Document Title

1st amendment of

Summary of the fate and behaviour in the environment for Fluopyram

Data Requirement(s)

Regulation (EC) No 1107/2009 & Regulation (EU) No 283/2013

Document MCA

Section 7: Fate and behaviour in the environment

According to the Guidance Document SANCO/10181/2013 for applicants on preparing dossiers for the approval of a chemical active substance

Date

2021-06-25

Author(s)

[redacted]

Bayer AG

Crop Science Division

OWNERSHIP STATEMENT

This document, the data contained in it and copyright therein are owned by Bayer AG and/or affiliated entities. No part of the document or any information contained therein may be disclosed to any third party without the prior written authorisation of Bayer AG and/or affiliated entities.

The summaries and evaluations contained in this document are based on unpublished proprietary data submitted for the purpose of the assessment undertaken by the regulatory authority. Other registration authorities should not grant, amend, or renew a registration on the basis of the summaries and evaluation of unpublished proprietary data contained in this document unless they have received the data on which the summaries and evaluation are based, either:

- **from Bayer AG or respective affiliate; or**
- **from other applicants once the period of data protection has expired.**

Version history

Date [yyyy-mm-dd]	Data points containing amendments or additions[1] and brief description	Document identifier and version number
2021-03-09	Original MCA as submitted by applicant	M-301037-02-1
2021-06-25	Revision of document number of original MCA as submitted by applicant due to interal requirements	M-770117-01-1
2021-06-25	Update of information due to findings from literature search for the metabolite TFA: section 7.5 was modified by the applicant	M-770117-02-1

[1] It is suggested that applicants adopt a similar approach to showing revisions and version history as outlined in SANCO/10180/2013 Chapter 4, 'How to revise an Assessment Report'.

Table of Contents

CA 7 FATE AND BEHAVIOUR IN THE ENVIRONMENT

Fluopyram was included in Annex I to Council Directive 91/414/EEC in year (Regulation (EU) 802/2013, Entry into Force on August 22, 2013). This Supplementary Dossier contains only data which were not submitted at the time of the Annex I inclusion of Fluopyram under Council Directive 91/414/EEC and which were therefore not evaluated during the first EU review. All data which were already submitted by Bayer AG (former Bayer CropScience) for the Annex I inclusion under Council Directive 91/414/EEC are contained in the Draft Assessment Report (DAR) and its Addenda, and are included in the Baseline Dossier provided by Bayer AG.

Relevant information for classification as detailed in the "*Combined Draft (Renewal) Assessment Report prepared according to Regulation (EC) N° 1107/2009 and Proposal for Harmonised Classification and Labelling (CLH Report) according to Regulation (EC) N° 1272/2008 – Volume 1, Level 2*" is provided in Document N1, Sections 8.2 and 8.3, and highlighted in light grey.

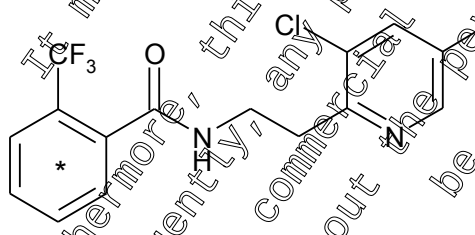
Note by the applicant: Information on study is provided in grey colour for all study that have been previously submitted for Annex I inclusion of fluopyram. The summary was updated according to the recent format and is thus given in black colour.

Information is provided in the following pages with respect to the fate and behaviour of fluopyram. This active substance is a broad-spectrum fungicide which is intended to be sprayed on cereals, grapes and apples in the field and lettuce in greenhouse.

The chemical structures and report names of fluopyram and its degradation products are given in Document N3. The following summary provides an overview of the behaviour of fluopyram in soil, water and air. The full details of the studies conducted to substantiate the information here are given in section CA 7.1 to CA 7.3.

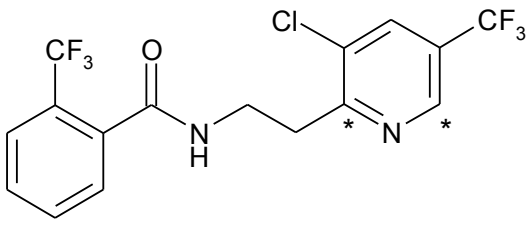
CA 7.1 Fate and behaviour in soil

The fate and behaviour of fluopyram in soil have been investigated in a comprehensive series of laboratory studies and, when required, extended by data from field experiments. The laboratory studies were all conducted with ^{14}C-labelled active substance. When required to fully define the fate of the molecule, studies have been separately performed with labelling in each of the two rings, uniformly labelled phenyl-ring or labelled in the 2- and 6-positions of the pyridyl-ring as illustrated in the figure below.



* denotes position of radiolabel, uniformly labelled in the phenyl ring

[phenyl-UL-^{14}C]fluopyram



* denotes position of radiolabel, labelled in the 2- and 6-position of the pyridyl ring

[pyridyl-2,6-^{14}C]fluopyram

Figure 7- 1: Radiolabel positions used for investigation of environmental fate of fluopyram

CA 7.1.1 Route of degradation in soil

The primary metabolic pathway in soil is hydroxylation in the 7-position of the active substance to form the metabolite fluopyram-7-hydroxy. Fluopyram-7-hydroxy has been observed in aerobic soil at a maximum of 5.8% AR. In a next step, fluopyram-benzamide (max. 3.8% AR) and pyridyl-carboxylic acid (PCA, max. 0.7% AR) were observed following cleavage at the 'central' bond of the molecule. Metabolite PCA may be further degraded in soil via fluopyram-methyl-sulfoxide (max. 1.0% AR). The metabolites fluopyram-benzamide, PCA and fluopyram-methyl-sulfoxide were formed at insignificant levels in aerobic soil testing and thus not considered in environmental risk assessment. Additionally, trifluoroacetate (TFA) can be formed following microbial degradation of fluopyram residues in aerobic soil (max. 7.4% on molar basis from active substance). Finally, fluopyram residues in aerobic soil were degraded ultimately to carbon dioxide (max. 27.2% AR), accompanied by the formation of non-extractable residues (NER, max. 15.1% AR), the latter as an indication for substantial integration into the soil matrix. Other unknown components occurred to an insignificant extent (< 2.7% AR for both label positions) in the studies investigating the route and rate of degradation in aerobic soil. An overview of the maximum occurrences of degradation products of fluopyram in aerobic laboratory soil as given in the table below and the degradation pathway is illustrated in Figure 7.1.1- 1.

Table 7.1.1- 1: Distribution of degradation products of fluopyram in aerobic laboratory soils

Fluopyram metabolites	Maximum formation (%AR)	Day of maximum formation	Fraction at study end (%AR)	Respective soil
Fluopyram-7-hydroxy	5.8	118	5.8	Brannens
Fluopyram -benzamide	3.8	30	0.2	Argissolo
Fluopyram -pyridyl-carboxylic acid (PCA)	0.7	30	n.d.	Dollendorf
Fluopyram -methyl-sulfoxide	1.0	128	1.0	Hoefchen
Trifluoroacetate (TFA) [1]	7.4	120	7.4	Wurmwiese
Maximum formation CO_2	27.2% AR after 365 d (end of study duration)			Springfield
Maximum formation NER	15.1% after 128 d (end of study duration)			Dollendorf

[1] Expressed as % of theoretical amount of TFA contained in applied fluopyram
n.d. = not detected

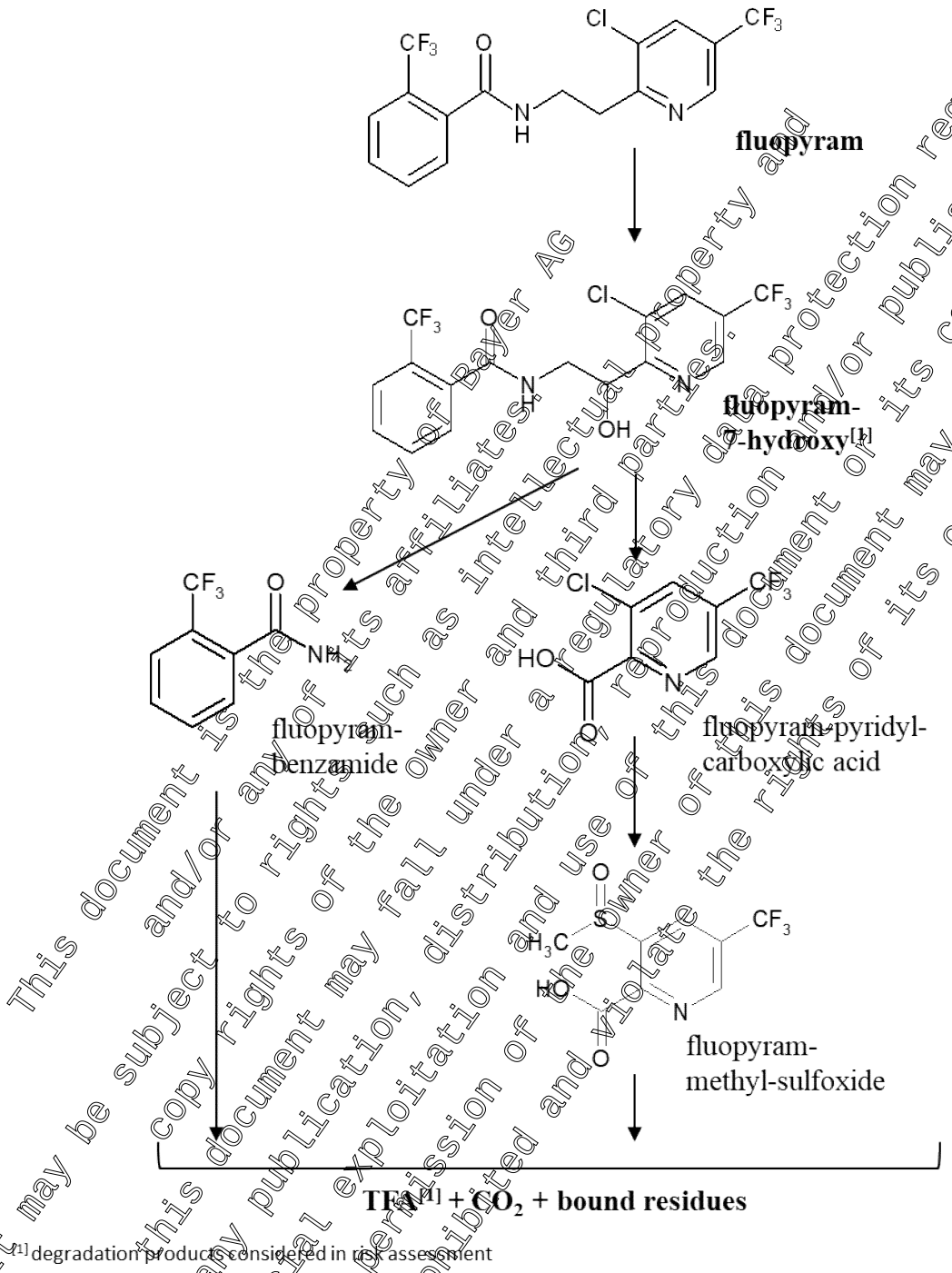


Figure 7.1.1- 1: Proposed degradation pathway of fluopyram in soil

Following an aerobic incubation phase, the degradation of fluopyram in soil was examined under anaerobic conditions in one soil for both radiolabels. Fluopyram was found to be slowly degraded under the conditions of the test. Formation of degradation products was insignificant for both positions of radiolabel applied. Two unidentified radioactive components were observed, each occurring at ≤ 3.3% AR in the course of the study. Mineralisation to CO_2 was less than 1.1% (phenyl-) and 0.8% AR (pyridyl-label). NER formation was 12.2% (phenyl-) and 12.9% AR (pyridyl-label) in maximum. In the absence of significant degradation observed in the test, no half-life could be calculated for fluopyram.

The photo-transformation on soil surfaces was studied for [phenyl-UL-^{14}C]fluopyram in one soil following exposure to artificial sunlight. Fluopyram was found to be stable under the conditions of the test as indicated by the recovery of parent compound in the extractable fraction at all sampling intervals. NER formation was 2.3% AR (phenyl-) and 2.7% AR (pyridyl-label) in maximum. In conclusion, photolytic transformation on soil surfaces is not regarded to be a relevant process for the degradation of fluopyram in the soil environment.

CA 7.1.1.1 Aerobic degradation

1. Information on the study

Data Point:	KCA 7.1.1.1/01
Report Author:	[redacted]
Report Year:	2008
Report Title:	[Pyridyl-2,6-14C]AE C656948: Aerobic metabolism/degradation and time dependent sorption in soils
Report No:	MEF-07/424
Document No:	M-298413-01-1
Guideline(s) followed in study:	OECD: Guideline 307, Aerobic and Anaerobic Transformation in Soil (2002); Commission Directive 95/36/EC amending Council Directive 91/414/EEC (Annexes I and II Fate and Behavior in the Environment) (1995); SETAC Procedures for Assessing the Environmental Fate and Ecotoxicity of Pesticides (1995); US EPA Subdivision N, Section 162-1 Aerobic soil metabolism (1982); OECD Guideline 106, Adsorption/desorption (2001) (only where applicable); Equivalent to US EPA OPPTS Guideline No. 835.4100
Deviations from current test guideline:	Current Guideline: OECD 307 (2002), OECD 106 (2000) (Only in parts) None
Previous evaluation:	yes, evaluated and accepted DAR (2006)
GLP/Officially recognised testing facilities:	Yes, conducted under GLP/Officially recognised testing facilities
Acceptability/Reliability:	Yes

2. Full summary of KCA 7.1.1.1/01

Executive Summary

The degradation and time-dependent sorption of [pyridyl-2,6-^{14}C]fluopyram was investigated in four soils for 128 days under aerobic conditions in the dark at 19.8 °C (mean over study duration) and a soil moisture of 55% of maximum water holding capacity. The study design considered in its conduct aspects of time dependent sorption (see also KCA 7.1.2.2/01).

Soil	Soil ID	Source	Texture (USDA)	pH [1]	OC [%]
Hoefchen am Hohensen	HF	Burscheid, Germany	silt loam	6.7	2.4
Laacherhof AXXa	AX	Monheim, Germany	sandy loam	6.2	2.2
Laacherhof Wurmwiese	WU	Monheim, Germany	sandy loam	5.2	1.8
Dollendorf II	DD	Blankenheim, Germany	clay loam	7.3	5.1

[1] in 0.01 M $CaCl_2$

The study application rate was 0.67 mg/kg soil (dry weight), equivalent to a single field application rate of 250 g fluopyram/ha (assuming incorporation into the top 2.5 cm of soil and a bulk density of 1.5 g/mL).

Duplicate samples were processed and analysed 0, 1, 3, 7, 15, 30, 58 and 128 days after treatment (DAT).
Mean material balances of radioactivity ranged from 97.6 to 101.0% AR for soil Hoefchen am Hohenseh, from 98.0 to 100.9% AR for soil Laacherhof AXXa, from 98.2 to 103.6% AR for soil Laacherhof Wurmwiese and from 96.5 to 102.6% AR for soil Dollendorf.

The maximum amount of carbon dioxide was 18.3, 4.7, 19.5 and 24.0% AR at study end (DAT-128) in soil Hoefchen am Hohenseh, Laacherhof AXXa, Laacherhof Wurmwiese and Dollendorf, respectively.
No significant amounts of organic volatile degradates were found for any soil at any sampling interval (≤0.1% AR).

Total extractable residues decreased from DAT 0 to DAT-128 from 98.1 to 68.4% AR in soil Hoefchen am Hohenseh, from 98.2 to 86.6% AR in soil Laacherhof AXXa, from 97.9 to 71.2% AR in soil Laacherhof Wurmwiese and from 96.6 to 59.9% AR in soil Dollendorf. The major portion of radioactivity was recovered in the 'ambient' extracts at all sampling intervals, whereas 'aggressive' extracts contributed only 2.8-3.8% AR.

Non-extractable residues (NER) increased from DAT 0 to DAT-128 from 1.9 to 13.2% AR in soil Hoefchen am Hohenseh, from 1.8 to 8.6% AR in soil Laacherhof AXXa, from 2.1 to 11.7% AR in soil Laacherhof Wurmwiese and from 3.4 to 15.1% AR in soil Dollendorf.

The amount of fluopyram in soil extracts decreased from DAT-0 to DAT-120 from 97.4 to 64.1% AR in soil Hoefchen am Hohenseh, from 97.5 to 81.0% AR in soil Laacherhof AXXa, from 97.3 to 68.4% AR in soil Laacherhof Wurmwiese and from 96.1 to 56.5% AR in soil Dollendorf.

A single minor transformation product was identified as fluopyram-7-hydroxy. Two additional minor metabolites, fluopyram-pyridyl-carboxylic acid and fluopyram-methyl-sulfoxide, were tentatively identified. Maximum levels were 3.3% AR (DAT-30) in soil Dollendorf for fluopyram-7-hydroxy, 0.7% AR (DAT-15) in soil Dollendorf for fluopyram-pyridyl-carboxylic acid and 1.0% AR (DAT-128) in soil Hoefchen for fluopyram-methyl-sulfoxide.

Up to three minor unidentified radioactive peaks (maximum concentration of 2.5% AR for a single peak) were detected. The total of unknown extracted radioactivity did not exceed 3.2% AR.

For details and results of degradation kinetics and time-dependent sorption investigations see respective sections later.

I. MATERIALS AND METHODS

A. MATERIALS

1. Test Item

[Pyridyl-2,6-^{14}C]AE C656948 (fluopyram)
Sample ID: BECH 2160
Specific Activity: 3.85 MBq/mg
Radiochemical Purity: > 99%
Chemical Purity: > 99%

2. Soil

Soils were sampled freshly from the field (upper horizon of 0 to 20 cm) and sieved to a particle size of ≤ 2 mm. Soils were chosen to represent an agricultural use area of Europe. Soils were stored at ambient

temperature for max. seven days prior use. Characteristics of the test soil are presented in the table below.

Table 7.1.1.1-1: Characteristics of test soil

Parameter	Results			
Soil designation	**Hoefchen am Hohenseh (HF)**	**Laacherhof AXXa (AX)**	**Laacherhof Wurmwiese (WU)**	**Dollendorf II (DD)**
Geographic Location (City / State / Country)	Burscheid / NRW / Germany	Monheim / NRW / Germany	Monheim/ NRW/ Germany	Blankenheim/ NRW/ Germany
Pesticide use history	No pesticide use for the previous 5 years			
Collection procedures	Sample taken with shovel and placed in plastic bag			
Sampling depth	0 – 20 cm			
Storage conditions	Room temperature (20°C ± 1°C)			
Storage length	Max. 7 days before application			
Soil preparation	Sieved (2 mm)			
Soil Taxonomic Classification (USDA)	Loamy, mixed, mesic Typic Argudalfs	Sandy, mixed, mesic Typic Cambudolls	Loamy, mixed, mesic Typic Argudalfs	n.d.
Texture Class (USDA)	silt loam	sandy loam	sandy loam	clay loam
Sand [50 µm - 2 mm] (%)	27	75	59	35
Silt [2 µm - 50 µm] (%)	56	14	24	36
Clay [< 2 µm] (%)	17	11	17	29
pH in Water	7.1	6.6	5.6	7.5
pH in 0.01 M $CaCl_2$	6.7	6.2	5.2	7.3
pH in 1 M KCl	6.5	6.0	4.8	7.0
Organic Matter [1] (%)	4.1	3.8	3.1	8.8
Organic Carbon (%)	2.4	2.2	1.8	5.1
Microbial biomass (mg $C_{microbial}$/ kg dry soil)				
Day 0	723	569	429	1951
Day 58	565	382	301	1812
Day 128	466	305	217	1488
CEC (meq/100 g)	12.4	9.5	9.6	21.2
55% MWHC (g/100 g)	32.7	26.6	30.5	46.5
Moisture at 1/3 bar ≙ pF 2.5 (g H_2O /100 g dry soil)	22.5	11.9	15.2	33.2

NRW: North Rhine-Westphalia; CEC: Cation exchange capacity; MWHC: Maximum Water Holding Capacity; n.d.: not determined
[1] % organic matter =% organic carbon x 1.724

B. STUDY DESIGN

1. Experimental Conditions

Four soils were incubated in the dark at 19.8 °C (18.9 – 20.7 °C) with [pyridyl-2,6-^{14}C]fluopyram at a target rate of 0.67 mg/kg soil for 128 d corresponding to a field rate of 250 g/ha (assuming incorporation into the top 2.5 cm of soil and a bulk density of 1.5 g/mL). The test substance was dissolved in methanol and applied dropwise with a volume of 402 µL onto 50 g subsamples of each soil using an adjustable pipette. After the application of the test item and evaporation of the organic solvent, the soil subsample was thoroughly mixed using a mortar and pestle and then added to the bulk (moist) soil (1950 g dry weight) to give the intended test item concentration. The spiked soil was then thoroughly mixed in a tumble mixer for one hour. Soil moisture was adjusted to 55% of the maximum water holding capacity (and at 29, 58 and 91 days after treatment). The test system was static and consisted of Erlenmeyer flasks, each containing 100 g of soil dry matter equivalents, attached with solid phase traps (soda lime and polyurethane foam) for the collection of $^{14}CO_2$ and volatile organics.

The test systems were incubated under aerobic conditions in the dark for 128 days at 20 °C and a soil moisture of 55% of the maximum water holding capacity in a climatic chamber.

2. Sampling

Duplicate samples were collected at 0, 1, 3, 7, 15, 30, 58 and 128 d after application. The soil was immediately processed after sampling. The soils from each flask were extracted completely. HPLC analysis was usually performed within 3 days. Extracts were stored in a refrigerator until further analysis. For confirmatory analyses, samples were stored frozen for six months. Storage stability investigations were performed.

Microbial soil biomass was determined at DAT-0, DAT-58 and DAT-128.

3. Analytical Procedures

The entire amount of soil in each test vessel was transferred into a centrifuge beaker. The first extraction was for 24 h by means of a mechanical shaker with 0.01 M aqueous $CaCl_2$ (soil/solution ratio = 1:4 accounting for soil moisture). The aqueous supernatant was separated by centrifugation and decantation and the fluopyram residues were analysed by LSC and HPLC (LOQ was equal to or less than 0.53% AR). The remaining soil was further processed in four extraction steps with acetonitrile and water (80 mL, 1 x 50/50 (v/v), 1 x 80/20 (v/v) and 2 x 100% acetonitrile) at ambient temperature (30 min shaking). Additionally, an aggressive microwave extraction was performed at 70 °C with acetonitrile/water (80/20 (v/v)) for 10 minutes. After each extraction step, the suspension was centrifuged for about 15 minutes and the clear supernatant was decanted and filtered. The four ambient organic extracts were combined and volume and radioactivity content were determined. An aliquot of the combined organic extracts was concentrated to a small volume and analysed by HPLC. The LOQ for a single HPLC peak in the organic soil extracts was equal to 0.23% AR. The microwave extracts (aggressive extracts) were also analysed by HPLC. The LOQ for the microwave soil extracts was equal to or less than 0.1% AR.

Residual radioactivity in air-dried, homogenized soils was determined by combustion followed by LSC analysis. For structural elucidation of the degradation products, 200 mL of organic extracts of day 30, 58 and 128 from soil HF were merged and afterwards concentrated, purified by solid phase extraction and fractionated by RP-HPLC. The two fractions were analysed by HPLC-MS-MS.

II. RESULTS AND DISCUSSION

A. EXTRACTION AND DISTRIBUTION OF RADIOACTIVITY IN SOIL SAMPLES

Table 7.1.1.1-2 to Table 7.1.1.1-3 summarize the degradation of [pyridyl-2,6-^{14}C]fluopyram as a function of time.

Table 7.1.1.1-2: Degradation of fluopyram in soil Hoefchen am Hohenseh under aerobic conditions

Compound	Replicate No.	Residues (% AR) on the following days after treatment (DAT)							
		0	1	3	7	15[1]	30	58	128
Fluopyram	A	97.2	95.9	95.1	93.9	91.7[2]	87.4	79.8	63.3
	B	97.5	96.7	97.2	93.4	93.9	86.6	77.7	64.9
	Mean	**97.4**	**96.3**	**96.2**	**93.7**	**93.9**[3]	**87.0**	**78.8**	**64.1**
Fluopyram-7-hydroxy	A	n.d.	n.d.	0.9	1.4	2.1[2]	2.2	2.3	2.0
	B	n.d.	n.d.	0.9	1.6	1.7	2.3	2.3	1.3
	Mean	**n.c.**	**n.c.**	**0.9**	**1.5**	**1.7**[3]	**2.3**	**2.3**	**1.7**
Fluopyram-pyridyl-carboxylic acid	A	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	B	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	Mean	**n.c.**	**n.c.**	**n.c.**	**n.c.**	**n.c.**	**n.c.**	**n.c.**	**n.c.**
Fluopyram-methyl-sulfoxide	A	n.d.	n.d.	n.d.	n.d.	n.d.	0.6	0.8	1.0
	B	n.d.	n.d.	n.d.	n.d.	n.d.	0.6	1.0	1.0
	Mean	**n.c.**	**n.c.**	**n.c.**	**n.c.**	**n.c.**	**0.6**	**0.9**	**1.0**
Total Unidentified Residues	A	0.6	0.4	0.6	0.7	0.5	1.4	1.7	1.3
	B	0.7	0.3	0.4	0.5	0.5	1.2	1.1	1.9
	Mean	**0.7**	**0.4**	**0.5**	**0.6**	**0.5**	**1.3**	**1.7**	**1.6**
Total Extractable Residues	A	97.9	96.3	96.7	96.0	94.3[2]	91.7	84.7	67.6
	B	98.2	97.1	98.5	95.5	96.1	90.8	82.6	69.1
	Mean	**98.1**	**96.7**	**97.6**	**95.7**	**96.1**[3]	**91.2**	**83.7**	**68.4**
Carbon Dioxide	A	n.a.	<0.1	<0.1	0.2	0.7	2.3	6.9	18.2
	B	n.a.	<0.1	<0.1	0.2	0.7	2.3	6.6	18.3
	Mean	**n.c.**	**<0.1**	**<0.1**	**0.2**	**0.7**	**2.3**	**6.8**	**18.3**
Volatile Organic Compounds	A	n.a.	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
	B	n.a.	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
	Mean	**n.c.**	**<0.1**	**<0.1**	**<0.1**	**<0.1**	**<0.1**	**<0.1**	**<0.1**
Non-Extractable Residues	A	1.9	2.1	2.5	3.3	4.0	5.5	8.6	13.1
	B	2.0	2.4	2.5	2.9	3.7	5.6	8.4	13.3
	Mean	**1.9**	**2.3**	**2.5**	**3.1**	**3.8**	**5.5**	**8.5**	**13.2**
Total Recovery	A	99.8	98.5	99.2	99.4	99.0[2]	99.5	100.1	99.0
	B	100.2	99.8	101.0	98.6	100.6	98.7	97.6	100.8
	Mean	**100.0**	**99.0**	**100.1**	**99.0**	**100.6**[3]	**99.1**	**98.9**	**99.9**

n.d.: not detected, n.a.: not analysed, n.c.: not calculated, DAT: days after treatment, SD: standard deviation

[1] The values for the extracts of replicate 1 of DAT-15 were invalidated, only replicate 2 will be used as single value in further calculations

[2] Accidentally a part of the organic extract was poured into the $CaCl_2$ solution

[3] Single value

Table 7.1.1.1-3: Degradation of fluopyram in soil Laacherhof AXXa under aerobic conditions

Compound	Replicate No.	Residues (% AR) on the following days after treatment (DAT)							
		0	**1**	**3**	**7**	**15**	**30**	**58**	**128**
Fluopyram	A	97.6	96.3	97.8	95.4	94.5	88.8	88.3	79.8
	B	97.4	96.5	97.3	95.4	95.2	91.3	86.2	82.2
	Mean	**97.5**	**96.4**	**97.6**	**95.4**	**94.8**	**90.0**	**87.2**	**81.0**
Fluopyram-7-hydroxy	A	n.d.	n.d.	n.d.	0.6	1.7	2.0	1.6	2.3
	B	n.d.	n.d.	n.d.	0.4	1.9	2.1	1.9	1.7
	Mean	**n.c.**	**n.c.**	**n.c.**	**0.5**	**1.8**	**2.1**	**1.7**	**2.0**
Fluopyram-pyridyl-carboxylic acid	A	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	B	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	Mean	**n.c.**	**n.c.**	**n.c.**	**n.c.**	**n.c.**	**n.c.**	**n.c.**	**n.c.**
Fluopyram-methyl-sulfoxide	A	n.d.	n.d.	n.d.	n.d.	n.d.	0.5	0.6	1.0
	B	n.d.	n.d.	n.d.	n.d.	n.d.	0.5	0.6	0.7
	Mean	**n.c.**	**n.c.**	**n.c.**	**n.c.**	**n.c.**	**0.5**	**0.6**	**0.8**
Total Unidentified Residues	A	0.6	0.4	0.3	0.5	0.4	1.3	2.1	3.2
	B	0.6	0.6	0.7	0.5	0.4	1.2	1.8	2.2
	Mean	**0.6**	**0.5**	**0.5**	**0.5**	**0.4**	**1.2**	**2.0**	**2.7**
Total Extractable Residues	A	98.2	96.7	98.1	96.6	96.6	92.6	92.5	86.3
	B	98.1	97.2	98.1	96.4	97.4	95.1	90.5	86.9
	Mean	**98.2**	**96.9**	**98.1**	**96.5**	**97.0**	**93.9**	**91.5**	**86.6**
Carbon Dioxide	A	n.a.	<0.1	<0.1	<0.1	0.2	0.7	2.0	4.7
	B	n.a.	<0.1	<0.1	0.1	0.2	0.7	1.9	4.7
	Mean	**n.c.**	**<0.1**	**<0.1**	**0.0**	**0.2**	**0.7**	**1.9**	**4.7**
Volatile Organic Compounds	A	n.a.	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
	B	n.a.	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
	Mean	**n.c.**	**<0.1**	**<0.1**	**<0.1**	**<0.1**	**<0.1**	**<0.1**	**<0.1**
Non-extractable Residues	A	1.9	2.1	2.0	2.7	2.8	4.7	6.0	8.8
	B	1.7	2.3	2.0	2.8	3.4	4.6	6.1	8.5
	Mean	**1.8**	**2.2**	**2.0**	**2.7**	**3.1**	**4.6**	**6.1**	**8.6**
Total Recovery	A	100.2	98.8	100.2	99.3	99.6	98.0	100.5	99.8
	B	99.8	99.5	100.1	99.2	100.9	100.4	98.6	100.1
	Mean	**100.0**	**99.2**	**100.1**	**99.2**	**100.3**	**99.2**	**99.5**	**99.9**

n.d. : not detected, n.a. : not analysed, n.c.: not calculated, DAT : days after treatment

Table 7.1.1.1-4: Degradation of fluopyram in soil Laacherhof Wurmwiese under aerobic conditions

Compound	Replicate No.	Residues (% AR) on the following days after treatment (DAT)							
		0	1	3	7	15	30	58	128
Fluopyram	A	97.2	95.0	97.0	95.1	91.1	89.1	80.6	69.6
	B	97.4	96.2	94.2	92.8	93.1	87.4	79.7	67.1
	Mean	**97.3**	**95.6**	**95.6**	**93.9**	**92.1**	**88.2**	**80.1**	**68.4**
Fluopyram-7-hydroxy	A	n.d.	1.0	1.7	2.8	3.3	2.6	2.5	2.3
	B	n.d.	1.0	1.7	2.4	2.3	3.0	2.7	2.0
	Mean	**n.c.**	**1.0**	**1.7**	**2.6**	**2.8**	**2.8**	**2.6**	**2.2**
Fluopyram-pyridyl-carboxylic acid	A	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	B	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	Mean	**n.c.**	**n.c.**	**n.c.**	**n.c.**	**n.c.**	**n.c.**	**n.c.**	**n.c.**
Fluopyram-methyl-sulfoxide	A	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	B	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	Mean	**n.c.**	**n.c.**	**n.c.**	**n.c.**	**n.c.**	**n.c.**	**n.c.**	**n.c.**
Total Unidentified Residues	A	0.6	0.7	0.6	0.6	0.6	0.6	1.4	0.6
	B	0.6	0.6	0.5	0.4	0.5	0.5	0.7	0.7
	Mean	**0.6**	**0.7**	**0.6**	**0.5**	**0.5**	**0.5**	**1.0**	**0.6**
Total Extractable Residues	A	97.8	96.7	99.3	98.5	95.0	92.2	84.4	72.7
	B	98.0	97.8	96.4	95.5	95.9	90.9	83.1	69.8
	Mean	**97.9**	**97.2**	**97.9**	**97.0**	**95.4**	**91.5**	**83.8**	**71.2**
Carbon Dioxide	A	n.a.	<0.1	0.1	0.3	1.1	3.2	7.7	19.3
	B	n.a.	<0.1	0.1	0.3	1.1	3.2	7.9	19.6
	Mean	**n.c.**	**<0.1**	**0.1**	**0.3**	**1.1**	**3.2**	**7.8**	**19.5**
Volatile Organic Compounds	A	n.a.	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
	B	n.a.	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
	Mean	**n.c.**	**<0.1**	**<0.1**	**<0.1**	**<0.1**	**<0.1**	**<0.1**	**<0.1**
Non-Extractable Residues	A	2.2	2.2	2.3	3.4	3.9	5.7	8.1	11.6
	B	2.1	2.4	2.3	2.4	4.2	6.0	8.0	11.7
	Mean	**2.1**	**2.3**	**2.3**	**2.9**	**4.0**	**5.9**	**8.0**	**11.7**
Total Recovery	A	100.0	98.9	101.7	102.1	99.9	101.2	100.2	103.6
	B	100.0	100.3	98.7	98.2	101.2	100.1	99.0	101.1
	Mean	**100.0**	**99.6**	**100.2**	**100.1**	**100.6**	**100.6**	**99.6**	**102.4**

n.d. : not detected, n.a. : not analysed, n.c.: not calculated, DAT : days after treatment

Table 7.1.1.1-5: Degradation of fluopyram in soil Dollendorf under aerobic conditions

Compound	Replicate No.	Residues (% AR) on the following days after treatment (DAT)							
		0	**1**	**3**	**7**	**15**	**30**	**58**	**128**
Fluopyram	A	95.4	95.4	93.6	88.4	85.3	79.5	73.0	58.5
	B	96.8	95.2	93.0	90.4	90.1	82.7	69.5	54.4
	Mean	**96.1**	**95.3**	**93.3**	**89.4**	**87.7**	**81.1**	**71.2**	**56.5**
Fluopyram-7-hydroxy	A	n.d.	0.8	2.2	2.9	2.7	3.3	2.7	1.0
	B	n.d.	0.7	1.5	2.8	3.3	3.4	2.5	1.2
	Mean	**n.c.**	**0.7**	**1.9**	**2.8**	**3.0**	**3.3**	**2.6**	**1.1**
Fluopyram-pyridyl-carboxylic acid	A	n.d.	n.d.	n.d.	0.4	0.8	0.7	0.6	n.d.
	B	n.d.	n.d.	n.d.	0.3	0.4	0.7	0.3	n.d.
	Mean	**n.c.**	**n.c.**	**n.c.**	**0.4**	**0.6**	**0.7**	**0.4**	**n.c.**
Fluopyram-methyl-sulfoxide	A	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	B	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	Mean	**n.c.**	**n.c.**	**n.c.**	**n.c.**	**n.c.**	**n.c.**	**n.c.**	**n.c.**
Total Unidentified Residues	A	0.5	0.6	0.4	1.4	1.6	2.4	2.3	1.9
	B	0.5	0.6	0.7	1.2	1.4	2.5	3.0	2.6
	Mean	**0.5**	**0.6**	**0.6**	**1.3**	**1.5**	**2.4**	**2.6**	**2.3**
Total Extractable Residues	A	95.9	96.8	96.3	93.1	90.4	85.9	78.5	61.5
	B	97.3	96.4	95.2	94.7	95.2	89.2	75.2	58.2
	Mean	**96.6**	**96.6**	**95.7**	**93.9**	**92.8**	**87.5**	**76.9**	**59.9**
Carbon Dioxide	A	n.a.	<0.1	<0.1	0.2	1.1	4.0	11.0	24.3
	B	n.a.	<0.1	<0.1	0.2	1.1	4.1	10.8	23.6
	Mean	**n.c.**	**<0.1**	**<0.1**	**0.2**	**1.1**	**4.1**	**10.9**	**24.0**
Volatile Organic Compounds	A	n.a.	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
	B	n.a.	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
	Mean	**n.c.**	**<0.1**	**<0.1**	**<0.1**	**<0.1**	**<0.1**	**<0.1**	**<0.1**
Non-Extractable Residues	A	2.9	4.4	3.3	5.8	6.0	8.7	11.5	15.5
	B	3.9	3.4	3.1	4.4	6.2	8.7	11.4	14.7
	Mean	**3.4**	**3.9**	**3.5**	**5.1**	**6.1**	**8.7**	**11.4**	**15.1**
Total Recovery	A	98.9	101.2	99.6	99.1	97.5	98.5	101.0	101.2
	B	101.1	99.9	98.9	99.3	102.6	102.0	97.4	96.5
	Mean	**100.0**	**100.5**	**99.3**	**99.2**	**100.0**	**100.3**	**99.2**	**98.9**

n.d. : not detected, n.a. : not analysed, n.c.: not calculated, DAT : days after treatment

B. MATERIAL BALANCE

The total radioactive material balances showed complete recovery of the applied radioactivity for each individual test flask (overall range 96.5-103.6% AR), indicating that no significant portion had dissipated from the test vessels or was lost upon processing. Mean material balances of radioactivity ranged from 97.6 to 101.0% AR for soil Hoefchen am Hohenseh, from 98.0 to 100.9% AR for soil Laacherhof AXXa, from 98.2 to 103.6% AR for soil Laacherhof Wurmwiese and from 96.5 to 102.6% AR for soil Dollendorf.

C. EXTRACTABLE AND NON-EXTRACTABLE RESIDUES

Total extractable residues decreased from DAT 0 to DAT-128 from 98.1 to 68.4% AR in soil Hoefchen am Hohenseh, from 98.2 to 86.6% AR in soil Laacherhof AXXa, from 97.9 to 71.2% AR in soil Laacherhof Wurmwiese and from 96.6 to 59.9% AR in soil Dollendorf. The major portion of radioactivity was recovered in the 'ambient' extracts at all sampling intervals, whereas 'aggressive' extracts contributed only 2.8-3.8% AR at the maximum.

Non-extractable residues (NER) increased from DAT 0 to DAT-128 from 1.9 to 13.2% AR in soil Hoefchen am Hohenseh, from 1.8 to 8.6% AR in soil Laacherhof AXXa, from 2.1 to 11.7% AR in soil Laacherhof Wurmwiese and from 3.4 to 15.1% AR in soil Dollendorf.

D. VOLATILIZATION

The maximum amount of carbon dioxide was 18.3, 4.5, 19.5 and 24.0% AR at study end (DAT-128) in soil Hoefchen am Hohenseh, Laacherhof AXXa, Laacherhof Wurmwiese and Dollendorf, respectively. No significant amounts of organic volatile degradates were found for any soil at any sampling interval (≤0.1% AR).

E. DEGRADATION OF TEST ITEM

The amount of fluopyram in soil extracts decreased from DAT-0 to DAT-120 from 97.4 to 64.1% AR in soil Hoefchen am Hohenseh, from 97.5 to 81.0% AR in soil Laacherhof AXXa, from 97.3 to 68.4% AR in soil Laacherhof Wurmwiese and from 96.1 to 56.5% AR in soil Dollendorf.

A single minor transformation product was identified as fluopyram-7-hydroxy. Two additional minor metabolites pyridyl-carboxylic acid and methyl-sulfoxide were tentatively identified. Maximum levels were 3.3% AR (DAT-30) in soil Dollendorf for fluopyram-7-hydroxy, 0.7% AR (DAT-15) in soil Dollendorf for pyridyl-carboxylic acid and 1.0% AR (DAT-128) in soil Hoefchen for methyl-sulfoxide.

Up to three minor unidentified radioactive peaks (maximum concentration of 2.5% AR for a single peak) were detected. The total of unknown extracted radioactivity did not exceed 3.2% AR.

F. KINETICS

New kinetic calculations based on more recent guidance are necessary, therefore the information included in this study is not considered relevant. Evaluation of the rate of degradation is reported under KCA 7.1.2.1.1/09 (M-761966-01-1).

G. TIME-DEPENDENCE OF SORPTION

Results of the time-dependent sorption experiment can be found in KCA 7.1.3.2/01.

III. CONCLUSIONS

[Pyridyl-2,6-^{14}C]fluopyram was moderately degraded in soil under aerobic conditions in the dark in the laboratory.

Formation of carbon dioxide was significant (up to 24.0% AR) at study end indicating the potential for a complete mineralization of report fluopyram and its degradation products. Formation of non-extractable residues (NER) was up to 15.1% AR at study end.

Besides NER and carbon dioxide, a single degradation product was identified and two metabolites were tentatively identified with the following maximum occurrences: 3.3% AR (DAT-30) in soil Dollendorf for fluopyram-7-hydroxy, 0.7% AR (DAT-15) in soil Dollendorf for pyridyl-carboxylic acid and 1.0% AR (DAT-128) in soil Hoefchen for methyl-sulfoxide. The total of unknown extracted radioactivity did not exceed 3.2% AR.

The results of study indicate that sorption of fluopyram to soil increases with its residence time in soil which should be acknowledged in mobility assessments. Since fluopyram was slowly degraded in soil when kept under aerobic lab conditions the TDS factor was well measurable over the entire study duration (see more details under section KCA 7.1.3.2/01).

3. Assessment and conclusion

Assessment and conclusion by applicant:
The study and its data are considered as valid and reliable for use in risk assessment.

Assessment and conclusion by RMS:
Outcome and conclusion of the study: RMS should indicate if they agree to the results and conclusions of the APPL.

1. Information on the study

Data Point:	KCA 7.1.1.1/02
Report Author:	[redacted]
Report Year:	2008
Report Title:	[Phenyl-UL-^{14}C]AE C656948: Aerobic soil metabolism/degradation and time-dependent sorption in four soils
Report No:	MEF-06/295
Document No:	M-298296-01-1
Guideline(s) followed in study:	OECD Guideline 307, Aerobic and Anaerobic Transformation in Soil (2002); Commission Directive 95/36/EC amending Council Directive 91/414/EEC (Annexes I and II, Fate and Behavior in the Environment) (1995); SETAC Procedures for Assessing the Environmental Fate and Ecotoxicity of Pesticides (1995); US EPA Subdivision N, Section 162-1, Aerobic soil metabolism (1982); OECD Guideline 106, Adsorption/Desorption (2001) (only where applicable); Equivalent to US EPA OPPTS Guideline No. 835.4100
Deviations from current test guideline:	Current Guideline: OECD 307 (2002), OECD 106 (2000) (Only in parts) None
Previous evaluation:	Yes, evaluated and accepted DAR (2011)
GLP/officially recognised testing facilities:	Yes, conducted under GLP/Officially recognised testing facilities
Acceptability/Reliability:	Yes

2. Full summary of KCA 7.1.1.1/02

Executive Summary

The degradation and time-dependent sorption of [phenyl-UL-^{14}C]fluopyram was investigated in four soils under aerobic conditions in the dark in the laboratory for 121 days at 19.8 °C (mean over study duration) and at a soil moisture of 55% of the maximum water holding capacity. The study design considered in its conduct aspects of time dependent sorption (see also KCA 7.1.3.2/02).

Soil	Soil ID	Source	Texture (USDA)	pH [1]	OC [%]
Hoefchen am Hohenseh	HH	Burscheid, Germany	silt loam	6.6	2.1
Laacherhof AXXa	LX	Monheim, Germany	sandy loam	6.6	1.5
Laacherhof Wurmwiese	WW	Monheim, Germany	loam	5.5	2.0
Laacherhof AIIIa	LA	Monheim, Germany	loam	6.6	1.3

[1] in 0.01 M $CaCl_2$

The study application rate was 0.67 mg/kg soil (dry weight), equivalent to a single field application rate of 250 g/ha (assuming incorporation into the top 2.5 cm of soil and a bulk density of 1.5 g/mL) [phenyl-UL-^{14}C]fluopyram.

Duplicate samples were processed and analyzed 0, 1, 2, 7, 14, 30, 62 and 121 days after treatment (DAT).

Mean material balances of radioactivity were in a range of 98.5 to 101.8% AR for soil Hoefchen am Hohenseh, from 97.7 to 101.3% AR for soil Laacherhof AXXa, from 101.2 to 105.9% AR for soil Laacherhof Wurmwiese and from 95.1 to 101.2% AR for soil Laacherhof AIIIa.

The maximum amount of carbon dioxide was 14.5, 13.9, 13.4 and 16.2% AR study end (DAT-121) in soil Hoefchen am Hohenseh, Laacherhof AXXa, Laacherhof Wurmwiese and Laacherhof AIIIa, respectively. Formation of volatile organic compounds was insignificant as demonstrated by values of ≤0.1% AR at all sampling intervals for all soils.

Total extractable residues significantly decreased from DAT-0 to DAT-121 from 99.7 to 73.2% AR in soil Hoefchen am Hohenseh, from 95.7 to 73.1% AR in soil Laacherhof AXXa, from 99.5 to 81.3% AR in soil Laacherhof Wurmwiese and from 97.9 to 65.1% AR in soil Laacherhof AIIIa.

Non-extractable residues (NER) significantly increased from DAT-0 to DAT-121 from 1.8 to 11.3% AR in soil Hoefchen am Hohenseh, from 2.0 to 10.8% AR in soil Laacherhof AXXa, from 2.3 to 10.1% AR in soil Laacherhof Wurmwiese and from 1.3 to 13.8% AR in soil Laacherhof AIIIa.

The amount of fluopyram in the total soil extracts (i.e. in aqueous desorption solution and organic soil extracts) significantly decreased from DAT-0 to DAT-128 from 97.8 to 67.6% AR in soil Hoefchen am Hohenseh, from 93.5 to 66.7% AR in soil Laacherhof AXXa, from 97.7 to 76.1% AR in soil Laacherhof Wurmwiese and from 96.5 to 57.3% AR in soil Laacherhof AIIIa.

Degradation of fluopyram was accompanied by the formation of two degradation products, identified as fluopyram-7-hydroxy with a maximum occurrence of 4.2% AR at DAT-62 in soil Laacherhof AIIIa and benzamide with a maximum occurrence of 1.1% AR at DAT-30, DAT-62 and DAT-121 in soil Laacherhof AIIIa. Up to six minor radioactive peaks (maximum concentration of 0.3% AR for a single peak) were detected. The total of unknown extracted radioactivity did not exceed 2.7% AR.

For details and results of degradation kinetics and time-dependent sorption investigations see respective sections later.

I. MATERIALS AND METHODS

A. MATERIALS

1. Test Item

[Phenyl-UL-^{14}C]fluopyram

Batch No	BECH 1813
Specific activity	3.85 MBq/mg
Radiochemical purity	> 98% (HPLC, radiodetection), > 99% (TLC radiodetection)
Chemical purity	>99% (HPLC, UV det., 210 nm)

2. Test Soils

Soil samples were collected freshly from the field. A few days before starting the test, the air-dried soils were sieved through a 2 mm sieve. Sil characteristics are summarised in the table below.

Table 7.1.1.1-6: Physico-chemical properties of test soils

Parameter	Results			
Soil Designation	**Hoefchen am Hohensch**	**Laacherhof AXXa**	**Laacherhof Wurmwiese**	**Laacherhof AIIIa**
Geographic Location (City / State / Country)	Burscheid / NRW / Germany	Monheim / NRW / Germany	Monheim / NRW / Germany	Monheim / NRW / Germany
Pesticide use history	No pesticide used			
Collection procedures	Sample taken with shovel and placed in plastic bag			
Sampling depth	0 – 20 cm			
Storage conditions	Room temperature (20 ± 1°C)			
Storage length	Max. 3 days before application			
Soil preparation	Sieved (2 mm)			
Soil Taxonomic Classification (USDA)	Loamy, mixed, mesic Typic Argudalfs	Sandy, mixed, mesic Typic Cambudolls	Loamy, mixed, mesic Typic Argudalfs	Loamy, mixed, mesic Typic Argudalfs
Texture Class (USDA)	silt loam	sandy loam	loam	loam
Sand [50 µm - 2 mm] (%)	7.8	72.9	48.2	42.3
Silt [2 µm - 50 µm] (%)	75.2	16.2	35.9	40.3
Clay [<2 µm] (%)	17.0	10.9	15.9	17.3
pH in Water	7.3	7.2	6.3	7.3
pH in 0.01 M $CaCl_2$	6.6	6.6	5.5	6.6
pH in 1 M KCl	6.8	6.8	5.7	6.8
Organic Matter [1] (%)	3.6	2.6	3.5	2.2
Organic Carbon (%)	2.1	1.5	2.0	1.3
Microbial biomass (mg $C_{microbial}$/kg dry soil)				
Day 0	866	913	147	107
Day 121	591	484	235	165
CEC (meq/100 g)	14.4	9.4	11.6	11.3
55% MWHC (g/100 g)	34.8	26.7	37.7	28.4

NRW: North Rhine-Westphalia; CEC: Cation exchange capacity; MWHC: Maximum Water Holding Capacity
[1] % organic matter =% organic carbon × 1.724

B. STUDY DESIGN

1. Experimental Conditions

Four soils were incubated at 19.8 °C (19.1–20.7 °C) with [phenyl-UL-^{14}C]fluopyram at a target rate of 0.67 mg/kg soil for 121 d corresponding to a field rate of 250 g/ha (assuming incorporation into the top 2.5 cm of soil and a bulk density of 1.5 g/mL). The test substance was dissolved in methanol and applied dropwise with a volume of 803 µL onto 50 g subsamples of each soil using an adjustable pipette. After

the application of the test item and evaporation of the organic solvent, the soil subsample was thoroughly mixed using a mortar and pestle and then added to the bulk (moist) soil (2250 g dry weight) to give the intended test item concentration. The spiked soil was then thoroughly mixed in a tumble mixer for one hour. Soil moisture was adjusted to 55% of the maximum water holding capacity (and at 43 days after treatment). The test system was static and consisted of Erlenmeyer flasks, each containing 100 g of soil dry matter equivalents, attached with solid phase traps (soda lime and polyurethane foam) for the collection of $^{14}CO_2$ and volatile organics.

The test systems were incubated under aerobic conditions in the dark for 121 days at 20 °C and a soil moisture of 55% of the maximum water holding capacity in a climatic chamber.

2. Sampling

Duplicate samples were collected at 0, 1, 2, 7, 14, 30, 62 and 121 days after application. The soil was immediately processed after sampling. The soils from each flask were extracted completely. HPLC analysis was usually performed within 3 days. Extracts were stored in a refrigerator until further analysis. For confirmatory analyses, samples were stored frozen for 29 weeks. Storage stability investigations were performed.

Microbial soil biomass was determined at DAT-0 and DAT-121.

3. Analytical Procedures

The entire amount of soil in each test vessel was transferred into a centrifuge beaker. The first extraction was for 24 h by means of a mechanical shaker with 0.01 M aqueous $CaCl_2$ (soil/solution ratio = 1:4 accounting for soil moisture). The aqueous supernatant was separated by centrifugation and decantation and the fluopyram residues were analysed by LSC and HPLC (LOQ was equal to or less than 0.12% AR). The remaining soil was further processed in four extraction steps with acetonitrile and water (80 mL, 1 x 50/50 (v/v), 1 x 80/20 (v/v) and 2 x 100% acetonitrile) at ambient temperature (30 min shaking). Additionally, an aggressive microwave extraction was performed at 70 °C with acetonitrile/water (80/20 (v/v)) for 10 minutes. After each extraction step the suspension was centrifuged for about 15 minutes and the clear supernatant was decanted and filtered.

The four ambient organic extracts were combined and volume and radioactivity content were determined. An aliquot of the combined organic extracts was concentrated to a small volume and analysed by HPLC. The LOQ for a single peak in the organic soil extracts was equal to 0.1% AR. The microwave extracts (aggressive extracts) were also analysed by HPLC. The LOQ for the microwave soil extracts was equal to or less than 0.1% AR. Residual radioactivity in air-dried, homogenized soils was determined by combustion followed by LSC analysis. The PU foam was extracted with 50 mL ethyl acetate by ultrasonication. Aliquots of 5mL of the extract were submitted to LSC measurement. Carbon dioxide absorbed by soda lime was liberated and trapped in a scintillation cocktail and radioactivity was subsequently measured by LSC. To proof the identity of CO_2, precipitation of liberated radioactivity as $BaCO_3$ was determined by adding $BaCl_2$ solution.

II. RESULTS AND DISCUSSION

A. EXTRACTION AND DISTRIBUTION OF RADIOACTIVITY IN SOIL SAMPLES

Table 7.1.1.1-7 to Table 7.1.1.1-10 summarise the degradation of [phenyl-UL-^{14}C]fluopyram as a function of time.

Table 7.1.1.1-7: Degradation of fluopyram in soil Hoefchen am Hohenseh under aerobic conditions

Compound	Replicate No.	Residues (% AR) on the following days after treatment (DAT)							
		0	1	2	7	14	30	62	121
Fluopyram	A	97.3	97.2	94.8	95.6	90.4	87.2	76.7	65.5
	B	98.4	96.6	96.1	95.0	91.7	88.1	78.4	69.6
	Mean	**97.8**	**96.9**	**95.5**	**95.3**	**91.0**	**87.6**	**77.5**	**67.6**
Fluopyram-benzamide	A	0.4	0.4	0.4	0.3	0.5	0.3	0.5	0.5
	B	0.5	0.2	0.1	0.1	0.2	0.4	0.4	0.5
	Mean	**0.4**	**0.3**	**0.3**	**0.2**	**0.4**	**0.5**	**0.6**	**0.6**
Fluopyram-7-hydroxy	A	0.1	0.5	0.8	0.6	2.1	2.6	2.7	2.6
	B	0.1	0.5	0.4	1.4	1.9	2.8	3.4	2.8
	Mean	**0.1**	**0.5**	**0.6**	**1.0**	**2.0**	**2.5**	**3.0**	**2.7**
Total Unidentified Residues	A	1.5	1.6	1.4	2.0	2.0	0.2	1.0	2.9
	B	1.2	2.0	1.2	1.6	2.5	0.2	1.1	1.9
	Mean	**1.4**	**1.8**	**1.3**	**1.8**	**2.2**	**0.2**	**1.1**	**2.4**
Total Extractable Residues	A	99.2	99.7	97.4	98.5	95.0	90.3	80.8	71.7
	B	100.2	99.3	97.9	98.2	96.3	91.4	83.5	74.8
	Mean	**99.7**	**99.5**	**97.6**	**98.3**	**95.6**	**90.9**	**82.2**	**73.2**
Carbon Dioxide	A	n.a.	0.1	0.1	0.5	1.1	2.8	8.1	14.4
	B	n.a.	0.1	0.1	0.6	1.4	3.2	7.5	14.5
	Mean	**n.c.**	**0.1**	**0.1**	**0.5**	**1.3**	**3.0**	**7.8**	**14.5**
Volatile Organic Compounds	A	n.a.	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
	B	n.a.	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	0.1
	Mean	**n.c.**	**<0.1**	**<0.1**	**<0.1**	**<0.1**	**<0.1**	**<0.1**	**<0.1**
Non-Extractable Residues	A	1.6	1.9	2.0	3.0	3.1	4.8	8.6	11.3
	B	2.0	1.8	2.1	2.8	3.5	4.5	8.5	11.4
	Mean	**1.8**	**1.9**	**2.0**	**2.9**	**3.3**	**4.7**	**8.5**	**11.3**
Total Recovery	A	100.9	101.3	99.5	102.0	99.2	97.9	97.5	97.4
	B	102.2	101.2	100.1	101.6	101.1	99.2	99.5	100.8
	Mean	**101.5**	**101.4**	**99.8**	**101.8**	**100.2**	**98.5**	**98.5**	**99.1**

n.d.: not detected, n.a.: not analysed, n.c.: not calculated, DAT: days after treatment

Table 7.1.1.1-8: Degradation of fluopyram in soil Laacherhof AXXa under aerobic conditions

Compound	Replicate No	Residues (% AR) on the following days after treatment (DAT)							
		0	1	2	7	14	30	62	121
Fluopyram	A	93.5	95.1	92.4	93.2	91.2	91.3	76.4	65.9
	B	93.5	93.9	95.9	96.3	93.1	86.7	77.2	68.5
	Mean	**93.5**	**94.5**	**94.1**	**94.8**	**92.2**	**89.0**	**76.8**	**66.7**
Fluopyram-benzamide	A	0.4	0.5	0.1	n.d.	0.5	0.6	0.6	0.8
	B	0.3	0.3	0.5	n.d.	0.4	0.5	0.8	0.8
	Mean	**0.4**	**0.4**	**0.3**	**n.c.**	**0.5**	**0.5**	**0.7**	**0.8**
Fluopyram-7-hydroxy	A	n.d.	0.2	0.2	1.2	2.1	3.5	3.7	3.7
	B	0.3	0.5	0.3	1.3	1.8	3.0	3.8	3.6
	Mean	**0.2**	**0.3**	**0.3**	**1.3**	**1.9**	**3.2**	**3.7**	**3.7**
Total Unidentified Residues	A	1.9	1.4	2.0	1.5	1.8	0.2	1.3	2.0
	B	1.3	1.5	1.1	2.2	1.6	0.3	1.2	1.8
	Mean	**1.6**	**1.5**	**1.5**	**1.8**	**1.7**	**0.3**	**1.2**	**1.9**
Total Extractable Residues	A	95.9	97.1	94.7	95.9	95.6	95.6	82.0	71.6
	B	95.5	96.2	97.7	99.8	96.9	90.4	82.9	74.7
	Mean	**95.7**	**96.7**	**96.2**	**97.9**	**96.3**	**93.0**	**82.4**	**73.1**
Carbon Dioxide	A	n.a.	0.1	0.1	0.5	1.1	3.1	7.3	20.4
	B	n.a.	<0.1	0.1	0.5	1.1	2.6	8.0	7.5
	Mean	**n.c.**	**<0.1**	**0.1**	**0.5**	**1.1**	**2.8**	**7.7**	**13.9**
Volatile Organic Compounds	A	n.a.	0.1	0.1	<0.1	<0.1	<0.1	<0.1	<0.1
	B	n.a.	<0.1	<0.1	<0.1	0.1	0.2	<0.1	0.1
	Mean	**n.c.**	**<0.1**	**<0.1**	**<0.1**	**<0.1**	**0.1**	**<0.1**	**0.1**
Non-Extractable Residues	A	2.2	1.6	2.1	2.9	3.0	4.4	7.8	10.8
	B	1.8	1.8	2.0	2.9	2.8	3.9	8.4	10.7
	Mean	**2.0**	**1.7**	**2.1**	**2.9**	**2.9**	**4.2**	**8.1**	**10.8**
Total Recovery	A	98.1	98.7	96.8	99.4	99.7	103.1	97.0	102.8
	B	97.3	98.0	99.8	103.2	100.9	97.1	99.3	93.1
	Mean	**97.7**	**98.4**	**98.3**	**101.3**	**100.3**	**100.1**	**98.1**	**97.9**

n.d.: not detected, n.a.: not analysed, n.c.: not calculated, DAT: days after treatment

Table 7.1.1.1-9: Degradation of fluopyram in soil Laacherhof Wurmwiese under aerobic conditions

Compound	Replicate No	Residues (% AR) on the following days after treatment (DAT)							
		0	1	2	7	14	30	62	121
Fluopyram	A	97.5	102.8	95.7	95.3	94.1	90.8	90.7	76.7
	B	97.8	102.1	100.0	98.8	93.2	92.4	89.9	81.4
	Mean	**97.7**	**102.4**	**97.9**	**97.1**	**93.6**	**91.6**	**90.3**	**76.1**
Fluopyram-benzamide	A	0.2	0.2	0.2	n.d.	0.4	0.2	0.1	0.3
	B	n.d.	n.d.	n.d.	n.d.	0.2	0.1	0.2	0.3
	Mean	**0.1**	**0.1**	**0.1**	**n.c.**	**0.3**	**0.2**	**0.1**	**0.3**
Fluopyram-7-hydroxy	A	n.d.	0.3	0.5	1.7	2.0	3.3	3.6	3.2
	B	n.d.	0.2	0.6	1.4	1.9	3.2	3.3	3.5
	Mean	**n.c.**	**0.3**	**0.6**	**1.5**	**2.0**	**3.3**	**3.5**	**3.3**
Total Unidentified Residues	A	1.7	1.9	2.8	2.2	2.1	0.4	0.7	1.8
	B	1.7	1.4	1.6	1.9	1.8	0.4	0.6	1.5
	Mean	**1.7**	**1.2**	**1.7**	**2.1**	**2.0**	**0.4**	**0.7**	**1.6**
Total Extractable Residues	A	99.4	104.5	98.3	99.2	98.6	94.7	95.1	75.9
	B	99.6	103.7	102.2	102.1	97.2	96.1	93.9	86.7
	Mean	**99.5**	**104.1**	**100.3**	**100.6**	**97.9**	**95.4**	**94.5**	**81.3**
Carbon Dioxide	A	n.a.	0.1	0.1	0.4	0.8	2.0	4.3	15.6
	B	n.a.	0.1	0.1	0.3	0.6	1.6	3.8	11.1
	Mean	**n.c.**	**0.1**	**0.1**	**0.4**	**0.7**	**1.8**	**4.0**	**13.4**
Volatile Organic Compounds	A	n.a.	0.1	0.1	0.1	0.1	0.1	0.2	<0.1
	B	n.a.	<0.1	0.1	<0.1	0.2	<0.1	<0.1	0.1
	Mean	**n.c.**	**<0.1**	**<0.1**	**<0.1**	**0.1**	**<0.1**	**0.1**	**<0.1**
Non-Extractable Residues	A	2.4	1.4	2.1	3.1	3.2	3.9	6.8	10.8
	B	2.3	1.9	2.3	2.9	3.0	4.0	7.4	9.5
	Mean	**2.3**	**1.7**	**2.2**	**3.0**	**3.1**	**3.9**	**7.1**	**10.1**
Total Recovery	A	101.8	106.1	100.6	102.8	102.7	100.6	106.4	102.3
	B	101.9	105.6	104.7	105.3	101.0	101.7	105.1	107.4
	Mean	**101.8**	**105.9**	**102.6**	**104.0**	**101.9**	**101.2**	**105.8**	**104.9**

n.d.: not detected, n.a.: not analysed, n.c.: not calculated, DAT: days after treatment

Table 7.1.1.1-10: Degradation of fluopyram in soil Laacherhof AIIIa under aerobic conditions

Compound	Replicate No	Residues (% AR) on the following days after treatment (DAT)							
		0	1	2	7	14	30	62	121
Fluopyram	A	94.7	95.0	94.6	92.7	88.2	84.5	74.4	58.9
	B	98.2	98.2	96.6	92.9	90.8	85.9	76.7	55.6
	Mean	**96.5**	**96.6**	**95.6**	**92.8**	**89.5**	**85.2**	**75.5**	**57.3**
Fluopyram-benzamide	A	0.5	0.4	0.5	0.7	0.9	1.1	1.2	1.1
	B	0.4	0.4	0.4	0.6	0.9	1.1	1.0	1.2
	Mean	**0.4**	**0.4**	**0.5**	**0.6**	**0.9**	**1.1**	**1.1**	**1.1**
Fluopyram-7-hydroxy	A	n.d.	0.4	0.5	1.7	2.7	3.1	4.0	4.1
	B	n.d.	0.4	0.5	1.7	2.4	3.3	4.3	3.9
	Mean	**n.c.**	**0.4**	**0.5**	**1.7**	**2.6**	**3.2**	**4.2**	**4.0**
Total Unidentified Residues	A	1.2	1.8	1.4	2.7	3.8	0.2	0.9	2.6
	B	0.7	0.9	1.2	1.6	3.0	0.1	0.5	2.8
	Mean	**1.0**	**1.3**	**1.3**	**1.6**	**2.4**	**0.2**	**0.7**	**2.7**
Total Extractable Residues	A	96.4	97.6	97.1	96.8	93.6	88.9	80.5	66.7
	B	99.4	99.9	98.7	96.8	97.2	90.4	82.4	63.4
	Mean	**97.9**	**98.7**	**97.9**	**96.8**	**95.4**	**89.7**	**81.4**	**65.1**
Carbon Dioxide	A	n.a.	<0.1	0.1	0.6	1.5	3.9	10.3	14.6
	B	n.a.	<0.1	0.1	0.5	1.5	3.7	9.4	17.7
	Mean	**n.c.**	**<0.1**	**0.1**	**0.5**	**1.5**	**3.8**	**9.8**	**16.2**
Volatile Organic Compounds	A	n.a.	<0.1	<0.1	<0.1	<0.1	0.1	0.1	0.1
	B	n.a.	<0.1	<0.1	0.1	<0.1	<0.1	0.1	0.1
	Mean	**n.c.**	**<0.1**	**0.1**	**<0.1**	**<0.1**	**<0.1**	**0.1**	**0.1**
Non-Extractable Residues	A	1.2	1.4	1.7	2.8	3.1	5.1	10.2	13.4
	B	1.4	1.5	1.8	2.9	3.0	5.1	9.5	14.1
	Mean	**1.3**	**1.5**	**1.7**	**2.9**	**3.1**	**5.1**	**9.9**	**13.8**
Total Recovery	A	97.6	99.0	99.0	100.1	98.3	98.0	101.0	94.8
	B	100.7	101.5	100.6	100.2	101.8	99.2	101.4	95.3
	Mean	**99.1**	**100.2**	**99.8**	**100.2**	**100.0**	**98.6**	**101.2**	**95.1**

n.d.: not detected, n.a.: not analysed, n.c.: not calculated, DAT: days after treatment

B. MATERIAL BALANCE

Mean material balances of radioactivity were in a range of 98.5 to 101.8% AR for soil Hoefchen am Hohenseh, from 97.7 to 101.3% AR for soil Laacherhof AXXa, from 101.2 to 105.9% AR for soil Laacherhof Wurmwiese and from 95.1 to 101.2% AR for soil Laacherhof AIIIa.

C. EXTRACTABLE AND NON-EXTRACTABLE RESIDUES

Total extractable residues significantly decreased from DAT-0 to DAT-121 from 99.7 to 73.2% AR in soil Hoefchen am Hohenseh, from 95.7 to 73.1% AR in soil Laacherhof AXXa, from 99.5 to 81.3% AR in soil Laacherhof Wurmwiese and from 97.9 to 65.1% AR in soil Laacherhof AIIIa.

Non-extractable residues (NER) significantly increased from DAT-0 to DAT-121 from 1.8 to 11.3% AR in soil Hoefchen am Hohenseh, from 2.0 to 10.8% AR in soil Laacherhof AXXa, from 2.3 to 10.1% AR in soil Laacherhof Wurmwiese and from 1.3 to 13.8% AR in soil Laacherhof AIIIa.

D. VOLATILIZATION

The maximum amount of carbon dioxide was 14.5, 13.9, 13.4 and 16.2% AR study end (DAT-121) in soil Hoefchen am Hohenseh, Laacherhof AXXa, Laacherhof Wurmwiese and Laacherhof AIIIa, respectively. Formation of volatile organic compounds was insignificant as demonstrated by values of ≤ 0.1% AR at all sampling intervals for all soils.

E. DEGRADATION OF TEST ITEM

The amount of fluopyram in the total soil extracts (i.e. in aqueous desorption solution and organic soil extracts) significantly decreased from DAT-0 to DAT-128 from 97.8 to 67.6% AR in soil Hoefchen am Hohenseh, from 93.5 to 66.7% AR in soil Laacherhof AXXa, from 97.7 to 76.1% AR in soil Laacherhof Wurmwiese and from 96.3 to 57.3% AR in soil Laacherhof AIIIa.

Degradation of fluopyram was accompanied by the formation of two degradation products, identified with the following maximum occurrence in at least one soil: fluopyram-7-hydroxy with 4.2% AR at DAT-62 in soil Laacherhof AIIIa and benzamide1.1% AR at DAT-30, DAT-62 and DAT-121 in soil Laacherhof AIIIa. Up to six very minor radioactive peaks (maximum concentration of 0.3% AR for a single peak) were detected. The total of unknown extracted radioactivity did not exceed 2.7% AR.

F. KINETICS

New kinetic calculations based on more recent guidance are necessary, therefore the information included in this study is not considered relevant. Evaluation of the rate of degradation is reported under KCA 7.1.2.1.1/09 (M-761966-01-1).

G. TIME-DEPENDENCE OF SORPTION

Results of the time-dependent sorption experiment can be found in KCA 7.1.3.2/02.

III. CONCLUSIONS

[Phenyl-UL-^{14}C]fluopyram moderately degraded in soil under aerobic conditions in the dark in the laboratory within the duration of the study.

Formation of carbon dioxide was significant (up to 16.2% AR) at study end. Formation of non-extractable residues (NER) was up to 13.8% AR at study end.

Degradation of fluopyram was accompanied by the formation of two degradation products, identified as fluopyram-7-hydroxy with a maximum occurrence of 4.2% AR at DAT-62 in soil Laacherhof AIIIa and benzamide with a maximum occurrence of 1.1% AR at DAT-30, DAT-62 and DAT-121 in soil Laacherhof AIIIa. Up to six minor radioactive peaks (maximum concentration of 0.3% AR for a single peak) were detected. The total of unknown extracted radioactivity did not exceed 2.7% AR.

The results of study indicate that sorption of fluopyram to soil increases with its residence time in soil, which should be acknowledged in mobility assessments. Since fluopyram was slowly degraded in soil when kept under aerobic lab conditions the TDS factor was well measurable over the entire study duration (see more details under section KCA 7.1.3.2/02).

3. Assessment and conclusion

Assessment and conclusion by applicant:
The study and its data are considered as valid and reliable for use in risk assessment.

Assessment and conclusion by RMS:
Outcome and conclusion of the study: RMS should indicate if they agree to the results and conclusions of the APPL.

1. Information on the study

Data Point:	KCA 7.1.1.1/03
Report Author:	[redacted]
Report Year:	2008
Report Title:	[Phenyl-UL-^{14}C] and [pyridyl-2,6-^{14}C]AE B656948: Aerobic soil metabolism in two US soils
Report No:	MEGME069-1
Document No:	M-299548-02-1
Guideline(s) followed in study:	US EPA: Pesticide Assessment Guidelines, Subdivision N, Section, 162-1: Aerobic Soil Metabolism Studies, 1982. US EPA OPPTS Guideline No. 835.4100
Deviations from current test guideline:	Current Guideline: OECD 307 (2002) None
Previous evaluation:	yes, evaluated and accepted DAR (2011)
GLP/Officially recognised testing facilities:	Yes, conducted under GLP/officially recognised testing facilities
Acceptability/Reliability:	Yes

2. Full summary of KCA 7.1.1.1/03

Executive Summary
The route and rate of degradation of [phenyl-UL-^{14}C] and [pyridyl-2,6-^{14}C]fluopyram was investigated in two US soils under aerobic conditions in the dark in the laboratory at 25 ± 1 °C and 75% of the water holding capacity at 1/3 bar for 365 days.

Soil	Source	Texture (USDA)	pH [1]	OC [%]
Springfield	Nebraska, USA	silty clay loam	6.5	1.7
Porterville	California, USA	sandy loam	7.9	0.5

[1] pH value was derived from aqueous 0.1 M $CaCl_2$ suspension (1:1)

The test was performed in flow-through test systems, consisting of flasks filled with soil and connected to a series of traps for collection of carbon dioxide and volatile organic compounds.

The application rate was 0.11-0.13 mg fluopyram/kg soil (dry weight), corresponding an intended maximum single field application rate of fluopyram of 250 g/ha (assuming incorporation into top 15 cm of soil and 1.5 g/cm^3 bulk density).

Duplicate samples from each system were processed and analysed at 0, 3, 7, 14, 30, 60, 91, 133, 167, 183, 273 and 365 days after treatment (DAT) for the Springfield soil and 0, 3, 7, 14, 30, 59, 90, 120, 150, 182, 272 and 365 DAT for the Porterville soil.

The volatile traps were assayed at each sampling interval to determine the amount of carbon dioxide and volatile organic compounds. The soil samples were extracted three times by shaking at ambient temperature with acetonitrile/water (80/20 v/v) and once using accelerated solvent extraction (ASE) at 80 °C with acetonitrile/water (9/1, v/v) in case the total radioactivity in the ambient soil extract was less than 90% of the total applied activity. Identification of the parent compound was accomplished by co-chromatography and liquid chromatography-electrospray ionization mass spectrometry (LC-ESI/MS).

In Springfield soil, the average material balance of radioactivity for the phenyl label ranged from 92.7 to 103.3% of the applied radioactivity (AR), for the pyridyl label, the range was 97.4 to 107.0% AR. In Porterville soil, the average material balance of radioactivity for the phenyl label ranged from 95.5 to 103.0% AR, for the pyridyl label, the range was 91.1 to 99.9% AR.

For the Springfield test systems, radioactive carbon dioxide increased from 0.5% AR at DAT-3 to 24.4% AR at DAT-273 (phenyl label) and from 0.8% AR at DAT-3 to 27.2% AR at DAT-365 (pyridyl label). For the Porterville test systems, radioactive carbon dioxide increased from 0.3% AR at DAT-3 to 9.4% AR at DAT-365 (phenyl label) and from 0.2% AR at DAT-3 to 14.0% AR at DAT-272 (pyridyl label). Other volatile components were insignificant with ≤0.1% AR.

For the Springfield test systems, the average extracted radioactive residues decreased from DAT-0 to DAT-365 from 97.4 to 60.8% AR in the phenyl label experiment and from 98.0 to 60.5% AR in the pyridyl label experiment. For the Porterville test systems, the average extracted radioactive residues decreased DAT-0 to DAT-365 from 99.3 to 80.2% AR in the phenyl label experiment and from 99.3 to 70.4% AR in the pyridyl label experiment.

For the Springfield test systems applied with the phenyl label, non-extractable residues (NER) increased from 2.6% AR at DAT-0 to 14.9% AR at DAT-273 and decreased then slightly to 14.1% AR at DAT-365. For the pyridyl label, NER increased in soil Springfield from 2.0% AR at DAT-0 to 14.7% AR at DAT-365. For the Porterville test systems applied with the phenyl label, NER increased from 0.7% AR at DAT-0 to 9.4% AR at DAT-272 and decreased then slightly to 9.0% AR at DAT-365. For the pyridyl label, NER increased in soil Porterville from 0.7% AR at day 0 to 10.6% AR at DAT-272 and decreased then slightly to 8.3% AR at DAT-365.

In Springfield soil, extractable fluopyram decreased from 96.3% AR at DAT-0 to 60.7% AR at DAT-365 in the phenyl label experiment and from 97.4% AR at DAT-0 to 60.3% AR at DAT-365 in the pyridyl label experiment. In Porterville soil, extractable fluopyram decreased from 98.9% AR at DAT-0 to 71.2% AR at DAT-365 (phenyl label) and from 98.5% AR at DAT-0 to 61.3% AR at DAT-365 (pyridyl label). The total unidentified residues amounted to a maximum of 1.7% AR and no single component exceeded 1.3% AR at any sampling interval in any soil.

I. MATERIALS AND METHODS

A. MATERIALS

1. Test Items

[phenyl-UL-^{14}C]AE C656948 (fluoypram)

Sample ID:	BECH 1910
Specific Activity:	3.85 MBq/mg
Radiochemical Purity:	98.5% (HPLC/radiodetection)
Chemical Purity:	>99.8% (unlabelled, HPLC UV 210 nm)

[pyridyl-2,6-^{14}C]AE C656948 (fluoypram)

Sample ID:	BECH1905
Specific Activity:	3.85 MBq/mg
Radiochemical Purity:	98.9% (HPLC/radiodetection)
Chemical Purity:	>99.8% (unlabelled, HPLC UV 210 nm)

2. Soil

Soil samples were collected freshly from the field. A few days before starting the test the air dried soils were sieved through a 2 mm sieve. The two soils used in this study are representative of agricultural soils. Soils were stored 4-6 °C for a maximum of 57 days prior use. Characteristics of the test soils are presented in the table below.

Table 7.1.1.1-11: Characteristics of test soils

Geographic Location	Springfield, Nebraska	Porterville, California
Pesticide use history	2000 -2003 Cyfluthrin	No application within past 5 years
Sampling depth	0 – 15/20 cm	0 – 20 cm
Soil preparation	2 mm sieve	
Texture Class (USDA)	Silty Clay Loam	Sandy Loam
Sand (%)	12.1	64.9
Silt (%)	55.9	20.8
Clay (%)	32.0	14.3
pH		
(soil/water 1:1)	7.0	8.3
(saturated paste)	6.9	8.1
(soil/0.1 M $CaCl_2$ 1:1)	6.5	7.9
Organic Matter (%) [1]	2.8	0.9
Organic Carbon (%)	1.7	0.5
Microbial Biomass (mg Microbial C/kg soil):		
Initial (Day 0)	404 [2]	96 [2]
Intermediate (Day 212)	234 [2]	66 [2]
Final (Day 365)	143 [3] /158 [2]	63 [3] /55 [2]
Cation Exchange Capacity (CEC)	18.7	11.5
Moisture Content (%)		
at 0.33 bar	28.3	14.6
at 0.1 bar	41.3	25.1
at 15 bar	16.6	5.9
MWHC [g /100 g dry soil] c)	43.1	31.1
Bulk Density (disturbed)(g/cm³)	1.13	1.14

DAT: days after treatment, DW: dry weight, USDA: United States Department of Agriculture, MWHC: Maximum Water Holding Capacity

[1] calculated as: OM [%] = OC [%] · 1.724

[2] Biomass samples not dosed with solvent

[3] Biomass samples dosed with solvent

B. STUDY DESIGN

1. Experimental conditions

For each soil, flow-through test systems were used, consisting of 250 mL Erlenmeyer flasks filled with 100 g of sieved soil (dry weight equivalents). The test vessels were connected to a series of traps containing 2 M KOH solution to collect carbon dioxide, ethylene glycol to collect volatile organic compounds or 1 M H_2SO_4 to trap alkaline compounds. Humidified air was continually drawn through the test systems. The moisture content of all the soils was adjusted to 75% of 1/3 bar water holding capacity and the test systems were placed in a dark, temperature controlled incubation chamber set to 25 ± 1 °C. The test systems were set up and pre-equilibrated for 6 days (Springfield) or 8 days (Porterville) prior to treatment.

The amount of fluopyram was targeted as 0.11 µg/g, corresponding to a field application rate of 250 g/ha. The test item was applied in methanol dropwise by an adjustable pipette. For the phenyl labeled fluopyram the final test item concentrations were 0.107 and 0.131 µg/g soil (dry weight) for the Porterville soil and Springfield soil, respectively. For the pyridyl labeled fluopyram the test concentration was 0.116 µg/g soil (dry weight) for both soils. After treatment, the soil was mixed gently by rotating the flask and the test systems were transferred to an environmental chamber and each system was attached to a series of volatile traps.

Test systems were incubated under aerobic conditions in the dark for 365 days at 25 ± 1°C and 75% of the water holding capacity at 1/3 bar.

2. Sampling
Duplicate test systems samples were collected at 0, 3, 7, 14, 30, 60, 91, 133, 157, 183, 273 and 365 days after treatment (DAT) for the Springfield soil and at 0, 3, 7, 14, 30, 59, 90, 120, 150, 182, 272 and 365 days after treatment for the Porterville soil. Volatile traps were analysed at each sampling interval. Ethylene glycol traps and the first KOH traps of all remaining test systems were replaced on DAT-141 in case of the Springfield soil. Biomass sampling intervals were on DAT-0, DAT-188 and DAT-365 for the Springfield soil and on day DAT-0, DAT-182 and DAT-365 in case of the Porterville soil.

3. Analytical procedures
At each interval, duplicate treated samples were collected. The entire samples was extracted on the sampling day. The ambient extraction was performed by shaking for 20 min with acetonitrile/water (80/20, v/v). After centrifugation, the solvent was decanted and filtered. This was repeated twice more, using 75 mL of CH_3CN/H_2O (80:20) and all extracts were combined prior to LSC measurement. If the total radioactivity in the ambient soil extract was less than 90% of the total applied activity, the soil was subjected to aggressive extraction with acetonitrile/water (9/1 v/v) at 80°C for 5 min in an ASE cell. The radioactivity in the aggressive extract was determined by LSC after separation of soil and extract as described before. The amount of volatiles and non-extractable residues was determined by LSC and combustion/LSC, respectively.

Quantitative HPLC measurement was performed after concentration for all ambient extracts and for aggressive extracts containing > 10% of applied radioactivity (% AR). The limit of quantification (LOQ) for the HPLC/radiodetection method was 1.0% AR.

Metabolite identification and characterization procedures were performed by HPLC co-chromatography using non-radioactive reference standards. Confirmation of the test item was performed by LC/ESI/MS.

II. RESULTS AND DISCUSSION

A. EXTRACTION AND DISTRIBUTION OF RADIOACTIVITY IN SOIL SAMPLES
Radioactive mass balance and distribution of [phenyl-UL-^{14}C] and [pyridyl-2,6-^{14}C]fluopyram and metabolites in soils Springfield and Porterville are summarised in Table 7.1.1.1-12 to Table 7.1.1.1-15.

Table 7.1.1.1-12: Degradation of [phenyl-UL-^{14}C]fluopyram in soil Springfield under aerobic conditions (expressed as percent of applied radioactivity)

Compound	Rep. No.	Days after treatment (DAT)											
		0	3	7	14	30	60	91	133	157	183	273	365
Fluopyram	A	96.0	95.4	89.2	76.6	74.6	75.8	68.4	77.1	70.2	69.8	60.1	59.0
	B	96.6	92.2	90.9	79.8	81.7	73.0	68.0	69.0	72.8	69.4	59.6	62.4
	Mean	**96.3**	**93.8**	**90.1**	**78.2**	**78.2**	**74.4**	**68.2**	**73.0**	**71.5**	**69.6**	**59.9**	**60.7**
Unknown A	A	0.2	0.6	0.6	0.9	0.8	0.0	0.0	0.0	0.0	0.0	0.2	0.0
	B	0.3	0.6	0.8	0.9	1.1	0.9	0.5	0.8	0.0	0.0	0.3	0.2
	Mean	**0.2**	**0.6**	**0.7**	**0.9**	**1.0**	**0.5**	**0.2**	**0.4**	**0.0**	**0.0**	**0.2**	**0.1**
Unknown B	A	0.3	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
	B	0.4	0.4	0.0	0.3	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
	Mean	**0.3**	**0.2**	**0.0**	**0.2**	**0.0**	**0.0**	**0.0**	**0.0**	**0.0**	**0.0**	**0.0**	**0.0**
Sum of Unidentified RA	A	1.1	0.6	0.6	0.9	0.8	0.0	0.0	0.0	0.0	0.0	0.2	0.0
	B	1.0	1.0	0.8	1.2	1.1	0.9	0.5	0.8	0.0	0.0	0.3	0.2
	Mean	**1.1** [1]	**0.8**	**0.7**	**1.0**	**1.0**	**0.5**	**0.2**	**0.4**	**0.0**	**0.0**	**0.2**	**0.1**
Ambient Extract	A	97.1	96.0	89.8	77.4	75.4	75.8	68.4	65.4	58.7	58.3	46.4	46.3
	B	97.6	93.2	91.7	81.0	82.8	73.8	68.5	59.6	60.8	57.8	46.3	49.6
	Mean	**97.4**	**94.6**	**90.8**	**97.2**	**79.1**	**74.9**	**68.5**	**62.5**	**59.8**	**58.1**	**46.4**	**47.9**
Aggressive Extract	A	ND	ND	ND	7.7	10.0	10.0	9.5	11.6	11.5	11.5	13.9	12.7
	B				7.7	8.8	10.7	10.4	10.1	12.0	11.6	13.6	13.0
	Mean				**7.7** [2]	**9.4** [2]	**10.4** [2]	**9.9** [2]	**10.9** [3]	**11.8** [3]	**11.6** [3]	**13.7** [3]	**12.9** [3]
Total Extractable RA	A	97.1	96.0	89.8	85.1	85.4	85.8	77.9	77.1	70.2	69.8	60.3	59.0
	B	97.6	93.2	91.7	88.6	91.6	84.7	78.9	69.7	72.9	69.4	59.9	62.6
	Mean	**97.4**	**94.6**	**90.8**	**86.9**	**88.5**	**85.2**	**78.4**	**73.4**	**71.5**	**69.6**	**60.1**	**60.8**
CO_2	A	ND	0.7	0.8	2.2	5.3	8.3	12.8	14.4	16.1	17.4	23.5	23.9
	B		0.4	0.9	2.2	4.8	8.7	11.5	14.3	16.5	16.6	25.3	19.3
	Mean		**0.5**	**0.8**	**2.2**	**5.1**	**8.5**	**12.2**	**14.3**	**16.3**	**17.0**	**24.4**	**21.6**
Volatile Organic Compounds	A	ND	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
	B		0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
	Mean		**0.0**	**0.0**	**0.0**	**0.0**	**0.0**	**0.0**	**0.0**	**0.0**	**0.0**	**0.0**	**0.0**
Non-extractable Residues	A	2.9	8.7	9.2	3.4	8.1	9.1	11.1	11.0	13.0	12.5	14.4	14.4
	B	2.4	7.6	9.2	3.8	6.4	9.1	9.8	11.0	13.4	13.5	15.3	13.8
	Mean	**2.6**	**8.2**	**9.2**	**3.6**	**7.3**	**9.1**	**10.5**	**11.0**	**13.2**	**13.0**	**14.9**	**14.1**
Material balance	A	100.0	105.4	99.9	90.8	98.9	103.2	101.8	102.5	99.3	99.8	98.2	97.3
	B	100.0	101.2	101.8	94.6	102.8	102.4	100.3	95.1	102.8	99.5	100.6	95.7
	Mean	**100.0**	**103.3**	**100.9**	**92.7**	**100.9**	**102.8**	**101.0**	**98.8**	**101.0**	**99.7**	**99.4**	**96.5**

DAT = days after treatment, ND = not done, RA = radioactivity
[1] Includes Unknown C, 0.5% (mean).
[2] Extracts not analysed
[3] Extracts were analysed. Characterized amounts are included above.

Table 7.1.1.1-13: Degradation of [pyridyl-2,6-^{14}C]fluopyram in soil Springfield under aerobic conditions (expressed as percent of applied radioactivity)

Compound	Rep. No.	Days after treatment (DAT)											
		0	3	7	14	30	60	91	133	157	183	273	365
Fluopyram	A	101.2	95.6	89.5	80.7	84.6	76.2	71.1	76.6	74.2	66.4	64.7	61.4
	B	93.7	89.0	89.8	83.5	86.2	77.9	70.0	76.7	72.2	70.1	61.7	59.3
	Mean	**97.4**	**92.3**	**89.6**	**82.1**	**85.4**	**77.1**	**70.5**	**76.7**	**73.2**	**68.2**	**63.2**	**60.3**
Unknown A	A	0.0	0.5	0.7	0.9	1.3	0.0	1.1	0.0	0.0	0.0	0.2	0.3
	B	0.3	0.6	0.7	1.0	1.1	0.0	0.6	0.0	0.0	0.0	0.0	0.0
	Mean	**0.1**	**0.6**	**0.7**	**0.9**	**1.2**	**0.0**	**0.8**	**0.0**	**0.0**	**0.0**	**0.1**	**0.1**
Unknown B	A	0.0	0.6	0.0	0.4	0.4	0.0	0.0	0.0	0.0	0.0	0.0	0.0
	B	0.4	0.0	0.0	0.5	0.4	0.0	0.0	0.0	0.0	0.0	0.0	0.0
	Mean	**0.2**	**0.3**	**0.0**	**0.4**	**0.4**	**0.0**	**0.0**	**0.0**	**0.0**	**0.0**	**0.0**	**0.0**
Sum of Unidentified RA	A	0.0	1.0	0.7	1.3	1.7	0.0	1.1	0.0	0.0	0.0	0.2	0.3
	B	1.0	0.6	0.7	1.5	1.5	0.0	0.6	0.0	0.0	0.0	0.0	0.0
	Mean	**0.5** [1]	**0.8**	**0.7**	**1.4**	**1.6**	**0.0**	**0.8**	**0.0**	**0.0**	**0.0**	**0.1**	**0.1**
Ambient Extract	A	101.2	96.6	90.2	81.9	86.3	76.2	72.2	64.7	61.7	52.9	50.4	47.6
	B	94.8	89.7	90.5	85.0	87.6	77.8	70.5	64.7	59.6	56.1	47.6	45.2
	Mean	**98.0**	**93.1**	**90.4**	**83.5**	**87.0**	**77.1**	**71.4**	**64.7**	**60.6**	**54.5**	**48.8**	**46.4**
Aggressive Extract	A	ND	ND	ND	7.4	8.0	11.3	11.3	11.9	12.6	13.5	14.6	14.1
	B				6.9	8.3	9.8	12.1	12.0	12.7	14.0	14.4	14.1
	Mean				7.1 [2]	8.2 [2]	10.5 [2]	11.7 [2]	12.0 [3]	12.6 [3]	13.7 [3]	14.5 [3]	14.1 [3]
Total Extractable RA	A	101.2	96.6	90.2	89.3	94.4	87.4	83.5	76.6	74.2	66.4	64.9	61.7
	B	94.8	89.7	90.5	91.9	96.0	87.6	82.7	76.7	72.2	70.1	61.7	59.3
	Mean	**98.0**	**93.1**	**90.4**	**90.6**	**95.2**	**87.6**	**83.1**	**76.7**	**73.2**	**68.2**	**63.3**	**60.5**
CO_2	A	ND	0.9	0.8	1.8	4.5	8.3	11.5	14.5	19.0	18.8	24.2	25.0
	B		0.8	0.8	1.7	4.5	7.3	12.7	14.0	17.7	19.2	23.5	29.4
	Mean		**0.8**	**0.8**	**1.7**	**4.5**	**7.8**	**12.1**	**14.3**	**18.3**	**19.0**	**23.9**	**27.2**
Volatile Organic Compounds	A	ND	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
	B		0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.1
	Mean		**0.0**	**0.0**	**0.0**	**0.0**	**0.0**	**0.0**	**0.0**	**0.0**	**0.0**	**0.0**	**0.1**
Non-extractable Residues	A	2.0	7.0	9.5	4.9	7.3	9.6	10.2	11.9	14.0	14.3	13.0	14.3
	B	2.0	7.0	11.3	5.1	7.4	9.1	10.1	11.4	13.3	13.2	14.2	15.1
	Mean	**2.0**	**7.0**	**10.4**	**5.0**	**7.3**	**9.4**	**10.2**	**11.6**	**13.7**	**13.8**	**13.6**	**14.7**
Material balance	A	103.2	104.5	100.6	96.0	106.2	105.4	105.3	103.2	107.3	99.5	102.2	101.0
	B	96.8	97.5	102.6	98.7	107.9	104.2	105.5	102.1	103.2	102.5	99.5	103.9
	Mean	**100.0**	**101.0**	**101.6**	**97.4**	**107.0**	**104.8**	**105.4**	**102.6**	**105.2**	**101.0**	**100.8**	**102.4**

DAT = days after treatment, ND = not done, RA = radioactivity
[1] Includes Unknown C, 0.2% (mean).
[2] Extracts not analysed.
[3] Extracts were analysed. Characterized amounts are included above.

Table 7.1.1.1-14: Degradation of [phenyl-UL-^{14}C]fluopyram in soil Porterville under aerobic conditions (expressed as percent of applied radioactivity)

Compound	Rep. No.	Days after treatment (DAT)											
		0	3	7	14	30	59	90	120	150	182	272	365
Fluopyram	A	99.7	98.0	96.9	90.9	87.6	91.2	86.6	85.9	82.2	78.9	73.2	71.0
	B	98.2	98.5	100.2	97.6	88.4	94.2	91.8	80.6	82.0	79.7	78.3	71.4
	Mean	**98.9**	**98.2**	**98.6**	**94.2**	**88.0**	**92.7**	**89.2**	**83.2**	**82.1**	**79.3**	**75.8**	**71.2**
Unknown A	A	0.0	1.2	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
	B	0.7	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
	Mean	**0.4**	**0.6**	**0.0**	**0.0**	**0.0**	**0.0**	**0.0**	**0.0**	**0.0**	**0.0**	**0.0**	**0.0**
Unknown B	A	0.0	0.4	0.3	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.6	0.0
	B	0.0	0.0	0.3	0.8	0.0	0.0	0.0	0.0	0.0	0.0	0.6	0.0
	Mean	**0.0**	**0.2**	**0.3**	**0.4**	**0.0**	**0.0**	**0.0**	**0.0**	**0.0**	**0.0**	**0.6**	**0.0**
Sum of Unidentified RA	A	0.0	1.6	0.3	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.6	0.0
	B	0.7	0.0	0.3	0.8	0.0	0.0	0.0	0.0	0.0	0.0	0.6	0.0
	Mean	**0.4**	**0.8**	**0.3**	**0.4**	**0.0**	**0.0**	**0.0**	**0.0**	**0.0**	**0.0**	**0.6**	**0.0**
Ambient Extract	A	99.7	99.6	97.2	90.9	87.6	91.2	86.6	85.9	82.2	78.9	73.9	71.0
	B	98.9	98.5	100.5	98.4	88.4	94.2	91.8	80.6	82.0	79.7	78.9	71.4
	Mean	**99.3**	**99.0**	**98.9**	**94.6**	**88.0**	**92.7**	**89.2**	**83.2**	**82.1**	**79.3**	**76.4**	**71.2**
Aggressive Extract [1]	A	ND	ND	ND	ND	ND	3.2	3.2	3.1	3.0	3.8	5.9	8.9
	B						2.5	2.2	3.6	3.3	3.8	5.6	9.1
	Mean						**2.8**	**2.7**	**3.3**	**3.1**	**3.8**	**5.7**	**9.0**
Total Extractable RA	A	99.7	99.6	97.2	90.9	87.6	94.5	89.8	88.9	85.2	82.7	79.7	79.9
	B	98.9	98.5	100.5	98.4	88.4	96.6	94.1	84.2	85.3	83.5	84.4	80.5
	Mean	**99.3**	**99.0**	**98.9**	**94.6**	**88.0**	**95.6**	**91.9**	**86.6**	**85.2**	**83.1**	**82.1**	**80.2**
CO_2	A	ND	0.3	0.5	0.8	0.3	2.9	4.1	3.4	5.2	6.8	8.0	9.7
	B		0.3	0.6	0.5	1.5	2.9	2.9	4.9	4.9	6.6	5.6	9.1
	Mean		**0.3**	**0.6**	**0.6**	**0.9**	**2.9**	**3.5**	**4.1**	**5.1**	**6.7**	**6.8**	**9.4**
Volatile Organic Compounds	A	ND	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.2	0.0	0.0	0.1
	B		0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.1	0.0	0.0	0.0
	Mean		**0.0**	**0.0**	**0.0**	**0.0**	**0.0**	**0.0**	**0.0**	**0.1**	**0.0**	**0.0**	**0.1**
Non-extractable Residues	A	0.7	2.0	2.5	4.3	6.9	5.0	7.2	6.5	6.5	8.8	9.5	9.0
	B	0.7	2.1	2.9	4.8	6.2	4.0	4.9	7.4	6.6	7.7	9.3	9.1
	Mean	**0.7**	**2.1**	**2.7**	**4.5**	**6.6**	**4.5**	**6.1**	**7.0**	**6.5**	**8.3**	**9.4**	**9.0**
Material balance	A	100.4	101.9	100.3	95.9	94.8	102.4	101.1	98.8	97.1	98.4	97.2	98.7
	B	99.6	100.9	104.0	103.7	96.2	103.6	102.0	96.6	96.9	97.8	99.3	98.8
	Mean	**100.0**	**101.4**	**102.1**	**99.8**	**95.5**	**103.0**	**101.5**	**97.7**	**97.0**	**98.1**	**98.3**	**98.7**

DAT = days after treatment, ND = not done, RA = radioactivity
[1] Extracts not analysed

Table 7.1.1.1-15: Degradation of [pyridyl-2,6-^{14}C]fluopyram in soil Porterville under aerobic conditions (expressed as percent of applied radioactivity)

Compound	Rep. No.	Days after treatment (DAT)											
		0	3	7	14	30	59	90	120	150	182	272	365
Fluopyram	A	98.0	99.0	90.7	86.7	89.6	80.9	86.0	77.1	81.4	79.4	68.5	67.5
	B	99.0	94.1	87.7	88.0	87.9	85.7	86.9	80.8	78.4	77.3	54.3	55.2
	Mean	**98.5**	**96.5**	**89.2**	**87.4**	**88.7**	**83.3**	**86.5**	**78.9**	**79.9**	**78.3**	**61.4**	**61.3**
Unknown A	A	0.3	0.4	1.7	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
	B	0.0	0.7	0.8	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.5	0.0
	Mean	**0.2**	**0.6**	**1.3**	**0.0**	**0.0**	**0.0**	**0.0**	**0.0**	**0.0**	**0.0**	**0.3**	**0.0**
Unknown B	A	0.4	0.0	0.5	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.5	0.0
	B	0.4	0.5	0.4	0.5	0.0	0.0	0.0	0.0	0.0	0.0	0.8	0.0
	Mean	**0.4**	**0.3**	**0.4**	**0.3**	**0.0**	**0.0**	**0.0**	**0.0**	**0.0**	**0.0**	**0.7**	**0.0**
Sum of Unidentified RA	A	1.1	0.4	2.2	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.5	0.0
	B	0.4	1.3	1.2	0.5	0.0	0.0	0.0	0.0	0.0	0.0	1.3	0.0
	Mean	**0.8** [1]	**0.8**	**1.7**	**0.3**	**0.0**	**0.0**	**0.0**	**0.0**	**0.0**	**0.0**	**0.9**	**0.0**
Ambient Extract	A	99.1	99.4	92.9	86.7	89.6	80.9	86.0	77.1	81.4	79.4	69.1	67.5
	B	99.4	95.3	88.8	88.6	87.9	85.7	86.9	80.8	78.4	77.3	55.6	55.2
	Mean	**99.3**	**97.4**	**90.9**	**87.6**	**88.7**	**83.3**	**86.5**	**78.9**	**79.9**	**78.3**	**62.3**	**61.3**
Aggressive Extract [2]	A	ND	ND	ND	ND	ND	2.8	2.3	3.8	3.6	3.9	5.1	7.9
	B						2.9	2.2	3.6	3.3	4.3	7.3	10.2
	Mean						**2.9**	**2.3**	**3.7**	**3.4**	**4.1**	**6.2**	**9.1**
Total Extractable RA	A	99.1	99.4	92.9	86.7	89.6	83.7	88.3	80.9	85.0	83.3	74.2	75.4
	B	99.4	95.3	88.9	88.6	87.9	88.6	89.2	84.4	81.7	81.6	62.9	65.4
	Mean	**99.3**	**97.4**	**90.9**	**87.6**	**88.7**	**86.2**	**88.8**	**82.7**	**83.3**	**82.4**	**68.5**	**70.4**
CO_2	A	ND	0.2	0.4	0.6	1.0	2.9	3.6	4.8	5.4	6.6	11.6	9.8
	B		0.2	0.4	0.6	1.3	2.1	3.6	5.1	5.3	6.4	16.3	15.0
	Mean		**0.2**	**0.4**	**0.6**	**1.2**	**2.5**	**3.6**	**4.9**	**5.4**	**6.5**	**14.0**	**12.4**
Volatile Organic Compounds	A	ND	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.1	0.0	0.0	0.0
	B		0.0	0.0	0.0	0.0	0.0	0.0	0.1	0.0	0.0	0.0	0.0
	Mean		**0.0**	**0.0**	**0.0**	**0.0**	**0.0**	**0.0**	**0.0**	**0.1**	**0.0**	**0.0**	**0.0**
Non-extractable Residues	A	0.8	1.3	3.5	4.1	4.7	4.5	4.6	6.3	6.2	7.2	9.4	6.7
	B	0.6	1.6	2.7	4.1	4.8	4.8	4.9	6.0	6.0	6.3	11.8	9.9
	Mean	**0.7**	**1.4**	**3.1**	**4.1**	**4.7**	**4.7**	**4.8**	**6.2**	**6.1**	**6.8**	**10.6**	**8.3**
Material Balance	A	99.9	100.9	96.8	91.4	95.3	91.1	96.5	92.1	96.8	97.2	95.2	91.9
	B	100.0	97.1	92.0	93.2	94.0	95.6	97.7	95.6	93.0	94.3	91.0	90.2
	Mean	**99.9**	**99.0**	**94.4**	**92.3**	**94.6**	**93.3**	**97.1**	**93.8**	**94.9**	**95.7**	**93.1**	**91.1**

DAT = days after treatment, ND = not done, RA = radioactivity
[1] Includes Unknown C, 0.2% (mean).
[2] Extracts not analysed

B. MATERIAL BALANCE

In Springfield soil, the average material balance of radioactivity ranged from 92.7 to 103.3% of the applied radioactivity (AR) for the phenyl label and from 97.4 to 107.0% AR for the pyridyl label. In Porterville soil, the average material balance of radioactivity ranged from 95.5 to 103.0% AR for the phenyl label and from 91.1 to 99.9% AR for the pyridyl label.

C. EXTRACTABLE AND NON-EXTRACTABLE RESIDUES

For the Springfield test systems, the average extracted radioactive residues decreased from DAT-0 to DAT-365 from 97.4 to 60.8% AR in the phenyl label experiment and from 98.0 to 60.5% AR in the pyridyl label experiment. For the Porterville test systems, the average extracted radioactive residues decreased DAT-0 to DAT-365 from 99.3 to 80.2% AR in the phenyl label experiment and from 99.3 to 70.4% AR in the pyridyl label experiment.

For the Springfield test systems applied with the phenyl label, non-extractable residues (NER) increased from 2.6% AR at DAT-0 to 14.9% AR at DAT-273 and decreased then slightly to 14.1% AR at DAT-365. For the pyridyl label, NER increased in soil Springfield from 2.0% AR at DAT-0 to 14.7% AR at DAT-365. For the Porterville test systems applied with the phenyl label, NER increased from 0.7% AR at DAT-0 to 9.4% AR at DAT-272 and decreased then slightly to 9.0% AR at DAT-365. For the pyridyl label, NER increased in soil Porterville from 0.7% AR at day 0 to 10.6% AR at DAT-272 and decreased then slightly to 8.3% AR at DAT-365.

D. VOLATILE RADIOACTIVITY

For the Springfield test systems, radioactive carbon dioxide increased from 0.5% AR at DAT-3 to 24.4% AR at DAT-273 (phenyl label) and from 0.8% AR at DAT-3 to 27.2% AR at DAT-365 (pyridyl label). For the Porterville test systems, radioactive carbon dioxide increased from 0.3% AR at DAT-3 to 9.4% AR at DAT-365 (phenyl label) and from 0.2% AR at DAT-3 to 14.0% AR at DAT-272 (pyridyl label). Other volatile components were insignificant with ≤0.1% AR.

E. TRANSFORMATION OF THE TEST ITEM

In Springfield soil, extractable fluopyram decreased from 96.3% AR at DAT-0 to 60.7% AR at DAT-365 in the phenyl label experiment and from 97.4% AR at DAT-0 to 60.3% AR at DAT-365 in the pyridyl label experiment. In Porterville soil, extractable fluopyram decreased from 98.9% AR at DAT-0 to 71.2% AR at DAT-365 (phenyl label) and from 98.5% AR at DAT-0 to 61.3% AR at DAT-365 (pyridyl label). The total unidentified residues amounted to a maximum of 1.7% AR and no single component exceeded 1.3% AR at any sampling interval in any soil.

F. KINETICS

New kinetic calculations based on more recent guidance are necessary, therefore the information included in this study is not considered relevant. Evaluation of the rate of degradation is reported under KCA 7.1.2.1.1/10 (M-761880-01-1).

III. CONCLUSIONS

Fluopyram was slowly degraded in aerobic soil in the dark in the laboratory. Only very low amounts of transient degradation products were observed, which were either mineralised or integrated into the soil matrix as non-extractable residues.

3. Assessment and conclusion

Assessment and conclusion by applicant:
The study and its data are considered as valid and reliable for use in risk assessment.

Assessment and conclusion by RMS:
Outcome and conclusion of the study: RMS should indicate if they agree to the results and conclusions of the APPL.

1. Information on the study

Data Point:	KCA 7.1.1.1/04
Report Author:	[redacted]
Report Year:	2020
Report Title:	Amendment no. 01: Rate of degradation of [phenyl-ul-14C]-fluopyram in brazilian soils
Report No:	1962-BS120-135-08
Document No:	M-349303-02-1
Guideline(s) followed in study:	OECD - Guideline for the Testing of Chemicals, Method 307 "Aerobic and anaerobic transformation in soil" (Adopted: 24th April 2002)
Deviations from current test guideline:	Current Guideline: OECD 307 (2002) The cation exchange capacity is not reported. In the experimental set-up up to six flasks were connected to the same trapping system.
Previous evaluation:	No, not previously submitted
GLP/Officially recognised testing facilities:	Yes, conducted under GLP/Officially recognised testing facilities
Acceptability/Reliability:	Yes

2. Full summary of KCA 7.1.1.1/04

Executive Summary

The degradation of [phenyl-UL-^{14}C]fluopyram was investigated in four soils under aerobic conditions in the dark in the laboratory for 119 days at 19.9 °C (mean over duration) and soil moisture of about 40 % of the maximum water holding capacity.

Soil	Source	Texture (USDA)	pH [1]	OC [%]
Argissolo	Piracicaba, Brazil	Clay	5.9	2.6
Latossolo	Veranópolis, Brazil	Clay	4.6	1.6
Neossolo	Osório, Brazil	Sandy loam	5.1	0.9
Gleissolo	Viamão, Brazil	Clay loam	3.9	10.1

[1] in H_2O

The amount of fluopyram for the treatment of the soil was comparatively high, i.e. 0.94 mg/kg soil, corresponding to an application rate of 250 g/ha (assuming incorporation into top 1.8 cm of soil and 1.5 g/cm^3 bulk density, only).

Duplicate test systems were processed and analysed 0, 7, 14, 28, 63, 91 and 119 days after treatment (DAT).

Mean material balances of radioactivity were 100.1 % AR for soil Argissolo (range from 94.1 to 108.8 % AR), 99.3 % AR for soil Latossolo (range from 97.0 to 103.8 % AR), 98.1 % AR for soil Neossolo (95.1 to 101.1 % AR) and 96.1 % AR for soil Gleissolo (92.6 to 99.8 % AR).

The maximum amount of carbon dioxide was 2.6, 4.9, 5.9 and 2.1 % AR at study end (DAT-119) in soil Argissolo, Latossolo, Neossolo and Gleissolo, respectively. Formation of volatile organic compounds (VOC) was insignificant as demonstrated by values below the limit of quantitation (0.133 µg, 0.25 % AR) at all sampling intervals for all soils.

Total extractable residues decreased from DAT-0 to DAT-119 from 100.0 to 92.4 % AR in soil Argissolo, from 98.9 to 88.3 % AR in soil Latossolo, from 100.5 to 87.4 % AR in soil Neossolo and from 96.2 to 91.9 % AR in soil Gleissolo.

Non-extractable residues (NER) at the end of the study reached values of 4.7, 7.5, 3.8 and 4.4 % AR for soils Argissolo, Latossolo, Neossolo and Gleissolo, respectively.

The amount of fluopyram in the total soil extracts (ambient and soxhlet) decreased from DAT-0 to DAT-119 from 96.21 to 91.01 % AR in soil Agrissolo, from 95.72 to 86.20 % AR in soil Latossolo, from 97.98 to 76.79 % AR in soil Neossolo and from 90.84 to 86.32 % AR in soil Gleissolo.

Weak degradation of fluopyram was accompanied by the formation of two degradation products. Fluopyram-7-hydroxy reached maximum values of 2.10, 2.37, 10.28 and 4.42 % AR in soils Argissolo, Latossolo, Neossolo and Gleissolo, respectively. Fluopyram-benzamide reached maximum values of 3.79, 1.38, 2.97 and 5.39 % AR in soils Argissolo, Latossolo, Neossolo and Gleissolo, respectively. Fluopyram-Benzamide never exceeded 5% of AR in two subsequent intervals and did not indicate an increasing trend to the end of study.

The degradation of floupyram was calculated according to single first order (SFO) kinetics. The DT_{50} values for fluopyram under aerobic conditions in the dark at a temperature of 20 ± 2 °C were 365 days in all soils.

I. MATERIALS AND METHODS

A. MATERIALS

1. Test Item

[phenyl-UL-^{14}C]fluopyram	
Batch No	KATH 6093
Specific activity	5.85 MBq/mg
Radiochemical purity	98.56%

2. Test Soils

The soils were sampled freshly from the field (upper horizon of 0 to 20 cm). The soil moisture content was adjusted to about 40 % of the maximum water holding capacity (MWHC) of the soils. The soils were taken from agricultural areas representing different Brazilian origins and different soil properties. Soil characteristics are summarized in the table below.

Table 7.1.1.1- 16: Physico-chemical properties of test soils

Soil Designation	Argissolo	Latossolo	Neossolo	Gleissolo
Geographic Location				
City	Piracicaba	Veranópolis	Osório	Viamão
State	São Paulo	Rio Grande do Sul	Rio Grande do Sul	Rio Grande do Sul
Country	Brazil	Brazil	Brazil	Brazil
Soil batch	A03-08	L01-08	N02-08	G02-08
Textural Class (USDA)	Clay	Clay	Sandy loam	Clay loam
Sand [%] [50 µm – 2 mm]	36	22	81	35
Silt [%] [2 µm – 50 µm]	22	22	4	34
Clay [%] [< 2 µm]	42	56	15	31
pH (H_2O)	5.9	4.6	5.1	3.9
Organic Carbon (combustion) (%)	2.6	1.6	0.9	10.1
Organic Matter (%)	4.5	2.7	1.5	17.4
Water Holding Capacity maximum (g water/g dried soil)	0.61	0.76	0.48	1.03
40 % maximum water holding capacity (g water/g dried soil)	0.24	0.30	0.19	0.41
Microbial Biomass (µg glucose/g soil)				
DAT-0	18.0	23.0	24.0	22.5
DAT-119	15.9	21.3	20.0	25.5

USDA: United States Department of Agriculture, DAT: days after treatment, DW: dry weight

B. STUDY DESIGN

1. Experimental Conditions

Flow-through test systems were used, consisting of 300 mL (for Argissolo, Latossolo and Neossolo soil) or 500 mL (for Gleissolo soil) Erlenmeyer flasks filled with soil and connected to an open air flow trapping system for collection of carbon dioxide and volatile organic compounds.

Portions of 60 g of the soil (dry weight) were weighed into each tube. The soils were ventilated continuously with moistened air. The amount of fluopyram for the treatment of the soil was comparatively high, i.e. 0.94 mg/kg soil, corresponding to an application rate of 250 g/ha (assuming incorporation into top 1.8 cm of soil and 1.5 g/cm³ bulk density, only). The application solution was prepared in methanol/water (1/4, v/v). The flasks were treated with 600 µL of the application solution and the applied amounts were uniformly spread on the surface.

The test systems were incubated under aerobic conditions in the dark for 119 days at 20 ± 2 °C and a soil moisture of about 40 % of the maximum water holding capacity.

2. Sampling

Seven sampling intervals were distributed over the entire incubation period of 119 days. Duplicate test systems were processed and analysed 0, 7, 14, 28, 63, 91 and 119 days after treatment (DAT).
Microbial soil biomass was determined at DAT-0 and at the end of the study.

3. Analytical Procedures

At each sampling interval, two Erlenmeyer flasks from each soil were removed from incubation and the soil was transferred into centrifugation flasks. The radioactivity in the trap solutions was measured by LSC. Since the volatiles represent the cumulative amount for several samples purged through the same trapping system, the measured radioactivity was divided by the number of flasks in the line.

Each soil was sequentially extracted four times at ambient temperature and once by soxhlet. Extractions were performed using a mechanical shaker. Extraction solvents were: Acetonitrile/water (30:70, 200 mL, 60 min), Acetonitrile/water (50:50, 100 mL, 30 min), Acetonitrile/water (80:20, 100 mL, 30 min), Acetonitrile (100 mL, 30 min) and Acetonitrile/water (80:20, 150 mL, 3 hours, soxhlet).

After each extraction, the suspensions were centrifuged for 10 min and the supernatant were transferred into a volumetric flask. Aliquots were measured by liquid scintillation counting (LSC) for radioactivity. Extracts were combined (soxhlet was treated separately) and concentrated about 20-fold. Non-extractable residues were determined by combustion/LSC.

The limit of detection (LOD) for the LSC method was 0.31 % AR for the extractables, 0.56 % AR for soil combustion, 0.17 % AR for volatiles and 0.08 % AR for $^{14}CO_2$.

The quantification of the test item and the degradation products in the soil extracts was performed by HPLC. Degradation products were identified by co-chromatography with reference items.

II. RESULTS AND DISCUSSION

A. EXTRACTION AND DISTRIBUTION OF RADIOACTIVITY IN SOIL SAMPLES

Table 7.1.1.1-17 to Table 7.1.1.1-20 summarize the degradation of [phenyl-UL-^{14}C]fluopyram as a function of time.

Table 7.1.1.1-17: Degradation of fluopyram in soil Argissolo under aerobic conditions (expressed as percent of applied radioactivity)

Compound	Replicate No.	DAT 0	7	14	28	63	91	119
Fluopyram	1	95.74	95.11	91.81	93.54	92.34	88.74	87.44
	2	96.68	86.35	93.57	91.29	94.36	96.65	94.58
	Mean	**96.21**	**90.73**	**92.69**	**92.41**	**93.35**	**92.70**	**91.01**
Fluopyram-7-hydroxy	1	n.d.	n.d.	1.87	1.73	1.90	1.32	1.20
	2	n.d.	0.83	1.49	2.47	1.09	2.28	1.15
	Mean	**n.c.**	**0.83**	**1.68**	**2.10**	**1.50**	**1.80**	**1.17**
Fluopyram-benzamide	1	3.80	n.d.	1.20	0.33	n.d.	2.11	0.14
	2	3.79	1.16	1.39	0.07	n.d.	0.81	0.25
	Mean	**3.79**	**1.16**	**1.30**	**0.20**	**n.c.**	**1.46**	**0.20**
Total Extractable Residues	1	99.5	95.1	94.9	95.6	94.2	92.4	88.8
	2	100.5	92.3	96.5	93.8	95.5	99.8	96.0
	Mean	**100.0**	**93.7**	**95.7**	**94.7**	**94.8**	**96.1**	**92.4**
Carbon Dioxide	1	n.a.	0.8	1.3	1.3	2.0	2.3	2.6
	2	n.a.	0.9	1.3	1.3	2.1	2.4	2.7
	Mean	**n.c.**	**0.8**	**1.3**	**1.3**	**2.0**	**2.4**	**2.6**
Volatile Organic Compounds	1	n.a.	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
	2	n.a.	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
	Mean	**n.c.**	**<LOQ**	**<LOQ**	**<LOQ**	**<LOQ**	**<LOQ**	**<LOQ**
Non-Extractable Residues	1	<LOQ	0.9	1.6	4.7	5.0	9.9	5.3
	2	<LOQ	0.9	1.2	2.5	3.0	6.6	4.1
	Mean	**<LOQ**	**0.9**	**1.4**	**3.6**	**4.0**	**8.2**	**4.7**
Total Recovery	1	99.5	96.9	97.8	101.6	101.2	104.6	96.7
	2	100.5	94.1	99.0	97.7	100.6	108.8	102.8
	Mean	**100.0**	**95.5**	**98.4**	**99.6**	**100.9**	**106.7**	**99.7**

n.d.: not detected, n.a.: not analyzed, n.c.: not calculated, DAT: days after treatment

Table 7.1.1.1-18: Degradation of fluopyram in soil Latossolo under aerobic conditions (expressed as percent of applied radioactivity)

Compound	Replicate No.	DAT 0	7	14	28	63	91	119
Fluopyram	1	97.74	93.46	93.68	93.42	90.60	87.06	91.30
	2	93.70	90.57	91.27	92.51	91.11	90.72	81.09
	Mean	**95.72**	**92.01**	**92.48**	**92.97**	**90.86**	**88.89**	**86.20**
Fluopyram-7-hydroxy	1	1.27	1.84	1.36	2.82	2.36	2.27	2.48
	2	2.28	2.76	0.71	1.88	2.38	1.93	1.57
	Mean	**1.78**	**2.30**	**1.04**	**2.35**	**2.37**	**2.10**	**2.03**
Fluopyram-benzamide	1	0.95	0.38	0.87	n.d.	0.31	n.d.	n.d.
	2	1.81	0.82	1.74	n.d.	n.d.	n.d.	0.06
	Mean	1.38	0.60	1.30	**n.c.**	0.31	**n.c.**	0.06
Total Extractable Residues	1	100.0	95.7	95.9	96.2	93.3	89.3	93.8
	2	97.8	96.5	93.7	94.4	93.5	92.7	82.7
	Mean	**98.9**	**96.1**	**94.8**	**95.3**	**93.4**	**91.0**	**88.3**
Carbon Dioxide	1	n.a.	0.9	1.5	1.5	3.2	3.9	4.4
	2	n.a.	0.8	1.3	1.3	3.5	4.5	5.4
	Mean	**n.c.**	**0.9**	**1.4**	**1.4**	**3.4**	**4.2**	**4.9**
Volatile Organic Compounds	1	n.a.	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
	2	n.a.	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
	Mean	**n.c.**	**<LOQ**	**<LOQ**	**<LOQ**	**<LOQ**	**<LOQ**	**<LOQ**
Non-Extractable Residues	1	<LOQ	2.0	1.7	2.2	3.0	3.8	5.7
	2	<LOQ	2.0	2.0	2.2	3.0	4.8	9.4
	Mean	**<LOQ**	**2.0**	**1.9**	**2.2**	**3.0**	**4.3**	**7.5**
Total Recovery	1	100.0	98.6	99.1	100.0	99.4	97.1	103.8
	2	97.8	99.3	97.0	98.0	100.0	102.0	97.5
	Mean	**98.9**	**98.9**	**98.1**	**99.0**	**99.7**	**99.5**	**100.7**

n.d.: not detected, n.a.: not analyzed, n.c.: not calculated, DAT: days after treatment

Table 7.1.1.1-19: Degradation of fluopyram in soil Neossolo under aerobic conditions (expressed as percent of applied radioactivity)

Compound	Replicate No.	DAT 0	7	14	28	63	91	119
Fluopyram	1	97.65	90.42	90.60	87.82	84.14	79.33	76.81
	2	98.32	87.90	84.84	79.48	82.23	79.78	76.77
	Mean	**97.98**	**88.30**	**87.72**	**83.65**	**83.18**	**79.55**	**76.79**
Fluopyram-7-hydroxy	1	1.03	2.37	5.18	6.44	4.38	9.48	9.74
	2	n.d.	4.09	6.02	12.69	9.15	11.08	10.82
	Mean	**1.03**	**3.23**	**5.60**	**9.57**	**6.76**	**10.28**	**10.28**
Fluopyram-benzamide	1	1.19	1.08	1.26	1.70	n.d.	0.20	0.49
	2	2.78	2.44	0.93	4.23	0.32	n.d.	0.15
	Mean	**1.99**	**1.76**	**1.09**	**2.97**	**0.32**	**0.20**	**0.32**
Total Extractable Residues	1	99.9	93.9	97.0	96.0	88.5	89.0	87.0
	2	101.1	94.4	91.8	96.4	91.7	90.7	87.7
	Mean	**100.5**	**94.2**	**94.4**	**96.2**	**90.1**	**89.8**	**87.4**
Carbon Dioxide	1	n.a.	1.2	2.1	2.1	4.7	5.5	6.5
	2	n.a.	1.4	2.6	2.6	3.8	4.7	5.3
	Mean	**n.c.**	**1.3**	**2.3**	**2.4**	**4.3**	**5.1**	**5.9**
Volatile Organic Compounds	1	n.a.	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
	2	n.a.	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
	Mean	**n.c.**	**<LOQ**	**<LOQ**	**<LOQ**	**<LOQ**	**<LOQ**	**<LOQ**
Non-Extractable Residues	1	<LOQ	<LOQ	1.3	1.2	2.2	3.3	3.2
	2	<LOQ	<LOQ	1.3	1.5	3.5	3.8	4.5
	Mean	**<LOQ**	**<LOQ**	**1.3**	**1.3**	**2.9**	**3.6**	**3.8**
Total Recovery	1	99.9	95.1	100.4	99.2	95.5	97.8	96.7
	2	101.1	95.8	95.5	100.5	99.0	99.2	97.6
	Mean	**100.5**	**95.4**	**98.0**	**99.9**	**97.2**	**98.5**	**97.1**

n.d.: not detected, n.a.: not analyzed, n.c.: not calculated, DAT: days after treatment

Table 7.1.1.1-20: Degradation of fluopyram in soil Gleissolo under aerobic conditions (expressed as percent of applied radioactivity)

Compound	Replicate No.	DAT 0	7	14	28	63	91	119
Fluopyram	1	89.31	87.19	87.82	88.67	84.87	89.23	87.93
	2	92.36	80.16	88.78	89.73	90.52	85.19	84.70
	Mean	**90.84**	**83.68**	**88.30**	**89.20**	**87.70**	**87.21**	**86.32**
Fluopyram-7-hydroxy	1	n.d.	3.17	3.85	3.00	6.85	1.21	5.74
	2	n.d.	4.73	1.11	3.56	1.99	2.83	3.06
	Mean	**n.c.**	**3.95**	**2.48**	**3.28**	**4.42**	**2.02**	**4.40**
Fluopyram-benzamide	1	5.31	5.11	1.44	n.d.	n.d.	n.d.	n.d.
	2	5.47	3.77	0.71	n.d.	n.d.	n.d.	2.37
	Mean	**5.39**	**4.44**	**1.08**	**n.c.**	**n.c.**	**n.c.**	**2.37**
Total Extractable Residues	1	94.6	95.5	93.3	91.7	91.7	90.4	93.7
	2	97.8	97.6	90.6	93.3	92.5	88.0	90.1
	Mean	**96.2**	**96.5**	**91.9**	**92.5**	**92.1**	**89.2**	**91.9**
Carbon Dioxide	1	n.a.	0.6	0.9	0.9	1.6	1.9	2.2
	2	n.a.	0.7	1.1	1.1	1.6	1.9	2.0
	Mean	**n.c.**	**0.6**	**1.0**	**1.0**	**1.6**	**1.9**	**2.1**
Volatile Organic Compounds	1	n.a.	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
	2	n.a.	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
	Mean	**n.c.**	**<LOQ**	**<LOQ**	**<LOQ**	**<LOQ**	**<LOQ**	**<LOQ**
Non-Extractable Residues	1	2.2	0.9	<LOQ	<LOQ	1.7	3.7	3.9
	2	1.3	<LOQ	1.6	<LOQ	3.5	4.0	4.9
	Mean	**1.7**	**<LOQ**	**1.6**	**<LOQ**	**2.6**	**3.9**	**4.4**
Total Recovery	1	96.8	96.9	94.0	92.6	95.0	96.1	99.8
	2	99.1	98.3	93.5	94.4	97.7	93.9	97.0
	Mean	**97.9**	**97.6**	**93.6**	**93.5**	**96.3**	**95.0**	**98.4**

n.d.: not detected, n.a.: not analyzed, n.c.: not calculated, DAT: days after treatment

B. MATERIAL BALANCE

Mean material balances of radioactivity were 100.1 % AR for soil Argissolo (range from 94.1 to 108.8 % AR), 99.3 % AR for soil Latossolo (range from 97.0 to 103.8 % AR), 98.1 % AR for soil Neossolo (95.1 to 101.1 % AR) and 96.1 % AR for soil Gleissolo (92.6 to 99.8 % AR).

C. EXTRACTABLE AND NON-EXTRACTABLE RESIDUES

Total extractable residues decreased from DAT-0 to DAT-119 from 100.0 to 92.4 % AR in soil Argissolo, from 98.9 to 88.3 % AR in soil Latossolo, from 100.5 to 87.4 % AR in soil Neossolo and from 96.2 to 91.9 % AR in soil Gleissolo.

Non-extractable residues (NER) at the end of the study reached values of 4.7, 7.5, 3.8 and 4.4 % AR for soils Argissolo, Latossolo, Neossolo and Gleissolo, respectively.

D. VOLATILIZATION

The maximum amount of carbon dioxide was 2.6, 4.9, 5.9 and 2.1 % AR at study end (DAT-119) in soil Argissolo, Latossolo, Neossolo and Gleissolo, respectively. Formation of volatile organic compounds (VOC) was insignificant as demonstrated by values below the limit of quantitation (0.133 µg, 0.25 % AR) at all sampling intervals for all soils.

E. DEGRADATION OF TEST ITEM

The amount of fluopyram in the total soil extracts (ambient and soxhlet) decreased from DAT-0 to DAT-119 from 96.21 to 91.01 % AR in soil Agrissolo, from 95.72 to 86.20 % AR in soil Latossolo, from 97.98 to 76.79 % AR in soil Neossolo and from 90.84 to 86.32 % AR in soil Gleissolo.

Weak degradation of fluopyram was accompanied by the formation of two degradation products. Fluopyram-7-Hydroxy reached maximum values of 2.10, 2.37, 10.28 and 4.42 % AR in soils Argissolo, Latossolo, Neossolo and Gleissolo, respectively. Fluopyram-Benzamide reached maximum values of 3.79, 1.38, 2.97 and 5.39 % AR in soils Argissolo, Latossolo, Neossolo and Gleissolo, respectively. Fluopyram-benzamide never exceeded 5% of AR in two subsequent intervals and did not indicate an increasing trend to the end of study.

F. KINETICS

New kinetic calculations based on more recent guidance are necessary, therefore the information included in this study is not considered relevant. Evaluation of the rate of degradation is reported under KCA 7.1.2.1.1/11 (M-761965-01-1).

III. CONCLUSIONS

[phenyl-UL-^{14}C]fluopyram was slowly degraded in soil under aerobic conditions in the dark in the laboratory.

Formation of carbon dioxide was low (up to 5.9 % AR) at study end, indicating low potential for complete mineralization of fluopyram. Formation of non-extractable residues (NER) was up to 7.5 % AR at study end, only.

Weak degradation of fluopyram was accompanied by the formation of two degradation products. Fluopyram-7-Hydroxy reached maximum values of 2.10, 2.37, 10.28 and 4.42 % AR in soils Argissolo, Latossolo, Neossolo and Gleissolo, respectively. Fluopyram-Benzamide reached maximum values of 3.79, 1.38, 2.97 and 5.39 % AR in soils Argissolo, Latossolo, Neossolo and Gleissolo, respectively. Fluopyram-Benzamide never exceeded 5% of AR in two subsequent intervals and did not indicate an increasing trend to the end of study.

The DT_{50} value for fluopyram was >365 days in the EU relevant soil (Argissolo) tested under aerobic conditions in the dark at a temperature of 20 °C.

3. Assessment and conclusion

Assessment and conclusion by applicant:
The study and its data are considered as valid and reliable for use in risk assessment, however, it should be noted that the fluopyram treatment rate investigated in this study was comparatively high.

Assessment and conclusion by RMS:
Outcome and conclusion of the study: RMS should indicate if they agree to the results and conclusions of the APPL.

1. Information on the study

Data Point:	KCA 7.1.1.1/05
Report Author:	[redacted]
Report Year:	2020
Report Title:	Amendment no. 01: Fluopyram: Aerobic metabolism / Degradation and time - Dependent sorption in 6 soils
Report No:	EnSa-20-0072
Document No:	M-681092-02-1
Guideline(s) followed in study:	OECD Test Guideline No. 307 (2002). OECD Test Guideline No. 106 (2000, only in parts). Guidance on how aged sorption studies for pesticides should be conducted, analyzed and used in the regulatory process (2012, revised draft 2016). Current revision dates Sep 2016 [this draft guidance was updated based on the PPR statement on aged sorption, EFSA Journal 2015;13(7):4175].
Deviations from current test guideline:	Current Guideline: OECD 307 (2002), OECD 106 (2000) (only in parts) None
Previous evaluation:	No, not previously submitted
GLP/Officially recognised testing facilities:	Yes, conducted under GLP/Officially recognised testing facilities
Acceptability/Reliability:	Yes

2. Full summary of KCA 7.1.1.1/05

Executive Summary

The degradation and time-dependence of sorption of [phenyl-UL-^{14}C]fluopyram was studied in six soils under aerobic conditions in the laboratory in the dark at 20 ±2 °C (mean 19.4 °C) and 55 ± 5% (mean 53.8%) of the respective maximum water holding capacity of soils for 118 days. The study design considered in its conduct aspects of time dependent sorption (see also KCA 7.1.3.2/04).

Soil	Soil ID	Source	Texture (USDA)	pH [1]	OC [%]
Little Oliver	LO	Malton, UK	sandy loam	5.5	1.5
Auchy les Mines	AM	Armancourt, France	silt loam	7.5	2.0
Urbanowice	UW	Urbanowice, Poland	silt loam	4.9	1.1
Charles River Farm	FA	Lleida, Spain	clay	7.7	1.6
Snidos	SD	Thessaloniki, Greece	loam	7.2	1.3
Paradiso San Zenone	PZ	Lodi, Italy	sandy loam	5.4	1.2

[1] in 0.01 M $CaCl_2$

An actual study application rate of 166 µg/kg soil dry weight was applied based on a maximum single field application rate of 250 g active substance/ha (assuming incorporation into top 10 cm of soil and 1.5 g/cm^3 bulk density).

Duplicate samples were processed and analysed 0, 3, 7, 12, 26, 48, 82 and 118 days after treatment (DAT).

At each sampling interval, the soil was extracted five times. The first extraction step was carried out at ambient temperature with aqueous 0.01 M $CaCl_2$ solution (soil to solution ratio of 1:4 (v/v); shaking for 48 hours) to determine the desorbable portion of the test item from the aged soil. Then, one ambient extraction of soil using acetonitrile/water 1/1 (*v*/*v*) followed. Furthermore, one ambient extraction step using acetonitrile/water 4/1 (*v*/*v*) and one with pure acetonitrile were performed. Finally, one microwave-assisted extraction step was performed using acetonitrile/water 4/1 (v/v) at 70 °C. The

amounts of test item and degradation products in soil extracts were determined by liquid scintillation counting (LSC) and by AMD-TLC/radiodetection analysis. Test item identity was confirmed by HPLC-MS(/MS) including accurate mass determination. One degradation product was identified in the extracts by AMD-TLC co-chromatography using a reference item.

Mean material balances of radioactivity were 98.2% AR for soil LO (range from 96.6 to 99.5% AR), 98.1% AR for soil AM (range from 96.7 to 102.3% AR), 97.6% AR for soil UW (range from 95.7 to 99.7% AR), 98.0% AR for soil FA (range from 95.9 to 99.4% AR), 97.0% AR for soil SD (range from 95.5 to 98.0% AR) and 97.2% AR for soil PZ (range from 96.8 to 98.4% AR).

The maximum amount of carbon dioxide was 1.6, 4.4, 1.8, 6.6, 13.1 and 11.2% AR in soil LO, AM, UW, FA, SD and PZ, respectively. Formation of volatile organic compounds (VOC) was insignificant as demonstrated by values of <0.1% AR at all sampling intervals for all soils.

Desorbable radioactive residues in aqueous 0.01 M $CaCl_2$ solution decreased from DAT-0 to DAT-118 from 36.2 to 15.3% AR in soil LO, from 23.4 to 10.2% AR in soil AM, from 44.4 to 24.0% AR in soil UW, from 43.1 to 21.9% AR in soil FA, from 45.7 to 24.1% AR in soil SD and from 44.4 to 21.1% AR from soil PZ.

Total extractable radioctivity (i.e. residues desorbed by aqueous 0.01 M $CaCl_2$ solution and residues in combined soil extracts) slightly decreased from DAT-0 to DAT-118 from 95.6 to 91.6% AR in soil LO, from 95.2 to 91.0% AR in soil AM, from 95.6 to 91.8% AR in soil UW, from 94.6 to 83.0% AR in soil FA, from 94.2 to 73.1% AR in soil SD and from 96.3 to 78.3% AR in soil PZ.

Non-extractable residues (NER) increased from DAT-0 to DAT-118 from 1.0 to 6.3% AR in soil LO, from 1.5 to 6.8% AR in soil AM, from 0.8 to 6.0% AR in soil UW, from 1.4 to 9.7% AR in soil FA, from 1.3 to 11.7% AR in soil SD and from 1.1 to 8.9% AR in soil PZ.

The total amount of fluopyram extractable (i.e. in aqueous desorption solution and organic soil extracts) decreased from DAT-0 to DAT-118 from 93.6 to 90.7% AR in soil LO, from 93.3 to 88.2% AR in soil AM, from 93.4 to 88.6% AR in soil UW, from 92.0 to 79.9% AR in soil FA, from 92.1 to 69.0% AR in soil SD and from 94.2 to 76.1% AR in soil PZ.

Degradation of fluopyram was accompanied by the formation of fluopyram-7-hydroxy observed at a maximum of 1.4% AR at DAT-82 in soil SD. The total unidentified components amounted to a maximum of 2.0% AR and no single compound exceeded 1.3% AR at any sampling interval in all soils.

For details and results of degradation kinetics and time-dependent sorption investigations see respective sections later.

I. MATERIALS AND METHODS

A. MATERIALS

1. Test Item

[phenyl-UL-^{14}C]fluopyram

Sample ID	KML 10699
Specific activity	5.15 MBq/mg
Radiochemical purity	> 98% (HPLC with radioactivity detector)
Chemical purity	> 98% (HPLC, UV- detector, 210 nm)

2. Test Soils

The soils were sampled freshly from the field (upper horizon of 0 to 10 cm as this is the respective top soil layer sampled and evaluated in the parallel field dissipation study M-758583-01-1, see

KCA 7.1.2.2.1/14), air-dried and sieved to a particle size of ≤ 2 mm. Afterwards, soils were stored at 6 °C for max. approx. 2 months. The soils were taken from agricultural areas. The physico-chemical characteristics of the test soils are summarized in the tables below.

Table 7.1.1.1-21: Physico-chemical properties of test soils LO, AM and UW

Soil Designation	LO	AM	UW
Geographic Location			
City	Malton	Armancourt	Urbanowice
State	North Yorkshire	Hauts de France	Opole
Country	UK	France	Poland
Soil Taxonomic Classification (USDA)	No information available		
Soil Series	No information available		
Textural Class (USDA)	sandy loam	silt loam	silt loam
Sand (%) [50 µm – 2 mm]	55	23	35
Silt (%) [2 µm – 50 µm]	26	58	62
Clay (%) [< 2 µm]	19	19	3
pH (soil/0.01 M $CaCl_2$ 1/2)	5.5	7.5	4.9
pH (soil/water 1/1)	5.7	7.7	5.0
pH (saturated paste)	5.6	7.6	5.0
pH (soil/1 N KCl 1/1)	5.3	7.1	4.5
Organic Carbon (combustion) (%)	1.5	2.0	1.1
Organic Matter (%) [1]	2.6	3.4	1.9
Cation Exchange Capacity (meq/100 g)	13.6	15.0	9.0
Water Holding Capacity maximum (g H_2O *ad* 100 g soil DW)	49.3	53.2	43.9
Bulk Density (disturbed, (g/cm³)	1.22	1.11	1.22
Microbial Biomass (mg microbial carbon / kg soil DW)			
DAT-0 (BIO- / BIO+)	359 / 348	426 / 446	206 / 192
DAT-62 (BIO- / BIO+)	235 / 229	377 / 381	129 / 141
DAT-118 (BIO- / BIO+)	182 162	322 / 300	94 / 95

USDA: United States Department of Agriculture, DAT: days after treatment, DW: dry weight

[1] calculated as: OM (%) = OC (%) 1.724

BIO- samples were applied with water, BIO+ samples were applied with solvent

Table 7.1.1.1-22: Physico-chemical properties of test soils FA, SD and PZ

Soil Designation	FA	SD	PZ
Geographic Location			
City	Lleida	Thessaloniki	Lodi
State	Catalunya	Central Macedonia	Lombardia
Country	Spain	Greece	Italy
Soil Taxonomic Classification (USDA)	No information available		
Soil Series	No information available		
Textural Class (USDA)	clay	loam	sandy loam
Sand [50 µm – 2 mm] (%)	19	35	45
Silt (%) [2 µm – 50 µm]	38	38	50
Clay (%) [< 2 µm]	43	27	5
pH (soil/0.01 M $CaCl_2$ 1/2)	7.7	7.2	5.4
pH (soil/water 1/1)	7.8	7.1	5.8
pH (saturated paste)	7.6	7.5	5.8
pH (soil/1 N KCl 1/1)	7.5	6.7	4.7
Organic Carbon (combustion) (%)	1.6	1.3	1.2
Organic Matter (%)[1]	2.8	2.2	2.1
Cation Exchange Capacity (meq/100 g)	18.2	16.8	11.8
Water Holding Capacity maximum (g H_2O *ad* 100 g soil DW)	55.4	55.0	51.1
Bulk Density (disturbed) (g/cm³)	1.11	1.10	1.11
Microbial Biomass (mg microbial carbon / kg soil DW)			
DAT-0 (BIO- / BIO+)	463 / 378	717 / 740	797 / 735
DAT-62 (BIO- / BIO+)	390 / 362	788 / 661	752 / 720
DAT-118 (BIO- / BIO+)	298 / 301	436 / 482	181 / 182

USDA: United States Department of Agriculture, DAT: days after treatment, DW: dry weight

[1] calculated as: OM (%) = OC (%) * 1.724

B. STUDY DESIGN

1. Experimental Conditions

Static test systems were used, consisting of 300 mL Erlenmeyer flasks filled with soil and equipped with a trap attachment (permeable for oxygen) containing soda lime for absorption of carbon dioxide and a polyurethane (PU) foam plug for adsorption of volatile organic compounds (VOC).

100 g of the sieved soil (dry weight equivalents) were weighed into each test vessel and the soil moisture was adjusted to 55 ± 5% of the maximum water holding capacity (MWHC) by addition of de-ionized water. The test vessels were then fitted with trap attachments. The untreated test systems were equilibrated to study conditions for 5 days prior to application.

An actual study application rate of 166 µg/kg soil dry weight was applied based on a maximum single field application rate of fluopyram of 250 g/ha (assuming incorporation into top 10 cm of soil and 1.5 g/cm³ bulk density)..

The application solution was prepared by diluting 2.51 mL of a stock solution (1.0 mg test item/mL methanol) in 57.49 mL water. 387 µL of the application solution were applied drop wise onto the soil surface of the respective equilibrated test systems using a pipette.

After application the test vessels (except DAT-0 samples) were fitted with trap attachments and incubated under aerobic conditions in the dark for 118 days at 20 ± 2 °C and a soil moisture of 55 ± 5% of the maximum water holding capacity in a walk-in climatic chamber.

2. Sampling

Duplicate samples were processed and analysed 0, 3, 7, 12, 26, 48, 82 and 118 days after treatment (DAT).

Microbial soil biomass was determined at start, middle and end of the study (DAT-2, DAT-62 and DAT-118).

3. Analytical Procedures

Following purging of the samples, the trap attachment was removed and the soil was extracted completely.

At each sampling interval, a so-called batch equilibrium shaking test was performed firstly to determine the time-dependent sorption of fluopyram. Therefore, the trap attachments were removed from the test systems and the entire soil of each test system was supplemented with 400 mL 0.01 M $CaCl_2$ solution, corresponding to a soil-to-solution ratio of approximately 1:4, and shaken for 48 h in the dark at 20 °C. Afterwards, supernatant and soil were separated by centrifugation and decantation. Thereafter, the soil was extracted three times at ambient temperature using a mechanical shaker followed by one extraction using a microwave (70 °C) with a magnetic stirrer. Extractions were performed with 80 mL ACN/water (1/1, v/v), ACN/water (4/1, v/v), ACN and ACN/water (4/1, v/v) in the first, second, third and last extraction, respectively.

To prove that the selected method of organic soil extraction is adequate, T0-samples were prepared and processed immediately after application in the same way as described for the other days, but without the $CaCl_2$ extraction step. The mean recovery of the test item at DAT-0 was between 93.5 and 96.1% AR for all soils without prior $CaCl_2$ extraction (T0) and between 92.0 and 94.2% AR for all soils with an additional $CaCl_2$ extraction step (T1).

The desorption solution of the batch equilibrium shaking test as well as the combined soil extracts were characterized separately by liquid scintillation counting and by AMD-TLC/radiodetection. The limit of detection (LOD) for the AMD-TLC/radiodetection method was 1.3% AR and for the LSC ≤0.4% AR for the different extracts/solutions and the combustions samples. Identity of the test item was confirmed by HPLC-MS(/MS). The amounts of volatiles and non-extractable residues were determined by LSC and combustion/LSC, respectively.

Selected desorption solutions were cochromatographed with a reference standard. Unlabeled metabolite fluopyram-7-hydroxy was spotted on the same plat as well as spiked to the radioactive sample.

II. RESULTS AND DISCUSSION

A. EXTRACTION AND DISTRIBUTION OF RADIOACTIVITY IN SOIL SAMPLES

Table 7.1.1.1-23 to Table 7.1.1.1-28 summarize the degradation of [phenyl-UL-^{14}C]fluopyram as a function of time.

Table 7.1.1.1-23: Degradation of fluopyram in soil Little Oliver under aerobic conditions

Compound	Replicate No.	Residues (% AR) on the following days after treatment (DAT)							
		0	3	7	12	26	48	82	118
Fluopyram	1	93.8	94.1	92.8	92.9	92.2	89.6	91.4	90.8
	2	93.4	94.2	93.8	92.4	93.2	89.0	91.7	90.6
	Mean	**93.6**	**94.1**	**93.3**	**92.7**	**92.7**	**89.3**	**91.6**	**90.7**
ROI 1	1	<LOD	n.d.	<LOD	n.d.	n.d.	n.d.	n.d.	n.d.
	2	<LOD	<LOD	<LOD	n.d.	n.d.	n.d.	n.d.	<LOD
	Mean	**<LOD**	**<LOD**	**<LOD**	**n.c.**	**n.c.**	**n.c.**	**n.c.**	**<LOD**
ROI 2	1	<LOD	<LOD	<LOD	<LOD	n.d.	n.d.	n.d.	n.d.
	2	<LOD	<LOD	<LOD	n.d.	n.d.	n.d.	n.d.	n.d.
	Mean	**<LOD**	**<LOD**	**<LOD**	**<LOD**	**n.c.**	**n.c.**	**n.c.**	**n.c.**
Fluopyram-7-hydroxy	1	<LOD	n.d.	<LOD	n.d.	n.d.	n.d.	n.d.	n.d.
	2	<LOD	n.d.	<LOD	n.d.	n.d.	n.d.	n.d.	n.d.
	Mean	**<LOD**	**n.c.**	**<LOD**	**n.c.**	**n.c.**	**n.c.**	**n.c.**	**n.c.**
ROI 4	1	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	2	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	Mean	**n.c.**	**n.c.**	**n.c.**	**n.c.**	**n.c.**	**n.c.**	**n.c.**	**n.c.**
ROI 5	1	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	2	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	Mean	**n.c.**	**n.c.**	**n.c.**	**n.c.**	**n.c.**	**n.c.**	**n.c.**	**n.c.**
ROI 6	1	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	2	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	Mean	**n.c.**	**n.c.**	**n.c.**	**n.c.**	**n.c.**	**n.c.**	**n.c.**	**n.c.**
Diffuse Residues	1	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
	2	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
	Mean	**<LOD**	**<LOD**	**<LOD**	**<LOD**	**<LOD**	**<LOD**	**<LOD**	**<LOD**
Sum of Unid./Diff. Residues [1]	1	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
	2	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
	Mean	**<LOD**	**<LOD**	**<LOD**	**<LOD**	**<LOD**	**<LOD**	**<LOD**	**<LOD**
Total Extractable Residues	1	95.8	95.2	93.9	93.7	93.0	90.9	91.9	91.8
	2	93.4	95.9	94.7	93.2	93.8	89.8	92.3	91.3
	Mean	**95.6**	**95.6**	**94.3**	**93.5**	**93.4**	**90.3**	**92.1**	**91.6**
Carbon Dioxide	1	n.a.	0.1	0.7	0.6	1.0	1.3	1.5	1.6
	2	n.a.	0.1	0.7	0.7	1.0	1.2	1.4	1.6
	Mean	**n.a.**	**0.1**	**0.7**	**0.7**	**1.0**	**1.3**	**1.4**	**1.6**
Volatile Organic Compounds	1	n.a.	<0.1	0.1	0.1	0.1	<0.1	<0.1	0.1
	2	n.a.	0.1	0.1	0.1	<0.1	<0.1	<0.1	<0.1
	Mean	**n.a.**	**0.1**	**0.1**	**0.1**	**<0.1**	**<0.1**	**<0.1**	**<0.1**
Non-Extractable Residues	1	1.1	1.8	3.2	2.7	4.6	6.0	5.7	6.4
	2	1.0	2.3	2.9	2.7	3.9	5.5	5.5	6.2
	Mean	**1.0**	**2.0**	**3.0**	**2.7**	**4.3**	**5.7**	**5.6**	**6.3**
Material Balance	1	96.8	97.2	97.9	97.1	98.7	98.2	99.1	99.9
	2	96.3	98.5	98.4	96.7	98.8	96.5	99.2	99.1
	Mean	**96.6**	**97.8**	**98.1**	**96.9**	**98.7**	**97.3**	**99.2**	**99.5**

n.d.: not detected, n.a.: not analysed, n.c.: not calculated, DAT: days after treatment
[1] Minor components (unidentified metabolites and diffuse residues) are summed up to unidentified residues.

Table 7.1.1.1-24: Degradation of fluopyram in soil Auchy les Mines under aerobic conditions

Compound	Replicate No.	Residues (% AR) on the following days after treatment (DAT)							
		0	3	7	12	26	48	82	118
Fluopyram	1	93.5	93.2	92.5	93.1	90.4	87.9	88.1	88.9
	2	93.0	94.1	94.0	93.8	90.7	88.8	88.1	87.4
	Mean	**93.3**	**93.6**	**93.3**	**93.5**	**90.6**	**88.3**	**88.1**	**88.2**
ROI 1	1	<LOD	n.d.	<LOD	n.d.	n.d.	n.d.	<LOD	<LOD
	2	<LOD	n.d.	<LOD	n.d.	n.d.	<LOD	<LOD	<LOD
	Mean	**<LOD**	**n.c.**	**<LOD**	**n.c.**	**n.c.**	**<LOD**	**<LOD**	**<LOD**
ROI 2	1	<LOD	<LOD	<LOD	n.d.	n.d.	n.d.	n.d.	n.d.
	2	<LOD	<LOD	<LOD	n.d.	n.d.	n.d.	n.d.	n.d.
	Mean	**<LOD**	**<LOD**	**<LOD**	**n.c.**	**n.c.**	**n.c.**	**n.c.**	**n.c.**
Fluopyram-7-hydroxy	1	n.d.	n.d.	<LOD	n.d.	n.d.	n.d.	n.d.	<LOD
	2	n.d.	n.d.	<LOD	n.d.	n.d.	n.d.	n.d.	<LOD
	Mean	**n.c.**	**n.c.**	**<LOD**	**n.c.**	**n.c.**	**n.c.**	**n.c.**	**<LOD**
ROI 4	1	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	2.6
	2	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	Mean	**n.c.**	**n.c.**	**n.c.**	**n.c.**	**n.c.**	**n.c.**	**n.c.**	**1.3**
ROI 5	1	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	2	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	Mean	**n.c.**	**n.c.**	**n.c.**	**n.c.**	**n.c.**	**n.c.**	**n.c.**	**n.c.**
ROI 6	1	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	2	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	Mean	**n.c.**	**n.c.**	**n.c.**	**n.c.**	**n.c.**	**n.c.**	**n.c.**	**n.c.**
Diffuse Residues	1	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
	2	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
	Mean	**<LOD**	**<LOD**	**<LOD**	**<LOD**	**<LOD**	**<LOD**	**<LOD**	**<LOD**
Sum of Unid./Diff. Residues [1]	1	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	2.6
	2	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
	Mean	**<LOD**	**<LOD**	**<LOD**	**<LOD**	**<LOD**	**<LOD**	**<LOD**	**1.3**
Total Extractable Residues	1	95.5	94.4	93.8	93.5	91.3	88.3	88.8	93.2
	2	94.9	95.6	95.2	94.2	91.7	89.8	89.2	88.9
	Mean	**95.2**	**95.0**	**94.5**	**93.8**	**91.5**	**89.0**	**89.0**	**91.0**
Carbon Dioxide	1	n.a.	0.3	0.4	1.1	1.5	2.2	3.3	4.7
	2	n.a.	0.3	0.5	1.0	1.5	2.2	3.2	4.2
	Mean	**n.c.**	**0.3**	**0.5**	**1.0**	**1.5**	**2.2**	**3.2**	**4.4**
Volatile Organic Compounds	1	n.a.	0.1	<0.1	0.1	<0.1	<0.1	0.1	<0.1
	2	n.a.	0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
	Mean	**n.c.**	**0.1**	**<0.1**	**<0.1**	**<0.1**	**<0.1**	**0.1**	**<0.1**
Non-Extractable Residues	1	1.5	2.4	2.7	3.2	4.3	5.6	5.9	7.0
	2	1.6	2.3	2.5	3.1	4.2	5.3	5.7	6.6
	Mean	**1.5**	**2.3**	**2.6**	**3.2**	**4.2**	**5.4**	**5.8**	**6.8**
Material Balance	1	97.0	97.1	97.0	97.8	97.2	96.1	98.0	104.8
	2	96.5	98.4	98.2	98.4	97.3	97.3	98.2	99.8
	Mean	**96.7**	**97.7**	**97.6**	**98.1**	**97.2**	**96.7**	**98.1**	**102.3**

n.d.: not detected, n.a.: not analysed, n.c.: not calculated DAT: days after treatment
[1] Minor components (unidentified metabolites and diffuse residues) are summed up to unidentified residues.

Table 7.1.1.1-25: Degradation of fluopyram in soil Urbanowice under aerobic conditions

Compound	Replicate No.	Residues (% AR) on the following days after treatment (DAT)							
		0	3	7	12	26	48	82	118
Fluopyram	1	93.1	94.8	93.3	91.9	92.9	88.4	91.9	90.2
	2	93.7	93.3	92.2	96.0	92.7	89.4	90.4	87.0
	Mean	**93.4**	**94.1**	**92.8**	**93.9**	**92.8**	**88.9**	**91.1**	**88.6**
ROI 1	1	<LOD	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	<LOD
	2	<LOD	n.d.	n.d.	n.d.	n.d.	n.d.	<LOD	<LOD
	Mean	**<LOD**	**n.c.**	**n.c.**	**n.c.**	**n.c.**	**n.c.**	**<LOD**	**<LOD**
ROI 2	1	<LOD	<LOD	<LOD	n.d.	n.d.	n.d.	n.d.	n.d.
	2	<LOD	<LOD	<LOD	n.d.	n.d.	n.d.	n.d.	n.d.
	Mean	**<LOD**	**<LOD**	**<LOD**	**n.c.**	**n.c.**	**n.c.**	**n.c.**	**n.c.**
Fluopyram-7-hydroxy	1	<LOD	n.d.	<LOD	n.d.	n.d.	n.d.	n.d.	<LOD
	2	<LOD	n.d.	<LOD	n.d.	n.d.	n.d.	n.d.	<LOD
	Mean	**<LOD**	**n.c.**	**<LOD**	**n.c.**	**n.c.**	**n.c.**	**n.c.**	**<LOD**
ROI 4	1	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	2	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	Mean	**n.c.**	**n.c.**	**n.c.**	**n.c.**	**n.c.**	**n.c.**	**n.c.**	**n.c.**
ROI 5	1	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	2	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	Mean	**n.c.**	**n.c.**	**n.c.**	**n.c.**	**n.c.**	**n.c.**	**n.c.**	**n.c.**
ROI 6	1	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	2	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	Mean	**n.c.**	**n.c.**	**n.c.**	**n.c.**	**n.c.**	**n.c.**	**n.c.**	**n.c.**
Diffuse Residues	1	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
	2	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	3.9
	Mean	**<LOD**	**<LOD**	**<LOD**	**<LOD**	**<LOD**	**<LOD**	**<LOD**	**2.0**
Sum of Unid./Diff. Residues [1]	1	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
	2	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	3.9
	Mean	**<LOD**	**<LOD**	**<LOD**	**<LOD**	**<LOD**	**<LOD**	**<LOD**	**2.0**
Total Extractable Residues	1	95.3	96.2	94.4	92.8	93.7	89.3	92.4	91.8
	2	95.8	94.6	93.7	96.5	93.4	90.1	91.3	91.9
	Mean	**95.6**	**95.4**	**94.0**	**94.6**	**93.6**	**89.7**	**91.8**	**91.8**
Carbon Dioxide	1	n.a.	0.2	0.5	0.7	1.0	1.2	1.5	1.8
	2	n.a.	0.2	0.5	0.8	1.0	1.2	1.5	1.8
	Mean	**n.c.**	**0.2**	**0.5**	**0.7**	**1.0**	**1.2**	**1.5**	**1.8**
Volatile Organic Compounds	1	n.a.	0.1	<0.1	<0.1	<0.1	0.1	0.1	<0.1
	2	n.a.	0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
	Mean	**n.c.**	**<0.1**	**<0.1**	**<0.1**	**<0.1**	**<0.1**	**<0.1**	**<0.1**
Non-Extractable Residues	1	0.8	1.7	2.3	2.3	3.7	4.9	4.9	6.2
	2	0.8	2.0	2.4	2.3	3.5	4.6	5.4	5.9
	Mean	**0.8**	**1.9**	**2.4**	**2.3**	**3.6**	**4.7**	**5.1**	**6.0**
Material Balance	1	96.2	98.2	97.2	95.8	98.3	95.4	98.8	99.8
	2	96.6	96.8	96.7	99.5	97.9	96.0	98.2	99.5
	Mean	**96.4**	**97.5**	**96.9**	**97.7**	**98.1**	**95.7**	**98.5**	**99.7**

n.d.: not detected, n.a.: not analysed, n.c.: not calculated, DAT: days after treatment
[1] Minor components (unidentified metabolites and diffuse residues) are summed up to unidentified residues.

Table 7.1.1.1-26: Degradation of fluopyram in soil Charles River Farm under aerobic conditions

Compound	Replicate No.	Residues (% AR) on the following days after treatment (DAT)							
		0	3	7	12	26	48	82	118
Fluopyram	1	92.9	92.7	90.4	91.6	91.7	86.6	83.7	80.6
	2	91.0	98.5	90.5	93.1	90.8	87.6	83.2	79.2
	Mean	**92.0**	**95.6**	**90.5**	**92.4**	**91.3**	**87.1**	**83.4**	**79.9**
ROI 1	1	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	<LOD	<LOD
	2	n.d.	n.d.	n.d.	n.d.	n.d.	<LOD	<LOD	<LOD
	Mean	**n.c.**	**n.c.**	**n.c.**	**n.c.**	**n.c.**	**<LOD**	**<LOD**	**<LOD**
ROI 2	1	<LOD	n.d.	<LOD	<LOD	n.d.	n.d.	n.d.	<LOD
	2	<LOD	n.d.	<LOD	n.d.	n.d.	<LOD	<LOD	<LOD
	Mean	**<LOD**	**n.c.**	**<LOD**	**<LOD**	**n.c.**	**<LOD**	**<LOD**	**<LOD**
Fluopyram-7-hydroxy	1	<LOD	n.d.	<LOD	<LOD	n.d.	<LOD	<LOD	<LOD
	2	<LOD	n.d.	<LOD	n.d.	n.d.	<LOD	<LOD	<LOD
	Mean	**<LOD**	**n.c.**	**<LOD**	**<LOD**	**n.c.**	**<LOD**	**<LOD**	**<LOD**
ROI 4	1	<LOD	n.d.	<LOD	n.d.	n.d.	n.d.	n.d.	n.d.
	2	<LOD	n.d.	<LOD	n.d.	n.d.	n.d.	n.d.	n.d.
	Mean	**<LOD**	**n.c.**	**<LOD**	**n.c.**	**n.c.**	**n.c.**	**n.c.**	**n.c.**
ROI 5	1	<LOD	n.d.	<LOD	<LOD	n.d.	n.d.	n.d.	n.d.
	2	<LOD	n.d.	<LOD	<LOD	n.d.	n.d.	n.d.	n.d.
	Mean	**<LOD**	**n.c.**	**<LOD**	**<LOD**	**n.c.**	**n.c.**	**n.c.**	**n.c.**
ROI 6	1	<LOD	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	2	<LOD	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	Mean	**<LOD**	**n.c.**	**n.c.**	**n.c.**	**n.c.**	**n.c.**	**n.c.**	**n.c.**
Diffuse Residues	1	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
	2	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
	Mean	**<LOD**	**<LOD**	**<LOD**	**<LOD**	**<LOD**	**<LOD**	**<LOD**	**<LOD**
Sum of Unid./Diff. Residues [1]	1	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
	2	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
	Mean	**<LOD**	**<LOD**	**<LOD**	**<LOD**	**<LOD**	**<LOD**	**<LOD**	**<LOD**
Total Extractable Residues	1	95.2	93.3	91.7	92.9	92.5	88.5	85.7	83.2
	2	93.9	99.1	92.3	93.8	91.7	89.8	85.5	82.8
	Mean	**94.6**	**96.2**	**92.0**	**93.4**	**92.1**	**89.2**	**85.6**	**83.0**
Carbon Dioxide	1	n.a.	0.4	0.8	1.1	1.6	2.8	5.0	6.5
	2	n.a.	0.1	0.8	1.1	1.6	2.8	4.9	6.7
	Mean	**n.c.**	**0.3**	**0.8**	**1.1**	**1.6**	**2.8**	**5.0**	**6.6**
Volatile Organic Compounds	1	n.a.	0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
	2	n.a.	0.1	<0.1	<0.1	<0.1	0.1	<0.1	<0.1
	Mean	**n.c.**	**<0.1**	**<0.1**	**<0.1**	**<0.1**	**<0.1**	**<0.1**	**<0.1**
Non-Extractable Residues	1	1.3	3.2	3.3	3.1	5.0	7.0	8.0	9.7
	2	1.5	2.7	3.0	3.0	5.2	7.0	8.0	9.8
	Mean	**1.4**	**2.9**	**3.1**	**3.1**	**5.1**	**7.0**	**8.0**	**9.7**
Material Balance	1	96.5	97.0	95.8	97.1	99.1	98.3	98.8	99.3
	2	95.4	101.9	96.1	97.9	98.5	99.6	98.4	99.4
	Mean	**95.9**	**99.4**	**95.9**	**97.5**	**98.8**	**99.0**	**98.6**	**99.4**

n.d.: not detected, n.a.: not analysed, n.c.: not calculated DAT: days after treatment
[1] Minor components (unidentified metabolites and diffuse residues) are summed up to unidentified residues.

Table 7.1.1.1-27: Degradation of fluopyram in soil Sindos under aerobic conditions

Compound	Replicate No.	Residues (% AR) on the following days after treatment (DAT)							
		0	3	7	12	26	48	82	118
Fluopyram	1	92.2	94.1	89.8	92.4	87.1	77.8	75.6	67.8
	2	92.1	93.2	91.6	89.7	86.7	82.9	75.4	70.2
	Mean	**92.1**	**93.7**	**90.7**	**91.1**	**86.9**	**80.3**	**75.5**	**69.0**
ROI 1	1	n.d.	n.d.	<LOD	<LOD	n.d.	<LOD	<LOD	<LOD
	2	n.d.	n.d.	n.d.	n.d.	n.d.	<LOD	<LOD	<LOD
	Mean	**n.c.**	**n.c.**	**<LOD**	**<LOD**	**n.c.**	**<LOD**	**<LOD**	**<LOD**
ROI 2	1	<LOD	n.d.	<LOD	<LOD	<LOD	n.d.	n.d.	<LOD
	2	<LOD	n.d.	<LOD	<LOD	<LOD	<LOD	n.d.	<LOD
	Mean	**<LOD**	**n.c.**	**<LOD**	**<LOD**	**<LOD**	**<LOD**	**n.c.**	**<LOD**
Fluopyram-7-hydroxy	1	<LOD	n.d.	<LOD	<LOD	n.d.	<LOD	1.3	<LOD
	2	<LOD	n.d.	<LOD	n.d.	n.d.	<LOD	1.4	<LOD
	Mean	**<LOD**	**n.c.**	**<LOD**	**<LOD**	**n.c.**	**<LOD**	**1.4**	**<LOD**
ROI 4	1	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	2	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	Mean	**n.c.**	**n.c.**	**n.c.**	**n.c.**	**n.c.**	**n.c.**	**n.c.**	**n.c.**
ROI 5	1	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	2	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	Mean	**n.c.**	**n.c.**	**n.c.**	**n.c.**	**n.c.**	**n.c.**	**n.c.**	**n.c.**
ROI 6	1	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	2	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	Mean	**n.c.**	**n.c.**	**n.c.**	**n.c.**	**n.c.**	**n.c.**	**n.c.**	**n.c.**
Diffuse Residues	1	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
	2	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
	Mean	**<LOD**	**<LOD**	**<LOD**	**<LOD**	**<LOD**	**<LOD**	**<LOD**	**<LOD**
Sum of Unid./Diff. Residues [1]	1	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
	2	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
	Mean	**<LOD**	**<LOD**	**<LOD**	**<LOD**	**<LOD**	**<LOD**	**<LOD**	**<LOD**
Total Extractable Residues	1	94.3	94.7	91.6	94.3	88.6	80.8	78.5	71.9
	2	94.1	94.1	92.9	90.7	88.8	85.7	78.0	74.4
	Mean	**94.2**	**94.4**	**92.2**	**92.5**	**88.7**	**83.2**	**78.3**	**73.1**
Carbon Dioxide	1	n.a.	0.5	1.1	1.6	2.8	5.5	10.0	13.0
	2	n.a.	0.6	1.1	1.5	2.9	5.6	9.3	13.2
	Mean	**n.c.**	**0.6**	**1.1**	**1.5**	**2.9**	**5.5**	**9.6**	**13.1**
Volatile Organic Compounds	1	n.a.	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
	2	n.a.	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
	Mean	**n.c.**	**<0.1**	**<0.1**	**<0.1**	**<0.1**	**<0.1**	**<0.1**	**<0.1**
Non-Extractable Residues	1	1.3	2.5	3.0	3.5	5.3	7.7	9.5	11.6
	2	1.3	2.7	2.9	3.3	5.2	8.2	9.3	11.9
	Mean	**1.3**	**2.6**	**3.0**	**3.4**	**5.2**	**7.9**	**9.4**	**11.7**
Material Balance	1	95.5	97.7	95.8	99.4	96.7	94.0	98.0	96.5
	2	95.4	97.3	96.9	95.5	96.9	99.5	96.7	99.5
	Mean	**95.5**	**97.5**	**96.3**	**97.4**	**96.8**	**96.7**	**97.3**	**98.0**

n.d.: not detected, n.a.: not analysed, n.c.: not calculated, DAT: days after treatment
[1] Minor components (unidentified metabolites and diffuse residues) are summed up to unidentified residues.

Table 7.1.1.1-28: Degradation of fluopyram in soil Paradiso San Zenone under aerobic conditions

Compound	Replicate No.	Residues (% AR) on the following days after treatment (DAT)							
		0	3	7	12	26	48	82	118
Fluopyram	1	95.6	92.9	91.6	90.3	86.3	79.7	77.1	75.1
	2	92.7	92.2	91.4	89.7	87.3	82.0	78.9	77.1
	Mean	**94.2**	**92.6**	**91.5**	**90.0**	**86.8**	**80.8**	**78.0**	**76.1**
ROI 1	1	n.d.	n.d.	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
	2	n.d.	n.d.	n.d.	<LOD	<LOD	<LOD	<LOD	<LOD
	Mean	**n.c.**	**n.c.**	**<LOD**	**<LOD**	**<LOD**	**<LOD**	**<LOD**	**<LOD**
ROI 2	1	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	n.d.	<LOD
	2	<LOD	<LOD	<LOD	<LOD	<LOD	n.d.	n.d.	<LOD
	Mean	**<LOD**	**<LOD**	**<LOD**	**<LOD**	**<LOD**	**<LOD**	**n.c.**	**<LOD**
Fluopyram-7-hydroxy	1	<LOD	n.d.	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
	2	<LOD	n.d.	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
	Mean	**<LOD**	**n.c.**	**<LOD**	**<LOD**	**<LOD**	**<LOD**	**<LOD**	**<LOD**
ROI 4	1	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	2	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d
	Mean	**n.c.**	**n.c.**	**n.c.**	**n.c.**	**n.c.**	**n.c.**	**n.c.**	**n.c.**
ROI 5	1	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d
	2	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d
	Mean	**n.c.**	**n.c.**	**n.c.**	**n.c.**	**n.c.**	**n.c.**	**n.c.**	**n.c.**
ROI 6	1	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	2	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	Mean	**n.c.**	**n.c.**	**n.c.**	**n.c.**	**n.c.**	**n.c.**	**n.c.**	**n.c.**
Diffuse Residues	1	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
	2	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
	Mean	**<LOD**	**<LOD**	**<LOD**	**<LOD**	**<LOD**	**<LOD**	**<LOD**	**<LOD**
Sum of Unid./Diff. Residues [1]	1	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
	2	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
	Mean	**<LOD**	**<LOD**	**<LOD**	**<LOD**	**<LOD**	**<LOD**	**<LOD**	**<LOD**
Total Extractable Residues	1	97.7	94.3	93.3	92.3	88.6	82.7	79.2	77.2
	2	95.0	93.6	93.0	91.6	89.3	85.0	81.3	79.4
	Mean	**96.3**	**94.0**	**93.1**	**91.9**	**89.0**	**83.8**	**80.3**	**78.3**
Carbon Dioxide	1	n.a.	0.5	1.2	1.8	3.5	6.2	9.2	12.0
	2	n.a.	0.6	1.2	1.8	3.3	6.4	8.8	10.4
	Mean	**n.c.**	**0.6**	**1.2**	**1.8**	**3.4**	**6.3**	**9.0**	**11.2**
Volatile Organic Compounds	1	n.a.	<0.1	<0.1	0.1	0.1	0.2	0.1	0.1
	2	n.a.	<0.1	<0.1	<0.1	<0.1	0.1	<0.1	<0.1
	Mean	**n.c.**	**<0.1**	**<0.1**	**<0.1**	**<0.1**	**0.1**	**<0.1**	**<0.1**
Non-Extractable Residues	1	1.1	2.1	2.7	3.2	4.8	6.9	7.7	9.1
	2	1.1	2.7	2.7	2.9	4.6	6.9	7.3	8.6
	Mean	**1.1**	**2.4**	**2.7**	**3.1**	**4.7**	**6.9**	**7.5**	**8.9**
Material Balance	1	98.8	97.0	97.2	97.3	96.9	95.9	96.2	98.3
	2	96.1	96.9	96.9	96.4	97.2	98.4	97.3	98.4
	Mean	**97.4**	**97.0**	**97.0**	**96.9**	**97.1**	**97.1**	**96.8**	**98.4**

n.d.: not detected, n.a.: not analysed, n.c.: not calculated, DAT: days after treatment
[1] Minor components (unidentified metabolites and diffuse residues) are summed up to unidentified residues.

B. MATERIAL BALANCE

Mean material balances of radioactivity were 98.2% AR for soil LO (range from 96.6 to 99.5% AR), 98.1% AR for soil AM (range from 96.7 to 102.3% AR), 97.6% AR for soil UW (range from 95.7 to 99.7% AR), 98.0% AR for soil FA (range from 95.9 to 99.4% AR), 97.0% AR for soil SD (range from 95.5 to 98.0% AR) and 97.2% AR for soil PZ (range from 96.8 to 98.4% AR).

The complete material balances found at all sampling intervals for all soils demonstrated that there was no significant loss of radioactivity from the test systems or during sample processing.

C. EXTRACTABLE AND NON-EXTRACTABLE RESIDUES

Desorbable residues in aqueous 0.01 M $CaCl_2$ solution decreased from DAT-0 to DAT-118 from 36.2 to 15.3% AR in soil LO, from 23.4 to 11.2% AR in soil AM, from 44.4 to 24.0% AR in soil UW, from 43.1 to 21.9% AR in soil FA, from 45.7 to 24.1% AR in soil SD and from 44.4 to 21.1% AR from soil PZ.

Total extractable residues (i.e. residues desorbed by aqueous 0.01 M $CaCl_2$ solution and residues in combined soil extracts) slightly decreased from DAT-0 to DAT-118 from 95.6 to 94.6% AR in soil LO, from 95.2 to 91.0% AR in soil AM, from 95.6 to 91.8% AR in soil UW, from 94.6 to 87.0% AR in soil FA, from 94.2 to 73.1% AR in soil SD and from 96.3 to 78.3% AR in soil PZ.

Non-extractable residues (NER) increased from DAT-0 to DAT-118 from 1.0 to 6.3% AR in soil LO, from 1.5 to 6.8% AR in soil AM, from 0.8 to 6.0% AR in soil UW, from 1.4 to 9.7% AR in soil FA, from 1.3 to 11.7% AR in soil SD and from 1.1 to 8.9% AR in soil PZ.

D. VOLATILIZATION

The maximum amount of carbon dioxide was 1.6, 4.4, 1.8, 6.6, 13.1 and 11.2% AR in soil LO, AM, UW, FA, SD and PZ, respectively. Formation of volatile organic compounds (VOC) was insignificant as demonstrated by values of <0.1% AR at all sampling intervals for all soils.

E. DEGRADATION OF TEST ITEM

The amount of fluopyram in the total soil extracts (i.e. in aqueous desorption solution and organic soil extracts) decreased from DAT-0 to DAT-118 from 93.6 to 90.7% AR in soil LO, from 93.3 to 88.2% AR in soil AM, from 93.4 to 88.6% AR in soil UW from 92.0 to 79.9% AR in soil FA, from 92.1 to 69.0% AR in soil SD and from 94.2 to 76.1% AR in soil PZ.

Degradation of fluopyram was accompanied by the formation of: fluopyram-7-hydroxy with a maximum amount of 1.4% AR at DAT-82 in soil SD. The total unidentified residues amounted to a maximum of 2.0% AR and no single compound exceeded 1.3% AR at any sampling interval in all soils.

F. KINETICS

Evaluation of trigger endpoints was done in the course of the study and can be found in KCA 7.1.2.1.1/06. Evaluation of modelling endpoints can be found in KCA 7.1.2.1.1/12 (M-761882-01-1).

G. TIME-DEPENDENCE OF SORPTION

Results of the time-dependent sorption experiment can be found in KCA 7.1.3.2/04.

III. CONCLUSIONS

Fluopyram was slowly degraded and mineralized in soil under aerobic conditions in the dark in the laboratory.

Formation of carbon dioxide was up to 13.1% AR and formation of non-extractable residues (NER) was up to 11.7% AR. Besides NER and carbon dioxide, degradation of fluopyram was accompanied by the formation of fluopyram-7-hydroxy with a maximum amount of 1.4% AR.

For results of degradation kinetics and time-dependent sorption investigations see respective sections later.

3. Assessment and conclusion

Assessment and conclusion by applicant: The study and its data are considered as valid and reliable for use in risk assessment.

Assessment and conclusion by RMS: Outcome and conclusion of the study: RMS should indicate if they agree to the results and conclusions of the APPL.

1. Information on the study

Data Point:	KCA 7.1.1.1/06
Report Author:	[redacted]
Report Year:	2020
Report Title:	Fluopyram: Aerobic Metabolism - degradation and time - Dependent sorption in 6 soils
Report No:	M12505406-3
Document No:	M-753426-01-1
Guideline(s) followed in study:	OECD Test Guideline No. 307 (2002) OECD Test Guideline No. 106 (2000, only in parts) Guidance on how aged sorption studies for pesticides should be conducted, analysed and used in the regulatory process (2012, revised draft 2016). Current revision dates: Sep 2016 [this draft guidance was updated based on the PPR statement on aged sorption, EFSA Journal 2015;13(7):4175]
Deviations from current test guideline:	Current Guideline: OECD 307 (2002), OECD 106 (2000) (Only in parts) None
Previous evaluation:	No, not previously submitted
GLP/Officially recognised testing facilities:	Yes, conducted under GLP/Officially recognised testing facilities
Acceptability/Reliability:	Yes

2. Full summary of KCA 7.1.1.1/06

Executive Summary

The degradation and time-dependence of sorption of [phenyl-UL-^{14}C]fluopyram was studied in six soils under aerobic conditions in the laboratory in the dark at 20 ± 2 °C (mean 19.4 °C) and 55 ± 5% (mean 54.6%) of the maximum water holding capacity for 118 days. The study design considered in its conduct aspects of time dependent sorption (see also KCA 7.1.3.2/05).

Soil	Soil ID	Source	Texture (USDA)	pH [1]	OC [%]
Hoeltinghausen	HS	Emstek, Germany	sand	4.5	0.9
Hornton	HT	Banbury, UK	loam	5.9	2.1
Le Thour	LT	Pontgivart-Auménancourt, France	silt loam	7.4	2.8
Brannens	BS	Tonneins, France	sandy loam	4.7	0.6
Balbiano	BB	Caleppio di Settala, Italy	sandy loam	7.1	1.1
Almayate East	AE	Malaga-Velez, Spain	loam	7.2	1.2

[1] in 0.01 M $CaCl_2$

An actual study application rate of 167 µg/kg soil dry weight was applied based on a maximum single field application rate of fluopyram of 250 g/ha (assuming incorporation into top 10 cm of soil and 1.5 g/cm^3 bulk density).

Duplicate samples were processed and analysed 0, 2, 7, 14, 27, 48, 83 and 118 days after treatment (DAT).

At each sampling interval, the soil was extracted five times. The first ambient extraction step was carried out at ambient temperature with aqueous 0.01 M $CaCl_2$ solution (soil to solution ratio of 1:4 (v/v); shaking for 48 hours) to determine the desorbable portion of the test item from the aged soil. Then, two ambient extractions of soil using acetonitrile/water 1/1 (v/v) and one with pure acetonitrile were performed. Finally, one microwave-assisted extraction step was performed using acetonitrile/water 4/1 (v/v) at 70 °C. The amounts of test item and degradation products in soil extracts were determined by liquid scintillation counting (LSC) and by HPLC/radiodetection analysis. Test item identity was confirmed by HPLC-MS/MS including accurate mass determination. One degradation product was identified in the extracts by co-chromatography with HPLC/radiodetection using a reference item and its enantiomeric composition was determined by a chiral chromatographic method.

Mean material balances of radioactivity were 102.4% AR for soil HS (range from 101.3 to 104.1% AR), 100.6% AR for soil HT (range from 95.8 to 104.3% AR), 100.9% AR for soil LT (range from 97.5 to 103.1% AR), 102.4% AR for soil BS (range from 100.5 to 106.2% AR), 101.9% AR for soil BB (range from 99.1 to 104.4% AR) and 101.4% AR for soil AE (range from 98.2 to 107.9% AR).

The maximum amount of carbon dioxide was 2.4, 4.5, 19.5, 5.9, 8.4 and 6.7% AR in soil HS, HT, LT, BS, BB and AE, respectively. Formation of volatile organic compounds (VOC) was insignificant as demonstrated by values of ≤ 0.1% AR at all sampling intervals for all soils.

Desorbable residues in aqueous 0.01 M $CaCl_2$ solution decreased from DAT-0 to DAT-118 from 41.1 to 21.0% AR in soil HS, from 27.2 to 10.9% AR in soil HT, from 26.1 to 14.0% AR in soil LT, from 62.9 to 39.4% AR in soil BS, from 36.3 to 17.2% in soil BB and from 36.5 to 11.7% from soil AE.

Total extractable residues (i.e. residues desorbed by aqueous 0.01 M $CaCl_2$ solution and residues in combined soil extracts) slightly decreased from DAT-0 to DAT-118 from 101.9 to 95.4% AR in soil HS, from 101.6 to 85.9% AR in soil HT, from 100.7 to 65.8% AR in soil LT, from 102.9 to 88.2% AR in soil BS, from 101.7 to 81.8% AR in soil BB and from 100.7 to 78.0% AR in soil AE.

Non-extractable residues (NER) increased from DAT-0 to DAT-118 from 0.6 to 3.5% AR in soil HS, from 1.9 to 9.2% AR in soil HT, from 2.4 to 13.7% AR in soil LT, from 0.7 to 6.4% in soil BS, from 1.6 to 8.9% AR in soil BB and from 1.8 to 13.4% AR in soil AE.

The amount of fluopyram in the total soil extracts (i.e. in aqueous desorption solution and organic soil extracts) decreased from DAT-0 to DAT-118 from 101.9 to 92.8% AR in soil HS, from 100.2 to 85.9% AR in soil HT, from 100.4 to 63.3% AR in soil LT, from 102.0 to 82.4% AR in soil BS, from 99.6 to 80.5% AR in soil BB and from 100.3 to 76.7% AR in soil AE.

Degradation of fluopyram was accompanied by the formation of fluopyram-7-hydroxy with a maximum amount of 5.8% AR at DAT-118 in soil BS. The total unidentified residues amounted to a maximum of 2.1% AR and no single compound exceeded 2.1% AR at any sampling interval in all soils.

I. MATERIALS AND METHODS

A. MATERIALS

1. Test Item

[phenyl-UL-^{14}C]fluopyram

Sample ID	KML 10699
Specific activity	5.15 MBq/mg
Radiochemical purity	> 98% (HPLC with radioactivity detector)
Chemical purity	> 98% (HPLC, UV- detector, 210 nm)

2. Test Soils

The soils were sampled freshly from the field (upper horizon of 0 to 10 cm as this is the respective top soil layer sampled and evaluated in the parallel field dissipation study M-758589-01-1, see KCA 7.1.2.2.1/15), air-dried and sieved to a particle size of ≤ 2 mm. Afterwards, soils were stored at 6 °C for approx. 1 month. The soils were taken from agricultural areas. The physico-chemical characteristics of the test soils are summarized in the tables below.

Table 7.1.1.1-29: Physico-chemical properties of test soils HS, HT and LT

Soil Designation	HS	HT	LT
Geographic Location			
City	Emstek	Banbury	Pontgivart-Auménancourt
State	Lower Saxony	South East	Grand Est
Country	Germany	UK	France
Soil Taxonomic Classification (USDA)	No information available		
Soil Series	No information available		
Textural Class (USDA)	sand	loam	silt loam
Sand (%) [50 µm – 2 mm]	85	35	25
Silt (%) [2 µm – 50 µm]	10	40	66
Clay (%) [< 2 µm]	3	25	9
pH (soil/0.01 M $CaCl_2$ 1/2)	4.5	5.9	7.4
pH (soil/water 1/1)	4.8	6.2	7.6
pH (saturated paste)	4.8	6.2	7.5
pH (soil/1 N KCl 1/1)	4.0	5.5	7.1
Organic Carbon (combustion) (%)	0.9	2.1	2.8
Organic Matter (%) [1]	1.6	3.6	4.8
Cation Exchange Capacity (meq/100 g)	5.3	16.5	15.6
Water Holding Capacity maximum (g H_2O *ad* 100 g soil DW)	29.0	54.3	62.5
at 1/10 bar (pF 2.0) (%)	7.5	30.9	31.2
Bulk Density (disturbed) (g/cm³)	1.44	1.21	1.03
Microbial Biomass (mg microbial carbon /			

Soil Designation	HS	HT	LT
kg soil DW) DAT-6 (BIO-)	71	396	1117
DAT-70 (BIO- / BIO+)	58 / 65	388 / 401	899 / 864
DAT-121 (BIO- / BIO+)	39 / 29	334 / 339	663 / 679

USDA: United States Department of Agriculture, DAT: days after treatment, DW: dry weight
[1] calculated as: OM (%) = OC (%) · 1.724
BIO- samples were applied with water, BIO+ samples were applied with solvent

Table 7.1.1.1-30: Physico-chemical properties of test soils BS, BB and AE

Soil Designation	BS	BB	AE
Geographic Location City State Country	Tonneins Nouvelle-Aquitaine France	Caleppio di Settala Lombardy Italy	Malaga-Velez Andalusia Spain
Soil Taxonomic Classification (USDA)	No information available		
Soil Series	No information available		
Textural Class (USDA)	sandy loam	sandy loam	loam
Sand (%) [50 µm – 2 mm]	65	57	33
Silt (%) [2 µm – 50 µm]	28	26	42
Clay (%) [< 2 µm]	7	17	25
pH (soil/0.01 M $CaCl_2$ 1/2)	4.7	7.1	7.7
pH (soil/water 1/1)	5.1	7.4	7.9
pH (saturated paste)	5.1	7.3	7.8
pH (soil/1 N KCl 1/1)	4.3	6.8	7.3
Organic Carbon (combustion) (%)	0.6	1.7	1.2
Organic Matter (%)[1]	1.0	2.9	2.1
Cation Exchange Capacity (meq/100 g)	4.6	13.8	18.2
Water Holding Capacity maximum (g H_2O *ad* 100 g soil DW)	39.4	48.7	46.6
at 1/10 bar (pF 2.0) (%)	12.4	18.7	27.7
Bulk Density (disturbed) (g/cm^3)	1.35	1.19	1.19
Microbial Biomass (mg microbial carbon / kg soil DW)			
DAT-6 (BIO-)	121	349	607
DAT-70 (BIO- / BIO+)	84 / 10	297 / 284	539 / 571
DAT-121 (BIO- / BIO+)	46 / 41	244 / 251	427 / 445

USDA: United States Department of Agriculture, DAT: days after treatment, DW: dry weight
[1] calculated as: OM (%) = OC (%) 1.724
BIO- samples were applied with water, BIO+ samples were applied with solvent

B. STUDY DESIGN

1. Experimental Conditions

Static test systems were used, consisting of 300 mL Erlenmeyer flasks filled with soil and equipped with a trap attachment (permeable for oxygen) containing soda lime for absorption of carbon dioxide and a polyurethane (PU) foam plug for adsorption of volatile organic compounds (VOC).

100 g of the sieved soils (dry weight equivalents) were weighed into each test vessel and the soil moisture was adjusted to 55% of the maximum water holding capacity (MWHC) by addition of de-ionized water. The test vessels were then fitted with trap attachments. The untreated test systems were equilibrated to study conditions for 2 days prior to application.

An actual study application rate of 167 µg/kg soil dry weight was applied based on a maximum single field application rate of fluopyram of 250 g/ha (assuming incorporation into top 10 cm of soil and 1.5 g/cm^3 bulk density)..

The application solution was prepared by diluting 2.51 mL of a stock solution (1.0 mg test item/mL methanol) in 57.49 mL water. An aliquot of 400 µL of the application solution were applied each drop wise onto the soil surface of the respective equilibrated test systems using a pipette.

After application the test vessels (except DAT-0 samples) were fitted with trap attachments and incubated under aerobic conditions in the dark for 118 days at 20 ± 2 °C and a soil moisture of 55 ± 5% of the maximum water holding capacity in a walk-in climatic chamber.

2. Sampling

Eight sampling intervals were distributed over the entire incubation period of 118 days. Duplicate samples were processed and analysed 0, 3, 7, 14, 27, 48, 83 and 118 days after treatment (DAT).

Microbial soil biomass was determined at start, middle and end of the study (i.e. DAT-6, DAT-70 and DAT-121).

3. Analytical Procedures

Following purging of the samples, the trap attachment was removed and the soil was extracted completely.

At each sampling interval, a so-called batch equilibrium shaking test was performed firstly to determine the time-dependent sorption of fluopyram. Therefore, the trap attachments were removed from the test systems and the entire soil of each test system was supplemented with 400 mL 0.01 M $CaCl_2$ solution, corresponding to a soil-to-solution ratio of approximately 1:4, and shaken in the dark at 20 °C for 48 h. Afterwards, supernatant and soil were separated by centrifugation and decantation. Thereafter, the soil was extracted three times at ambient temperature using a mechanical shaker followed by one extraction using a microwave (70 °C) with a magnetic stirrer. Extractions were performed with 80 mL ACN/water (1/1, v/v), ACN/water (4/1, v/v), ACN and ACN/water (4/1, v/v) in the first, second, third and last extraction, respectively.

For confirmation of extraction efficiency, T0-samples were prepared separately and processed immediately after application as described for the other samples, but without the aqueous $CaCl_2$ extraction step. The mean recovery of the test item at DAT-0 was between 98.7 and 104.7% AR for all soils without prior $CaCl_2$ extraction (T0) and between 99.6 and 102.0% AR for all soils with an additional $CaCl_2$ extraction step (T1).

The aqueous desorption solution of the batch equilibrium shaking test and the combined soil extracts were analysed separately each by liquid scintillation counting and by HPLC/radiodetection. The limit of detection (LOD) for the HPLC/radiodetection method was 1.9% AR and for the LSC ≤0.4% AR for

the different extracts/solutions and the combustion samples. Identity of the test item was confirmed by HPLC-MS(/MS). The amount of non-extractable residues was determined by combustion/LSC.

The metabolite fluopyram-7-hydroxy as observed in desorption solution and soil extracts was identified by co-chromatography in HPLC with unlabelled reference item.

In addition, attempts were made to resolve the two enantiomers of fluopyram-7-hydroxy potentially formed, by a chiral analysis incomparison to non-labelled racemic reference item.

II. RESULTS AND DISCUSSION

A. EXTRACTION AND DISTRIBUTION OF RADIOACTIVITY IN SOIL SAMPLES

Table 7.1.1.1-31 to Table 7.1.1.1-36 summarize the degradation of [phenyl-UL-^{14}C]fluopyram as a function of time.

Table 7.1.1.1-31: Degradation of fluopyram in soil Hoeltinghausen under aerobic conditions

Compound	Replicate No.	Residues (% AR) on the following days after treatment (DAT)							
		0	3	7	14	27	48	83	118
Fluopyram	1	102.3	99.5	100.8	100.0	99.9	98.0	97.6	95.2
	2	101.4	101.8	100.3	101.4	102.3	98.7	96.9	90.3
	Mean	**101.9**	**100.6**	**100.5**	**100.7**	**101.1**	**98.4**	**97.3**	**92.8**
Fluopyram-7-hydroxy	1	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	< LOQ
	2	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	< LOQ
	Mean	**n.c.**	**n.c.**	**n.c.**	**n.c.**	**n.c.**	**n.c.**	**n.c.**	**< LOQ**
u2	1	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	2	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	Mean	**n.c.**	**n.c.**	**n.c.**	**n.c.**	**n.c.**	**n.c.**	**n.c.**	**n.c.**
u3	1	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	2	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	Mean	**n.c.**	**n.c.**	**n.c.**	**n.c.**	**n.c.**	**n.c.**	**n.c.**	**n.c.**
u4	1	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	2	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	Mean	**n.c.**	**n.c.**	**n.c.**	**n.c.**	**n.c.**	**n.c.**	**n.c.**	**n.c.**
u5	1	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	2	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	Mean	**n.c.**	**n.c.**	**n.c.**	**n.c.**	**n.c.**	**n.c.**	**n.c.**	**n.c.**
u6	1	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	< LOQ
	2	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	< LOQ
	Mean	**n.c.**	**n.c.**	**n.c.**	**n.c.**	**n.c.**	**n.c.**	**n.c.**	**< LOQ**
u7	1	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	< LOQ
	2	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	< LOQ
	Mean	**n.c.**	**n.c.**	**n.c.**	**n.c.**	**n.c.**	**n.c.**	**n.c.**	**< LOQ**
u8	1	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	2	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	Mean	**n.c.**	**n.c.**	**n.c.**	**n.c.**	**n.c.**	**n.c.**	**n.c.**	**n.c.**
u9	1	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	2	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	Mean	**n.c.**	**n.c.**	**n.c.**	**n.c.**	**n.c.**	**n.c.**	**n.c.**	**n.c.**
Sum of Unid./Diff. Residues [1]	1	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	< LOQ
	2	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	< LOQ
	Mean	**n.c.**	**n.c.**	**n.c.**	**n.c.**	**n.c.**	**n.c.**	**n.c.**	**< LOQ**
Total Extractable Residues	1	102.3	99.5	100.8	100.0	99.9	98.0	97.6	97.9
	2	101.4	101.8	100.3	101.4	102.3	98.7	96.9	92.9
	Mean	**101.9**	**100.6**	**100.5**	**100.7**	**101.1**	**98.4**	**97.3**	**95.4**
Carbon Dioxide	1	n.a.	< 0.1	n.d.	< 0.1	1.5	1.6	2.5	2.4
	2	n.a.	< 0.1	n.d.	n.d.	0.7	1.8	2.4	2.3
	Mean	**n.a.**	**< 0.1**	**n.c.**	**< 0.1**	**1.1**	**1.7**	**2.4**	**2.3**
Volatile Organic compounds	1	n.a.	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	0.2	< 0.1
	2	n.a.	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1
	Mean	**n.a.**	**< 0.1**	**< 0.1**	**< 0.1**	**< 0.1**	**< 0.1**	**0.1**	**< 0.1**
Non-Extractable Residues	1	0.6	1.0	1.4	1.9	1.9	2.4	2.7	3.5
	2	0.7	1.1	1.5	1.8	2.0	2.4	3.0	3.5
	Mean	**0.6**	**1.0**	**1.5**	**1.8**	**1.9**	**2.4**	**2.8**	**3.5**
Material Balance	1	102.9	100.4	102.2	101.9	103.3	102.1	103.0	103.8
	2	102.1	102.9	101.8	103.2	105.0	102.9	102.2	98.7
	Mean	**102.5**	**101.7**	**102.0**	**102.5**	**104.1**	**102.5**	**102.6**	**101.3**

n.d.: not detected, n.a.: not analysed, n.c.: not calculated, DAT: days after treatment
[1] Minor components (unidentified metabolites and diffuse residues) are summed up to unidentified residues.

Table 7.1.1.1-32: Degradation of fluopyram in soil Hornton under aerobic conditions

Compound	Replicate No.	Residues (% AR) on the following days after treatment (DAT)							
		0	3	7	14	27	48	83	118
Fluopyram	1	102.3	106.0	97.9	89.5	90.3	90.5	86.4	85.3
	2	98.1	96.3	96.1	93.9	96.2	90.3	88.7	86.6
	Mean	**100.2**	**101.2**	**97.0**	**91.7**	**93.3**	**90.4**	**87.6**	**85.9**
Fluopyram-7-hydroxy	1	n.d.	n.d.	n.d.	n.d.	n.d.	< LOQ	n.d.	n.d.
	2	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	Mean	**n.c.**	**n.c.**	**n.c.**	**n.c.**	**n.c.**	**< LOQ**	**n.c.**	**n.c.**
u2	1	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	2	< LOQ	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	Mean	**< LOQ**	**n.c.**	**n.c.**	**n.c.**	**n.c.**	**n.c.**	**n.c.**	**n.c.**
u3	1	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	2	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	Mean	**n.c.**	**n.c.**	**n.c.**	**n.c.**	**n.c.**	**n.c.**	**n.c.**	**n.c.**
u4	1	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	2	< LOQ	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	Mean	**< LOQ**	**n.c.**	**n.c.**	**n.c.**	**n.c.**	**n.c.**	**n.c.**	**n.c.**
u5	1	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	2	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	Mean	**n.c.**	**n.c.**	**n.c.**	**n.c.**	**n.c.**	**n.c.**	**n.c.**	**n.c.**
u6	1	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	2	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	Mean	**n.c.**	**n.c.**	**n.c.**	**n.c.**	**n.c.**	**n.c.**	**n.c.**	**n.c.**
u7	1	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	2	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	Mean	**n.c.**	**n.c.**	**n.c.**	**n.c.**	**n.c.**	**n.c.**	**n.c.**	**n.c.**
u8	1	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	2	n.d.	< LOQ	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	Mean	**n.c.**	**< LOQ**	**n.c.**	**n.c.**	**n.c.**	**n.c.**	**n.c.**	**n.c.**
u9	1	n.d.	< LOQ	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	2	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	Mean	**n.c.**	**< LOQ**	**n.c.**	**n.c.**	**n.c.**	**n.c.**	**n.c.**	**n.c.**
Sum of Unid./Diff. Residues [1]	1	n.d.	< LOQ	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	2	< LOQ	< LOQ	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	Mean	**< LOQ**	**< LOQ**	**n.c.**	**n.c.**	**n.c.**	**n.c.**	**n.c.**	**n.c.**
Total Extractable Residues	1	102.3	106.4	97.9	89.5	90.3	91.6	86.4	85.3
	2	100.8	96.6	96.1	93.9	96.2	90.3	88.7	86.6
	Mean	**101.6**	**101.5**	**97.0**	**91.7**	**93.3**	**90.9**	**87.6**	**85.9**
Carbon Dioxide	1	n.a.	< 0.1	< 0.1	n.d.	2.1	3.1	3.9	4.5
	2	n.a.	< 0.1	< 0.1	n.d.	1.8	3.5	3.9	4.5
	Mean	**n.a.**	**< 0.1**	**< 0.1**	**n.d.**	**1.9**	**3.3**	**3.9**	**4.5**
Volatile Organic compounds	1	n.a.	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	0.1
	2	n.a.	< 0.1	< 0.1	< 0.1	< 0.1	0.1	0.1	< 0.1
	Mean	**n.a.**	**< 0.1**	**< 0.1**	**< 0.1**	**< 0.1**	**< 0.1**	**0.1**	**0.1**
Non-Extractable Residues	1	1.8	2.8	3.4	4.4	5.7	6.4	8.1	8.2
	2	2.1	2.8	3.1	3.8	6.1	6.1	8.4	10.3
	Mean	**1.9**	**2.8**	**3.3**	**4.1**	**5.9**	**6.3**	**8.2**	**9.2**
Material Balance	1	104.1	109.2	101.4	93.9	98.1	101.1	98.4	98.1
	2	102.9	99.4	99.3	97.8	104.1	100.0	101.1	101.4
	Mean	**103.5**	**104.3**	**100.3**	**95.8**	**101.1**	**100.6**	**99.8**	**99.7**

n.d.: not detected, n.a.: not analysed, n.c.: not calculated, DAT: days after treatment
[1] Minor components (unidentified metabolites and diffuse residues) are summed up to unidentified residues.

Table 7.1.1.1-33: Degradation of fluopyram in soil Le Thour under aerobic conditions

Compound	Replicate No.	Residues (% AR) on the following days after treatment (DAT)							
		0	3	7	14	27	48	83	118
Fluopyram	1	100.6	99.2	94.8	95.5	89.8	79.9	70.8	62.8
	2	100.3	96.6	89.9	94.5	91.3	83.1	67.7	63.7
	Mean	**100.4**	**97.9**	**92.4**	**95.0**	**90.6**	**81.5**	**69.2**	**63.3**
Fluopyram-7-hydroxy	1	n.d.	n.d.	n.d.	2.0	2.7	4.6	3.9	2.5
	2	n.d.	n.d.	< LOQ	2.2	3.6	2.2	5.0	2.5
	Mean	**n.c.**	**n.c.**	**< LOQ**	**2.1**	**3.2**	**3.4**	**4.4**	**2.5**
u2	1	< LOQ	n.d.	n.d.	n.d.	n.d.	< LOQ	n.d.	n.d.
	2	n.d.	n.d.	< LOQ	n.d.	n.d.	n.d.	n.d.	n.d.
	Mean	**< LOQ**	**n.c.**	**< LOQ**	**n.c.**	**n.c.**	**< LOQ**	**n.c.**	**n.c.**
u3	1	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	2	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	Mean	**n.c.**	**n.c.**	**n.c.**	**n.c.**	**n.c.**	**n.c.**	**n.c.**	**n.c.**
u4	1	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	2	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	Mean	**n.c.**	**n.c.**	**n.c.**	**n.c.**	**n.c.**	**n.c.**	**n.c.**	**n.c.**
u5	1	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	2	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	Mean	**n.c.**	**n.c.**	**n.c.**	**n.c.**	**n.c.**	**n.c.**	**n.c.**	**n.c.**
u6	1	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	2	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	Mean	**n.c.**	**n.c.**	**n.c.**	**n.c.**	**n.c.**	**n.c.**	**n.c.**	**n.c.**
u7	1	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	2	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	Mean	**n.c.**	**n.c.**	**n.c.**	**n.c.**	**n.c.**	**n.c.**	**n.c.**	**n.c.**
u8	1	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	2	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	Mean	**n.c.**	**n.c.**	**n.c.**	**n.c.**	**n.c.**	**n.c.**	**n.c.**	**n.c.**
u9	1	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	2	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	Mean	**n.c.**	**n.c.**	**n.c.**	**n.c.**	**n.c.**	**n.c.**	**n.c.**	**n.c.**
Sum of Unid./Diff. Residues [1]	1	< LOQ	n.d.	n.d.	n.d.	n.d.	< LOQ	n.d.	n.d.
	2	n.d.	n.d.	< LOQ	n.d.	n.d.	n.d.	n.d.	n.d.
	Mean	**< LOQ**	**n.c.**	**< LOQ**	**n.c.**	**n.c.**	**< LOQ**	**n.c.**	**n.c.**
Total Extractable Residues	1	101.1	99.2	94.8	97.5	92.5	85.3	74.7	65.3
	2	100.3	96.6	92.5	96.7	95.0	85.3	72.7	66.2
	Mean	**100.7**	**97.9**	**93.7**	**97.1**	**93.7**	**85.3**	**73.7**	**65.8**
Carbon Dioxide	1	n.a.	< 0.1	< 0.1	< 0.1	4.5	7.7	14.9	19.6
	2	n.a.	< 0.1	n.d.	< 0.1	4.8	8.5	14.9	19.3
	Mean	**n.a.**	**< 0.1**	**< 0.1**	**< 0.1**	**4.6**	**8.1**	**14.9**	**19.5**
Volatile Organic compounds	1	n.a.	< 0.1	< 0.1	< 0.1	< 0.1	0.1	0.2	0.1
	2	n.a.	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	0.1
	Mean	**n.a.**	**< 0.1**	**< 0.1**	**< 0.1**	**< 0.1**	**0.1**	**0.1**	**0.1**
Non-Extractable Residues	1	2.5	3.1	3.3	4.6	4.3	8.4	12.2	13.9
	2	2.3	2.7	4.3	4.2	4.4	8.8	11.1	13.6
	Mean	**2.4**	**2.9**	**3.8**	**4.4**	**4.3**	**8.6**	**11.6**	**13.7**
Material Balance	1	103.6	102.3	98.2	102.1	101.3	101.5	101.9	98.9
	2	102.6	99.3	96.8	100.9	104.1	102.6	98.7	99.2
	Mean	**103.1**	**100.8**	**97.5**	**101.5**	**102.7**	**102.0**	**100.3**	**99.1**

n.d.: not detected, n.a.: not analysed, n.c.: not calculated, DAT: days after treatment
[1] Minor components (unidentified metabolites and diffuse residues) are summed up to unidentified residues.

Table 7.1.1.1-34: Degradation of fluopyram in soil Brannens under aerobic conditions

Compound	Replicate No.	Residues (% AR) on the following days after treatment (DAT)							
		0	3	7	14	27	48	83	118
Fluopyram	1	101.1	99.0	99.0	96.7	100.0	91.7	86.1	82.2
	2	103.0	100.0	99.3	98.6	97.8	89.1	92.0	82.6
	Mean	**102.0**	**99.5**	**99.2**	**97.6**	**98.9**	**90.4**	**89.0**	**82.4**
Fluopyram-7-hydroxy	1	n.d.	n.d.	n.d.	< LOQ	< LOQ	5.0	6.6	7.0
	2	n.d.	n.d.	n.d.	n.d.	2.0	4.5	4.3	4.5
	Mean	**n.c.**	**n.c.**	**n.c.**	**< LOQ**	**< LOQ**	**4.7**	**5.5**	**5.8**
u2	1	< LOQ	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	2	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	Mean	**< LOQ**	**n.c.**	**n.c.**	**n.c.**	**n.c.**	**n.c.**	**n.c.**	**n.c.**
u3	1	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	2	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	Mean	**n.c.**	**n.c.**	**n.c.**	**n.c.**	**n.c.**	**n.c.**	**n.c.**	**n.c.**
u4	1	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	2	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	Mean	**n.c.**	**n.c.**	**n.c.**	**n.c.**	**n.c.**	**n.c.**	**n.c.**	**n.c.**
u5	1	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	2	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	Mean	**n.c.**	**n.c.**	**n.c.**	**n.c.**	**n.c.**	**n.c.**	**n.c.**	**n.c.**
u6	1	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	2	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	Mean	**n.c.**	**n.c.**	**n.c.**	**n.c.**	**n.c.**	**n.c.**	**n.c.**	**n.c.**
u7	1	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	2	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	Mean	**n.c.**	**n.c.**	**n.c.**	**n.c.**	**n.c.**	**n.c.**	**n.c.**	**n.c.**
u8	1	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	2	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	Mean	**n.c.**	**n.c.**	**n.c.**	**n.c.**	**n.c.**	**n.c.**	**n.c.**	**n.c.**
u9	1	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	2	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	Mean	**n.c.**	**n.c.**	**n.c.**	**n.c.**	**n.c.**	**n.c.**	**n.c.**	**n.c.**
Sum of Unid./Diff. Residues [1]	1	LOQ	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	2	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	Mean	**< LOQ**	**n.c.**	**n.c.**	**n.c.**	**n.c.**	**n.c.**	**n.c.**	**n.c.**
Total Extractable Residues	1	102.7	99.0	99.0	97.9	101.1	96.7	92.7	89.2
	2	103.0	100.0	99.3	98.6	99.8	93.6	96.3	87.2
	Mean	**102.9**	**99.5**	**99.2**	**98.3**	**100.5**	**95.1**	**94.5**	**88.2**
Carbon Dioxide	1	n.a.	n.d.	< 0.1	< 0.1	3.0	3.3	4.8	5.9
	2	n.a.	n.d.	0.1	n.d.	2.8	3.5	4.8	5.9
	Mean	**n.a.**	**n.d.**	**< 0.1**	**< 0.1**	**2.9**	**3.4**	**4.8**	**5.9**
Volatile Organic compounds	1	n.a.	< 0.1	< 0.1	n.d.	< 0.1	0.1	< 0.1	0.1
	2	n.a.	n.d.	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	0.1
	Mean	**n.a.**	**< 0.1**	**< 0.1**	**< 0.1**	**< 0.1**	**0.1**	**< 0.1**	**0.1**
Non-Extractable Residues	1	0.6	1.2	1.7	2.3	2.9	4.0	5.3	6.2
	2	0.8	1.2	1.6	2.3	2.7	3.9	5.1	6.5
	Mean	**0.7**	**1.2**	**1.6**	**2.3**	**2.8**	**3.9**	**5.2**	**6.4**
Material Balance	1	103.3	100.1	100.7	100.2	107.1	104.0	102.8	101.4
	2	103.7	101.2	100.9	100.9	105.3	101.0	106.2	99.6
	Mean	**103.5**	**100.7**	**100.8**	**100.5**	**106.2**	**102.5**	**104.5**	**100.5**

n.d.: not detected, n.a.: not analysed, n.c.: not calculated, DAT: days after treatment
[1] Minor components (unidentified metabolites and diffuse residues) are summed up to unidentified residues.

Table 7.1.1.1-35: Degradation of fluopyram in soil Balbiano under aerobic conditions

Compound	Replicate No.	Residues (% AR) on the following days after treatment (DAT)							
		0	3	7	14	27	48	83	118
Fluopyram	1	99.6	99.9	98.1	97.5	98.4	93.7	83.8	82.0
	2	99.6	97.2	97.9	97.2	96.2	92.2	85.7	78.9
	Mean	**99.6**	**98.5**	**98.0**	**97.3**	**97.3**	**92.9**	**84.8**	**80.5**
Fluopyram-7-hydroxy	1	n.d.	n.d.	n.d.	n.d.	n.d.	< LOQ	< LOQ	n.d.
	2	n.d.	n.d.	n.d.	< LOQ	n.d.	< LOQ	< LOQ	2.6
	Mean	**n.c.**	**n.c.**	**n.c.**	**< LOQ**	**n.c.**	**< LOQ**	**< LOQ**	**< LOQ**
u2	1	2.1	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	2	2.0	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	Mean	**2.1**	**n.c.**	**n.c.**	**n.c.**	**n.c.**	**n.c.**	**n.c.**	**n.c.**
u3	1	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	2	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	Mean	**n.c.**	**n.c.**	**n.c.**	**n.c.**	**n.c.**	**n.c.**	**n.c.**	**n.c.**
u4	1	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	2	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	Mean	**n.c.**	**n.c.**	**n.c.**	**n.c.**	**n.c.**	**n.c.**	**n.c.**	**n.c.**
u5	1	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	2	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	Mean	**n.c.**	**n.c.**	**n.c.**	**n.c.**	**n.c.**	**n.c.**	**n.c.**	**n.c.**
u6	1	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	2	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	Mean	**n.c.**	**n.c.**	**n.c.**	**n.c.**	**n.c.**	**n.c.**	**n.c.**	**n.c.**
u7	1	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	2	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	Mean	**n.c.**	**n.c.**	**n.c.**	**n.c.**	**n.c.**	**n.c.**	**n.c.**	**n.c.**
u8	1	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	2	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	Mean	**n.c.**	**n.c.**	**n.c.**	**n.c.**	**n.c.**	**n.c.**	**n.c.**	**n.c.**
u9	1	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	2	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	Mean	**n.c.**	**n.c.**	**n.c.**	**n.c.**	**n.c.**	**n.c.**	**n.c.**	**n.c.**
Sum of Unid./Diff. Residues [1]	1	2.1	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	2	2.0	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	Mean	**2.1**	**n.c.**	**n.c.**	**n.c.**	**n.c.**	**n.c.**	**n.c.**	**n.c.**
Total Extractable Residues	1	101.7	99.9	98.1	97.5	98.4	94.6	85.4	82.0
	2	101.6	97.2	97.9	98.1	96.2	93.3	87.2	81.5
	Mean	**101.7**	**98.5**	**98.0**	**97.8**	**97.3**	**93.9**	**86.3**	**81.8**
Carbon Dioxide	1	n.a.	< 0.1	n.d.	n.d.	3.0	4.2	5.7	7.9
	2	n.a.	n.d.	< 0.1	< 0.1	3.0	4.1	5.9	8.9
	Mean	**n.a.**	**< 0.1**	**< 0.1**	**< 0.1**	**3.0**	**4.1**	**5.8**	**8.4**
Volatile Organic compounds	1	n.a.	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1
	2	n.a.	< 0.1	< 0.1	< 0.1	< 0.1	0.1	< 0.1	0.1
	Mean	**n.a.**	**< 0.1**	**< 0.1**	**< 0.1**	**< 0.1**	**0.1**	**< 0.1**	**0.1**
Non-Extractable Residues	1	1.9	2.5	3.2	4.2	4.0	5.9	8.8	8.2
	2	1.4	2.5	3.2	4.0	4.1	5.9	7.9	9.5
	Mean	**1.6**	**2.5**	**3.2**	**4.1**	**4.1**	**5.9**	**8.3**	**8.9**
Material Balance	1	103.6	102.4	101.4	101.7	105.4	104.7	99.9	98.1
	2	103.0	99.7	101.2	102.0	103.3	103.4	101.0	100.0
	Mean	**103.3**	**101.0**	**101.3**	**101.8**	**104.4**	**104.0**	**100.5**	**99.1**

n.d.: not detected, n.a.: not analysed, n.c.: not calculated, DAT: days after treatment
[1] Minor components (unidentified metabolites and diffuse residues) are summed up to unidentified residues.

Table 7.1.1.1-36: Degradation of fluopyram in soil Almayate East under aerobic conditions

Compound	Replicate No.	Residues (% AR) on the following days after treatment (DAT)							
		0	3	7	14	27	48	83	118
Fluopyram	1	100.3	96.4	96.3	96.9	95.7	84.6	78.5	77.1
	2	100.3	96.2	96.4	98.2	99.9	86.3	82.0	76.4
	Mean	**100.3**	**96.3**	**96.3**	**97.5**	**97.8**	**85.4**	**80.2**	**76.7**
Fluopyram-7-hydroxy	1	n.d.	n.d.	n.d.	n.d.	n.d.	< LOQ	< LOQ	< LOQ
	2	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	< LOQ
	Mean	**n.c.**	**n.c.**	**n.c.**	**n.c.**	**n.c.**	**< LOQ**	**< LOQ**	**< LOQ**
u2	1	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	2	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	Mean	**n.c.**	**n.c.**	**n.c.**	**n.c.**	**n.c.**	**n.c.**	**n.c.**	**n.c.**
u3	1	n.d.	< LOQ	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	2	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	Mean	**n.c.**	**< LOQ**	**n.c.**	**n.c.**	**n.c.**	**n.c.**	**n.c.**	**n.c.**
u4	1	< LOQ	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	2	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	Mean	**< LOQ**	**n.c.**	**n.c.**	**n.c.**	**n.c.**	**n.c.**	**n.c.**	**n.c.**
u5	1	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	2	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	Mean	**n.c.**	**n.c.**	**n.c.**	**n.c.**	**n.c.**	**n.c.**	**n.c.**	**n.c.**
u6	1	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	2	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	Mean	**n.c.**	**n.c.**	**n.c.**	**n.c.**	**n.c.**	**n.c.**	**n.c.**	**n.c.**
u7	1	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	2	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	Mean	**n.c.**	**n.c.**	**n.c.**	**n.c.**	**n.c.**	**n.c.**	**n.c.**	**n.c.**
u8	1	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	2	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	Mean	**n.c.**	**n.c.**	**n.c.**	**n.c.**	**n.c.**	**n.c.**	**n.c.**	**n.c.**
u9	1	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	2	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	Mean	**n.c.**	**n.c.**	**n.c.**	**n.c.**	**n.c.**	**n.c.**	**n.c.**	**n.c.**
Sum of Unid./Diff. Residues [1]	1	< LOQ	< LOQ	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	2	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	Mean	**< LOQ**	**< LOQ**	**n.c.**	**n.c.**	**n.c.**	**n.c.**	**n.c.**	**n.c.**
Total Extractable Residues	1	101.1	96.7	96.3	96.9	95.7	86.3	79.5	78.5
	2	100.3	96.2	96.4	98.2	99.9	86.3	82.0	77.5
	Mean	**100.7**	**96.5**	**96.3**	**97.5**	**97.8**	**86.3**	**80.7**	**78.0**
Carbon Dioxide	1	n.a.	n.d.	< 0.1	< 0.1	3.2	3.8	5.6	6.8
	2	n.a.	n.d.	n.d.	< 0.1	3.0	4.1	5.3	6.7
	Mean	**n.a.**	**n.c.**	**< 0.1**	**< 0.1**	**3.1**	**4.0**	**5.5**	**6.7**
Volatile Organic compounds	1	n.a.	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1
	2	n.a.	< 0.1	< 0.1	< 0.1	0.1	< 0.1	< 0.1	< 0.1
	Mean	**n.a.**	**< 0.1**	**< 0.1**	**< 0.1**	**0.1**	**< 0.1**	**< 0.1**	**< 0.1**
Non-Extractable Residues	1	1.7	3.6	4.5	5.9	6.9	9.4	13.1	13.7
	2	1.8	3.2	4.6	5.8	7.0	9.4	12.4	13.1
	Mean	**1.8**	**3.4**	**4.6**	**5.9**	**7.0**	**9.4**	**12.7**	**13.4**
Material Balance	1	102.8	100.3	100.8	102.8	105.8	99.4	98.1	99.0
	2	102.1	99.5	101.0	104.0	110.0	99.8	99.7	97.3
	Mean	**102.5**	**99.9**	**100.9**	**103.4**	**107.9**	**99.6**	**98.9**	**98.2**

n.d.: not detected, n.a.: not analysed, n.c.: not calculated, DAT: days after treatment
[1] Minor components (unidentified metabolites and diffuse residues) are summed up to unidentified residues.

B. MATERIAL BALANCE

Mean material balances of radioactivity were 102.4% AR for soil HS (range from 101.3 to 104.1% AR), 100.6% AR for soil HT (range from 95.8 to 104.3% AR), 100.9% AR for soil LT (range from 97.5 to 103.1% AR), 102.4% AR for soil BS (range from 100.5 to 106.2% AR), 101.9% AR for soil BB (range from 99.1 to 104.4% AR) and 101.4% AR for soil AE (range from 98.2 to 107.9% AR).

The complete material balances found at all sampling intervals for all soils demonstrated that there was no significant loss of radioactivity from the test systems or during sample processing.

C. EXTRACTABLE AND NON-EXTRACTABLE RESIDUES

Desorbable residues in aqueous 0.01 M $CaCl_2$ solution decreased from DAT-0 to DAT-118 from 41.1 to 21.0% AR in soil HS, from 27.2 to 10.9% AR in soil HT, from 26.1 to 14.0% AR in soil LT, from 62.9 to 39.4% AR in soil BS, from 36.3 to 17.2% in soil BB and from 36.5 to 11.7% from soil AE.

Total extractable residues (i.e. residues desorbed by aqueous 0.01 M $CaCl_2$ solution and residues in combined soil extracts) slightly decreased from DAT-0 to DAT-118 from 101.9 to 95.4% AR in soil HS, from 101.6 to 85.9% AR in soil HT, from 100.7 to 65.8% AR in soil LT, from 102.9 to 88.2% AR in soil BS, from 101.7 to 81.8% AR in soil BB and from 100.7 to 78.0% AR in soil AE.

Non-extractable residues (NER) increased from DAT-0 to DAT-118 from 0.6 to 3.5% AR in soil HS, from 1.9 to 9.2% AR in soil HT, from 2.4 to 13.7% AR in soil LT, from 0.7 to 6.4% in soil BS, from 1.6 to 8.9% AR in soil BB and from 1.8 to 13.4% AR in soil AE.

D. VOLATILIZATION

The maximum amount of carbon dioxide was 2.4, 4.5, 19.5, 5.9, 8.4 and 6.7% AR in soil HS, HT, LT, BS, BB and AE, respectively. Formation of volatile organic compounds (VOC) was insignificant as demonstrated by values of ≤ 0.1% AR at all sampling intervals for all soils.

E. DEGRADATION OF TEST ITEM

The amount of fluopyram in the total soil extracts (i.e. in aqueous desorption solution and organic soil extracts) decreased from DAT-0 to DAT-118 from 101.9 to 92.8% AR in soil HS, from 100.2 to 85.9% AR in soil HT, from 100.4 to 63.3% AR in soil LT, from 102.0 to 82.4% AR in soil BS, from 99.6 to 80.5% AR in soil BB and from 100.3 to 76.7% AR in soil AE.

Degradation of fluopyram was accompanied by the formation of fluopyram-7-hydroxy with a maximum amount of 5.8% AR at DAT-118 in soil BS. The total unidentified residues amounted to a maximum of 2.1% AR and no single compound exceeded 2.1% AR at any sampling interval in all soils.

Attempts were made to investigate the occurring ratio of the two possible isomers of the metabolite of fluopyram-7-hydroxy but no clear conclusion on the enantiomeric behaviour can be drawn from this study.

F. KINETICS

New kinetic calculations including degradation products were conducted and reported under KCA 7.1.2.1.1/13 (M-761969-01-1).

G. TIME-DEPENDENCE OF SORPTION

Results of the time-dependent sorption experiment can be found in KCA 7.1.3.2/05.

III. CONCLUSIONS

Fluopyram was slowly degraded and mineralized in soil under aerobic conditions in the dark in the laboratory.

Formation of carbon dioxide was up to 19.5% AR and formation of non-extractable residues (NER) was up to 13.7% AR. Besides NER and carbon dioxide, degradation of fluopyram was accompanied by the formation of fluopyram-7-hydroxy with a maximum amount of 5.8% AR.

The results of the study indicate an 'ageing' of residues of fluopyram in soil with time that expressed by an increase of sorption to soil. The effect was considered further in mobility assessments (see KCA 7.1.3.2/05). For consideration in mobility assessments, this time dependnet sorption effect was quantified to result in TDS factors each determined for the various sampling points in the course of the study.

3. Assessment and conclusion

Assessment and conclusion by applicant:
The study and its data are considered as valid and reliable for use in risk assessment.

Assessment and conclusion by RMS:
Outcome and conclusion of the study: RMS should indicate if they agree to the results and conclusions of the APPL.

1. Information on the study

Data Point:	KCA 7.1.1/07
Report Author:	[redacted]
Report Year:	2021
Report Title:	Fluopyram: Aerobic degradation and determination of BCS-AA10065 and trifluoroacetic acid (TFA) in 4 soils
Report No:	EnSa-20-0811
Document No:	M-761739-01-1
Guideline(s) followed in study:	OECD Test Guideline No. 307 (2002); Commission Regulation (EU) No 283/2013 in accordance with Regulation (EC) No 1107/2009; US EPA OCSPP Test Guideline No. 835.4100 / 835.4200 (2008); SANCO/3029/99 rev. 4: EU guidance document for generating and reporting methods of analysis in support of pre-registration data requirements (2000)
Deviations from current test guideline:	Current Guideline: OECD 307 (2002) None
Previous evaluation:	No, not previously submitted
GLP/Officially recognised testing facilities:	Yes, conducted under GLP/Officially recognised testing facilities
Acceptability/Reliability:	Yes

2. Full summary of KCA 7.1.1.1/07

Executive Summary

The degradation of fluopyram (FLU) including the potential fr formation of the two mdegradation products BCS-AA10065 (fluopyram-7-hydroxy, FLU-7-OH) and trifluoroacetate (TFA) was investigated following application of [phenyl-UL-^{14}C]fluopyram to four soils under aerobic conditions in the dark in the laboratory at 19.2 °C (mean over duration) and 54.4% (mean over duration) of the maximum water holding capacity for 120 days.

Soil	Soil ID	Source	Texture (USDA)	pH [1]	OC [%]
Frankenforst	FF	Vinxel, Germany	silt loam	7.3	2.3
Wurmwiese	WW	Monheim, Germany	loam	5.1	2.1
Höfchen am Hohensee	HF	Burscheid, Germany	silt loam	5.7	2.3
Innerdeich	IN	Monheim, Germany	sandy loam	6.2	1.8

[1] pH value was derived from aqueous 0.01 M $CaCl_2$ suspension

The test was performed in static test systems, consisting of flasks filled with soil and equipped with solid trap attachments to collect carbon dioxide and volatile organic compounds.

The application rate was 331 µg/kg soil (dry weight), corresponding an intended maximum single field application rate of 250 g FLU/ha (assuming incorporation into top 5 cm of soil and 1.5 g/cm^3 bulk density).

Duplicate samples from each system were processed and analysed at 0, 6, 14, 21, 36, 56, 89 and 120 days after treatment (DAT). The volatile traps were assayed at each sampling interval to determine the amount of carbon dioxide and volatile organic compounds.

At each sampling interval, the soil was extracted at ambient temperature using acetonitrile/water 4/1 (v/v) followed by one ambient extraction using acetonitrile and a microwave-assisted extraction using acetonitrile/water 4/1 (v/v) at 70 °C. At DAT-0 to DAT-14 the soil was first extracted at ambient temperature using water prior to the above described extraction procedure.

The amounts of test item and degradation products in soil extracts were determined by liquid scintillation counting (LSC) and by HPLC/radiodetection analysis. The amounts of volatiles and non-extractable residues were determined by LSC and combustion/LSC, respectively.

Test item and degradation products were identified by HPLC-MS(/MS) including accurate mass determination or by retention time comparison with reference items. Additionally, the metabolite fluopyram-7-hydroxy was isolated from soil extracts and analysis by a chiral chromatographic method to investigate the ratio of both enantiomers in the course of the study. Furthermore, soil extracts were analysed by IC-MS to quantify the formation of TFA during the study.

The mean material balance of radioactivity ranged from 97.5 to 100.6% of applied radioactivity (% AR) for soil IN, from 95.0 to 103.0% AR for soil HF, from 97.2 to 102.6% AR for soil WW and from 98.8 to 101.2% AR for soil FF.

The maximum amount of carbon dioxide was 9.8, 8.8, 8.0 and 13.3% AR at study end (DAT-120) in soil IN, HF, WW and FF, respectively. Organic volatiles determined were ≤0.1% AR at all sampling points.

The amount of radioactivity extractable from the soil decreased from DAT-0 to DAT-120 from 95.5 to 76.4% AR in soil IN, from 97.5 to 74.6% AR in soil HF, from 99.6 to 78.8% AR in soil WW and from 94.9 to 72.1% AR in soil FF.

The amount of non-extractable residues (NER) increased from DAT-0 to DAT-89 from 2.2 to 11.6% AR in soil IN and from 3.9 to 14.8% AR in soil FF. Until DAT-120 NER decreased slightly to 11.3% AR (IN) and 13.4% AR (FF). Non-extractable residues (NER) increased from DAT-0 to DAT-120 from 4.0 to 13.8% AR in soil HF and from 3.0 to 12.8% AR in soil WW.

The amount of fluopyram in the soil extracts decreased from DAT-0 to DAT-120 from 91.4 to 70.9% AR in soil IN, from 94.2 to 70.1% AR in soil HF, from 95.2 to 73.9% AR in soil WW and from 91.2 to 67.8% AR in soil FF.

Degradation of fluopyram was accompanied by the formation of fluopyram-7-hydroxy with a maximum amount of 4.3% AR at DAT-89 in soil WW. No single unidentified component exceeded 1.3% AR at any sampling interval in any soil.

The degradation product TFA was detected with a maximum amount of 7.41% of the theoretical amount contained in applied fluopyram at study end (DAT-120).

I. MATERIALS AND METHODS

A. MATERIALS

1. Test Item

[phenyl-UL-^{14}C]fluopyram

Sample ID:	KML 10699
Specific Activity:	5.15 MBq/mg
Radiochemical Purity:	>98% (HPLC/radiodetection)
Chemical Purity:	>98% (HPLC UV 210 nm)

2. Soils

Soils were sampled freshly from the field (upper horizon of 0 to 20 cm) and sieved to a particle size of ≤ 2 mm. The soils were taken from agricultural use areas representing different geographical origin and different soil properties as required by the guidelines. No plant protection products used for previous 5 years. Soil were stored at ambient temperature for 12-14 days prior use. Characteristics of the test soils are presented in the table below.

Table 7.1.1.1-37: Characteristics of test soils

Soil	Innerdeich (IN)	Höfchen am Hohensee (HF)	Wurmwiese (WW)	Frankenforst (FF)
Geographic Location (City / State / Country)	Monheim / North Rhine-Westphalia / Germany	Burscheid / North Rhine-Westphalia / Germany	Burscheid / North Rhine-Westphalia / Germany	Vinxel / North Rhine-Westphalia / Germany
Textural Class (USDA)	sandy loam	silt loam	loam	silt loam
Sand [50 µm – 2 mm]	75%	21%	49%	25%
Silt [2 µm – 50 µm]	14%	62%	30%	54%
Clay [< 2 µm]	11%	17%	21%	21%
pH (soil/water 1/1)	6.5	6.6	5.5	7.6
pH (soil/0.01 M $CaCl_2$ 1/2)	6.2	5.7	5.1	7.3
pH (saturated paste)	6.5	6.1	5.5	7.5
pH (soil/1 N KCl 1/1)	6.1	5.5	4.9	7.0
Organic carbon [%]	1.8%	2.3%	2.1%	2.3%
Organic matter [%] [1]	3.1%	4.0%	3.6%	4.0%
Cation exchange capacity [meq/100 g]	9.6	11.3	11.5	17.7
Water Holding Capacity				
maximum [g H_2O ad 100 g soil DW]	39.4	58.3	55.1	54.5
at 1/10 bar (pF 2.0) [%]	13.4	28.8	20.9	34.7
Bulk Density (disturbed) [g/cm³]	1.33	1.03	1.15	1.10
Microbial biomass [mg C/kg soil dry weight]				
DAT-1 (BIO-/BIO+) [2]	592/633	856/926	776/845	1200/1236
DAT-61 (BIO-/BIO+) [2], [3]	412/418	635/656	568/558	956/943
DAT-120 (BIO-/BIO+) [2], [3]	291/307	483/389	259/385	776/688

DAT = days after treatment; USDA: United States Department for Agriculture
[1] % organic matter = % organic carbon × 1.724
[2] BIO- samples were left untreated
[3] BIO+ samples were applied with solvent of application solution

B. STUDY DESIGN

1. Experimental conditions

Static test systems were used consisting of Erlenmeyer flasks filled with soil and equipped with traps containing soda lime to collect carbon dioxide and a polyurethane (PU) foam plug to collect volatile organic compounds.

100 g of sieved soil (dry weight equivalents) were weighed into each test vessel and soil moisture was adjusted to 55 ± 5% of the maximum water holding capacity and the test systems were acclimated for 2 days at test conditions.

The actual application rate was 331 µg/kg soil (dry weight), corresponding an intended maximum single field application rate of 250 g FLU/ha (assuming incorporation into top 5 cm of soil and 1.5 g/cm³ bulk density). An application solution of [phenyl-UL-^{14}C] fluopyram with a concentration of 35.4 µg/mL was prepared in water from a stock solution prepared in methanol (methanol/water about 3/97, *v/v*). 940 µL of this solution were applied to each test system and after application the test vessels (except DAT-0), were closed with trap attachments.

Test systems were incubated under aerobic conditions in the dark for 120 days at 20 ± 2°C and 55 ± 5% of the maximum water holding capacity.

2. Sampling
Duplicate test systems were processed and analysed 0, 6, 14, 21, 36, 56, 89 and 120 days after treatment (DAT). The volatile traps were assayed at each sampling interval to determine the amount of carbon dioxide and volatile organic compounds. No maintenance of trap attachments for absorption of carbon dioxide was necessary.

Microbial soil biomass was determined at start, middle and end of the study (DAT-1, DAT-61 and DAT-120).

3. Analytical procedures
At each sampling interval, the soil was extracted once with water using a mechanical shaker (only DAT-0 to DAT-14) followed by two extraction steps using acetonitrile/water (4/1; *v/v*) and acetonitrile, respectively. All beforementioned extractions were performed at ambient temperature for 30 minutes. Finally, one extraction was conducted using a microwave with a magnetic stirrer at 70 °C for 30 minutes. Extracts and soil were separated by centrifugation and decantation. Afterwards, the ambient and microwave extracts were combined. The amounts of volatiles and non-extractable residues were determined by LSC and combustion/LSC, respectively.

The amounts of test item and degradation products in soil extracts were determined by liquid scintillation counting (LSC) and by HPLC/radiodetection analysis. The limit of quantification (LOQ) for the HPLC/radiodetection method was 0.86% AR. Test item and degradation products were identified by HPLC-MS(/MS) including accurate mass determination or by retention time comparison with reference items.

Following observation of metabolite fluopyram-7-hydroxy investigations were performed intothe ratio of the single enantiomers. Respective peaks in HPLC were isolated by fraction collection. Enantiomers in the isolated peak were separated by a chiral chromatographic method. The two separated enantiomers were collected as fractions and quantified each by LSC.

For determination of total TFA formed by microbial degradation of fluopyram, soil extracts were combined and analysed by ion chromatography coupled with mass spectroscopy (IC-MS) specific for TFA. Full details and acceptable validation data to support the analytical method are presented within document M-CA 4, which comply with the EU regulatory requirements outlined within SANTE/2020/12830, Rev.1.

II. RESULTS AND DISCUSSION

A. EXTRACTION AND DISTRIBUTION OF RADIOACTIVITY IN SOIL SAMPLES
Radioactive mass balance and distribution of [phenyl-UL-^{14}C] fluopyram and metabolites in soil extracts are summarised in Table 7.1.1.1-38 to Table 7.1.1.1-41. The ratio of enantiomers of fluopyram-7-hydroxy is summarised in Table 7.1.1.1-42 and the formation of TFA is summarised in Table 7.1.1.1-43.

Table 7.1.1.1-38: **Degradation of fluopyram in soil Innerdeich under aerobic conditions (expressed as percent of applied radioactivity)**

Compound	Replicate	DAT							
		0	6	14	21	36	56	89	120
Fluopyram	A	87.7	87.5	85.2	81.6	76.1	76.7	73.5	71.5
	B	95.0	91.0	83.3	85.4	80.7	79.4	72.9	70.4
	Mean	**91.4**	**89.2**	**84.2**	**83.5**	**78.4**	**78.1**	**73.2**	**70.9**
FLU-7-OH	A	n.d.	2.4	3.5	4.2	3.2	3.6	3.8	3.2
	B	< LOD	2.0	3.6	3.6	3.5	3.5	4.3	4.0
	Mean	**< LOD**	**2.2**	**3.5**	**3.9**	**3.4**	**3.5**	**4.1**	**3.6**
TFA [1] (Reg 9)	A	n.d.	n.d.	n.d.	n.d.	n.d.	< LOD	0.9	< LOD
	B	n.d.	< LOD	n.d.	n.d.	n.d.	< LOD	< LOD	< LOD
	Mean	**n.d.**	**< LOD**	**n.d.**	**n.d.**	**n.d.**	**< LOD**	**< LOD**	**< LOD**
Unknown 1 (Reg 1)	A	< LOD	< LOD	n.d.	< LOD	n.d.	n.d.	n.d.	n.d.
	B	1.0	n.d.	< LOD	n.d.	n.d.	n.d.	n.d.	n.d.
	Mean	**< LOD**	**< LOD**	**< LOD**	**< LOD**	**n.d.**	**n.d.**	**n.d.**	**n.d.**
Unknown 2 (Reg 2)	A	< LOD	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	B	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	Mean	**< LOD**	**n.d.**	**n.d.**	**n.d.**	**n.d.**	**n.d.**	**n.d.**	**n.d.**
Unknown 3 (Reg 4)	A	n.d.	n.d.	< LOD	< LOD	< LOD	n.d.	n.d.	n.d.
	B	n.d.	n.d.	n.d.	< LOD	n.d.	n.d.	n.d.	< LOD
	Mean	**n.d.**	**n.d.**	**< LOD**	**< LOD**	**< LOD**	**n.d.**	**n.d.**	**< LOD**
Unknown 4 (Reg 6)	A	0.9	< LOD	n.d.	< LOD	< LOD	n.d.	n.d.	n.d.
	B	< LOD	< LOD	n.d.	< LOD	n.d.	n.d.	n.d.	n.d.
	Mean	**< LOD**	**< LOD**	**n.d.**	**< LOD**	**< LOD**	**n.d.**	**n.d.**	**n.d.**
Unknown 5 (Reg 8)	A	n.d.	n.d.	n.d.	n.d.	< LOD	n.d.	n.d.	n.d.
	B	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	Mean	**n.d.**	**n.d.**	**n.d.**	**n.d.**	**< LOD**	**n.d.**	**n.d.**	**n.d.**
Diffuse Residues	A	2.4	< LOD	1.6	1.4	< LOD	1.0	n.d.	1.5
	B	1.6	1.6	6.4	1.5	< LOD	0.9	< LOD	1.0
	Mean	**2.0**	**< LOD**	**4.0**	**1.5**	**< LOD**	**0.9**	**< LOD**	**1.3**
Carbon dioxide	A	n.a.	0.9	2.1	3.5	4.7	7.1	8.6	9.0
	B	n.a.	0.9	1.9	3.4	4.8	6.9	8.9	10.6
	Mean	**n.a.**	**0.9**	**2.0**	**3.4**	**4.8**	**7.0**	**8.7**	**9.8**
Volatile organic compounds	A	n.a.	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1
	B	n.a.	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1
	Mean	**n.a.**	**< 0.1**	**< 0.1**	**< 0.1**	**< 0.1**	**< 0.1**	**< 0.1**	**< 0.1**
Total extractable residues	A	92.1	91.5	90.7	87.8	81.0	81.8	78.3	76.8
	B	98.8	95.3	93.6	91.2	84.9	84.3	78.4	76.0
	Mean	**95.5**	**93.4**	**92.2**	**89.5**	**83.0**	**83.1**	**78.3**	**76.4**
Non-extractable residues	A	2.5	4.9	6.2	7.5	9.6	10.2	11.4	11.2
	B	2.0	4.9	6.2	7.7	9.9	10.2	11.8	11.4
	Mean	**2.2**	**4.9**	**6.2**	**7.6**	**9.8**	**10.2**	**11.6**	**11.3**
Material balance	A	94.6	97.3	99.0	98.8	95.4	99.2	98.2	96.9
	B	100.8	101.0	101.8	102.3	99.7	101.4	99.1	98.0
	Mean	**97.7**	**99.1**	**100.4**	**100.6**	**97.5**	**100.3**	**98.7**	**97.5**

n.d.: not detected, n.a.: not analysed, DAT: days after treatment

[1] The metabolite TFA was not identified in the course of this study. Due to the low retention time of Reg 9 of approx. 4 minutes, this peak is considered to very likely represent the polar compound TFA which is a known degradation product of fluopyram. However, the peak is always < LOD in the HPLC/radiodetection analysis.

Table 7.1.1.1-39: **Degradation of fluopyram in soil Höfchen am Hohensee under aerobic conditions (expressed as percent of applied radioactivity)**

Compound	Replicate	DAT							
		0	6	14	21	36	56	89	120
Fluopyram	A	93.0	87.1	85.7	83.4	75.2	78.7	74.5	71.2
	B	95.5	87.4	89.0	86.2	78.3	78.8	73.3	69.1
	Mean	**94.2**	**87.2**	**87.4**	**84.8**	**76.8**	**78.8**	**73.9**	**70.1**
FLU-7-OH	A	< LOD	1.9	3.5	3.2	3.0	3.7	4.1	3.0
	B	< LOD	1.8	2.5	2.9	3.4	3.4	4.0	3.3
	Mean	**< LOD**	**1.9**	**3.0**	**3.1**	**3.2**	**3.6**	**4.1**	**3.2**
TFA [1] (Reg 9)	A	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	< LOD
	B	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	< LOD
	Mean	**n.d.**	**n.d.**	**n.d.**	**n.d.**	**n.d.**	**n.d.**	**n.d.**	**< LOD**
Unknown 1 (Reg 1)	A	< LOD	< LOD	n.d.	< LOD	n.d.	n.d.	n.d.	n.d.
	B	< LOD	< LOD	< LOD	n.d.	n.d.	n.d.	n.d.	n.d.
	Mean	**< LOD**	**< LOD**	**< LOD**	**< LOD**	**n.d.**	**n.d.**	**n.d.**	**n.d.**
Unknown 2 (Reg 2)	A	< LOD	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	B	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	Mean	**< LOD**	**n.d.**	**n.d.**	**n.d.**	**n.d.**	**n.d.**	**n.d.**	**n.d.**
Unknown 3 (Reg 4)	A	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	< LOD
	B	n.d.	n.d.	< LOD	n.d.	n.d.	n.d.	n.d.	n.d.
	Mean	**n.d.**	**n.d.**	**< LOD**	**n.d.**	**n.d.**	**n.d.**	**n.d.**	**< LOD**
Unknown 4 (Reg 6)	A	1.0	n.d.	< LOD	n.d.	n.d.	< LOD	n.d.	n.d.
	B	< LOD	n.d.	n.d.	< LOD	n.d.	n.d.	n.d.	n.d.
	Mean	**< LOD**	**n.d.**	**< LOD**	**< LOD**	**n.d.**	**< LOD**	**n.d.**	**n.d.**
Unknown 5 (Reg 8)	A	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	B	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	Mean	**n.d.**	**n.d.**	**n.d.**	**n.d.**	**n.d.**	**n.d.**	**n.d.**	**n.d.**
Diffuse Residues	A	< LOD	2.0	< LOD	1.4	< LOD	< LOD	< LOD	< LOD
	B	1.7	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
	Mean	**< LOD**	**1.0**	**< LOD**	**< LOD**	**< LOD**	**< LOD**	**< LOD**	**< LOD**
Carbon dioxide	A	n.a.	0.8	1.6	1.8	3.5	5.4	6.9	9.2
	B	n.a.	0.8	1.6	2.5	3.7	5.5	8.0	8.3
	Mean	**n.a.**	**0.8**	**1.6**	**2.1**	**3.6**	**5.5**	**7.5**	**8.8**
Volatile organic compounds	A	n.a.	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1
	B	n.a.	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1
	Mean	**n.a.**	**< 0.1**	**< 0.1**	**< 0.1**	**< 0.1**	**< 0.1**	**< 0.1**	**< 0.1**
Total extractable residues	A	95.8	91.6	90.3	88.2	78.9	83.5	78.9	75.4
	B	99.2	90.3	92.8	90.1	82.0	82.3	77.7	73.9
	Mean	**97.5**	**90.9**	**91.6**	**89.2**	**80.5**	**82.9**	**78.3**	**74.6**
Non-extractable residues	A	4.3	13.6	6.9	8.9	11.5	10.5	12.8	13.5
	B	3.7	9.0	7.0	9.2	10.4	11.9	13.2	14.1
	Mean	**4.0**	**11.3**	**7.0**	**9.0**	**11.0**	**11.2**	**13.0**	**13.8**
Material balance	A	100.1	105.9	98.8	98.9	94.0	99.5	98.6	98.0
	B	102.9	100.0	101.4	101.8	96.1	99.7	99.0	96.3
	Mean	**101.5**	**103.0**	**100.1**	**100.4**	**95.0**	**99.6**	**98.8**	**97.2**

n.d.: not detected, n.a.: not analysed, DAT: days after treatment

[1] The metabolite TFA was not identified in the course of this study. Due to the low retention time of Reg 9 of approx. 4 minutes, this peak is considered to very likely represent the polar compound TFA which is a known degradation product of fluopyram. However, the peak is always < LOD in the HPLC/radio-detection analysis.

Table 7.1.1.1-40: **Degradation of fluopyram in soil Wurmwiese under aerobic conditions (expressed as percent of applied radioactivity)**

Compound	Replicate	DAT 0	6	14	21	36	56	89	120
Fluopyram	A	95.1	89.3	89.7	87.6	80.2	80.9	76.2	73.3
	B	95.2	90.2	87.0	85.8	80.7	77.4	73.5	74.6
	Mean	**95.2**	**89.7**	**88.3**	**86.7**	**80.5**	**79.1**	**74.9**	**73.9**
FLU-7-OH	A	< LOD	1.8	3.0	2.9	2.8	4.0	4.6	3.4
	B	n.d.	1.5	3.0	3.3	3.4	3.4	4.0	3.4
	Mean	**< LOD**	**1.7**	**3.0**	**3.1**	**3.1**	**3.7**	**4.3**	**3.4**
TFA [1] (Reg 9)	A	n.d.	n.d.	n.d.	n.d.	n.d.	< LOD	< LOD	< LOD
	B	n.d.	n.d.	n.d.	n.d.	n.d.	< LOD	1.0	< LOD
	Mean	**n.d.**	**n.d.**	**n.d.**	**n.d.**	**n.d.**	**< LOD**	**< LOD**	**< LOD**
Unknown 1 (Reg 1)	A	1.0	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	B	1.0	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	Mean	**1.0**	**n.d.**	**n.d.**	**n.d.**	**n.d.**	**n.d.**	**n.d.**	**n.d.**
Unknown 2 (Reg 2)	A	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	B	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	Mean	**n.d.**	**n.d.**	**n.d.**	**n.d.**	**n.d.**	**n.d.**	**n.d.**	**n.d.**
Unknown 3 (Reg 4)	A	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	< LOD
	B	n.d.	n.d.	n.d.	< LOD	n.d.	n.d.	n.d.	n.d.
	Mean	**n.d.**	**n.d.**	**n.d.**	**< LOD**	**n.d.**	**n.d.**	**n.d.**	**< LOD**
Unknown 4 (Reg 6)	A	0.9	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	B	< LOD	< LOD	n.d.	< LOD	n.d.	n.d.	1.0	n.d.
	Mean	**< LOD**	**< LOD**	**n.d.**	**< LOD**	**n.d.**	**n.d.**	**< LOD**	**n.d.**
Unknown 5 (Reg 8)	A	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	B	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	Mean	**n.d.**	**n.d.**	**n.d.**	**n.d.**	**n.d.**	**n.d.**	**n.d.**	**n.d.**
Diffuse Residues	A	2.6	2.4	< LOD	< LOD	< LOD	< LOD	< LOD	1.0
	B	2.1	< LOD	1.2	1.0	< LOD	n.d.	1.1	0.9
	Mean	**2.3**	**1.2**	**< LOD**	**< LOD**	**< LOD**	**< LOD**	**< LOD**	**1.0**
Carbon dioxide	A	n.a.	1.0	1.7	2.7	3.8	3.1	7.5	7.9
	B	n.a.	1.0	1.7	2.0	3.7	5.4	7.5	8.1
	Mean	**n.a.**	**1.0**	**1.7**	**2.4**	**3.8**	**4.2**	**7.5**	**8.0**
Volatile organic compounds	A	n.a.	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1
	B	n.a.	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1
	Mean	**n.a.**	**< 0.1**	**< 0.1**	**< 0.1**	**< 0.1**	**< 0.1**	**< 0.1**	**< 0.1**
Total extractable residues	A	100.2	93.5	92.8	91.0	83.2	85.4	82.3	78.4
	B	99.0	92.8	91.2	90.7	84.5	81.1	79.6	79.1
	Mean	**99.6**	**93.2**	**92.0**	**90.9**	**83.8**	**83.3**	**80.9**	**78.8**
Non-extractable residues	A	3.0	6.7	6.7	8.1	10.0	10.7	11.1	12.4
	B	3.0	6.8	6.8	8.4	9.2	10.8	13.8	13.2
	Mean	**3.0**	**6.7**	**6.8**	**8.2**	**9.6**	**10.8**	**12.4**	**12.8**
Material balance	A	103.2	101.2	101.2	101.9	97.0	99.3	100.9	98.7
	B	102.0	100.4	99.8	101.1	97.4	97.4	100.9	100.5
	Mean	**102.6**	**100.8**	**100.5**	**101.5**	**97.2**	**98.3**	**100.9**	**99.6**

n.d.: not detected, n.a.: not analysed, DAT: days after treatment

[1] The metabolite TFA was not identified in the course of this study. Due to the low retention time of Reg 9 of approx. 4 minutes, this peak is considered to very likely represent the polar compound TFA which is a known degradation product of fluopyram. However, the peak is always < LOD in the HPLC/radiodetection analysis.

Table 7.1.1.1-41: **Degradation of fluopyram in soil Frankenforst under aerobic conditions (expressed as percent of applied radioactivity)**

Compound	Replicate	DAT 0	6	14	21	36	56	89	120
Fluopyram	A	88.1	88.4	91.3	86.3	83.7	79.5	68.9	69.0
	B	94.2	87.9	85.2	88.5	82.2	78.9	69.8	66.7
	Mean	**91.2**	**88.1**	**88.3**	**87.4**	**83.0**	**79.2**	**69.3**	**67.8**
FLU-7-OH	A	< LOD	1.2	1.6	1.8	2.1	2.4	2.4	1.8
	B	< LOD	1.3	1.3	2.0	1.8	2.1	2.8	1.8
	Mean	**< LOD**	**1.3**	**1.4**	**1.9**	**1.9**	**2.2**	**2.6**	**1.8**
TFA [1] (Reg 9)	A	n.d.	n.d.	n.d.	n.d.	< LOD	0.9	< LOD	< LOD
	B	n.d.	n.d.	n.d.	n.d.	< LOD	< LOD	< LOD	< LOD
	Mean	**n.d.**	**n.d.**	**n.d.**	**n.d.**	**< LOD**	**< LOD**	**< LOD**	**< LOD**
Unknown 1 (Reg 1)	A	1.2	< LOD	< LOD	< LOD	n.d.	n.d.	n.d.	n.d.
	B	1.5	n.d.	< LOD	n.d.	n.d.	n.d.	n.d.	n.d.
	Mean	**1.3**	**< LOD**	**< LOD**	**< LOD**	**n.d.**	**n.d.**	**n.d.**	**n.d.**
Unknown 2 (Reg 2)	A	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	< LOD
	B	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	< LOD
	Mean	**n.d.**	**n.d.**	**n.d.**	**n.d.**	**n.d.**	**n.d.**	**n.d.**	**< LOD**
Unknown 3 (Reg 4)	A	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	B	< LOD	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	Mean	**< LOD**	**n.d.**	**n.d.**	**n.d.**	**n.d.**	**n.d.**	**n.d.**	**n.d.**
Unknown 4 (Reg 6)	A	n.d.	n.d.	n.d.	< LOD	n.d.	n.d.	n.d.	n.d.
	B	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	Mean	**n.d.**	**n.d.**	**n.d.**	**< LOD**	**n.d.**	**n.d.**	**n.d.**	**n.d.**
Unknown 5 (Reg 8)	A	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	B	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	Mean	**n.d.**	**n.d.**	**n.d.**	**n.d.**	**n.d.**	**n.d.**	**n.d.**	**n.d.**
Diffuse Residues	A	2.0	1.2	< LOD	1.4	< LOD	1.3	1.0	1.3
	B	1.2	1.8	1.4	< LOD	1.4	1.2	< LOD	1.0
	Mean	**1.6**	**1.5**	**< LOD**	**< LOD**	**< LOD**	**1.2**	**< LOD**	**1.2**
Carbon dioxide	A	n.a.	1.0	1.8	0.2	4.8	7.5	12.3	13.5
	B	n.a.	1.0	2.0	3.1	4.5	7.3	11.7	13.2
	Mean	**n.a.**	**1.0**	**1.9**	**1.7**	**4.7**	**7.4**	**12.0**	**13.3**
Volatile organic compounds	A	n.a.	< 0.1	0.1	0.1	< 0.1	< 0.1	< 0.1	< 0.1
	B	n.a.	0.1	0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1
	Mean	**n.a.**	**< 0.1**	**< 0.1**	**< 0.1**	**< 0.1**	**< 0.1**	**< 0.1**	**< 0.1**
Total extractable residues	A	92.0	91.3	93.4	90.1	86.6	84.1	72.9	73.1
	B	97.9	91.0	88.3	91.4	85.9	82.4	74.0	71.1
	Mean	**94.9**	**91.1**	**90.8**	**90.8**	**86.3**	**83.3**	**73.5**	**72.1**
Non-extractable residues	A	4.2	8.4	6.9	8.0	9.0	10.7	15.2	12.7
	B	3.5	7.3	8.2	7.8	9.1	10.3	14.3	14.2
	Mean	**3.9**	**7.9**	**7.5**	**7.9**	**9.0**	**10.5**	**14.8**	**13.4**
Material balance	A	96.2	100.8	102.0	98.4	100.5	102.4	100.5	99.3
	B	101.4	99.3	98.4	102.3	99.5	100.0	100.0	98.4
	Mean	**98.8**	**100.1**	**100.2**	**100.3**	**100.0**	**101.2**	**100.2**	**98.9**

n.d.: not detected, n.a.: not analysed, DAT: days after treatment

[1] The metabolite TFA was not identified in the course of this study. Due to the low retention time of Reg 9 of approx. 4 minutes, this peak is considered to very likely represent the polar compound TFA which is a known degradation product of fluopyram. However, the peak is always < LOD in the HPLC/radiodetection analysis.

Table 7.1.1.1-42: **Ratio of enantiomers of fluopyram-7-hydroxy in soils under aerobic conditions (expressed as percent of total 100%)**

Soil/replicate	Compound	DAT							
		0	6	14	21	36	56	89	120
Soil IN rep 1	Enantiomer 1	<LOQ	68.9	67.0	52.2	57.3	64.6	83.0	36.2
	Enantiomer 2	<LOQ	31.1	33.0	47.8	42.7	35.4	17.0	63.8
Soil IN rep 2	Enantiomer 1	<LOQ	66.6	64.4	52.3	40.0 [1]	64.4	74.2	45.9
	Enantiomer 2	<LOQ	33.4	35.6	47.7	96.0 [1]	35.6	25.8	54.1
Soil IN mean	**Enantiomer 1**	**<LOQ**	**67.9**	**65.7**	**52.3**	**57.3**	**64.5**	**78.3**	**41.6**
	Enantiomer 2	**<LOQ**	**32.1**	**34.3**	**47.7**	**42.7**	**35.5**	**21.7**	**58.4**
Soil HF rep 1	Enantiomer 1	<LOQ	72.8	69.8	58.0	61.1	66.3	53.2	38.2
	Enantiomer 2	<LOQ	27.2	30.2	42.0	38.9	33.7	46.8	61.8
Soil HF rep 2	Enantiomer 1	<LOQ	74.2	74.8	57.9	59.4	65.2	53.4	40.4
	Enantiomer 2	<LOQ	25.8	25.2	42.1	40.6	34.8	46.6	59.6
Soil HF mean	**Enantiomer 1**	**<LOQ**	**73.5**	**71.9**	**57.9**	**60.2**	**65.8**	**53.3**	**39.3**
	Enantiomer 2	**<LOQ**	**26.5**	**28.1**	**42.1**	**39.8**	**34.2**	**46.7**	**60.7**
Soil IWW rep 1	Enantiomer 1	<LOQ	71.3	60.1	39.1	39.9	47.7	33.1	24.0
	Enantiomer 2	<LOQ	28.7	39.9	60.9	60.1	52.3	66.9	76.0
Soil WW rep 2	Enantiomer 1	<LOQ	68.3	45.4	39.2	37.5	43.6	31.0	27.5
	Enantiomer 2	<LOQ	31.7	54.6	60.8	62.5	56.4	69.0	72.5
Soil WW mean	**Enantiomer 1**	**<LOQ**	**70.0**	**52.8**	**39.2**	**38.6**	**45.8**	**32.1**	**25.8**
	Enantiomer 2	**<LOQ**	**30.0**	**47.2**	**60.8**	**61.4**	**54.2**	**67.9**	**74.2**
Soil FF rep 1	Enantiomer 1	<LOQ	78.3	66.5	67.9	73.1	53.9	62.2	27.3
	Enantiomer 2	<LOQ	21.7	33.5	32.1	26.9	46.1	37.8	72.7
Soil FF rep 2	Enantiomer 1	<LOQ	78.2	67.5	68.7	72.0	31.9	58.0	37.3
	Enantiomer 2	<LOQ	21.8	32.5	31.3	28.0	68.1	42.0	62.7
Soil FF mean	**Enantiomer 1**	**<LOQ**	**78.2**	**66.9**	**68.3**	**72.6**	**43.6**	**59.9**	**32.3**
	Enantiomer 2	**<LOQ**	**21.8**	**33.1**	**31.7**	**27.4**	**56.4**	**40.1**	**67.7**

[1] Outlier not considered for calculation of mean value

The limit of quantification (LOQ) of the chiral chromatographic method was not determined. As the amount of fluopyram-7-hydroxy was below the LOQ of the primary chromatographic method at DAT-0 the fraction of each enantiomer was set to <LOQ here.

Table 7.1.1.1-43: **Formation of TFA in soils under aerobic conditions (expressed as% of theoretical amount of TFA contained in applied fluopyram [1])**

Soil	Replicate No.	DAT 0	6	14	21	36	56	89	120
Innerdeich	A	0.20	0.25	0.89	1.55	1.76	2.56	3.03	~~1.94~~ [2]
	B	0.28	0.28	0.68	2.69	1.97	2.56	2.83	3.10
	Mean	**0.24**	**0.26**	**0.79**	**2.12**	**1.87**	**2.56**	**2.93**	**3.10**
Höfchen am Hohensee	A	0.13	1.10	0.72	1.19	1.56	2.37	2.68	4.51
	B	0.12	0.26	0.85	1.32	1.58	2.39	2.97	4.57
	Mean	**0.12**	**0.68**	**0.79**	**1.26**	**1.57**	**2.38**	**2.83**	**4.54**
Wurmwiese	A	-0.04	0.56	1.09	1.71	2.19	3.52	4.28	6.74
	B	0.06	0.59	1.01	1.76	2.36	3.58	3.99	8.07
	Mean	**<LOQ [3]**	**0.58**	**1.04**	**1.73**	**2.28**	**3.55**	**4.14**	**7.41**
Frankenforst	A	0.05	0.49	0.78	1.66	1.92	3.60	5.03	5.65
	B	0.03	0.47	0.67	1.56	1.90	3.38	4.50	8.17
	Mean	**<LOQ [3]**	**0.48**	**0.72**	**1.61**	**1.91**	**3.49**	**4.76**	**6.91**

[1] 1 mole fluopyram can form a maximum of 2 mole of TFA. Fluopyram was applied with 83.45 nmole based on the applied amount of fluopyram of 33107 ng/test system and its molecular weight of 396.72 g/mole. The maximum theoretical amount of TFA formed during the study (100% conversion of fluopyram to TFA) is 18868 ng based on the molecular weight of TFA of 113 g/mole.
[2] Outlier not considered for calculation of mean value
[3] LOQ = 0.1%

B. MATERIAL BALANCE

The mean material balance of radioactivity ranged from 97.5 to 100.6% AR for soil IN, from 95.0 to 103.0% AR for soil HF, from 97.2 to 102.6% AR for soil WW and from 98.8 to 101.2% AR for soil FF.

C. EXTRACTABLE AND NON-EXTRACTABLE RESIDUES

The radioactivity extracted from soil decreased from DAT-0 to DAT-120 from 95.5 to 76.4% AR in soil IN, from 97.5 to 74.6% AR in soil HF, from 99.6 to 78.8% AR in soil WW and from 94.9 to 72.1% AR in soil FF.

The amount of non-extractable residues (NER) increased from DAT-0 to DAT-89 from 2.2 to 11.6% AR in soil IN and from 3.9 to 14.8% AR in soil FF. Until DAT-120 the amount decreased slightly to 11.3% AR (IN) and 13.4% AR (FF). Non-extractable residues (NER) increased from DAT-0 to DAT-120 from 4.0 to 13.8% AR in soil HF and from 3.0 to 12.8% AR in soil WW. No further characterization of NER was performed.

D. VOLATILE RADIOACTIVITY

The maximum amount of carbon dioxide was 9.8, 8.8, 8.0 and 13.3% AR at study end (DAT-120) in soil IN, HF, WW and FF, respectively. Formation of volatile organic compounds (VOC) was insignificant as demonstrated by values of < 0.1% AR at all sampling intervals for all soils.

E. TRANSFORMATION OF THE TEST ITEM

The amount of fluopyram in the soil extracts decreased from DAT-0 to DAT-120 from 91.4 to 70.9% AR in soil IN, from 94.2 to 70.1% AR in soil HF, from 95.2 to 73.9% AR in soil WW and from 91.2 to 67.8% AR in soil FF.

The metabolite fluopyram-7-hydroxy was the sole component observed at a maximum of 4.3% AR by DAT- 89 in soil WW. Chiral analysis of fluopyram-7-hydroxy indicated the metabolite to occur as

partial racemic mixture, i.e. though preference for formation of single enantiomer was observed dependent on sampling interval, no clear trend in enantiomer ratio could be observed during the test period.

The metabolite TFA was observed at a maximum of 7.4% at study end (DAT-120) in soil WW. The value refers to the theoretical molar ratio of formation based on fluopyram applied. No single unidentified component exceeded 1.3% AR at any sampling interval in any soil.

F. KINETICS

New kinetic calculations including degradation products were conducted and reported under KCA 7.1.2.1.1/14 (M-762167-01-1).

III. CONCLUSIONS

Fluopyram was slowly degraded under the conditions of the test.

Formation of carbon dioxide was up to a maximum of 13.3% AR and NER were up to 14.8% AR.

Besides carbon dioxide, fluopyram-7-hydroxy was observed at a of 4.3% AR by DAT-89. No single unidentified component exceeded 1.3% AR at any sampling interval in any soil.

Chiral analysis of fluopyram-7-hydroxy indicated the metabolite to occur as partial racemic mixture, i.e. though preference for formation of single enantiomer was observed dependent on sampling interval, no clear trend in enantiomer ratio could be observed during the test period.

The metabolite TFA was detected with a maximum amount of 7.4% of theoretical amount contained in applied fluopyram at study end (DAT-120).

3. Assessment and conclusion

Assessment and conclusion by applicant: The study and its data are considered as valid and reliable for use in risk assessment.

Assessment and conclusion by RMS: Outcome and conclusion of the study. RMS should indicate if they agree to the results and conclusions of the APPL.

CA 7.1.1.2 Anaerobic degradation

1. Information on the study

Data Point:	KCA 7.1.1.2/01
Report Author:	[redacted]
Report Year:	2008
Report Title:	[Phenyl-UL-14C] and [pyridyl-2,6-14C]AE C656948: Anaerobic soil metabolism
Report No:	MEGMP070-1
Document No:	M-292022-02-1
Guideline(s) followed in study:	US EPA Subdivision N, Section 162-2 US EPA OPPTS Guideline No. 835.4300 OECD Guidelines for Testing of Chemicals, Guideline 307 Canada PMRA DACO No. 8.2.3.4.4
Deviations from current test guideline:	Current Guideline: OECD 307 (2002) Biomass was only determined at study start (no determination at end of aerobic degradation and no determination of anaerobic microorganisms was performed)
Previous evaluation:	yes, evaluated and accepted DAR (2011)
GLP/Officially recognised testing facilities:	Yes, conducted under GLP/Officially recognised testing facilities
Acceptability/Reliability:	Yes

2. Full summary of KCA 7.1.1.2/01

Executive Summary

The degradation of [phenyl-UL-^{14}C]- and [pyridyl-2,6-^{14}C]fluopyram was investigated in a silt loam soil under anaerobic conditions in the dark in the laboratory at 20 ± 1 °C for 120 days applying an aerobic incubation phase of 28 days (at 50% of MWHC) before start of the anaerobic incubation phase (total study period 148 days).

Soil	Source	Texture (USDA)	pH [1]	OC [%]
Hoefchen	Burscheid, Germany	silt loam	6.1	2.5

[1] pH value was derived from aqueous 0.01 M $CaCl_2$ suspension

The test was performed in flow-through systems each containing 100 g of soil (dry weight) connected to traps for the collection of CO_2 and volatile organic compounds.

Fluopyram was applied at the rate of 0.17 mg/kg dry weight for phenyl label and 0.18 mg/kg dry weight for pyridyl label, equivalent to a field application rate of 250 g/ha (assuming incorporation into top 10 cm of soil and 1.5 g/cm^3 bulk density).

Samples were analysed at 0 and 15 days after treatment (DAT, aerobic phase) and at 0, 3, 7, 15, 30, 58, 92 and 120 days after soil flooding (DASF, anaerobic phase; DASF 0 = DAT 28).

Soil and water layer were separated by filtering and the water layer was analysed by LSC directly, with no extraction. The soil was extracted with acetonitrile/water (4/1, v/v) by three cycles of shaking, centrifugation and decanting at room temperature (‘ambient’ conditions). The soil of DASF-92 and -120 were transferred to an ASE cell for aggressive extraction at 100 °C (‘aggressive’ conditions).

The mean material balance of radioactivity was 96.6% of applied radioactivity (% AR) in the phenyl-labelled test system (range from 93.2 to 100.0% AR) and 97.5% AR in the pyridyl-labelled test system (range from 94.3 to 100.2% AR).

The maximum amount of carbon dioxide detected at 120 days after flooding was 1.1% AR for the phenyl-labelled and 0.8% AR for the pyridyl-labelled test system. Formation of volatile organic compounds (VOC) during the aerobic and anaerobic incubation phases was not detectable.

Total extractable residues decreased during the aerobic incubation phase (DAT-0 to DAT-28) from 96.0 to 90.2% AR in the phenyl-labelled test systems. During the anaerobic incubation phase (DASF-0 to DASF-120)total extractable residues remained more or less stable. The behaviour in the pyridyl-labelled test systems was comparable.

In the phenyl-labelled test systems, non-extractable residues (NER) increased during the aerobic incubation phase (DAT-0 to DAT-28) from 4.0 to 6.5% AR. During the anaerobic incubation phase, with an exceptional higher value of 12.2% AR at DASF-58, the NER remained more or less constant until study end. In the pyridyl-labelled test systems, NER increased during the aerobic incubation phase (DAT-0 to DAT-28) from 4.2 to 6.4% AR. The NER during the anaerobic incubation phase showed a similar behaviour as described for the first radiolabel.

In the entire phenyl-labelled test system, the amount of fluopyram decreased during the aerobic incubation phase (DAT-0 to DAT-28) from 96.0 to 88.8% AR. During the anaerobic incubation phase the amount of fluopyram in the entire system remained more or less constant. In the entire pyridyl-labelled test system, the amount of fluopyram decreased during the aerobic incubation phase (DAT-0 to DAT-28) from 95.8 to 89.6% AR. During the anaerobic incubation phase the amount of fluopyram in the entire system remained more or less constant.

There was essentially no degradation of fluopyram during the anaerobic phase of the study. No transformation products at >5% AR were detected for both labels during both, the aerobic and anaerobic phase of the study. The unidentified radioactivity which consisted of two separate components, was less than 3.3% of the applied amount throughout the study duration for both labels.

I. MATERIALS AND METHODS

A. MATERIALS

1. Test Items

[phenyl-UL-^{14}C]AE C656948 (fluopyram)

Sample ID:	BECH1910
Specific Activity:	3.85 MBq/mg
Radiochemical Purity:	>99% (HPLC/radiodetection)

[pyridyl-2,6-^{14}C]AE C656948 (fluopyram)

Sample ID:	BECH1905
Specific Activity:	3.85 MBq/mg
Radiochemical Purity:	>98% (HPLC/radiodetection)

2. Soil

The soil was collected to a depth of 0 - 20 cm from Hoefchen, Burscheid, Northrhine-Westfalia, Germany and is representative of a typical use area. It had not been in contact with any pesticides for at least 5 years. Prior to treatment with the test substance, the soil was maintained in a biologically active state at 20 °C at the testing facility. The soil was air-dried, sieved through a 2-mm sieve and soil moisture

was determined before use. The soil was acclimated to the study temperature of 20 °C and weighed on a dry-weight basis for individual test systems.

Table 7.1.1.2-1: Physico-chemical properties of test soil

Soil Designation	Hoefchen
Geographic Location	
City	Burscheid
Country	Germany
Soil Taxonomic Classification (USDA)	Loamy, mixed, mesic Typic Argudalf
Textural Class (USDA)	silt loam
Sand (%) [50 µm – 2 mm]	13.9
Silt (%) [2 µm – 50 µm]	65.4
Clay (%) [< 2 µm]	20.7
pH	
- Soil/0.01 M $CaCl_2$ 1/1	6.1
- Soil/water 1/1	6.4
Organic Carbon (%)	2.5
Organic Matter (%) [1]	4.3
Cation Exchange Capacity [meq/100 g]	12.3
Water Holding Capacity	
maximum (g H_2O *ad* 100 g soil DW)	47.8
at 1/3 bar (%)	22.5
at 15 bar(%)	11.0
Bulk Density (disturbed; g/cm³)	1.03
Microbial Biomass (aerobic phase, DAT-0) (mg microbial carbon / kg soil DW)	300.3

DAT: days after treatment, DW: dry weight, USDA: United States Department of Agriculture
[1] calculated as: OM [%] = OC [%] · 1.724

B. STUDY DESIGN

1. Experimental Conditions

The test system consisted of 250-mL Erlenmeyer flasks, each containing 100 g of soil (dry weight), with side arms for attachment to traps for the collection of CO_2 and volatile organic compounds. During the aerobic phase, each flask was equipped with a glass tower containing soda lime and mineral oil-coated glass wool for collection of volatiles. During the anaerobic (flooded) phase, the test system was equipped with an adaptor with gas-tight valves suitable for purging volatiles from the test system. The volatile organics were collected from the headspace of the treated test systems using 2 M KOH, ethylene glycol, and 1 M H_2SO_4.

The test items were applied to the aerobic soil in methanol/water (1/2) based on a field rate of 250 g/ha assuming homogeneous distribution in 10 cm topsoil layer and a bulk density of 1.5 g/mL. Phenyl label test systems were each treated at a rate of 16.63 µg/test system, corresponding to 0.17 µg/g) and the pyridyl label was applied at a rate of 16.7 µg/test system, corresponding to 0.18 µg/g), equivalent to

Samples were incubated under aerobic conditions for 28 days at a soil moisture of 50% of the maximum water holding capacity (23.9% soil moisture) in an environmental chamber at 20 ± 1 °C. At DAT-28 of the aerobic phase of the study, all static volatile traps were separated from the test systems after purging with nitrogen for 10 to 15 minutes at approximately 40 mL/min. Afterwards, deionized water, deoxygenated by purging with nitrogen, was used for flooding, resulting in a water layer of about 2 cm deep. The samples were purged with nitrogen for 10 min each at 40 mL/min to initiate the anaerobic phase of the study. The double valves were closed, and the samples were transferred to an upright incubator that was purged with nitrogen to ensure anaerobic conditions. The flooded test systems were kept in a temperature controlled incubator with a nitrogen filled atmosphere at 20 ± 1 °C for 120 days.

2. Sampling

Duplicate samples at day 0 and a single sample 15 days after treatment (DAT) were analysed under aerobic conditions (DAT-0 and DAT-15). The anaerobic phase started at DAT-28 corresponding to day 0 after soil flooding (DASF-0). Anaerobic samples were analysed at 0, 3, 7, 15, 30, 58, 92 and 120 days after soil flooding (DASF). During the aerobic incubation phase, the soil moisture of the test systems was adjusted to 50% of the maximum water holding capacity at day 0 and day 24. Samples were stored prior to analysis at 0°C for 1– 5 days.

3. Analytical Procedures

At each sampling interval of the aerobic phase, the trap attachments were removed from the test systems and soda lime and glass wool treated with mineral oil from were extracted with ethyl acetate. The soil was extracted at room temperature ('ambient' conditions) with acetonitrile/water (4/1, v/v) by three cycles of shaking, centrifugation and decanting through filtering. After each extraction step, supernatant and soil were separated by centrifugation and decantation.

At each interval during the anaerobic phase of the study, replicate treated test systems were removed from the incubator and the volatile components were collected from the headspace by purging with nitrogen through a series of traps at approximately 40 mL/min for 30 minutes. Soil and water layer were separated by filtering and the water layer was analysed by LSC directly, with no extraction. The soil was extracted with acetonitrile/water (4/1, v/v) by three cycles of shaking, centrifugation and decanting at room temperature ('ambient' conditions). The soil of DASF-92 and 120 were transferred to an ASE cell for aggressive extraction at 100 °C ('aggressive' conditions).

Fluopyram residues in water phases and soil extracts were assayed by HPLC/radiodetection using a flow through ^{14}C detector. Water samples were analysed by HPLC without concentration steps after fortification with a solution of non-radioactive standards. Aliquots of the soil extracts (ambient and aggressive) were evaporated under to approximately 3 mL, supplemented with acetonitrile and sonicated. The solution was filtered (0.45 µm), fortified with a solution of non-radioactive standards and analysed by HPLC. The amount of volatiles and non-extractable residues was determined by liquid scintillation counting (LSC) and combustion/LSC, respectively.

The limit of detection (LOD) for HPLC was determined empirically by a series of injections of increasing radioactivity. The lowest amount of radioactivity detected resulted in a peak height of approximately 3 times the background level in the chromatogram (416 dpm) and was considered to be the instrument LOD. The minimum amount of radioactivity injected was 3,797 dpm for any sample, which gives a limit of quantitation (LOQ) of 0.42% of the applied radioactivity.

Identification of the parent compound was achieved by mass spectrometry (LC/ESI/MS) and co-chromatography using authentic standards.

The water layers of the duplicate control samples (day 0) and test samples were measured for the rest of the intervals at each anaerobic sampling interval throughout the study for pH and dissolved oxygen content. The redox potential (E_h) of the water and soil layers were also determined.

II. RESULTS AND DISCUSSION

A. EXTRACTION AND DISTRIBUTION OF RADIOACTIVITY IN SOIL SAMPLES

The pH value of the water decreased during the study from 8.1 to 6.6 for the phenyl label and from 8.0 to 6.8 for the pyridyl label. The oxygen content in the water phase decreased during the study from 1.0 to 0.1 mg/L for the phenyl-label and from 0.9 to 0.0 mg/L for the pyridy label. The redox potential in the water phase decreased during the study from 462.4 to 92.7 mV for the phenyl label and from 425.4 to 101.6 mV for the pyridyl label. The redox potential in the soil decreased during the study from 530.4

to 62.2 mV for the phenyl label and from 455.8 to 77.1 mV for the pyridyl label. The following tables show the decline of the active ingredient and the development of volatiles and non-extractable residues in the aerobic and anaerobic phase of the study.

Table 7.1.1.2-2: Degradation of [phenyl-UL-^{14}C]fluopyam in soil under anaerobic conditions (values expressed as % AR)

Compound	Source	DAT	Sampling Intervals									
			0	15 [1]	28 [2]	31	35	43	58	86	120	148
		DASF	N/A		0	3	7	15	30	58	92	120
Fluopyram	Water	A	N/A		7.0	5.7	5.9	3.7	3.6	3.5	2.5	3.8
		B	N/A		6.0	5.1	4.8	3.4	3.4	3.4	2.9	2.4
		Mean	**N/A**		**6.5**	**5.4**	**5.3**	**3.5**	**3.5**	**3.5**	**2.7**	**3.1**
	Soil	A	96.0	92.0	81.8	81.8	80.7	84.5	82.5	80.0	79.7	83.3
		B	96.1	n.a.	82.8	83.7	83.9	84.1	82.8	79.3	84.9	82.6
		Mean	**96.0**	**92.0**	**82.3**	**82.7**	**82.3**	**84.3**	**82.6**	**79.6**	**82.3**	**83.0**
	Entire System	A	*96.0*	*92.0*	*88.8*	*87.2*	*86.6*	*88.2*	*86.1*	*83.5*	*83.2*	*87.1*
		B	*96.1*	*n.a.*	*88.8*	*88.8*	*88.7*	*87.5*	*86.2*	*82.7*	*87.8*	*85.0*
		Mean	**96.0**	**92.0**	**88.8**	**88.1**	**87.6**	**87.8**	**86.1**	**83.1**	**85.0**	**86.1**
Sum of unidentified and diffuse Residues [3]	Water	A	N/A		0.0	0.0	0.0	0.0	0.3	0.8	1.4	0.0
		B	N/A		0.0	0.3	0.0	0.3	0.3	0.8	0.8	1.4
		Mean	**N/A**		**0.0**	**0.1**	**0.0**	**0.2**	**0.5**	**0.8**	**1.1**	**0.7**
	Soil	A	0.0	1.3	1.3	1.5	1.4	2.0	1.3	2.2	1.3	2.5
		B	0.0	0.0	1.5	1.4	1.8	1.4	1.5	1.3	1.5	1.8
		Mean	**0.0**	**1.3**	**1.4**	**1.4**	**1.6**	**1.7**	**1.4**	**1.8**	**1.4**	**2.1**
	Entire System	A	*0.0*	*0.3*	*1.3*	*1.5*	*1.4*	*2.0*	*1.6*	*3.0*	*2.7*	*2.5*
		B	*0.0*	*0.0*	*1.5*	*1.7*	*1.8*	*1.7*	*2.2*	*2.0*	*2.3*	*3.2*
		Mean	**0.0**	**1.3**	**1.4**	**1.5**	**1.6**	**1.9**	**1.9**	**2.6**	**2.5**	**2.8**
Total Extractable Residues	Water	A	N/A		7.0	5.7	5.9	3.7	3.8	4.3	3.8	3.8
		B	N/A		6.0	5.4	4.8	3.7	4.1	4.1	3.7	3.8
		Mean	**N/A**		**6.5**	**5.5**	**5.3**	**3.7**	**4.0**	**4.2**	**3.8**	**3.8**
	Soil	A	96.0	93.3	83.0	83.3	82.1	86.5	83.8	82.2	81.0	85.8
		B	96.1	n.a.	84.3	85.0	85.7	85.5	84.3	80.6	86.3	84.5
		Mean	**96.0**	**93.3**	**83.7**	**84.2**	**83.9**	**86.0**	**84.0**	**81.4**	**83.7**	**85.1**
	Entire System	A	*96.0*	*93.3*	*90.0*	*89.0*	*88.0*	*90.2*	*87.6*	*86.5*	*84.8*	*89.6*
		B	*96.1*	*n.a.*	*90.3*	*90.4*	*90.5*	*89.2*	*88.4*	*84.7*	*90.0*	*88.3*
		Mean	**96.0**	**93.3**	**90.2**	**89.7**	**89.2**	**89.7**	**88.0**	**85.6**	**87.5**	**88.9**
Carbon Dioxide		A	0.0	0.0	0.9	0.9	0.9	1.0	1.0	0.9	1.1	1.1
		B	0.0	n.a.	0.9	0.9	0.9	1.0	1.0	1.0	1.1	1.1
		Mean	**0.0**	**0.0**	**0.9**	**0.9**	**0.9**	**1.0**	**1.0**	**1.0**	**1.1**	**1.1**
Volatile Organic Compounds		A	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
		B	0.0	n.a.	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
		Mean	**0.0**	**0.0**	**0.0**	**0.0**	**0.0**	**0.0**	**0.0**	**0.0**	**0.0**	**0.0**
Non-Extractable Residues		A	3.9	3.4	6.4	5.7	5.3	6.0	7.2	12.0	4.3	4.4
		B	4.0	n.a.	6.6	5.4	5.8	7.5	7.5	12.5	5.1	4.0
		Mean	**4.0**	**3.4**	**6.5**	**5.6**	**5.6**	**6.7**	**7.4**	**12.2**	**4.7**	**4.2**
Material Balance		A	99.9	96.7	97.3	95.7	94.2	97.2	95.8	99.4	90.2	95.1
		B	100.1	n.a.	97.9	96.8	97.2	97.7	96.9	98.2	96.2	93.4
		Mean	**100.0**	**96.7**	**97.6**	**96.2**	**95.7**	**97.5**	**96.4**	**98.8**	**93.2**	**94.2**

DAT: days after treatment; DASF: days after soil flooding; n.a.: not analysed
[1] Before soil flooding (aerobic incubation phase)
[2] After soil flooding (anaerobic incubation phase)
[3] Consists of 2 components, each less than 3% AR.
Values calculated during dossier preparation are given in *italics*.

Table 7.1.1.2-3: Degradation of [pyridyl-2,6-^{14}C]fluopyam in soil under anaerobic conditions (values expressed as % AR)

Compound	Source	DAT	Sampling Intervals									
			0	15 [1]	28 [2]	31	35	43	58	86	120	148
		DASF	N/A		0	3	7	15	30	58	92	120
Fluopyram	Water	A	N/A		5.9	6.8	6.7	5.1	3.4	2.9	3.1	3.7
		B	N/A		7.3	5.7	6.1	5.6	4.6	3.2	3.0	2.4
		Mean	**N/A**		**6.6**	**6.2**	**6.4**	**5.4**	**4.0**	**3.0**	**3.0**	**3.1**
	Soil	A	95.1	90.0	83.1	82.5	85.6	82.1	82.9	75.1	85.1	83.2
		B	96.5	n.a.	82.9	83.1	85.4	81.6	84.5	73.8	83.5	83.4
		Mean	**95.8**	**90.0**	**83.0**	**82.8**	**85.5**	**81.9**	**83.7**	**74.5**	**84.6**	**83.8**
	Entire System	A	*95.1*	*90.0*	*89.0*	*89.3*	*92.3*	*87.2*	*86.3*	*78.0*	*88.8*	*91.9*
		B	*96.5*	*n.a.*	*90.2*	*88.8*	*91.5*	*85.7*	*89.1*	*77.0*	*86.5*	*85.8*
		Mean	**95.8**	**90.0**	**89.6**	**89.0**	**91.9**	**87.2**	**87.7**	**77.5**	**87.7**	**88.8**
Sum of unidentified and diffuse Residues [3]	Water	A	N/A		0.0	0.0	0.0	0.0	1.3	1.3	0.7	0.0
		B	N/A		0.0	0.0	0.0	0.0	1.0	0.7	0.8	1.3
		Mean	**N/A**		**0.0**	**0.0**	**0.0**	**0.0**	**1.2**	**1.0**	**0.7**	**0.7**
	Soil	A	0.0	2.1	1.5	1.2	1.5	1.5	1.5	2.0	1.5	2.0
		B	0.0	n.a.	1.3	1.5	1.8	2.9	1.1	2.3	2.0	3.3
		Mean	**0.0**	**1.1**	**1.4**	**1.3**	**1.6**	**2.2**	**1.3**	**2.2**	**1.7**	**2.6**
	Entire System	A	*0.0*	*1.1*	*1.5*	*1.2*	*1.5*	*1.5*	*2.8*	*3.3*	*2.2*	*2.0*
		B	*0.0*	*n.a.*	*1.3*	*1.5*	*1.8*	*2.9*	*2.1*	*3.0*	*2.8*	*4.6*
		Mean	**0.0**	**1.1**	**1.4**	**1.3**	**1.6**	**2.2**	**2.5**	**3.2**	**2.4**	**3.3**
Total Extractable Residues	Water	A	N/A		5.9	6.8	6.7	5.1	4.7	4.2	3.8	3.7
		B	N/A		7.3	5.7	6.1	5.6	5.6	3.9	3.8	3.8
		Mean	**N/A**		**6.6**	**6.2**	**6.4**	**5.4**	**5.2**	**4.0**	**3.8**	**3.7**
	Soil	A	95.1	91.1	84.6	83.7	87.1	83.7	84.3	77.2	87.3	90.2
		B	96.5	n.a.	84.2	84.5	87.1	84.5	85.6	76.1	85.4	86.6
		Mean	**95.8**	**91.1**	**84.4**	**84.1**	**87.1**	**84.1**	**85.0**	**76.6**	**86.4**	**88.4**
	Entire System	A	*95.1*	*91.1*	*90.5*	*90.5*	*93.8*	*88.8*	*89.0*	*81.4*	*91.1*	*93.9*
		B	*96.5*	*n.a.*	*91.5*	*90.2*	*93.1*	*90.1*	*91.2*	*80.0*	*89.2*	*90.4*
		Mean	**95.8**	**91.1**	**91.0**	**90.3**	**93.5**	**89.5**	**90.2**	**80.6**	**90.2**	**92.1**
Carbon Dioxide		A	0.0	0.0	0.7	0.7	0.7	0.7	0.7	0.7	0.8	0.8
		B	0.0	n.a.	0.7	0.7	0.7	0.7	0.8	0.8	0.8	0.8
		Mean	**0.0**	**0.0**	**0.7**	**0.7**	**0.7**	**0.7**	**0.7**	**0.7**	**0.8**	**0.8**
Volatile Organic Compounds		A	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
		B	0.0	n.a.	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
		Mean	**0.0**	**0.0**	**0.0**	**0.0**	**0.0**	**0.0**	**0.0**	**0.0**	**0.0**	**0.0**
Non-Extractable Residues		A	3.8	5.1	6.1	5.3	6.0	6.8	8.2	12.9	4.9	5.0
		B	4.7	n.a.	6.6	5.4	6.0	7.3	8.0	12.9	4.7	4.8
		Mean	**4.2**	**5.1**	**6.4**	**5.3**	**6.0**	**7.1**	**8.1**	**12.9**	**4.8**	**4.9**
Material Balance		A	98.8	96.3	97.2	96.4	100.6	96.3	98.0	94.9	96.8	99.6
		B	101.2	n.a.	98.8	96.2	99.9	98.1	100.0	93.6	94.7	96.1
		Mean	**100.0**	**96.3**	**98.0**	**96.3**	**100.2**	**97.2**	**99.0**	**94.3**	**95.7**	**97.8**

DAT: days after treatment; DASF: days after soil flooding; n.a.: not analysed
[1] Before soil flooding (aerobic incubation phase)
[2] After soil flooding (anaerobic incubation phase)
[3] Consists of 2 components, each less than 3% AR.
Values calculated during dossier preparation are given in *italics*.

B. MATERIAL BALANCE

The mean material balance of radioactivity was 96.6% of applied radioactivity (% AR) in the phenyl-labelled test system (range from 93.2 to 100.0% AR) and 97.5% AR in the pyridyl-labelled test system (range from 94.3 to 100.2% AR).

C. EXTRACTABLE AND NON-EXTRACTABLE RESIDUES

Total extractable residues decreased during the aerobic incubation phase (DAT-0 to DAT-28) from 96.0 to 90.2% AR in the phenyl-labelled test systems. During the anaerobic incubation phase (DASF-0 to DASF-120) total extractable residues remained more or less stable. The behaviour in the pyridyl-labelled test systems was comparable.

In the phenyl-labelled test systems, non-extractable residues (NER) increased during the aerobic incubation phase (DAT-0 to DAT-28) from 4.0 to 6.5% AR. During the anaerobic incubation phase, with an exceptional higher value of 12.2% AR at DASF-58, the NER remained more or less constant until study end. In the pyridyl-labelled test systems, NER increased during the aerobic incubation phase (DAT-0 to DAT-28) from 4.2 to 6.4% AR. The NER during the anaerobic incubation phase showed a similar behaviour as described for the first radiolabel.

D. VOLATILIZATION

The maximum amount of carbon dioxide detected at 120 days after flooding was 1.1 % AR for the phenyl-labelled and 0.8% AR for the pyridyl-labelled test system. Formation of volatile organic compounds (VOC) during the aerobic and anaerobic incubation phases was not detectable.

E. DEGRADATION OF TEST ITEM

In the entire phenyl-labelled test system, the amount of fluopyram decreased during the aerobic incubation phase (DAT-0 to DAT-28) from 96.0 to 88.8% AR. During the anaerobic incubation phase the amount of fluopyram in the entire system remained more or less constant. In the entire pyridyl-labelled test system, the amount of fluopyram decreased during the aerobic incubation phase (DAT-0 to DAT-28) from 95.8 to 89.6% AR. During the anaerobic incubation phase s the amount of fluopyram in the entire system remained more or less constant.

There was essentially no degradation of fluopyram during the anaerobic phase of the study. No transformation products at > 5% AR were detected for both labels during both, the aerobic and anaerobic phase of the study. The unidentified radioactivity, which consisted of two separate components, was ≤ 3.3% of the applied amount throughout the study duration for both labels.

III. CONCLUSIONS

Fluopyram is considered stable under anaerobic conditions.

3. Assessment and conclusion

Assessment and conclusion by applicant:
The study is considered to be valid and reliable.

Assessment and conclusion by RMS:
Outcome and conclusion of the study: RMS should indicate if they agree to the results and conclusions of the APPL

1. Information on the study

Data Point:	KCA 7.1.1.2/02
Report Author:	[redacted]
Report Year:	2009
Report Title:	Fluopyram - Bayer CropScience response to PMRA comments regarding redox potential (Eh) in anaerobic soil and aquatic studies
Report No:	M-354014-01-1
Document No:	M-354014-01-1
Guideline(s) followed in study:	not applicable
Deviations from current test guideline:	Current Guideline: not applicable (notifier request)
Previous evaluation:	No, not previously submitted
GLP/Officially recognised testing facilities:	not applicable
Acceptability/Reliability:	Yes

2. Full Summary of KCA 7.1.1.2/02

Introduction

On 22nd June 2009, clarification if the "redox potential (Eh)" measurements reported in an anaerobic soil metabolism study (M-292022-02-1, KCA 7.1.1.3/01) indicate an "anaerobic" environment (email from S. Minoli, PMRA, June 22, 2009) was requested. The purpose of the statement summarised here was to answer to this request.

Reply

Anaerobic soil studies are conducted to mimic the conditions of a pesticide being applied in the field, where a heavy rain might create pockets of anaerobic conditions when the soil becomes flooded. The study itself was performed with field soil and consisted of an anaerobic soil phase, conducted under similar conditions as the aerobic soil metabolism study. Generally, test systems are incubated for approximately one half-life of the active ingredient or for 30 days, whichever is shorter. After this aerobic phase, test systems are flooded with water, and the head space of test systems are flushed with an inert gas (e.g. nitrogen). During the subsequent 120-day incubation period, test conditions move from an aerobic environment to an anaerobic environment. As PMRA has indicated, the OECD 308 and EPA's OPPTS 835.4400 guidance documents both state that "The sediment and water are regarded as anaerobic once the redox potential (Eh) is lower than –100 mV."

The feasibility of achieving an E_h value below -100 mV is limited in anaerobic soil and aquatic test systems. E_h values below +200 mV are sufficient to create a reducing or moderately reducing environment, which is relevant in determining the environmental fate of active ingredients under anaerobic conditions. The E_h in sediments ranging from -300 to +400 mV is described as anaerobic and Eh values greater than + 400 mV as aerobic. The Eh scale indicates that values of less than -100 mV are a highly reduced/reduced redox conditions while Eh values in the range of -100 to +400 mV are reduced/ moderately reduced redox conditions. The microbial populations below -100 mV are strictly anaerobic, and the microbial populations favored in the Eh range of -100 to +400 mV are facultative anaerobes. A facultative anaerobic microorganism is an organism, generating energy by aerobic respiration if oxygen is present but is also capable of switching to fermentation in the absence of oxygen. All microbial populations favored in an atmosphere with an Eh over +400 mV are considered aerobic.

Regarding the EPA and OECD guidance documents, the feasibility of achieving an Eh value below -100 mV is very limited in anaerobic soil test systems. Additionally, a highly reducing test system does not simulate environments where the introduction of pesticides would likely occur.

Therefore, Bayer proposed that the agencies consider conditions as anaerobic if Eh values are less than +200 mV, as opposed to the more unreachable level of -100 mV that is recommended in the current guidance.

Bayer CropScience has typically conducted anaerobic soil with resulting Eh values ranging from -100 to +200 mV. Eh values less than +200 mV are sufficient to create a reducing or moderately reducing anaerobic environment based on the comparison of the degradation pathways between aerobic and anaerobic water/sediment environments.

An anaerobic (reducing) environment has a different microbial population than that of an aerobic (oxidizing) environment. Since the microbial populations are different within anaerobic and aerobic test systems, the degradation pathway of a compound in an anaerobic environment will often be significantly different than in an aerobic environment. The variance in the metabolic pathways between aerobic and anaerobic conditions, observed in studies conducted with various compounds, suggests the existence of anaerobic vs. aerobic microbial populations within the different test systems.

Conclusion
Anaerobic soil studies are conducted to fulfil guideline requirements for the regulatory submission of developmental pesticides. The OECD 308 and EPA's OPPTS 835.4400 guidance documents both state that "The sediment and water are regarded as anaerobic once the redox potential (Eh) is lower than –100 mV." Based on the Eh scale, levels below -100 mV indicate a highly reduced environment. When considering past laboratory experiences, achieving an Eh value of -100 mV in anaerobic soil test systems is extremely difficult. Additionally, a highly reducing test system does not simulate environments where the introduction of pesticides would likely occur.

Bayer CropScience has typically conducted anaerobic soil studies with observed Eh values ranging from -100 to +200 mV. Eh values below +200 mV are sufficient to create a reducing/moderately reducing environment to determine the environmental fate of active ingredients under anaerobic conditions.
This notion is supported by the variance observed in the metabolic pathways of the aerobic and anaerobic aquatic studies of other test compounds suggests the existence of anaerobic vs. aerobic microbial populations within the different test systems.

3. Assessment and conclusion

Assessment and conclusion by applicant: The statement given by Bayer CropScience remains valid for anaerobic soil studies suggesting to consider anaerobic conditions being reached at Eh-values <+200 mV.

Assessment and conclusion by RMS: Outcome and conclusion of the study: RMS should indicate if they agree to the results and conclusions of the APPI.

CA 7.1.1.3 Soil photolysis

1. Information on the study

Data Point:	KCA 7.1.1.3/01
Report Author:	[redacted]
Report Year:	2007
Report Title:	[14C]-AE C656948: Soil photolysis
Report No:	CX/06/022
Document No:	M-286872-01-1
Guideline(s) followed in study:	EU 91/414/EEC amended by 94/37/EC, Section 7.1.1.1.2; US EPA Subdivision N, Paragraph 161-3 [OPPTS 835.2410]; Canadian PMRA DACO Number 8.2.3.3.1; SETAC-Europe Section 1.3 March 1995; OECD draft Documents January 2002
Deviations from current test guideline:	Current Guideline: SETAC-Europe Section 1.3 (1995); OECD draft guideline (2002) None
Previous evaluation:	yes, evaluated and accepted DAR (2011)
GLP/Officially recognised testing facilities:	Yes, conducted under GLP/Officially recognised testing facilities
Acceptability/Reliability:	Yes

2. Full summary of KCA 7.1.1.3/01

Executive Summary

The photolytic route and rate of degradation of [phenyl-UL-^{14}C]fluopyram was studied in a sandy loam soil under exposure to simulated sunlight in the laboratory for 23 days at 20 ± 2 °C and 75% of 1/3-bar soil moisture

Soil	Source	Texture (USDA)	pH [1]	OC [%]
Porterville	RFH Experimental Farm, Porterville, USA	Sandy loam	7.7	0.6

[1] pH value derived from aqueous 0.01 M $CaCl_2$ suspensions

A nominal study application rate of about 15.4 µg/test system of 6.16 cm^2 (approx. 7.8 mg/kg soil dry weight) was applied based on a maximum single field application rate of report name of 250 g/ha (assuming a spray onto 22 mm of soil and 1.5 g/cm^3 bulk density).

Samples were incubated for 23 days under simulated sunlight, which is equivalent to e.g. 30.4 days natural sunlight in Phoenix (Arizona, USA). For comparison, additional samples were incubated in the dark.

For irradiated test systems, the mean material balance of radioactivity ranged from 97.9 to 105.8% of the applied radioactivity (AR). For dark test systems, the mean material balances ranged from 97.8 to 105.8% AR.

Mineralisation was minimal. The amount of carbon dioxide was 0.2 and 0.1% AR at study end (DAT-23) in irradiated and dark samples, respectively. No organic volatiles were detected.

Extractable residues ranged for all sampling intervals between 97.3 and 105.2% AR in irradiated samples and from 97.4 and 105.2% AR in dark samples. Non-extractable residues (NER) increased from DAT-0 to DAT-23 from 0.7 to 2.3% AR in irradiated samples and from 0.7 to 2.7% AR in dark samples.

Fluopyram remained stable in the soil extracts during the incubation period. Amounts between 99.3 and 105.2% AR in irradiated samples and between 97.4 and 105.2% AR in dark samples were found. No degradation products of fluopyram were observed. Therefore, no identification of degradation products was performed.

Fluopyram can be considered as photolytically stable on soil surface. Therefore, no degradation rates for the decline of fluopyram were to be calculated.

I. MATERIALS AND METHODS

A. MATERIALS

1. Test Item

[Phenyl-UL-^{14}C]AE C656948 (fluopyram)

Batch No.:	BECH 1910
Specific Activity:	3.85 MBq/mg
Radiochemical Purity:	>98% (HPLC/radiodetection)

2. Test Soil

One soil was used, which was sampled freshly from the field and sieved to a particle size of ≤2 mm. Soil characteristics are sumamrised in the table below.

Table 7.1.1.3-1: Physico-chemical properties of test soil

Soil Designation	Porterville
Geographic Location	
City	Porterville (RFH Experimental Farm)
State	California
Country	USA
Textural Class (USDA)	loamy sand
Sand (%) [50 µm – 2 mm]	68
Silt (%) [2 µm – 50 µm]	22
Clay (%) [<2 µm]	10
pH	
- Soil/0.01 M $CaCl_2$ 1/1	7.7
- Soil/water 1/1	8.4
- Soil/1 N KCl 1/1	7.4
Organic Carbon (%)	0.6
Organic Matter [1] (%)	1.0
Cation Exchange Capacity [meq/100 g]	7.4
Water Holding Capacity at 1/10 bar (%) (pF 2.0)	21.0
Bulk Density (disturbed) [g/cm^3]	0.98
Microbial Biomass (DAT-0) [mg microbial C/kg soil DW]	85.9

[1] % organic matter = % organic carbon x 1.724
DW: dry weight, USDA: United States Department of Agriculture

B. STUDY DESIGN

1. Experimental Conditions

The static test system for photolytic degradation in soil consisted of glass photolysis vessels inserted into glass incubation units and capped using quartz lids for irradiated vessels. For untreated samples, the same photolysis incubation units were used, but with a solid cap instead of the cap containing a quartz window. All test vessels were connected to traps for the collection of volatiles and CO_2 (one ethylene glycol and two 2 M KOH traps).

For preparation of the test systems, 2.0 g dry weight equivalents of the sieved soil were weighed into each vessel.

The nominal study application rate (SAR) was 15.4 µg/test system of 6.16 cm^2 (approximately 7.8 mg per kg soil dry weight, actual: 7.5 mg per kg soil dry weight for the first treatment and 7.8 mg per kg soil dry weight for the second treatment). The test item was applied directly onto the soil surface of the respective test vessels (i.e. onto approx. 22 mm of soil) in 52 µL acetonitrile using an adjustable pipette.

The irradiated test systems were continuously irradiated under artificial sunlight for 23 days at 20 ± 2°C and a soil moisture of approx. 75% of WHC at 1/3 bar in a Heraeus Sun Test CPS+ unit containing a Xenon lamp simulating natural sunlight. The light emission was filtered with a 290 nm cut-off UV-filter, which eliminated all wavelengths < 290 nm. The intensity of the Xenon lamp was determined at the beginning and the end of the overall test period using an irradiance monitor and the global light intensity was calculated as 276 W/m^2 for 290 to 800 nm. The radiation intensity and exposure time under experimental conditions can be related to natural solar radiation at e.g. Phoenix (Arizona, USA) representing extraordinary conditions. At this light intensity, 23 days in the Suntest® unit are equal to 30.4 days solar summer sunlight in Phoenix.

The dark test systems were incubated for 23 days at 20 ± 2°C and approx. 75 % of at 1/3 bar soil moisture.
A water/ethylene glycol mixture circulating through the water jacket around the vessels, dissipated the heat generated by the xenon light source. The coolant passed through a flow heater/cooler for temperature control to keep samples at 20°C as monitored by a temperature probe. Soil photolysis vessels were removed once each day from the Suntest® unit, weighted and the moisture adjusted by addition of deionised water to the required weight.

2. Sampling

Seven sampling intervals were distributed over the entire incubation period of 23 days. Duplicate samples and associated traps were processed and analysed 1, 3, 7, 14 and 23 days after treatment (DAT) for both irradiated and dark samples. Duplicate samples were also taken for the 'air dried moisture' regime irradiated for 23 days. Samples of DAT-0 were processed and analysed immediately after application and were identical for irradiated and dark samples.

Microbial soil biomass was determined once for the test batch at the beginning of the study.

3. Analytical Procedures

At each sampling interval, test vessels were removed from the incubation system and the soil was carefully transferred into a suitable sized extraction vessel. The soils were extracted three times at ambient temperature using acetonitrile/water (4/1, v/v). After each extraction step, supernatant and soil were separated by centrifugation and decantation.

Soil extracts were characterized by liquid scintillation counting and the primary and confirmatory chromatographic methods (HPLC/radiodetection and TLC/radiodetection). The limit of quantification (LOQ) for the LSC measurements was 0.026% AR. The LOQ for the HPLC/radiodetection method was 2% AR. The amount of volatiles in the trapping solutions was determined at each sampling time except for time zero samples by liquid scintillation counting (LSC), additionally, non-extractable residues were determined by combustion/LSC.The test item was identified by HPLC-MS(/MS) and radiodetection. No identification of degradation products was performed. In addition, selected samples were analysed by TLC for confirmation of the identity of the test item.

II. RESULTS AND DISCUSSION

A. EXTRACTION AND DISTRIBUTION OF RADIOACTIVITY IN SOIL SAMPLES

In Table 7.1.1.3-2 and Table 7.1.1.3-3 the photodegradation of [phenyl-UL-^{14}C]fluopyram is shown for irradiated and dark samples.

Table 7.1.1.3-2: Photodegradation of [phenyl-UL-^{14}C]fluopyram in soil Porterville (mean values expressed as % AR) – irradiated samples

Compound	Source	Replicate	DAT					
			0 [1]	1	3	7	14	23
Fluopyram	Irradiated	A	104.0	94.8	98.6	96.5	97.1	99.4
		B	106.4	105.5	100.0	106.2	104.3	103.4
		Mean	**105.2**	**100.2**	**99.3**	**101.4**	**100.7**	**101.4**
Total Extractable Residues [2]	Irradiated	A	104.0	94.8	98.6	96.5	97.1	99.4
		B	106.4	105.5	100.0	106.2	104.3	103.4
		Mean	**105.2**	**100.2**	**99.3**	**101.4**	**100.7**	**101.4**
Carbon Dioxide [2]	Irradiated	A	n.a	n.d.	n.d.	0.2	0.2	0.2
		B	n.a	n.d.	n.d.	0.1	0.1	0.2
		Mean	**n.c**	**n.d.**	**n.d.**	**0.2**	**0.1**	**0.2**
Volatile Organic Compounds [2]	Irradiated	A	n.a	n.d.	n.a	n.d.	n.d.	n.d.
		B	n.a	n.d.	n.a	n.d.	n.d.	n.d.
		Mean	**n.c**	**n.d.**	**n.d.**	**n.d.**	**n.d.**	**n.d.**
Non-Extractable Residues [2]	Irradiated	A	0.6	0.4	0.7	0.7	1.6	2.0
		B	0.7	0.4	0.7	1.0	1.7	2.7
		Mean	**0.7**	**0.4**	**0.7**	**0.9**	**1.6**	**2.3**
Material Balance	Irradiated	A	104.6	95.2	99.4	97.4	98.8	101.5
		B	107.1	105.9	100.7	107.4	106.0	106.3
		Mean	**105.8**	**100.6**	**100.0**	**102.4**	**102.4**	**103.9**

n.a.: not analysed, n.c.: not calculated, n.d.: not detected, DAT: days after treatment

[1] DAT-0 samples were identical for irradiated and dark samples.

[2] Values taken from Material Balance

Table 7.1.1.3-3: Photodegradation of [phenyl-UL-^{14}C]fluopyram in soil Porterville (mean values expressed as % AR)– dark samples

Compound	Source	Replicate	DAT				
			0 [1]	1	7	14	23
Fluopyram	Dark	A	104.0	97.2	104.4	103.2	99.5
		B	106.4	97.7	103.7	102.7	99.5
		Mean	**105.2**	**97.4**	**104.0**	**103.0**	**99.5**
Total Extractable Residues [2]	Dark	A	104.0	97.2	104.4	103.2	99.5
		B	106.4	97.7	103.7	102.7	99.5
		Mean	**105.2**	**97.4**	**104.0**	**103.0**	**99.5**
Carbon Dioxide [2]	Dark	A	n.a	n.d.	0.2	0.1	0.1
		B	n.a	n.d.	0.2	0.1	0.1
		Mean	**n.c**	**n.d.**	**0.2**	**0.1**	**0.1**
Volatile Organic Compounds [2]	Dark	A	n.a	n.d.	n.d.	n.d.	n.d.
		B	n.a	n.d.	n.d.	n.d.	n.d.
		Mean	**n.c**	**n.d.**	**n.d.**	**n.d.**	**n.d.**
Non-Extractable Residues [2]	Dark	A	0.6	0.3	1.0	2.2	2.7
		B	0.7	0.5	0.8	2.3	2.6
		Mean	**0.7**	**0.4**	**0.9**	**2.2**	**2.7**
Material Balance	Dark	A	104.6	97.4	105.5	105.5	102.3
		B	107.1	98.2	104.6	105.1	102.2
		Mean	**105.8**	**97.8**	**105.1**	**105.3**	**102.3**

n.a.: not analysed, n.c.: not calculated, n.d.: not detected, DAT: days after treatment
[1] DAT-0 samples were identical for irradiated and dark samples.
[2] Values taken from Material Balance.

B. MATERIAL BALANCE

For irradiated test systems, the material balances of radioactivity as mean of duplicate test vessels ranged from 100.0 to 105.8% AR. Material balance of radioactivity for test vessels with air-dried soil was at 97.9% AR at DAT-23. For dark test systems, the material balances of radioactivity as mean of duplicate test vessels ranged from 97.8 to 105.8% AR. The complete material balances found at all sampling intervals for both irradiated and dark samples demonstrated that there was no significant loss of radioactivity from the test systems or during sample processing.

C. EXTRACTABLE AND NON-EXTRACTABLE RESIDUES

Extractable residues ranged for all sampling intervals between 99.3 and 105.2% AR in irradiated samples and from 97.4 and 105.2% AR in dark samples. Non-extractable residues (NER) increased from DAT-0 to DAT-23 from 0.7 to 2.3% AR in irradiated samples and from 0.7 to 2.7% AR in dark samples.

D. VOLATILES

The amount of carbon dioxide was 0.2 and 0.1% AR at study end (DAT-23) in irradiated and dark samples, respectively. No organic volatiles were detected at all sampling intervals for irradiated and dark samples.

E. DEGRADATION OF PARENT COMPOUND

The amount of fluopyram in the soil extracts was stable between 99.3 and 105.2% AR in irradiated samples and between 97.4 and 105.2% AR in dark samples. No degradation products of fluopyram were observed. Therefore, no identification of degradation products was performed.

F. KINETICS

Fluopyram is not photolytically degraded in soil. Therefore, no degradation rates for the decline of fluopyram were calculated.

III. CONCLUSIONS

The study showed that fluopyram was photolytically stable under the prevailing intensive test conditions. Therefore, no degradation rates for the decline of fluopyram were to be calculated.

Photolysis on soil surfaces is not considered as a relevant pathway for the degradation of fluopyram in the environment.

3. Assessment and conclusion

Assessment and conclusion by applicant: The study is considered to be valid and reliable.

Assessment and conclusion by RMS: Outcome and conclusion of the study: RMS should indicate if they agree to the results and conclusions of the APPL.

CA 7.1.2 Rate of degradation in soil

CA 7.1.2.1 Laboratory studies

Kinetic evaluations of the different laboratory soil degradation studies according to FOCUS degradation kinetics (2006, 2014) have been carried out to derive modelling and trigger endpoints.

Taking into account the results of a detailed visual and statistical assessment, the soil degradation of fluopyram for modelling purposes can mostly be described assuming a single first-order (SFO) approach. For soils regarded as relevant for the EU, the geometric mean half-live of fluopyram in the laboratory is calculated to 364 days.

For comparison with trigger values, soil degradation of fluopyram can best be described by applying SFO or biphasic models like the first-order multi compartment (FOMC), the double first order in parallel (DFOP) or the hockey-stick (HS) model. Trigger half-lives of fluopyram in the laboratory were estimated to ranged from 157 to >1000 days (geometric mean: 422.3 days). The respective DT_{90} values ranged from 521 to >1000 days.

Table 7.1.2.1- 1: Laboratory DT_{50} and DT_{90} values of fluopyram in aerobic soil (modelling endpoints)

Parent	**Dark aerobic laboratory conditions**						
Soil type	**References**	**pH[1]**	**t. °C / % MWHC**	**$DegT_{50}$ actual / DT_{90} actual (d)**	**$DegT_{50}$ mod (d) 20 °C, pF2/ 10kPa[2]**	**St. (χ^2)**	**Method of calculation**
[^{14}C-pyridyl-2,6]Fluopyram							
Hoefchen am Hohensch, silt loam	M-298413-01-1	6.7	20°C/ 55%	205.2 / 682	205.2	1.15	SFO
Laacherhof AXXa, sandy loam	M-298413-01-1	6.2	20°C/ 55%	441.5 / >1000	441.5	1.32	SFO

Parent	Dark aerobic laboratory conditions						
Soil type	**References**	**pH[1]**	**t. °C / % MWHC**	**DegT$_{50}$ actual / DT$_{90}$ actual (d)**	**DegT$_{50}$ $_{mod}$ (d) 20 °C, pF2/ 10kPa[2]**	**St. (χ^2)**	**Method of calculation**
Laacherhof Wurm-wiese, sandy loam	M-298413-01-1	5.2	20°C/ 55%	230.97 / 767	230.97	1.38	SFO
Dollendorf, clay loam	M-298413-01-1	7.3	20°C/ 55%	141.1 / 469	141.1	2.64	SFO
[^{14}C-phenyl-UL]Fluopyram							
Hoefchen am Hohenseh, silt loam	M-298296-01-1	6.6	20°C/ 55%	214.3 / 712.0	214.3	1.67	SFO
Laacherhof AXXa, sandy loam	M-298296-01-1	6.6	20°C/ 55%	223.7 / 743.3	223.7	1.19	SFO
Laacherhof Wurmwiese, loam	M-298296-01-1	5.5	20°C/ 55%	307.7 / >1000	307.7	1.81	SFO
Laacherhof AIIIa, loam	M-298296-01-1	6.6	20°C/ 55%	163.2 / 542.0	163.2	1.06	SFO
Argissolo, clay	M-344303-02-1	5.3 (5.9)[ ]	20°C/ 40%	707.1 / >1000	440.3	3.05	SFO
Little Oliver, sandy loam	M-681092-02-1	5.5	19.4°C/ 53.6%[2]	>1000 / >1000	1000 (default)	1.02	SFO
Auchy les Mines, silt loam	M-681092-02-1	7.5	19.4°C/ 54.0%[2]	1051.3 / >1000	993.2	1.12	SFO
Urbanowice, silt loam	M-681092-02-1	4.9	19.4°C/ 53.6%[2]	>1000 / >1000	1000 (default)	0.998	SFO
Charles River Farm, clay	M-681092-02-1	7.7	19.4°C/ 54.0%[2]	489.17 / >1000	462.12	1.10	SFO
Sindos, loam	M-681092-02-1	7.2	19.4°C/ 54.0%[2]	261.70 / 869	247.23	0.858	SFO
Paradiso San Zenone, sandy loam	M-681092-02-1	5.4	19.4°C/ 53.8%[2]	351.85 / >1000	332.40	1.84	SFO
Hoeltinghausen, sand	M-753426-01-1	4.5	19.4 / 54.1[4]	1054.2 / >1000	995.9	0.668	SFO
Hornton, loam	M-753426-01-1	5.9	19.4 / 54.8[4]	515.2 / >1000	474.0	2.27	SFO
Le Thour, silt loam	M-753426-01-1	7.4	19.4 / 55.0[4]	172.8 / 573.9	163.2	1.84	SFO
Brannens, sandy loam	M-753426-01-1	4.7	19.4 / 54.2[4]	413.1 / >1000	390.2	1.20	SFO
Balbiano, sandy loam	M-753426-01-1	7.1	19.4 / 54.5[4]	366.5 / >1000	346.3	0.999	SFO

Parent	Dark aerobic laboratory conditions						
Soil type	**References**	**pH[1]**	**t. °C / % MWHC**	**DegT$_{50}$ actual / DT$_{90}$ actual (d)**	**DegT$_{50}$ mod (d) 20 °C, pF2/ 10kPa[2]**	**St. (χ^2)**	**Method of calculation**
Almayate East, loam	M-753426-01-1	7.7	19.4 / 54.6[4]	292.9 / 972.9	260.7	2.08	SFO
Frankenforst, silt loam	M-761739-01-1	7.3	19.2 / 54.2[4]	246.4 / 818.4	204.0	1.84	SFO
Wurmwiese, loam	M-761739-01-1	5.1	19.2 / 54.4[4]	341.0 / >1000	DT$_{50\ fast}$ 4.735 d, **DT$_{50\ slow}$ 369.7 d,** g 0.0956	1.76	DFOP[5]
Hoefchen am Hohenseh, silt loam	M-761739-01-1	5.7	19.2 / 54.4[4]	327.8 / 1000	DT$_{50\ fast}$ 3.850 d, **DT$_{50\ slow}$ 373.1 d,** g 0.1208	2.15	DFOP[5]
Innerdeich, sandy loam	M-761739-01-1	6.2	19.2 / 54.5[4]	374.4 / >1000	DT$_{50\ fast}$ 4.488 d, **DT$_{50\ slow}$ 416.0 d,** g 0.1085	0.99	DFOP[5]
Both [^{14}C-pyridyl-2,6]Fluopyram and [^{14}C-phenyl-UL]Fluopyram							
Springfield, silty clay loam	M-299548-02-1	6.5	25°C/ 49.7%	483.4 / >1000	490.0	3.18	SFO
Porterville, sandy loam	M-299548-02-1	7.9	25°C/ 36.0%	864.5 / >1000	789.3	2.00	SFO
Geometric mean (if not pH dependent)					364.38		
pH dependence					No		

[1] Measured in $CaCl_2$
[2] Normalised using a Q10 of 2.58 and Walker Equation coefficient of 0.7
[3] pH $CaCl_2$ is calculated based on equation: pH H_2O = 0.953 pH $CaCl_2$ + 0.85; FOCUS, 2014b, value in brackets measured in H_2O
[4] Mean measured values
[5] Slow phase DT$_{50}$ used for geometric mean calculation

Table 7.1.2.1- 2: Best-fit DT_{50} and DT_{90} values of fluopyram in aerobic soil (EU trigger endpoints)

Parent	Dark aerobic laboratory conditions						
Soil type	**References**	**pH[1]**	**t. °C / % MWHC**	**$DegT_{50\ actual}$ / $DT_{90\ actual}$ (d)**	**$DegT_{50\ mod}$ (d) 20 °C pF2/ 10kPa[2]**	**St. (χ^2)**	**Method of calculation**
[^{14}C-pyridyl-2,6]Fluopyram							
Hoefchen am Hohenseh, silt loam	M-298413-01-1	6.7	20°C/ 55%	213.9 / 732	-	1.53	HS
Laacherhof AXXa, sandy loam	M-298413-01-1	6.2	20°C/ 55%	444.5 / >1000	-	1.39	SFO
Laacherhof Wurmwiese, sandy loam	M-298413-01-1	5.2	20°C/ 55%	245 / 843	-	1.06	HS
Dollendorf, clay loam	M-298413-01-1	7.3	20°C/ 55%	156.9 / 521	-	2.37	SFO
[^{14}C-phenyl-UL]Fluopyram							
Hoefchen am Hohenseh, silt loam	M-298296-01-1	6.6	20°C/ 55%	209.3 / 739	-	1.01	HS
Laacherhof AXXa, sandy loam	M-298296-01-1	6.6	20°C/ 55%	221.9 / 737	-	1.25	SFO
Laacherhof, Wurmwiese, loam	M-298296-01-1	5.5	20°C/ 55%	320.8 / >1000	-	1.89	SFO
Laacherhof, AIIIa, loam	M-298296-01-1	6.6	20°C/ 55%	160.5 / 552	-	0.779	HS
Argissolo, clay	M-349303-02-1	5.3 (5.9)[3]	20°C/ 40%	>1000 / >1000	-	1.87	SFO
Little Oliver, sandy loam	M-681092-02-1	5.5	19.4°C/ 53.6%	>1000 / >1000	-	0.75	FOMC
Auchy les Mines, silt loam	M-681092-02-1	7.5	19.4°C/ 54.0%	>1000 / >1000	-	0.65	FOMC
Urbanowice, silt loam	M-681092-02-1	4.9	19.4°C/ 53.6%	>1000 / >1000	-	0.97	FOMC
Charles River Farm, clay	M-681092-02-1	7.7	19.4°C/ 54.0%	501 / >1000	-	1.12	DFOP
Sindos, loam	M-681092-02-1	7.2	19.4°C/ 54.0%	464 / >1000	-	0.77	FOMC
Paradiso San Zenone, sandy loam	M-681092-02-1	5.4	19.4°C/ 53.8%	>1000 / >1000	-	0.87	FOMC

Hoeltinghausen, sand	M-753426-01-1	4.5	19.4 / 54.1[4]	>1000 / >1000	-	0.668	SFO
Hornton, loam	M-753426-01-1	5.9	19.4 / 54.8[4]	805.1 / >1000	-	0.742	HS
Le Thour, silt loam	M-753426-01-1	7.4	19.4 / 55.0[4]	173.2 / 575.4	-	1.84	SFO
Brannens, sandy loam	M-753426-01-1	4.7	19.4 / 54.2[4]	413.3 / >1000	-	1.26	SFO
Balbiano, sandy loam	M-753426-01-1	7.1	19.4 / 54.5[4]	366.5 / >1000	-	0.999	SFO
Almayate East, loam	M-753426-01-1	7.7	19.4 / 54.6[4]	292.9 / 972.9	-	2.08	SFO
Frankenforst, silt loam	M-761739-01-1	7.3	19.2 / 54.2[4]	245.0 / 857.5	-	1.48	DFOP
Wurmwiese, loam	M-761739-01-1	5.1	19.2 / 54.4[4]	457.1 / >1000	-	1.50	DFOP
Hoefchen am Hohenseh, silt loam	M-761739-01-1	5.7	19.2 / 54.4[4]	310.2 / >1000	-	2.13	DFOP
Innerdeich, sandy loam	M-761739-01-1	6.2	19.2 / 54.5[4]	427.3 / >1000	-	0.798	DFOP
Both [^{14}C-pyridyl-2,6]Fluopyram and [^{14}C-phenyl-UL]Fluopyram							
Springfield, silty clay loam	M-299548-02-1	6.5	25°C/ 49.7%	483.4 / >1000	-	3.18	SFO
Porterville, sandy loam	M-299548-02-1	7.9	25°C/ 36.0%	864.5 / >1000	-	2.00	SFO
Maximum (n=27)				1000			

[1] Measured in $CaCl_2$
[2] Normalised using a Q10 of 2.58 and Walker equation coefficient of 0.7
[3] pH $CaCl_2$ is calculated based on equation: pH H_2O = 0.953 pH $CaCl_2$ + 0.85; FOCUS, 2014b, value in brackets measured in H_2O
[4] Mean measured values

If possible, the available laboratory data on aerobic degradation in soil for the active substance also served for the kinetic evaluation of metabolites fluopyram-7-hydroxy and TFA via a pathway approach. Additionally, one study on the degradation rate of fluopyram-7-hydroxy in aerobic soil following separate application of the metabolite is available.

Kinetic evaluations were performed according to FOCUS degradation kinetics (2006, 2014) to derive modelling and trigger endpoints.

For modelling purposes, the kinetic evaluation resulted in a geometric mean DT_{50} of 17.5 days for metabolite fluopyram-7-hydroxy. From the pathway-fits, a formation fraction of fluopyram-7-hydroxy could be estimated to an arithmetic mean f.f. of 0.6342. For trigger purposes, half-lives of fluopyram-7-hydroxy ranged from 5.1 to 85.5 days (geometric mean: 19.1 days), respective DT_{90} values ranged from 17.0 to 284 days.

Following degradation tests on rate of TFA in aerobic soil, the compound is regarded to be stable under laboratory conditions. The half-life of TFA was calculated to be >1000 days for both, modelling and

trigger purposes. Correspondingly, a DT_{90} of moe than 1000 days applies as well. From degradation tests perfomed with the active substance, an arithmetic mean formation fraction of 0.2701 (per CF_3 moiety) was derived for TFA, overall via all metabolites and parallel pathways. Due to the potential formation of 2 TFA molecules from one fluopyram molecule in total, the total molar yield or overall formation fraction reflecting TFA formation per FLU molecule will be 2 x the overall formation fraction per CF_3 moiety, i.e. 0.5402.

Table 7.1.2.1- 3: DT_{50} and DT_{90} values of fluopyram-7-hydroxy in aerobic soil (modelling endpoints)

Fluopyram-7-hydroxy (FLU-7-OH)	**Dark aerobic conditions; metabolite dosed or the precursor from which the f.f. was derived was fluopyram, in pathway of max. occurrence in soil: 5.8 % (Brannens, d 118)**							
Soil type	**References**	**pH[1]**	**t. °C / % MWHC**	**$DegT_{50\ actual}$ / $DT_{90\ actual}$ (d)**	**f. f. k_f / k_{fm}**	**$DegT_{50\ mod}$ (d) 20 °C, pF2/ 10kPa[2]**	**St. (χ^2)**	**Method of calculation**
Hoefchen am Hohenseh, silt loam	M-298413-01-1	6.7	20°C/ 55%	5.618 / 18.7	0.9528	5.618	6.11	SFO-SFO
Laacherhof AXXa, sandy loam	M-298413-01-1	6.2	20°C/ 55%	18.75 / 62.3	0.6294	18.75	20.0	SFO-SFO (95th CI rate fixed)
Laacherhof Wurmwiese, sandy loam	M-298413-01-1	5.2	20°C/ 55%	7.865 / 26.1	1.00	7.865	22.6	SFO-SFO
Dollendorf , clay loam	M-298413-01-1	7.3	20°C/ 55%	5.109 / 17.0	1.00	5.109	19.0	SFO-SFO
Hoefchen m Hohenseh, silt loam	M-298296-01-1	6.6	20°C/ 55%	18.04 / 59.93	0.4837	18.04	10.3	SFO-SFO (95th CI rate fixed)
Laacherhof AXXa, sandy loam	M-298296-01-1	6.6	20°C/ 55%	20.27 / 67.35	0.5798	20.27	5.22	SFO-SFO (95th CI rate fixed)
Laacherhof Wurmwiese, loam	M-298296-01-1	5.3	20°C/ 55%	15.22 / 50.6	0.8690	15.22	7.35	SFO-SFO (95th CI rate fixed)
Laacherhof Alfa, loam	M-298296-01-1	6.6	20°C/ 55%	22.05 / 73.26	0.4603	22.05	9.70	SFO-SFO (95th CI rate fixed)
Argissolo, clay	M-349303-02-1	5.3 (5.9)[3]	20°C/ 40%	13.23 / 43.9	1.00	8.24	26.0	SFO - SFO
Le Thour, silt loam	M-753426-01-1	7.4	19.4 / 55.0[4]	18.67 / 62.01	0.4493	17.64	19.68	SFO-SFO
Brannens, sandy loam	M-753426-01-1	4.7	19.4 / 54.2[4]	93.35 / 310.1	0.5264	88.19	18.00	SFO-SFO (DT_{50} * 1.25 fixed)
Frankenforst, silt loam	M-761739-01-1	7.3	19.2 / 54.2[4]	10.48 / 34.80	0.6689	8.675	11.7	SFO-SFO

Fluopyram-7-hydroxy (FLU-7-OH)	**Dark aerobic conditions; metabolite dosed or the precursor from which the f.f. was derived was fluopyram, in pathway fit** **max. occurrence in soil: 5.8 % (Brannens, d 118)**							
Soil type	**References**	**pH[1]**	**t. °C / % MWHC**	**$DegT_{50\ actual}$ / $DT_{90\ actual}$ (d)**	**f. f. k_f / k_{dp}**	**$DegT_{50\ mod}$ (d) 20 °C pF2/ 10kPa[2]**	**St. (χ^2)**	**Method of calculation**
Wurmwiese, loam	M-761739-01-1	5.1	19.2 / 54.4[4]	66.55 / 221.1	0.3082	61.69	7.54	DFOP-SFO
Hoefchen am Hohenseh, silt loam	M-761739-01-1	5.7	19.2 / 54.4[4]	85.52 / 284.1	0.2430	79.28	7.02	DFOP-SFO
Innerdeich, sandy loam	M-761739-01-1	6.2	19.2 / 54.5[4]	61.31 / 203.7	0.3422	56.83	6.14	DFOP-SFO
Frankenforst, silt loam	M-757988-01-1	7.3	21.09 / 52.6[4]	5.371 / 17.84	-	5.210	7.64	SFO[6]
Wurmwiese, loam	M-757988-01-1	5.1	21.09 / 52.9[4]	13.92 / 91.87	-	30.68[5]	6.75	FOMC[6]
Hoefchen am Hohenseh, silt loam	M-757988-01-1	5.7	21.09 / 52.8[4]	11.50 / 38.21	-	12.75	3.43	SFO[6]
Innerdeich, sandy loam	M-757988-01-1	6.2	21.09 / 51.6[4]	17.63 / 284.2	-	94.92[5]	4.05	HS[6]
Geometric mean values of the 4 soils above (Innerdeich, Hoefchen a. Hohenseh, Wurmwiese, Frankenforst) which were examined in 2 different studies								
Frankenforst, silt loam	-	7.3	-	-	-	6.723	-	Geometric mean 2 DT_{50} s
Wurmwiese, loam	-	5.1	-	-	-	43.51	-	Geometric mean 2 DT_{50} s
Hoefchen am Hohenseh , silt loam	-	5.7	-	-	-	31.80	-	Geometric mean 2 DT_{50} s
Innerdeich, sandy loam	-	6.2	-	-	-	73.45	-	Geometric mean 2 DT_{50} s
Geometric mean (if not pH dependent)						17.53		
Arithmetic mean					0.6342			
pH dependence						No		

[1] Measured in $CaCl_2$
[2] Normalised using a Q10 of 2.58 and Walker equation coefficient of 0.7
[3] pH $CaCl_2$ is calculated based on equation: pH H_2O = 0.953 pH $CaCl_2$ + 0.85; FOCUS, 2014b, value in brackets measured in H_2O
[4] mean measured values
[5] pseudo DT_{50} = DT_{90} / 3.32 used as DT_{50} for modelling endpoints
[6] Metabolite applied study

Table 7.1.2.1- 4: Best-fit DT_{50} and DT_{90} values of fluopyram-7-hydroxy in aerobic soil (EU trigger endpoints)

Fluopyram-7-hydroxy	Dark aerobic laboratory conditions. Metabolite dosed or the precursor from which the f.f. was derived was Fluopyram							
Soil type	**Reference**	**pH[1]**	**t. °C / % MWHC**	**Deg$T_{50\ actual}$ / $DT_{90\ actual}$ (d)**	**f. f. k_f / k_{dp}**	**Deg$T_{50\ mod}$ (d) 20 °C pF2 / 10kPa[2]**	**St. (χ^2)**	**Method of calculation**
Hoefchen am Hohenseh, silt loam	M-298413-01-1	6.7	20°C/ 55%	12.07 / 40.1	0.4698	-	4.61	HS-SFO
Laacherhof AXXa, sandy loam	M-298413-01-1	6.2	20°C/ 55%	10.22 / 34.0	1.00	-	15.6	SFO-SFO
Laacherhof Wurmwiese, sandy loam	M-298413-01-1	5.2	20°C/ 55%	11.92 / 39.6	0.6829	-	5.47	HS-SFO
Dollendorf, clay loam	M-298413-01-1	7.3	20°C/ 55%	5.109 / 17.0	1.00	-	19.0	SFO-SFO
Hoefchen am Hohenseh, silt loam	M-298296-01-1	6.6	20°C/ 55%	17.71 / 58.82	0.4669	-	5.23	HS-SFO
Laacherhof AXXa, sandy loam	M-298296-01-1	6.6	20°C/ 55%	17.54 / 58.26	0.6430	-	4.15	SFO-SFO
Laacherhof Wurmwiese, loam	M-298296-01-1	5.5	20°C/ 55%	12.61 / 41.9	1.00	-	6.05	SFO-SFO
Laacherhof, AIIIa, loam	M-298296-01-1	6.6	20°C/ 55%	29.28 / 97.27	0.3589	-	3.39	HS-SFO
Argissolo, clay	M-349303-02-1	5.3 (5.9)[3]	20°C/ 40%	13.23 / 43.9	1.00	-	26.0	SFO - SFO
Le Thour, silt loam	M-753426-01-1	7.4	19.4 / 55.0[4]	18.67 / 62.01	0.4493	-	19.68	SFO-SFO
Brannens, sandy loam	M-753426-01-1	4.7	19.4 / 54.2[4]	74.68 / 248.1	0.5671	-	19.68	SFO-SFO
Frankenforst, silt loam	M-761739-01-1	7.3	19.2 / 54.2[4]	24.56 / 81.60	0.3109	-	9.04	DFOP-SFO
Wurmwiese, loam	M-761739-01-1	5.1	19.2 / 54.4[4]	66.55 / 221.1	0.3082	-	7.54	DFOP-SFO
Hoefchen am Hohenseh, silt loam	M-761739-01-1	5.7	19.2 / 54.4[4]	85.52 / 284.1	0.2430	-	7.02	DFOP-SFO
Innerdeich, sandy loam	M-761739-01-1	6.2	19.2 / 54.5[4]	61.31 / 203.7	0.3422	-	6.14	DFOP-SFO

Fluopyram-7-hydroxy	Dark aerobic laboratory conditions. Metabolite dosed or the precursor from which the f.f. was derived was Fluopyram							
Soil type	**Reference**	**pH[1]**	**t. °C / % MWHC**	**$DegT_{50\ actual}$ / $DT_{90\ actual}$ (d)**	**f. f. k_f / k_{dp}**	**$DeT_{50\ mod}$ (d) 20 °C pF2 / 10kPa[2]**	**St. (χ^2)**	**Method of calculation**
Frankenforst, silt loam	M-757988-01-1	7.3	21.09 / 52.6 [4]	5.371 / 17.84	-	-	7.64	SFO[5]
Wurmwiese, loam	M-757988-01-1	5.1	21.09 / 52.9 [4]	14.74 / 113.9	-	-	5.82	HS[5]
Hoefchen am Hohenseh , silt loam	M-757988-01-1	5.7	21.09 / 52.8 [4]	11.50 / 38.21	-	-	3.43	SFO[5]
Innerdeich, sandy loam	M-757988-01-1	6.2	21.09 / 51.6 [4]	17.63 / 284.2 $DT_{50\ fast}$ 17.63 d $DT_{50\ slow}$ 167.8 d tb 32.1 d = g 0.7167, $DT_{50\ pseudo}$ 85.6 d	-	-	4.05	HS[5]
Maximum (n=19)				85.52 / 284.1				

[1] Measured in $CaCl_2$
[2] Normalised using a Q10 of 2.58 and Walker equation coefficient of 0.7
[3] pH $CaCl_2$ is calculated based on equation: pH H_2O = 0.953 pH $CaCl_2$ + 0.85; FOCUS, 2014b, value in brackets measured in H_2O
[4] Mean measured values
[5] Metabolite applied study

Table 7.1.2.1- 5: DT_{50} and DT_{90} values of TFA in aerobic soil (modelling endpoints)

Trifluoroacetate (TFA)	Dark aerobic laboratory conditions overall formation, from parent to TFA via all metabolites and parallel pathways; max. occurrence in soil: 14.8 % per FLU molecule 7.41 % per CF_3 moiety								
Soil type (USDA)	**Reference**	**pH[4]**	**T (C°) / % MWHC**	**DT_{50} / DT_{90} (d)**	**$DT_{50\ mod}$ (d) 20°C pF2 / 10 kPa[3]**	**ff overall (FLU-TFA) per CF_3 ^{CF3}**	**ff overall (FLU-TFA) per FLU ^{FLU}**	**St. (χ^2)**	**Method of calculation *parent***
Frankenforst, silt loam	M-761739-01-1	7.3	19.2 / 54.2[2]	-[1]	-[1]	0.2555 ^{CF3}	0.5109 ^{FLU}	6.95	SFO
Wurmwiese, loam	M-761739-01-1	5.1	19.2 / 54.4[2]	-[1]	-[1]	0.4012 ^{CF3}	0.8024 ^{FLU}	12.5	DFOP
Hoefchen a. Hohenseh , silt loam	M-761739-01-1	5.7	19.2 / 54.4[2]	-[1]	-[1]	0.2630 ^{CF3}	0.5261 ^{FLU}	8.98	DFOP
Innerdeich, sandy loam	M-761739-01-1	6.3	19.2 / 54.5[2]	-[1]	-[1]	0.1608 ^{CF3}	0.3215 ^{FLU}	16.2	DFOP
Geometric mean									
Arithmetic mean						0.2701 ^{CF3}	**0.5402 ^{FLU}**		

[1] No degradation assumed
[2] Mean measured values used
[3] Normalised using a Q10 of 2.58 and Walker equation coefficient of 0.7
[4] Measured in $CaCl_2$
^{CF3} formation fraction, reflecting TFA formation per CF3 moiety of FLU
^{FLU} total molar yield; formation fraction, reflecting TFA formation per FLU molecule, i.e. 2 x formation fraction per CF3 moiety, as FLU has 2 CF3 moieties.

Table 7.1.2.1- 6: Best-fit DT_{50} and DT_{90} values of TFA in aerobic soil (EU trigger endpoints)

TFA	Dark aerobic laboratory conditions. Metabolite dosed							
Soil type	**Reference**	**pH[3]**	**t, °C / % MWHC**	**DT_{50}/ DT_{90} (d)**	**f. f. k_f / k_{dp}**	**DT_{50} (d) 20 °C pF2/10kPa[2]**	**St. (χ^2)**	**Method of calculation**
AX, Sandy loam	M-439283-01-1	6.2	20°C/ 55%	>1000 / >1000		-	1.01	SFO[1]
DD, Clay Loam	M-439283-01-1	7.3	20°C/ 55%	>1000 / >1000		-	1.09	SFO[1]
WW, Sandy loam	M-439283-01-1	5.1	20°C/ 55%	>1000 / >1000		-	1.20	SFO[1]
HH, Silt loam	M-439283-01-1	6.4	20°C/ 55%	>1000 / >1000		-	1.00	SFO[1]
Geometric mean (if not pH dependent)						-		
Arithmetic mean					-			

[1] Metabolite dosed study
[2] Normalised using a Q10 of 2.58 and Walker equation coefficient of 0.7
[3] Measured in $CaCl_2$

CA 7.1.2.1.1 Aerobic degradation of the active substance

Data Point:	KCA 7.1.2.1.1/01
Report Author:	[redacted]
Report Year:	2008
Report Title:	[Pyridyl-2,6-14C]AE C656948: Aerobic metabolism/degradation and time-dependent sorption in soils
Report No:	MEF-07/424
Document No:	M-298413-01-1
Guideline(s) followed in study:	OECD: Guideline 307, Aerobic and Anaerobic Transformation in Soil (2002); Commission Directive 95/36/EC amending Council Directive 91/414/EEC (Annexes I and II, Fate and Behavior in the Environment) (1995); SETAC Procedures for Assessing the Environmental Fate and Ecotoxicity of Pesticides (1995); US EPA Subdivision N, Section 162-1, Aerobic soil metabolism (1982); OECD: Guideline 106, Adsorption/Desorption (2001) (only where applicable); Equivalent to US EPA OPPTS Guideline No. 835.4100
Deviations from current test guideline:	Current Guideline: OECD 307 (2002), OECD 106 (2000) (Only in parts) None
Previous evaluation:	yes, evaluated and accepted DAR (2011)
GLP/Officially recognised testing facilities:	Yes, conducted under GLP/Officially recognised testing facilities
Acceptability/Reliability:	Yes

The experimental study is summarised and discussed under point KCA 7.1.1.1/01 of this document. The kinetic evaluation is summarised under KCA 7.1.2.1.1/09 (M-761966-01-1). The results of the aged sorption part of the study and is summarised under KCA 7.1.2.2/01.

Data Point:	KCA 7.1.2.1.1/02
Report Author:	[redacted]
Report Year:	2008
Report Title:	[Phenyl-UL-14C]AE C656948: Aerobic soil metabolism/degradation and time-dependent sorption in four soils
Report No:	MEF-06/295
Document No:	M-298296-01-1
Guideline(s) followed in study:	OECD: Guideline 307, Aerobic and Anaerobic Transformation in Soil (2002); Commission Directive 95/36/EC amending Council Directive 91/414/EEC (Annexes I and II, Fate and Behavior in the Environment (1995); SETAC Procedures for Assessing the Environmental Fate and Ecotoxicity of Pesticides (1995); US EPA Subdivision N, Section 162-1, Aerobic soil metabolism (1982); OECD: Guideline 106, Adsorption/Desorption (2000) (Only where applicable); Equivalent to US EPA OPPTS Guideline No. 835.4000
Deviations from current test guideline:	Current Guideline OECD 307 (2002), OECD 106 (2000) (Only in parts) None
Previous evaluation:	yes, evaluated and accepted DAR (2011)
GLP/Officially recognised testing facilities:	Yes, conducted under GLP/Officially recognised testing facilities
Acceptability/Reliability:	Yes

The experimental study is summarised and discussed under point KCA 7.1.1.1/02 of this document. The kinetic evaluation is summarised under KCA 7.1.2.1.1/09 (M-761966-01-1). The results of the aged sorption part of the study and is summarised under KCA 7.1.3.2.02.

Data Point:	KCA 7.1.2.1.1/03
Report Author:	Meyer, B. N.
Report Year:	2008
Report Title:	[Phenyl-UL-14C] and [pyridyl-2,6-14C]AE C656948: Aerobic soil metabolism in two US soils
Report No:	MEGM-1069-1
Document No:	M-298548-02-1
Guideline(s) followed in study:	US EPA: Pesticide Assessment Guidelines, Subdivision N, Section, 162-1: Aerobic Soil Metabolism Studies, 1982. US EPA OPPTS Guideline No. 835.4100
Deviations from current test guideline:	Current Guideline OECD 307 (2002) None
Previous evaluation:	yes, evaluated and accepted DAR (2011)
GLP/Officially recognised testing facilities:	Yes, conducted under GLP/Officially recognised testing facilities
Acceptability/Reliability:	Yes

The experimental study is summarised and discussed under point KCA 7.1.1.1/03 of this document. The kinetic evaluation is summarised under KCA 7.1.2.1.1/10 (M-761880-01-1).

Data Point:	KCA 7.1.2.1.1/04
Report Author:	[redacted].
Report Year:	2020
Report Title:	Amendment no. 01: Rate of degradation of [phenyl-ul-14C]-fluopyram in brazilian soils
Report No:	1962-BS120-135-08
Document No:	M-349303-02-1
Guideline(s) followed in study:	OECD - Guideline for the Testing of Chemicals. Method 307 "Aerobic and anaerobic transformation in soil" (Adopted: 24th April 2002)
Deviations from current test guideline:	Current Guideline: OECD 307 (2002) The cation exchange capacity is not reported. In the experimental set-up up to six flasks were connected to the same trapping system.
Previous evaluation:	No, not previously submitted
GLP/Officially recognised testing facilities:	Yes, conducted under GLP/Officially recognised testing facilities
Acceptability/Reliability:	Yes

The experimental study is summarised and discussed under point KCA 7.1.1.1/04 of this document. The kinetic evaluation was done in a separate study and is summarised under KCA 7.1.2.1.1/11 (M-761965-01-1). The representativeness of the tested Brazilian soils for European agricultural areas was assessed in a separate study and is summarised under KCA 7.1.2.1.1/05.

1. Information on the study

Data Point:	KCA 7.1.2.1.1/05
Report Author:	Ageert, J.; Kley, C.
Report Year:	2020
Report Title:	Fluopyram (FLU), Ecoregion crosswalk - Representativeness of Brazilian soils used for investigating degradation rates in soil for Europe
Report No:	EnSa-20-0640
Document No:	M-735268-01-1
Guideline(s) followed in study:	not applicable
Deviations from current test guideline:	Current Guideline: not applicable (calculation)
Previous evaluation:	No, not previously submitted
GLP/Officially recognised testing facilities:	No, not conducted under GLP/Officially recognised testing facilities
Acceptability/Reliability:	Yes

2. Full summary of KCA 7.1.2.1.1/05

Executive Summary

For the active substance fluopyram laboratory soil degradation studies with 4 Brazilian soils have been conducted (KCA 7.1.1.1/04, M-349303-01-1, amended report M-349303-02-1).

To assess whether these soils are representative for European agricultural areas and hence may be relevant for the European risk assessment, a comparison between soil types and properties of the soils used in the study and the occurrence of comparable soil types and properties in Europe is carried out.

Based on a comparison of soil types, soil properties and their spatial occurrence, only one of 4 soils, the Argissolo soil, is considered potentially relevant for Europe. However, its spatial extent is very limited (less than 1.1% of Europeans agriculturally used area, mainly in south-eastern Europe (Romania and Bulgaria, eastern Serbia), but also in Lithuania, Poland, Germany, Italy, on the Iberian Peninsula and to a smaller extent in UK, Denmark, and Greece).

The Latossolo soil batch is not representative, as similar soil types (Acrisols) only occur to a very limited spatial extent, but not in combination with similar soil pH (pH_{H2O} 4.6) and texture (clay).

The Neossolo soil batch is not representative for European agriculture, as similar soil types (luvic or gleyic Arenosols) do not occur on agriculturally used areas in Europe.

The Gleissolo soil batch is not representative for European agriculturally used soils, due to its extremely low soil pH (pH_{H2O} 3.9), its extremely high organic carbon content (10.1%) and no overlap with its similar soil types (Gleysol, Fluvisol).

I. METHODS

A comparison between soil types and properties of the 4 Brazilian soils used in the study (KCA 7.1.1.1/04, M-349303-01-1, amended report M-349303-02-1) and the occurrence of comparable soil types and properties in Europe was carried out to assess whether these soils are representative for European agricultural areas and hence may be relevant for the European risk assessment.

For the comparison of environmental conditions under which pesticides will degrade similarly between Europe and North America the ecoregion[1] crosswalk approach is often used. It comes along with a GIS-based software 'Europe-North America Soil Geographic Information for Pesticide Studies' (ENASGIPS) 3.0 developed by the Pest Management Regulatory Agency Health Canada and the US Environmental Protection Agency in collaboration with Agriculture and Agri-Food Canada and the EC Joint Research Centre as part of the OECD project 'Harmonized International Guidance for Pesticide Terrestrial Field Dissipation Studies and Crosswalk of North American and European Eco-regions'.

However, this tool does not include geographic information from other parts of the world, it compares individual soil parameters and does not necessary take into account the actual conditions at the site where the soil was taken from.

Therefore, to assess the representativeness of the Brazilian soils for European agricultural land a simple comparison of soil types and individual soil parameters is carried out.

The soil batches used were classified according to the Brazilian Soil Classification System SiBCS. This system aims at describing soil under tropical climate and uses a hierarchical structure ranging from order over suborder, great group, subgroup, family to series. The technical pedological manual also offers a table mapping SiBCS soil taxonomy classes to World Reference Base (WRB) soil taxonomy classes.

Additionally, expert statements are available which classify the typically required Brazilian lab study soils (with similar, but not exactly the same batches as used in the study) according to the World Reference Base for Soil Resources.

[1] Ecoregion are defined as "relatively large units of land containing a distinct assemblage of natural communities and species, which boundaries that approximate the original extent of natural communities prior to major land-use change." There are different ecoregion classification systems considering soil types, climate zonation, and (vegetation) ecology.

A spatial query for the corresponding soil types is conducted on the European Soil Database SGDBE. For querying the occurrence of individual soil parameters like texture, organic carbon content and soil pH similar to the soil used in the study, state of the art soil maps based on the LUCAS topsoil data are used. To account for variability of the parameters and uncertainty of the maps ranges of parameters are queried, i.e. the USDA soil texture class is used instead of the exact sand, silt and clay percentage. For organic carbon the value ± 0.5% and for pH the value ± 0.5 pH unit are queried as a pragmatic approach. In order to restrict the spatial queries to agricultural land, the Corine Land Cover data (Coordination of Information on the Environment Land Cover, CLC) is used.

II. RESULTS

The sites from which the 4 Brazilian soils are sampled are mapped in Figure 7.1.2.1.1- 1. One site is located in the federal state Sao Paulo (south-east region). Three are located in Rio Grande do Sul in the south region.

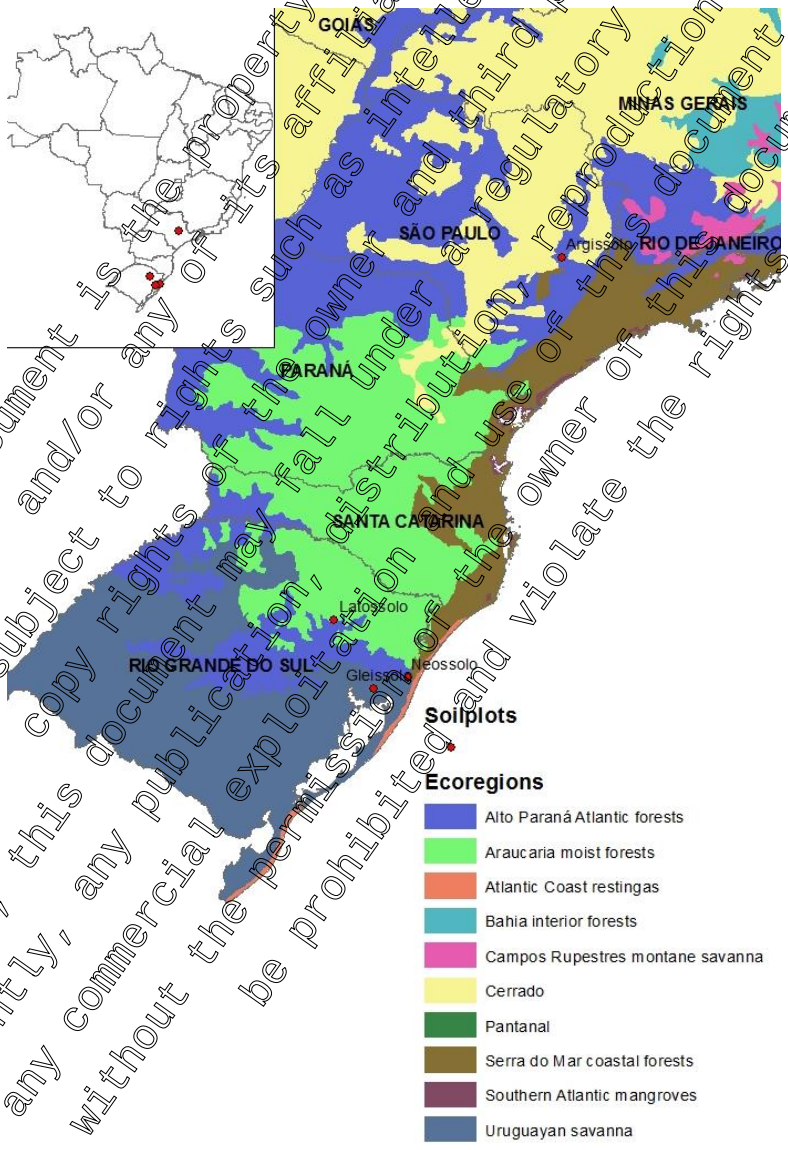


Figure 7.1.2.1.1- 1: Location of Brazilian sites where soil was collected, and ecoregions (WWF 2016)

A Argissolo soil

The Argissolo soil was sampled from an agricultural area in Piracicaba municipal district (22°40’50”S, 47°37’31”W) in the state Sao Paulo.

This area is located in the ecoregion “Alto Paraná Atlantic forests” (also denoted as NT0150). This region spreads from southern Brazil, north-eastern Argentina and eastern Paraguay, and the main natural vegetation type is semi-deciduous forest. The climate in this ecoregion is subtropical with more than 1200 mm of annual rainfall.

The soil batch used for the study is classified as Argissolo vermelho eutroferrico chernossolico. It has an organic carbon content of 2.8%. Its texture is clay according to USDA soil textural classification (42% clay, 22% silt, 36% sand), and it has a pH_{H2O} of 5.9. A soil classification according to World Reference Base of this soil batch is not available.

The soil batch classified to World Reference Base is from a location in about 5 km distance from the soil batch used in the study. It is classified as Argissolo vermelho-amarelo eutroferricos tipicos. This translation into World Reference Base yields a luvic Phaeozem due to the soil’s humus rich topsoil and clay enriched subsurface horizon.

The Brazilian Soil Classification System describes the soil order of Argissolos as mineral soil with an increase of clay from surface to the subsurface. The suborder “vermelho” denotes the red colour of the soil. The great group “eutroferrico” refers to the soil’s high base saturation and iron content and the subgroup “chernossolico” describes the A horizon’s type, i.e. it is a dark mineral horizon with high base saturation and high organic carbon content.

Given these descriptions, the soils from the different batches have very similar characteristics and this analysis is therefore considered to investigate the occurrence of similar soil on European agricultural area, meaning a spatial query for the occurrence of luvic Phaeozem is carried out.

Figure 7.1.2.1.1- 2 displays locations where luvic Phaeozems can be found on European agriculturally used area. The spatial extent displayed in the map represents soil mapping units which normally contain different soils, i.e. only a fraction (on average 58%) of the area is covered by luvic Phaeozems. According to this analysis, luvic Phaeozems sum up to 0.8% of Europeans agriculturally used area, mainly in south-eastern Europe (Romania and Bulgaria, eastern Serbia), but also in Lithuania, Poland, Germany and Italy.

The information available for the soil batch used in the study is limited and therefore a definitive attribution to WRB soil classification is not possible within the scope of this analysis. In case the soil batch used in the study does not fulfil all requirements to be classified as luvic Phaeozem, an additional query for the Reference Soil Groups according to the World Reference Base that correspond to the Brazilian soil order Argissolo according to IBGE is carried out. According to this mapping Argissolo corresponds to Acrisol, Lixisols or Alisols in WRB.

Acrisols on arable land occur in Europe mainly in Iberia and to a smaller extent in UK, Denmark, Serbia and Greece. These soils make up about 0.3% of Europe’s agriculturally used area. Lixisols do not occur on agricultural area. Alisols can be found in southern Portugal only (far less than 0.1% of Europe’s agriculturally used area).

Similar topsoil pH, organic carbon content and texture are as well displayed in Figure 7.1.2.1.1- 2. Soil pH and organic carbon content of the soil used in the study commonly occur in Central and Southern Europe. Clay soils, however, are not equally ubiquitously distributed, but can be found at different spots mainly in southern Spain, on Sicily an in Puglia, in Scandinavia around Stockholm and Helsinki and on smaller areas in Hungary and Bulgaria.

In principle, similar soils as the Argissolo can be found on Europe's arable land. However, the spatial extent is very limited.

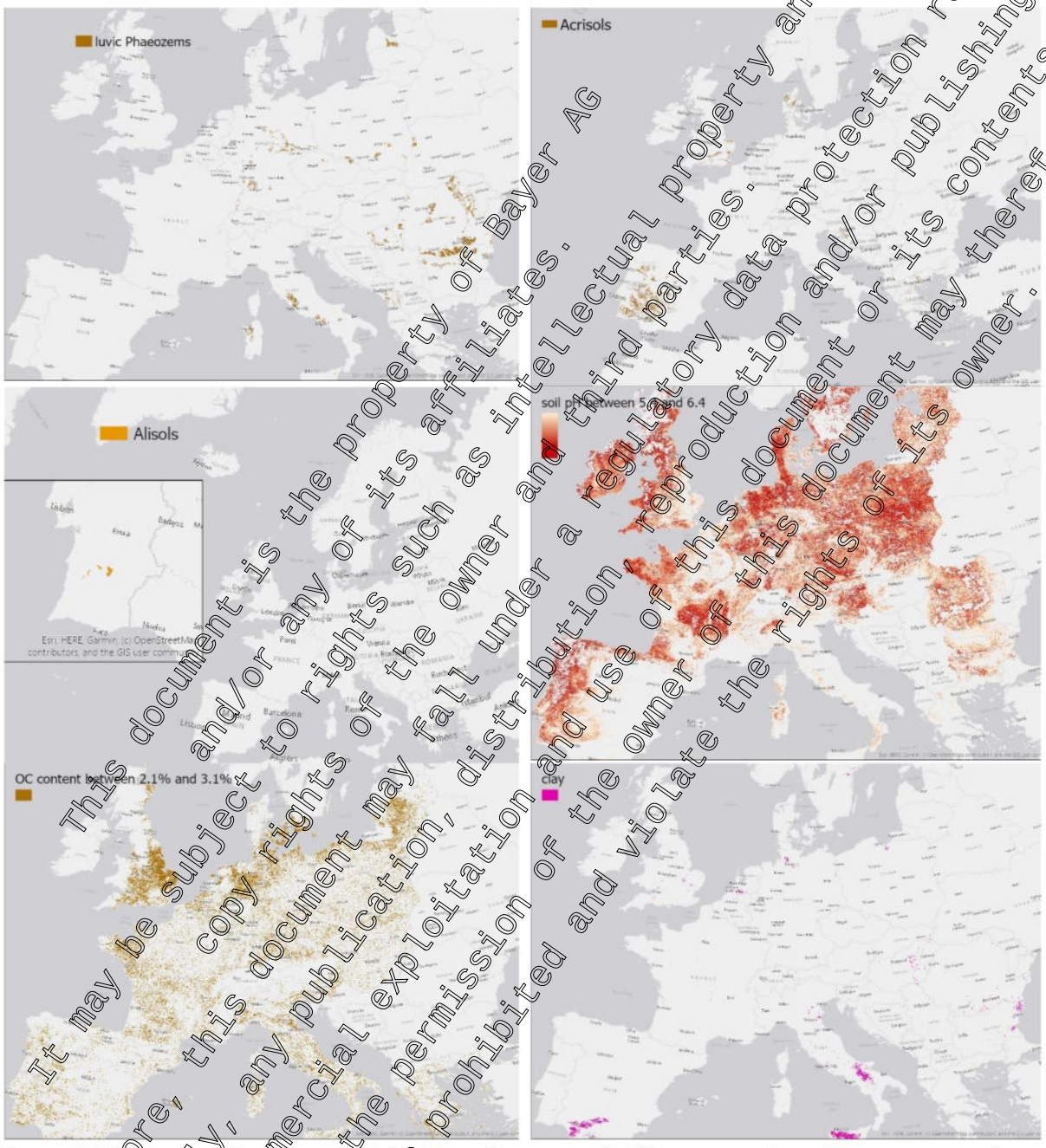


Figure 7.1.2.1.1- 2: Occurrence of similar soil types, soil pH_{H2O}, organic carbon content and texture compared to Argissolo Vermelho eutroferrico on European agriculturally used area

B Latossolo soil

The Latossolo soil was sampled from an agricultural area in Veranopolis municipal district (28°53'42"S, 51°33'05"W) in Rio Grande do Sul.

This area is located on the boundary between the ecoregions “Araucaria moist forests” (also denoted as NT0101) and “Alto Parana Atlantic forests (denoted as NT0150). These regions range from the southern Atlantic Brazil into north-eastern Argentina and southern Brazil, north-eastern Argentina and eastern Paraguay, respectively. The main natural vegetation types are mixed coniferous and broad-leafed trees as well as semi-deciduous forests. Climate in both ecoregions is subtropical with high annual rainfalls above 1300 mm/a.

The soil batch used in the study is classified as Latossolo Vermelho distroferrico tipico. Soil texture according to USDA is clay. The pH_{H2O} is 4.6 and the organic carbon content is 1.6%.

According to the Brazilian soil Classification System Latossolos correspond to the World Reference Base Soil Reference Group Ferrasols.

The soil batch classified to WRB is from a location in about 22 km distance from the soil batch used in the study. It is classified as Latossolo Vermelho-Amarelo aluminico argissolico. This soil has a highly weathered B horizon, a high aluminium exchange capacity and a clay enriched subsoil.

The Brazilian soil Classification System describes the soil order of Latossolos as highly weathered soils. The suborder Vermelho denotes the soil’s colour which is influenced by the high amount of iron oxides. The soil batch used in the study and the soil batch characterised differ and it is not sure whether it would be appropriate to base the spatial analysis on the full WRB classification, but rather only consider the Soil Reference Group Acrisol. Therefore, for the spatial analysis, solely Soil Reference Groups (both Ferrasols and Acrisols) are considered.

According to the European Soil Database Ferrasols do not occur on arable land in Europe. Figure 7.1.2.1.1- 3 displays locations where Acrisols can be found on European agriculturally used area. The spatial extent displayed in the map represents soil mapping units which normally contain different soils, i.e. only a fraction (on average 27%) of the area is covered by Acrisols. According to this analysis, Acrisols sum up to 0.3% of Europeans agriculturally used area, mainly in Iberia and to a smaller extent in UK, Denmark, Serbia and Greece.

The soil pH is rather low (pH_{H2O} 4.6). Similar soil pH values (with the tendency to lower values) are mainly found in Sweden and Finland. In the north-eastern part of central Europe, Ireland, Scotland, central France and in the northern parts of Romanian Carpathian mountains similar and slightly higher soil pH occurs. In Galicia and northern Portugal also similar soil pH occurs. Organic carbon content of 1.6% (±0.5%) are very typical for Central and Southern European arable land. Clay-textured soils can be found at different spots mainly in southern Spain, on Sicily an in Puglia, in Skandinavia around Stockholm and Helsinki and on smaller areas in Hungary and Bulgaria.

The spatial occurrence of Acrisols is very limited, even if the full range of Acrisols without further qualifiers is considered. Concerning the Latossolo, there is no overlap of similar soil types (Acrisol) and similar soil properties (pH_{H2O} = 4.6, organic carbon content 1.6 %, clay) in Europe.

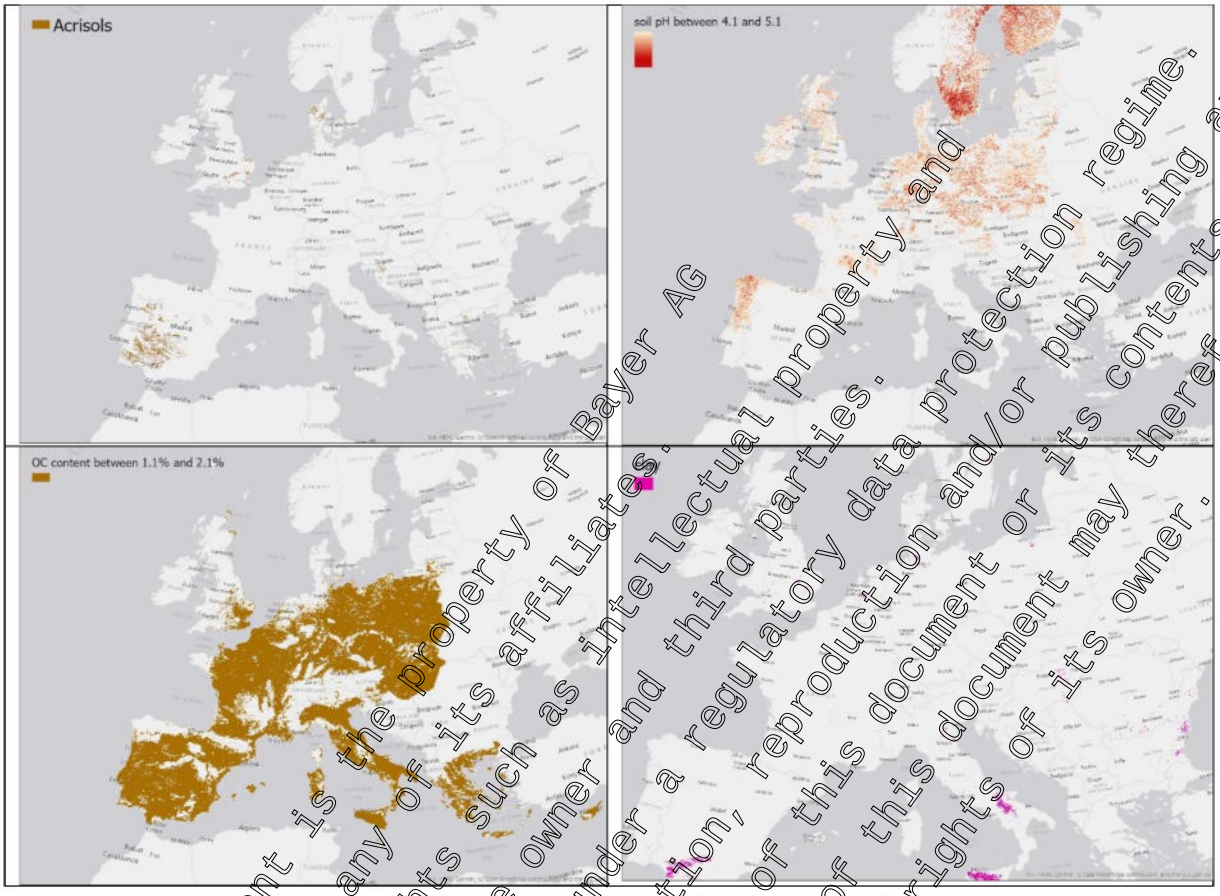


Figure 7.1.2.1.1- 3: Occurrence of similar soil type, soil pH_{H2O}, organic carbon content and texture compared to Latossolo on European agriculturally used area

C Neossolo soil

The Neossolo soil was sampled from an agricultural area in Osorio municipal district (29°53'44"S, 50°16'53"W) in Rio Grande do Sul.

This area is located on the boundary between the ecoregions "Serra do Mar coastal forests" (also denoted as NT0160) and "Uruguayan Savanna" (also denoted as NT0710). The "Serra do Mar coastal forests" ecoregions cover a 100 km wide strip along the Coast of South-east and South Brazil with montane forests. Climate is subtropical with annual average precipitation ranging from 1400 to 4000 mm without a dry period. The "Uruguayan Savanna" ecoregion includes southern Rio Grande do Sul in southern Brazil, Uruguay and some parts of Argentina. The ecoregion is mainly covered by semi-tall grasslands. Annual rainfall ranges from 1000 mm/a in the south to 1300 mm/a in the north, and annual average temperatures range from 16°C in the south to 19°C in the North.

The soil batch used in the study is classified as Neossolo quartzarenico ortico tipico. The USDA soil texture based on the reported grain size distribution is sandy loam. Soil pH_{H2O} is 5.1. The soil has a low organic carbon content of 0.9%.

The soil batch classified to World Reference Base is from the same location as the soil batch used in the study. It is classified as Neossolo quartzarenico ortico eutrico. This translation into World Reference Base yields a hypoluvic endogleyic Arenosol (dystric) due to its sandy texture, its small clay increase in the subsoil horizons, mottles in the subsoil originating from reducing conditions and its low base saturation.

The Brazilian soil Classification System describes the soil order of Neossolos quartzarenicos as similar to Arenosols in the WRB.

The study report does not include more information about the soil. However, as it was sampled at the same location it could be considered appropriate to base the spatial analysis on this detailed classification. The qualifiers hypoluvic and endogleyic are not available in the European soil database for a query. The specifier "hypo" describes a weak expression of a feature. Instead of querying "hypoluvic", the qualifier "luvic" is used for the query. As the specifier "endo" refers to the depth where a characteristic (in this case a gleyic properties) the qualifier "gleyic" is used for the query. However, according to the soil and land use databases no luvic or gleyic Arenosols are found in European areas used for agriculture.

Figure 7.1.2.1.1- 4 displays locations where Arenosols (also others than hypoluvic endogleyic) can be found on European agriculturally used area. The spatial extent displayed in the map represents soil mapping units which normally contain different soils, i.e. only a fraction (on average 33%) of the area is covered by Arenosols. According to this analysis Arenosols sum up to 2.5% of Europeans agriculturally used area, mainly in Poland, Denmark, and northern Germany.

The soil pH of the study soil batch is pH_{H2o} = 5.1 and can be found in northern Europe, especially in Scandinavia, the Baltic countries, Poland, and Germany, as well as in the UK, in parts of France an in north-western Spain and Portugal. Organic carbon content is rather low (0.9 %). Similar soil organic carbon contents are found in southern Europe (especially the Iberian Peninsula), but also in southern Poland, Czech Republic, Slovakia and Hungary. Sandy loams are found in large parts of northern Europe, UK, France and the Iberian Peninsula.

Although there is a small overlap of Arenosols in general and the soil properties similar to the study soil batch, it has to be noted that luvic or gleyic Arenosols, equivalent to the used Neossolo in the study, are not found and not relevant for European agriculturally used land.

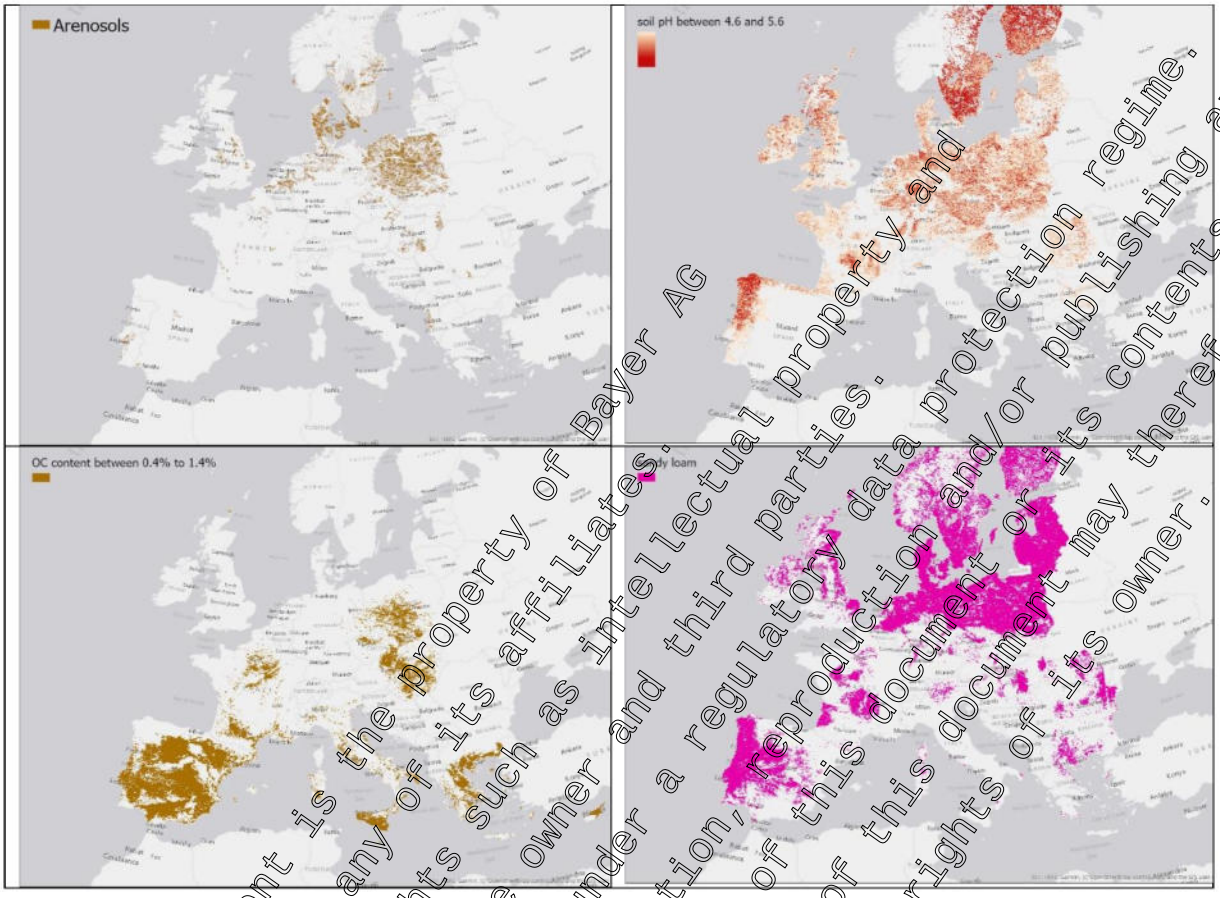


Figure 7.1.2.1.1- 4: Occurrence of similar soil type, soil pH_{H2O}, organic carbon content and texture compared to Neossolo on European agriculturally used area

D Gleissolo soil

The Gleissolo soil was sampled from an agricultural area in Viamao municipal district (30°04'09"S, 50°51'45"W) in Rio Grande do Sul.

This area is located in the ecoregion "Uruguayan Savanna" (also denoted as NT0710). This region includes southern Rio Grande do Sul in southern Brazil, Uruguay and some parts of Argentina. The ecoregion is mainly covered by semi-tall grasslands. Annual rainfall ranges from 1000 mm/a in the south to 1300 mm/a in the north, and annual average temperatures range from 16°C in the south to 19°C in the North.

The soil batch used in the study is classified as Gleissolo melanico aluminico tipico. Its organic carbon content is very high (10.1%). Soil texture is clay loam according to USDA soil texture classification. The soils pH_{H2O} is rather low with 5.9.

The soil batch classified to World Reference Base (WRB) is from a location in about 8.7 km distance from the soil batch used in the study. It is classified as Gleissolo haplico ta eutrofico neofluvissolico. That translation into World Reference Base yields a gleyic Fluvisol (humic, eutric) due to the soil's fluvitile, marine and lacustrine sediments, its organic carbon content distribution and the mottles which indicate a groundwater influence.

The Brazilian soil Classification System describes the soil order of Gleissolos as pasty soil with water saturation (allowing reducing conditions to occur). The suborder melanico denotes the occurrence of a dominant, humic, chernic horizon. The great group aluminico indicates that the soil is aluminous and

that the base saturation is lower than 50%. This characteristic does not apply to the soil batch for which the soil classification according to WRB was investigated. Additionally, the soil pH and organic carbon content differ significantly between the soil batches. Therefore, this analysis should not be based on this classification.

Instead, the spatial query is solely based on Soil Reference Groups without considering additional specifications in form of qualifiers. According to the Brazilian soil Classification System, Gleissolos correspond to the WRB Soil Reference Group Gleysols. As there have been some changes in the key to the Reference Groups in the WRB for Gleysols and Fluvisols and the European Soil Database Classification is not based on the latest WRB keys, Fluvisols are also considered.

Figure 7.1.2.1.1- 5 displays locations where Gleysols and Fluvisols can be found on European agriculturally used area. The spatial extent displayed in the map represents soil mapping units which normally contain different soils, i.e. only a fraction (on average 39% for Gleysols and 60% for Fluvisols) of the area is covered by the above mentioned soil types. Gleysols are mainly found in the UK and in (northern) Germany, in Poland, in the Baltic countries where groundwater is rather shallow. Fuvisols are typically along rivers. They can be predominantly found in the Po valley in northern Italy, in many eastern European countries, and along the Northern Sea coast of France, Belgium, the Netherlands and Germany. According to this analysis Gleysols cover about 6.2% of Europeans agriculturally used area. Fluvisols cover a slightly larger fraction of 6.7%.

The soil pH of the study soil batch is pH_{H2O} = 3.9 and extremely low for European conditions. There are only very small and scattered areas with similar low pH in southern Sweden and Finland. While the soil pH is extremely low, the soil organic carbon content is extremely high (10.1%). Similar organic carbon ranges are found in the Baltic countries, in Scandinavia in regions near the Baltic Sea, in Ireland, Scotland and Wales and in Galicia in north-western Spain. Clay loam textured soils are mainly found in Southern Europe and in England.

While similar soil types to the Gleissolo (Gleysol, Fluvisol) frequently occur on Europe's agriculturally used area, the soil pH and organic carbon content are extreme. Concerning the Gleissolo, there is no overlap of similar soil types (Gleysol, Fluvisol) and similar soil properties (low pH_{H2O} = 3.9, high organic carbon content 10.1 %) in Europe.

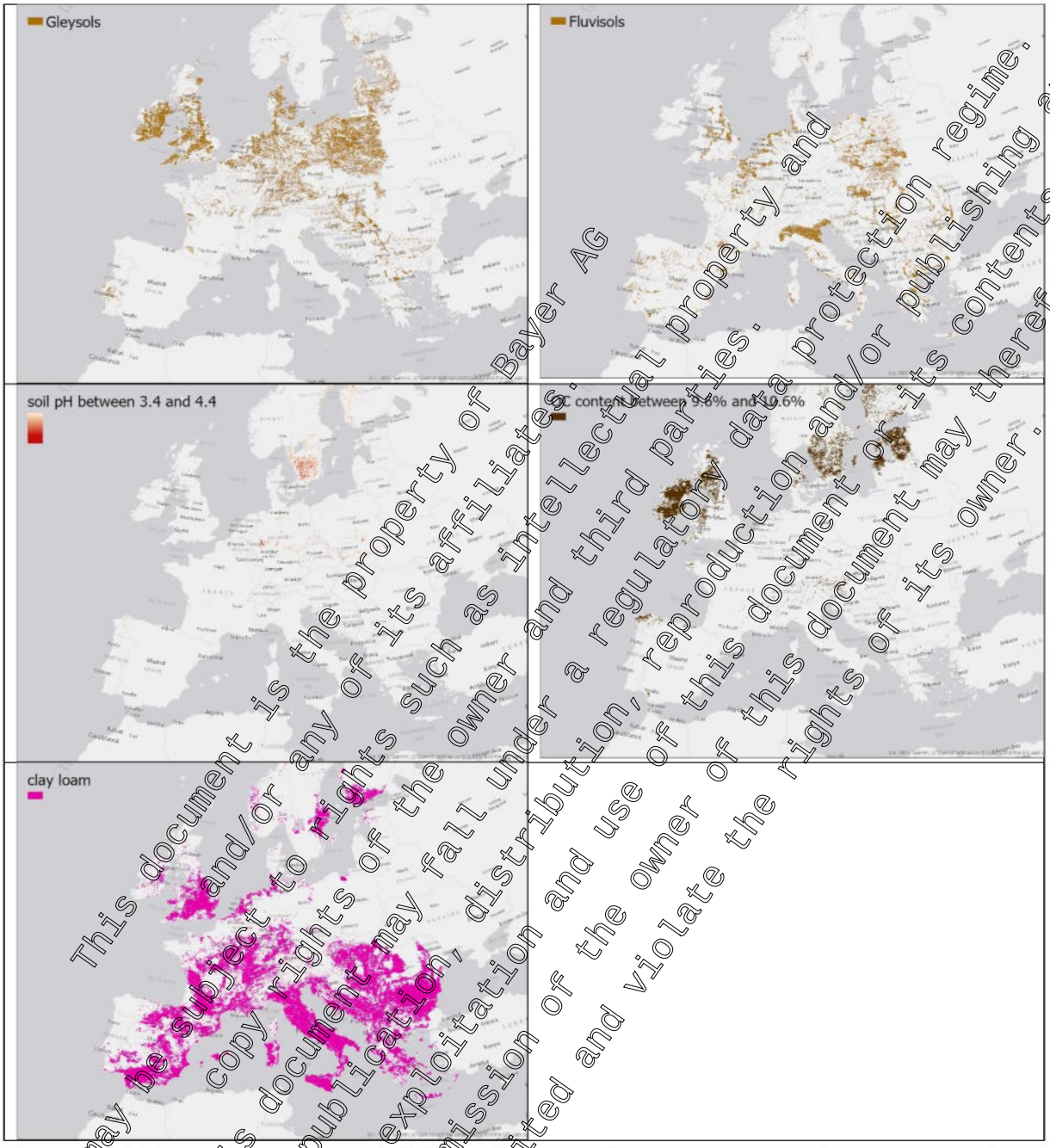


Figure 7.1.2.1.1- 5: Occurrence of similar soil type, soil pH_{H2O}, organic carbon content and texture compared to Gleissolo on European agriculturally used area

III. CONCLUSIONS

Based on a comparison of soil types, soil properties and their spatial occurrence, only one of 4 soils, the Argissolo soil, is considered potentially relevant for Europe. However, its spatial extent is very limited (less than 1.7% of Europeans agriculturally used area, mainly in south-eastern Europe (Romania and Bulgaria, eastern Serbia), but also in Lithuania, Poland, Germany, Italy, on the Iberian Peninsula and to a smaller extent in UK, Denmark, and Greece). Soils Latossolo, Neossolo and Gleissolo are not representative for European agriculturally used soils.

3. Assessment and conclusion

Assessment and conclusion by applicant: The crosswalk evaluation is considered valid and reliable.

Assessment and conclusion by RMS: Outcome and conclusion of the study: RMS should indicate if they agree to the results and conclusions of the APPL.

1. Information on the study

Data Point:	KCA 7.1.2.1.1/06
Report Author:	[redacted]
Report Year:	2020
Report Title:	Amendment no. 01: Fluopyram: Aerobic metabolism / Degradation and time - Dependent sorption in 6 soils
Report No:	EnSa-20-0072
Document No:	M-681092-02-1
Guideline(s) followed in study:	OECD Test Guideline No. 307 (2002). OECD Test Guideline No. 106 (2000 only in parts) Guidance on how aged sorption studies for pesticides should be conducted, analyzed and used in the regulatory process (2012, revised draft 2016). Current revision dates Sep 2016 (this draft guidance was updated based on the PPR statement on aged sorption, EFSA Journal 2015;13(7):4175].
Deviations from current test guideline:	Current Guideline: OECD 307 (2002), OECD 106 (2000) (Only in parts) None
Previous evaluation:	No, not previously submitted
GLP/Officially recognised testing facilities:	Yes, conducted under GLP/Officially recognised testing facilities
Acceptability/Reliability:	Yes

The experimental study is summarised and discussed under point KCA 7.1.1.1/05 of this document. A kinetic evaluation of trigger endpoints following current FOCUS guidance was conducted in the course of the study and is summarised below. Evaluation of modelling endpoints can be found in KCA 7.1.2.1.1/12 (M-681882-01-1). The results of the aged sorption part of the study and is summarised under KCA 7.1.3.2/04.

2. Full summary of KCA 7.1.2.1.1/06

The degradation of fluopyram followed first order multi compartment (FOMC) kinetics in all soils, except soil Sindos, where degradation followed double first order in parallel (DFOP) kinetics. The DT_{50} values for fluopyram were between 464 and >1000 days in the tested soils under aerobic conditions in the dark at a temperature of 20 °C.

1. MATERIALS AND METHODS

Kinetic Evaluation

The residue data for the test item were evaluated according to the FOCUS guidance document on degradation kinetics using the software KinGUI 2 to derive the DT_{50} and DT_{90} values for fluopyram.
Model input datasets were the residual test item amounts found in each replicate test system at each sampling interval. The initial total recovery (material balance) at DAT-0 was included in the parameter

optimization procedure, but for optimal goodness of fit, the value was allowed to be estimated by the model.
For the determination of the degradation kinetics the following procedure was applied:

- Values between LOD and LOQ were set to the measured values.
- All single values < LOD or non-detected (n.d.) were set to 0.5 × LOD. If they became < LOD/ n.d. for a second time the curve was cut off until a subsequent value >LOQ occurs.

For the evaluation of the data three different kinetic models were tested in order to determine the best-fit kinetic model. The best-fit kinetic model was selected on the basis of the chi² scaled error criterion and on the basis of a visual assessment of the goodness of the fits (diagrams of measured and calculated values vs. time, diagrams of residuals vs. time). DT_{50} and DT_{90} values (time until 50 or 90% degradation) were calculated from the resulting kinetic parameters.

II. RESULTS AND DISCUSSION

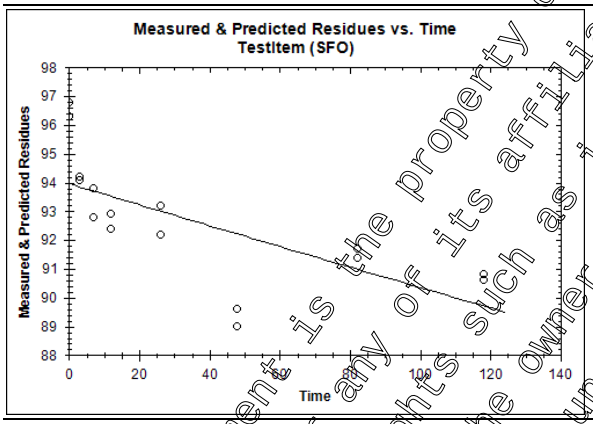
The degradation of fluopyram followed first order multi compartment (FOMC) kinetics in all soils, except soil Charles River Farm, where degradation followed double first order in parallel (DFOP) kinetics. The DT_{50} values for fluopyram under aerobic conditions in the dark at a temperature of 20 ± 2 °C were >1000, >1000, >1000, 301, 464 and >1000 days in soil LO, AM, UW, FA, SD and PZ, respectively.

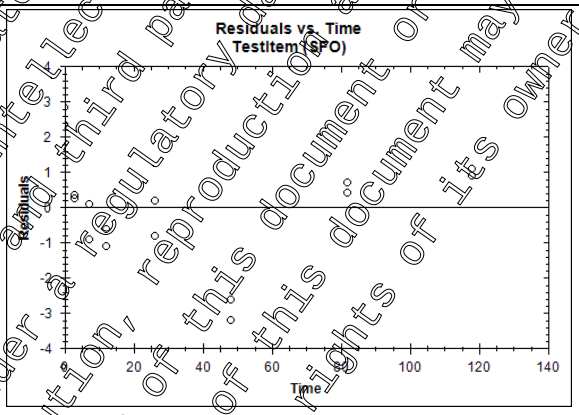
Table 7.1.2.1.1-1: Degradation kinetics of fluopyram in soil Little Oliver under aerobic conditions for trigger evaluation (Best-fit marked in bold)

Kinetic Model [1]	M_0 [%]	Parameters (k, k1, k2 [1/d], g [-], tb, α, β [d])	Chi^2 Error [%]	Prob >t [-]	Lower CI (k, k1, k2 [1/d], g, α [-], tb, β [d])	Upper CI (k, k1, k2 [1/d], g, α [-], tb, β [d])	DT_{50} [days]	DT_{90} [days]	VA
SFO	93.95	k: 3.917e-04	1.28	k: 0.002	M_0: 92.87	M_0: 95.04	> 1000	> 1000	-
DFOP	96.01	k1: 8.87e-02 k2: 2.43e-14 g: 5.41e-02	0.84	k1: 0.041 k2: 0.500	M_0: 94.42 g: 2.701e-02	M_0: 97.30 g: 0.081	> 1000	> 1000	+
FOMC	**96.56**	**α: 0.011190 β: 0.321102**	**0.75**	**n.r.**	**M_0: 95.22 α: 0.006 β: -0.479**	**M_0: 97.90 α: 0.016 β: 1.121**	**> 1000**	**> 1000**	+

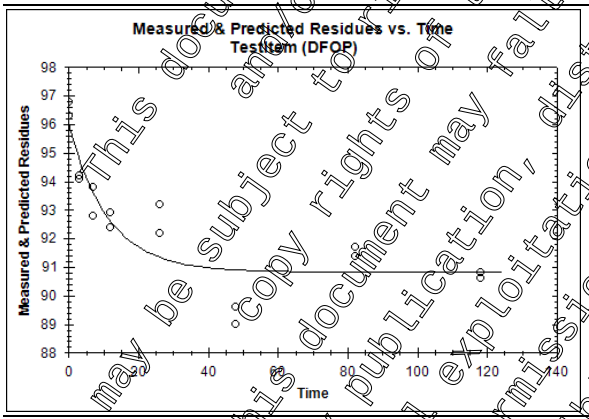
VA = visual assessment, + good, o acceptable, - poor; n.r.: not relevant
[1] SFO: single first order, FOMC: first order multi compartment, DFOP: double first order in parallel

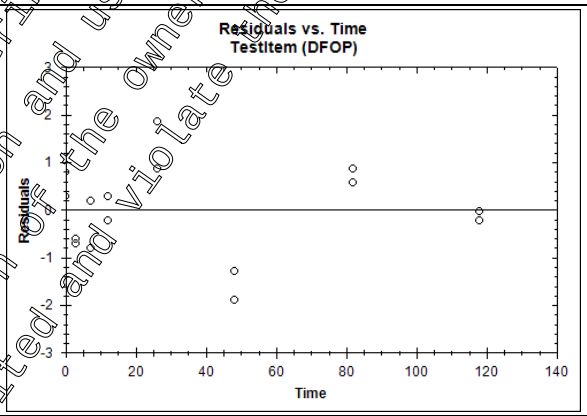
SFO



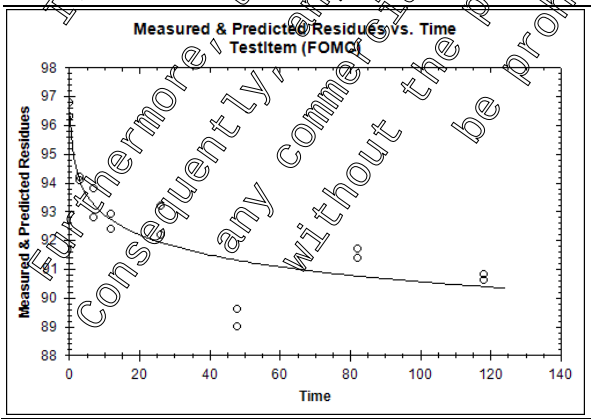


DFOP





FOMC



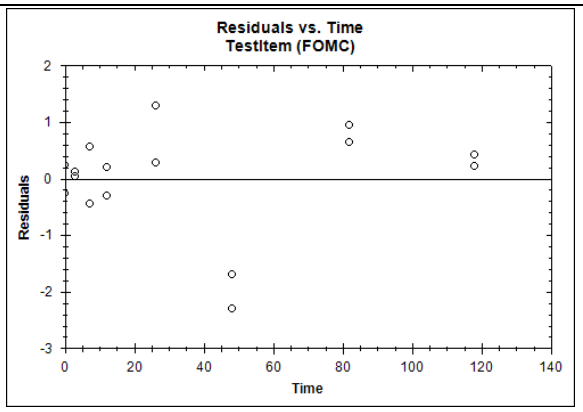
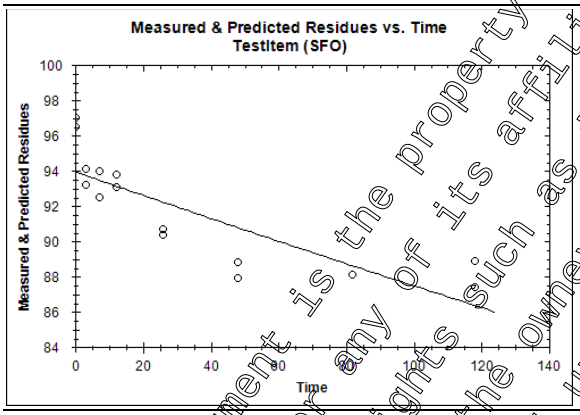


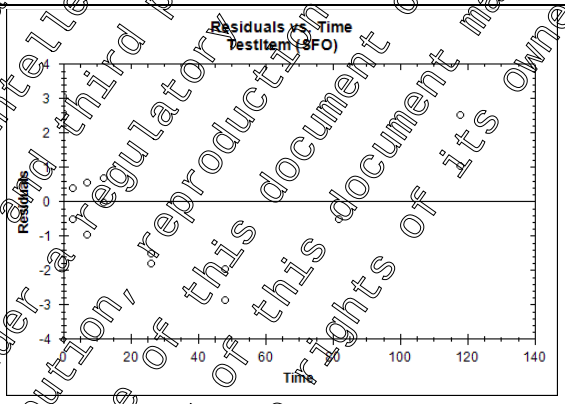
Table 7.1.2.1.1-2: Degradation kinetics of fluopyram in soil Auchy les Mines under aerobic conditions for trigger evaluation (Best-fit marked in bold)

Kinetic Model [1]	M_0 [%]	Parameters (k, k1, k2 [1/d], g [-], tb, α, β [d])	Chi^2 Error [%]	Prob >t [-]	Lower CI (k, k1, k2 [1/d], g, α [-], tb, β [d])	Upper CI (k, k1, k2 [1/d], g, α [-], tb, β [d])	DT_{50} [days]	DT_{90} [days]	VA
SFO	93.93	k: 7.11e-04	1.38	k: <0.001	M_0: 92.74	M_0: 95.13	975	> 1000	+
DFOP	95.88	k1: 0.045 k2: 0.000 g: 0.083	0.67	k1: 0.039 k2: 0.500	M_0: 94.82 g: 0.027	M_0: 96.95 k1: 0.023 k2: 0.0001 g: 0.140	> 1000	> 1000	+
FOMC	**96.59**	**α: 0.02380 β: 1.93165**	**0.65**	**n.r.**	**M_0: 95.33 α: 0.016 β: -0.569**	**M_0: 97.86 α: 0.031 β: 4.432**	**> 1000**	**> 1000**	**+**

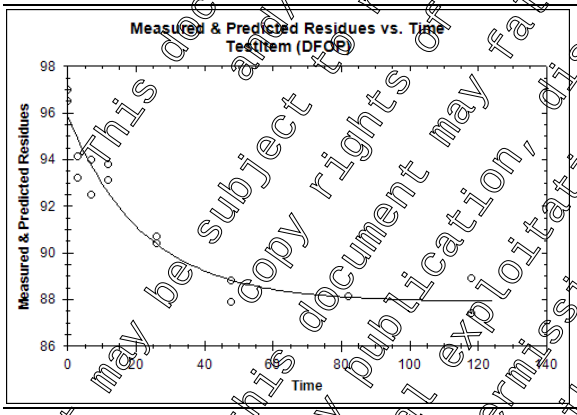
VA = visual assessment, + good, o acceptable, - poor; n.r.: not relevant
[1] SFO: single first order, FOMC: first order multi compartment, DFOP: double first order in parallel

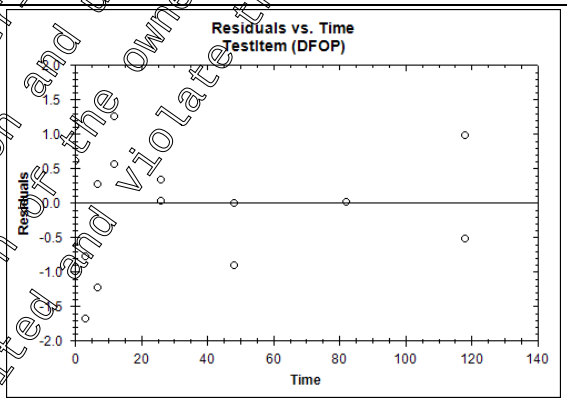
SFO



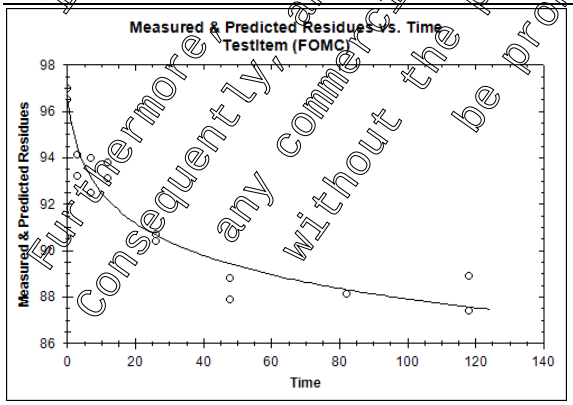


DFOP





FOMC



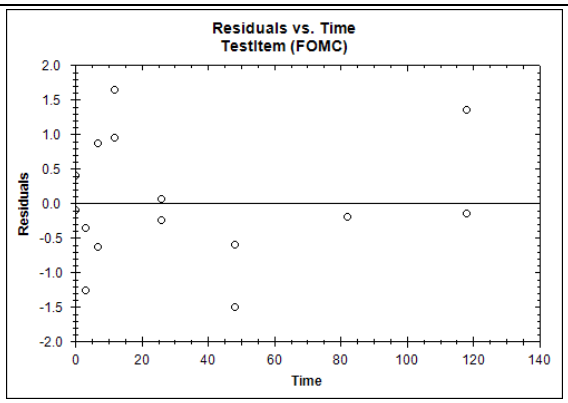
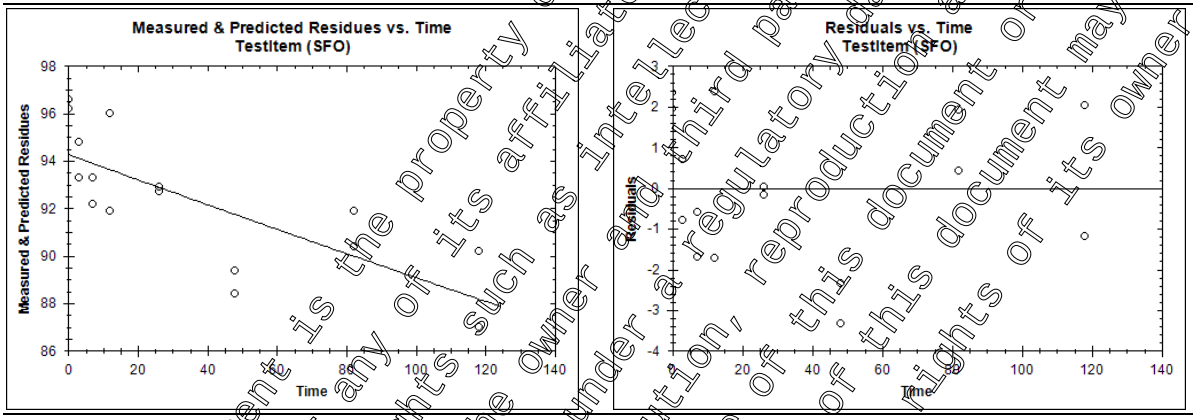


Table 7.1.2.1.1-3: Degradation kinetics of fluopyram in soil Urbanowice under aerobic conditions for trigger evaluation (Best-fit marked in bold)

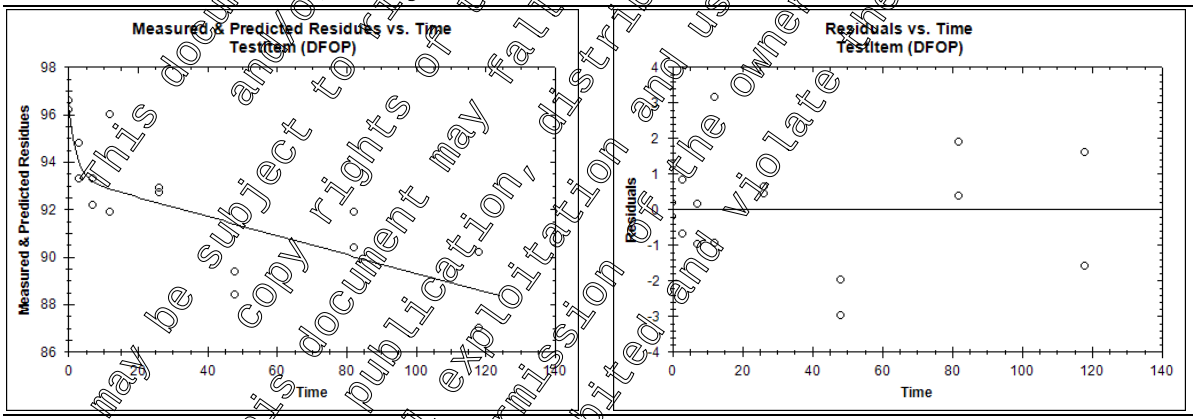
Kinetic Model [1]	M_0 [%]	Parameters (k, k1, k2 [1/d], g [-], tb, α, β [d])	Chi^2 Error [%]	Prob >t [-]	Lower CI (k, k1, k2 [1/d], g, α [-], tb, β [d])	Upper CI (k, k1, k2 [1/d], g, α [-], tb, β [d])	DT_{50} [days]	DT_{90} [days]	VA
SFO	94.25	k: 5.647e-04	1.20	k: <0.001	M_0: 93.00	M_0: 95.50	> 1000	> 1000	-
DFOP	96.41	k1: 0.462 k2: 0.0004 g: 0.032	1.06	k1: 0.240 k2: 0.006	M_0: 94.04 g: 0.002	M_0: 98.78 g: 0.062	> 1000	> 1000	o
FOMC	**96.21**	**α: 0.018122 β: 1.917807**	**0.97**	**n.r.**	**M_0: 93.98 α: 0.005 β: -3.804**	**M_0: 98.43 α: 0.031 β: 7.639**	**> 1000**	**> 1000**	**+**

VA = visual assessment, + good, o acceptable, - poor; n.r.: not relevant
[1] SFO: single first order, FOMC: first order multi compartment, DFOP: double first order in parallel

SFO



DFOP



FOMC

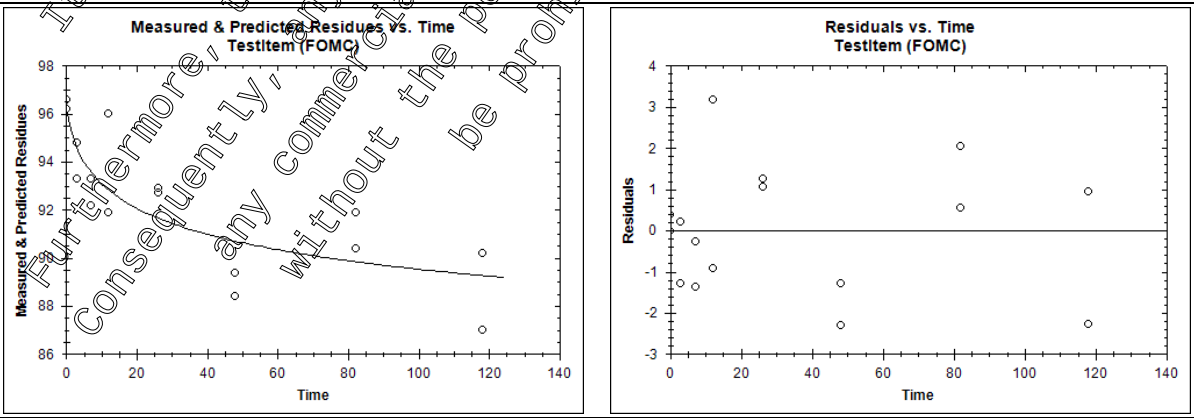
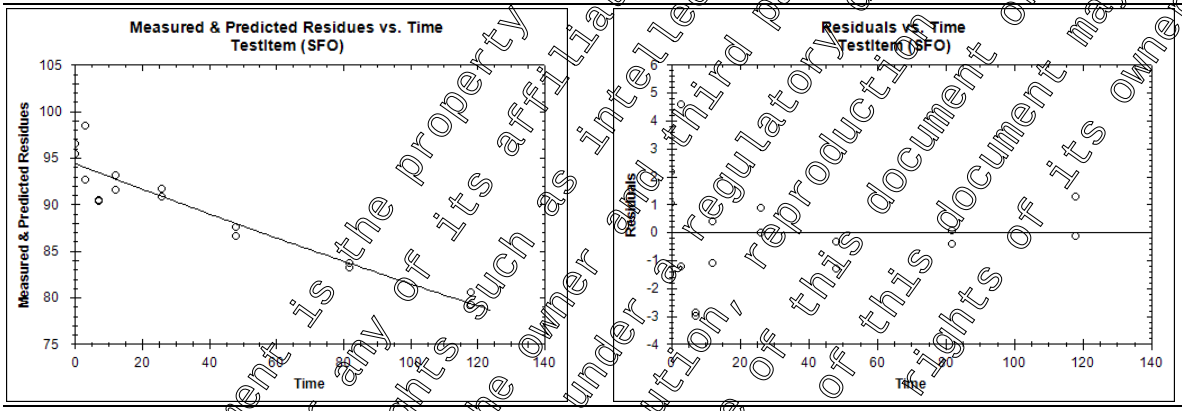


Table 7.1.2.1.1-4: Degradation kinetics of fluopyram in soil Charles River Farm under aerobic conditions for trigger evaluation (Best-fit marked in bold)

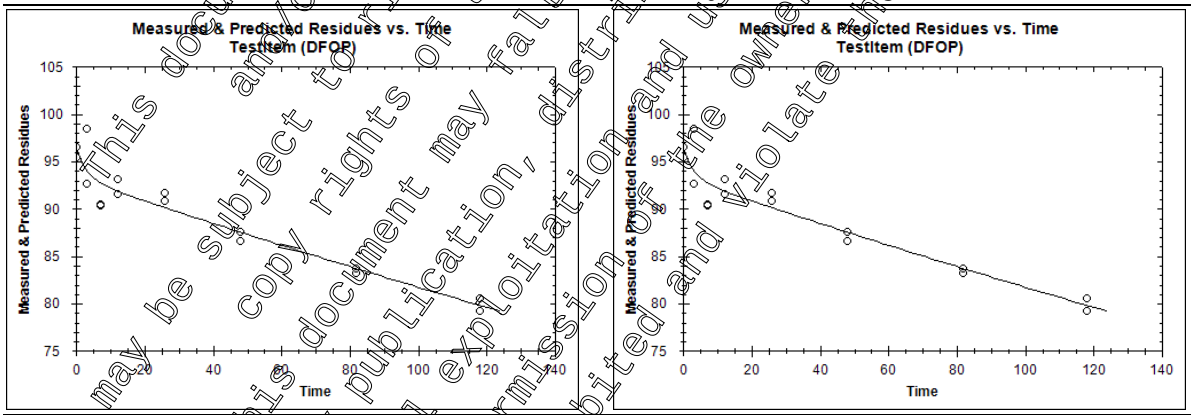
Kinetic Model [1]	M_0 [%]	Parameters (k, k1, k2 [1/d], g [-], tb, α, β [d])	Chi^2 Error [%]	Prob >t [-]	Lower CI (k, k1, k2 [1/d], g, α [-], tb, β [d])	Upper CI (k, k1, k2 [1/d], g, α [-], tb, β [d])	DT_{50} [days]	DT_{90} [days]	VA
SFO	94.35	k: 1.471e-03	1.23	k: <0.001	M_0: 93.00	M_0: 95.50	471	> 1000	o
DFOP	**96.29**	**k1: 0.297 k2: 0.001 g: 0.032**	**1.12**	**k1: 0.236 k2: <0.001**	**M_0: 93.79 g: -0.002**	**M_0: 98.78 g: 0.065**	**501**	**> 1000**	**+**
FOMC	94.96	α: 0.2038 β: 90.6181	1.23	n.r.	M_0: 93.20 α: 0.154 β: 137.4	M_0: 96.71 α: 0.561 β: 318.7	> 1000	> 1000	o

VA = visual assessment, + good, o acceptable, - poor; n.r.: not relevant
[1] SFO: single first order, FOMC: first order multi compartment, DFOP: double first order in parallel

SFO



DFOP



FOMC

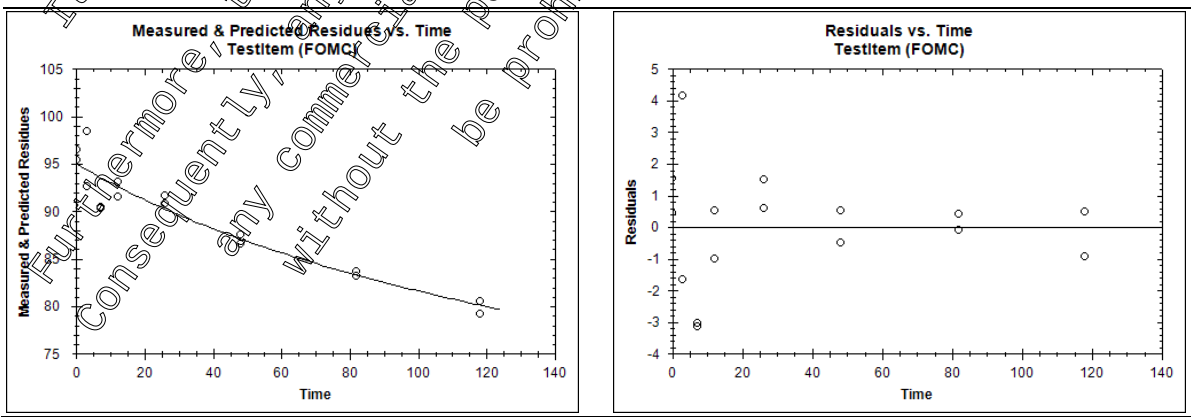
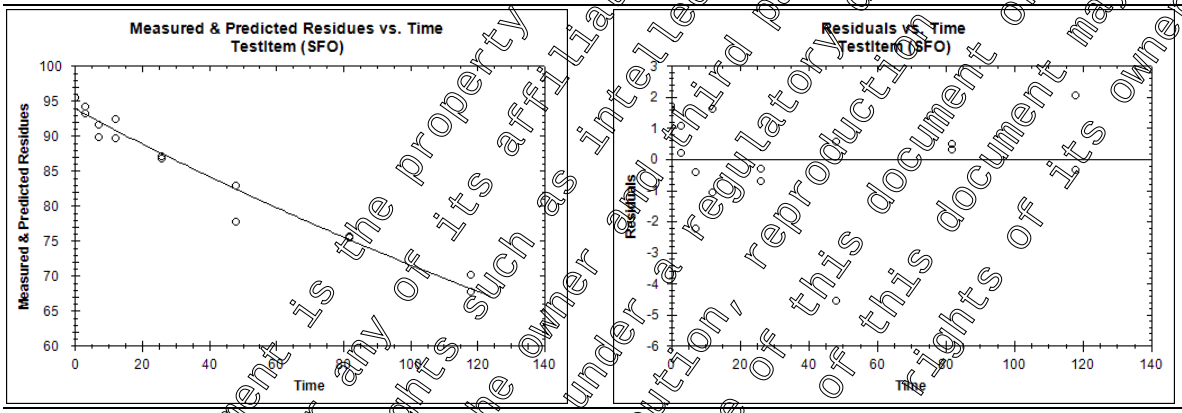


Table 7.1.2.1.1-5: Degradation kinetics of fluopyram in soil Sindos under aerobic conditions for trigger evaluation (Best-fit marked in bold)

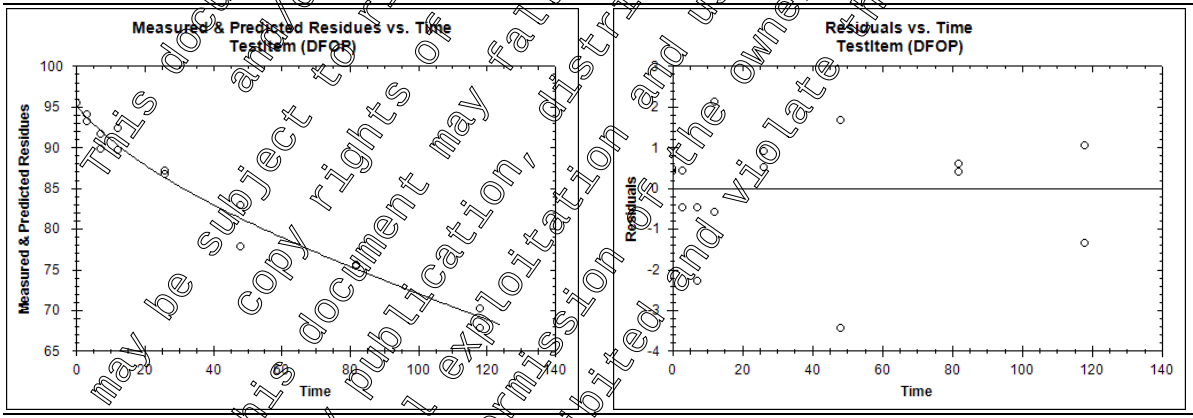
Kinetic Model [1]	M_0 [%]	Parameters (k, k1, k2 [1/d], g [-], tb, α, β [d])	Chi^2 Error [%]	Prob >t [-]	Lower CI (k, k1, k2 [1/d], g, α [-], tb, β [d])	Upper CI (k, k1, k2 [1/d], g, α [-], tb, β [d])	DT_{50} [days]	DT_{90} [days]	VA
SFO	93.78	k: 2.707e-03	1.05	k: <0.001	M_0: 92.58	M_0: 94.98	256	851	o
DFOP	95.01	k1: 0.052 k2: 0.002 g: 0.053	0.78	k1: 0.230 k2: <0.001	M_0: 93.17 g: -0.040	M_0: 96.84 g: 0.146	286.1	1000	+
FOMC	**94.72**	**α:** 0.40499 **β:** 102.249	**0.77**	**n.r.**	**M_0:** 93.29 **α:** 0.035 **β:** 27.27	**M_0:** 96.15 **α:** 0.775 **β:** 231.8	**464**	**> 1000**	+

VA = visual assessment, + good, o acceptable, - poor; n.r.: not relevant
[1] SFO: single first order, FOMC: first order multi compartment, DFOP: double first order in parallel

SFO



DFOP



FOMC

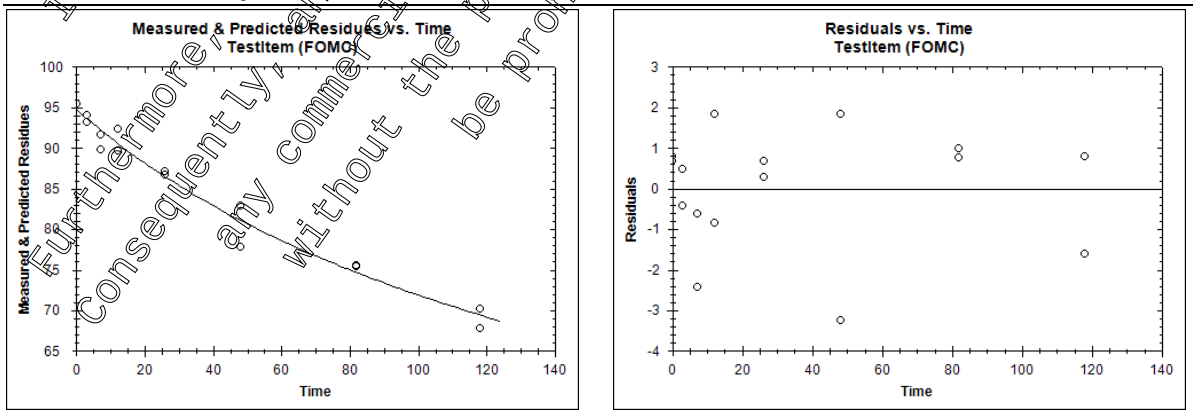
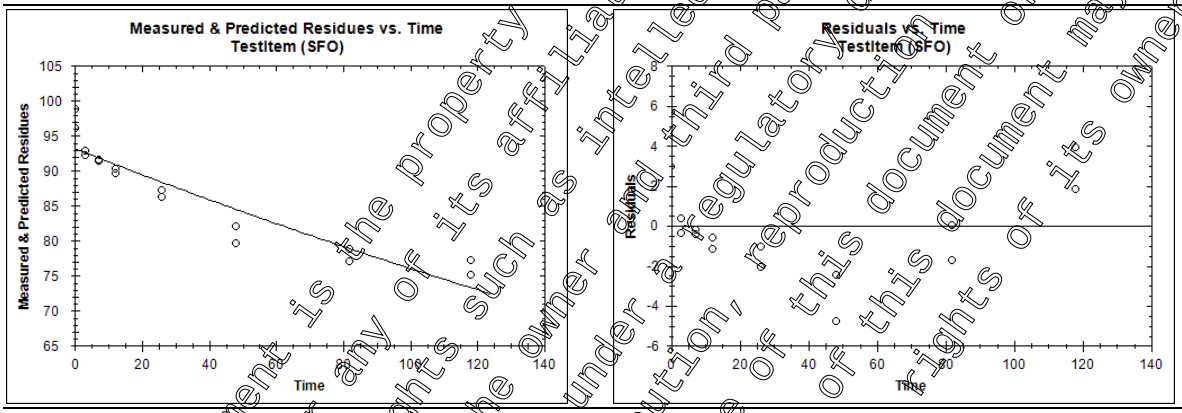


Table 7.1.2.1.1-6: Degradation kinetics of fluopyram in soil Paradiso San Zenone under aerobic conditions for trigger evaluation (Best-fit marked in bold)

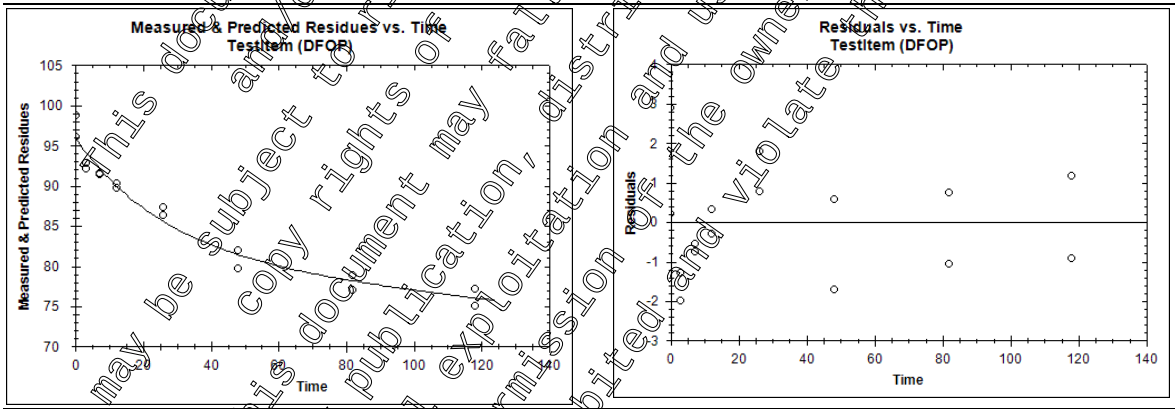
Kinetic Model [1]	M_0 [%]	Parameters (k, k1, k2 [1/d], g [-], tb, α, β [d])	Chi^2 Error [%]	Prob >t [-]	Lower CI (k, k1, k2 [1/d], g, α [-], tb, β [d])	Upper CI (k, k1, k2 [1/d], g, α [-], tb, β [d])	DT_{50} [days]	DT_{90} [days]	VA
SFO	93.11	k: 2.029e-03	2.18	k: <0.001	M_0: 91.29	M_0: 94.94	342	> 1000	o
DFOP	95.89	k1: 0.038 k2: 0.0006 g: 0.151	1.03	k1: 0.050 k2: 0.206	M_0: 94.26 g: 0.021	M_0: 97.52 g: 0.281	888	1000	+
FOMC	**96.54**	**α: 0.09256 β: 9.50714**	**0.87**	**n.r.**	**M_0: 94.91 α: 0.065 β: 1.825**	**M_0: 98.17 α: 0.12 β: 17.19**	**> 1000**	**> 1000**	+

VA = visual assessment, + good, o acceptable, - poor; n.r.: not relevant
[1] SFO: single first order, FOMC: first order multi compartment, DFOP: double first order in parallel

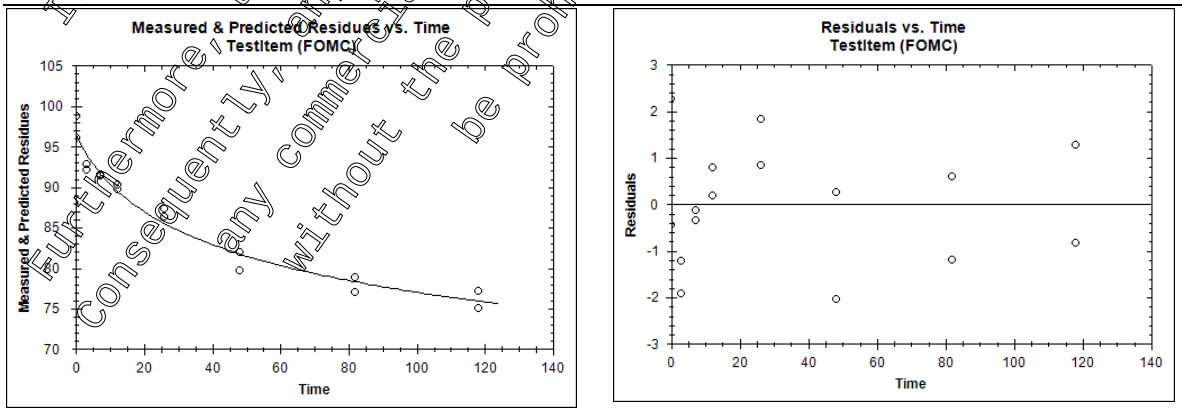
SFO



DFOP



FOMC



III. CONCLUSIONS

In the current study, fluopyram was slowly degraded and mineralized. The DT_{50} values for fluopyram were between 464 and >1000 days in the six tested soils under aerobic conditions in the dark at a mean temperature of 19.4 °C.

3. Assessment and conclusion

Assessment and conclusion by applicant: The kinetic evaluation followed FOCUS guidances and is considered valid and reliable.

Assessment and conclusion by RMS: Outcome and conclusion of the study: RMS should indicate if they agree to the results and conclusions of the APPL.

Data Point:	KCA 7.1.2.1.1/07
Report Author:	[redacted]
Report Year:	2020
Report Title:	Fluopyram: Aerobic Metabolism / degradation and time - Dependent sorption in 6 soils
Report No:	M12505406-3
Document No:	M-753426-01-1
Guideline(s) followed in study:	OECD Test Guideline No. 307 (2002) OECD Test Guideline No. 106 (2000, only in parts) Guidance on how aged sorption studies for pesticides should be conducted, analysed and used in the regulatory process (2012, revised draft 2016). Current revision dates Sep 2016 [this draft guidance was updated based on the PPR statement on aged sorption, EFSA Journal 2015;13(7):4175]
Deviations from current test guideline:	Current Guideline: OECD 307 (2002), OECD 106 (2000) (Only in parts) None
Previous evaluation:	No, not previously submitted
GLP/Officially recognised testing facilities:	Yes, conducted under GLP/Officially recognised testing facilities
Acceptability/Reliability:	Yes

The experimental study is summarised and discussed under point KCA 7.1.1.1/06 of this document. The kinetic evaluation is summarised under KCA 7.1.2.1.1/13 (M-761969-01-1). The results of the aged sorption part of the study and is summarized under KCA 7.1.3.2/05.

Data Point:	KCA 7.1.2.1.1/08
Report Author:	[redacted]
Report Year:	2021
Report Title:	Fluopyram: Aerobic degradation and determination of BCS-AA10065 and trifluoroacetic acid (TFA) in 4 soils
Report No:	EnSa-20-0811
Document No:	M-761739-01-1
Guideline(s) followed in study:	OECD Test Guideline No. 307 (2002); Commission Regulation (EU) No 283/2013 in accordance with Regulation (EC) No 1107/2009; US EPA OCSPP Test Guideline No. 835.4100, 835.4200 (2008); SANCO/3029/99 rev. 4: EU guidance document for generating and reporting methods of analysis in support of pre-registration data requirements (2000)
Deviations from current test guideline:	Current Guideline: OECD 307 (2002) None
Previous evaluation:	No, not previously submitted
GLP/Officially recognised testing facilities:	Yes, conducted under GLP/Officially recognised testing facilities
Acceptability/Reliability:	Yes

The experimental study is summarised and discussed under point KCA 7.1.2.1.1/07 of this document. The kinetic evaluation following current FOCUS guidance is summarised under KCA 7.1.2.1.1/14 (M-762167-01-1).

1. Information on the study

Data Point:	KCA 7.1.2.1.1/09
Report Author:	Klein, C.; Lange, N.
Report Year:	2021
Report Title:	Fluopyram (FLU): Kinetic evaluation of aerobic laboratory soil degradation in European soils (Bahczinski, 2008; Menke and Telscher, 2008) according to FOCUS kinetics using KinGUI 2.1
Report No:	EnSa-20-0335
Document No:	M-761966-01-1
Guideline(s) followed in study:	not applicable
Deviations from current test guideline:	Current Guideline: not applicable (kinetic evaluation)
Previous evaluation:	No, not previously submitted
GLP/Officially recognised testing facilities:	No, not conducted under GLP/Officially recognised testing facilities
Acceptability/Reliability:	Yes

2. Full summary of KCA 7.1.2.1.1/09

Executive Summary

A kinetic modelling analysis of aerobic laboratory soil residue data of fluopyram (FLU) and fluopyram-7-hydroxy (FLU-7-OH) was conducted in order to derive kinetic parameters suitable for modelling and for trigger purpose, using the software tool KinGUI 2.1. The identification of the appropriate kinetic model followed the recommendations given by FOCUS Kinetics.

For modelling purposes, the $DegT_{50,actual}$ values of fluopyram were calculated to be between 141.1 and 441.5 days and the $DegT_{50,mod}$ (normalised) were between 141.1 and 441.5 days (8 soils). For trigger purposes, the $DegT_{50,actual}$ values of fluopyram were calculated to be between 156.9 and 444.5 days (8 soils).

For modelling purposes, the $DegT_{50,actual}$ values of fluopyram-7-hydroxy were calculated to be between 5.109 and 22.05 days and the $DegT_{50,mod}$ (normalised) were between 5.109 and 22.05 days (8 soils). For trigger purposes, the $DegT_{50,actual}$ values of fluopyram were calculated to be between 5.109 and 29.28 days (8 soils).

I. METHODS

A kinetic modelling analysis of aerobic laboratory soil residue data of fluopyram (FLU) and fluopyram-7-hydroxy (FLU-7-OH) was conducted in order to derive kinetic parameters suitable for modelling and for trigger purpose, using the software tool KinGUI 2.1. The identification of the appropriate kinetic model followed the recommendations given by FOCUS Kinetics (FOCUS, 2006, 2014a) based on a detailed statistical analysis including visual assessment, χ^2 statistic, significance t-test and correlation analysis, using correspondingly pre-processed residue data. Additionally, the Scaled Weighted Area under Residue Curve (SWARC) was used as a further indicator for the visual assessment and to choose the appropriate model.

The modelling analysis is based on residue data from 2 aerobic laboratory soil degradation studies in European soils (KCA 7.1.1.1/02, M-298296-01-1; KCA 7.1.1.1/01, M-298413-01-1).

The soil metabolite fluopyram-7-hydroxy was found at relevant amounts in other soils (> 5% of applied radioactivity), and with sufficient data points above the limit of detection (LOD) in these soils here. Therefore, the metabolite degradation was included in the pathway even if it was not found at relevant amounts here (> 5 %).

In both studies partly the same soil names are reported. Due to the fact, that soils with the same name for both labels have been collected with a 2 year time difference, they are not considered as the same soils and were therefore not combined or averaged (EFSA, 2018). Thus, the 2 labels with the same soil name are evaluated separately.

Finally, the following degradation pathway was considered in the compartment model.

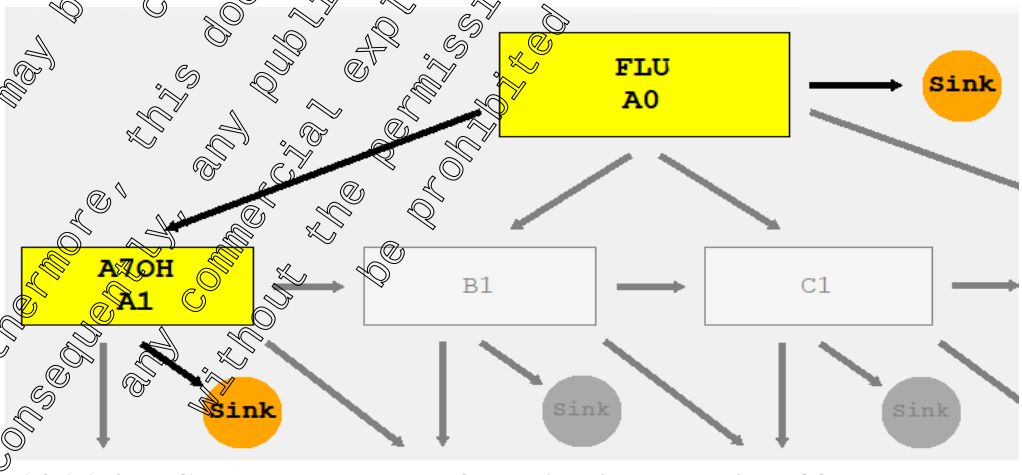


Figure 7.1.2.1.1-6: Compartment model of aerobic soil degradation of fluopyram (FLU = fluopyram, A7OH = FLU-7-OH)

For the evaluation of trigger endpoints, a two-step-process was followed. Initially, the parent was fitted alone and its trigger endpoints were derived from this fit. Secondly, for metabolite evaluation, the appropriate pathway scheme was chosen in combination with the best-fit kinetic model selected for parent only. Trigger endpoints for the metabolites were derived from this free fitted pathway fit, if appropriate.

II. RESULTS

Results of the kinetic evaluations for trigger points and modelling purposes based on residue data from the two laboratory studies are summarised in the tables below.

Degradation of fluopyram

Hoefchen am Hohenseh

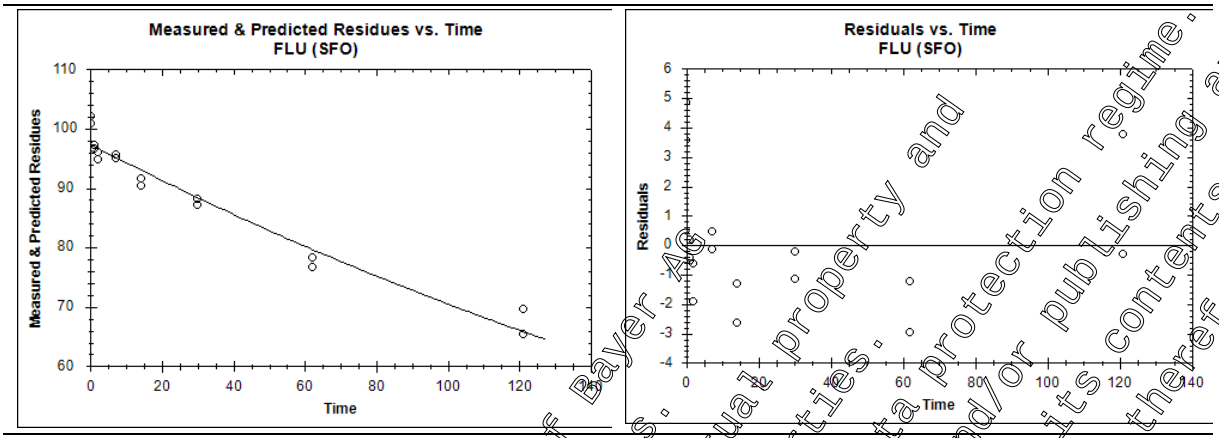
Table 7.1.2.1.1-7: Fluopyram (M-298296-01-1): kinetic and statistical results of degradation in soil Hoefchen am Hohenseh for modelling endpoints

Kinetic model	DT_{50} actual	DT_{90} actual	DT_{50} fast / slow	VA	χ^2err / SWARC	k_1	k_2	g	t-test k_1 / k_2	95th CI of k_1	95th CI of k_2
	(d)	(d)	(d)		(% / -)	(1/d)	(1/d)	(-)	(-)	(1/d)	(1/d)
SFO, free fit	214.3	711.9	-	+	1.97 / 4.28	0.003234	-	-	<0.001	0.00284 to 0.004	-
DFOP	231.0	814.0	7.343 / 281.0		1.50 / 0.054	0.09439	0.002581	0.0540	0.019 / <0.001	0.01015 to 0.179	0.00219 to 0.003
SFO, fixed fit	**214.3** fix	712.0 fix	-	+	1.67 / 4.28	0.003234	-		-	-	-

VA = visual assessment, + = good, o = acceptable, - = poor
SWARC = Scaled Weighted Area under Residue Curve
CI = confidence intervall
fixed fit: parent parameters fixed to free fit values, DT50 FLU-7-OH fixed to 95th CI rate of free fit.

Modelling Endpoints: SFO fit is statistically and visually good (χ^2err <15%, t-test <0.05). SWARC value is < 40, not indicating a biphasic decline. Consequently, **SFO** degradation model is appropriate for modelling endpoints.
However, metabolite FLU-7-OH is rising until the end of study. The pathway fit (free fit) was therefore modified with a fixed DT_{50} value for FLU-7-OH (fixed fit). The DT_{50} value of FLU-7-OH was fixed to a conservative value (95% confidence interval k of free fit), formation fractions were fitted and parent parameters were fixed to values derived from the free fit. Finally, this **fixed SFO fit** was considered appropriate.

SFO free



SFO fixed

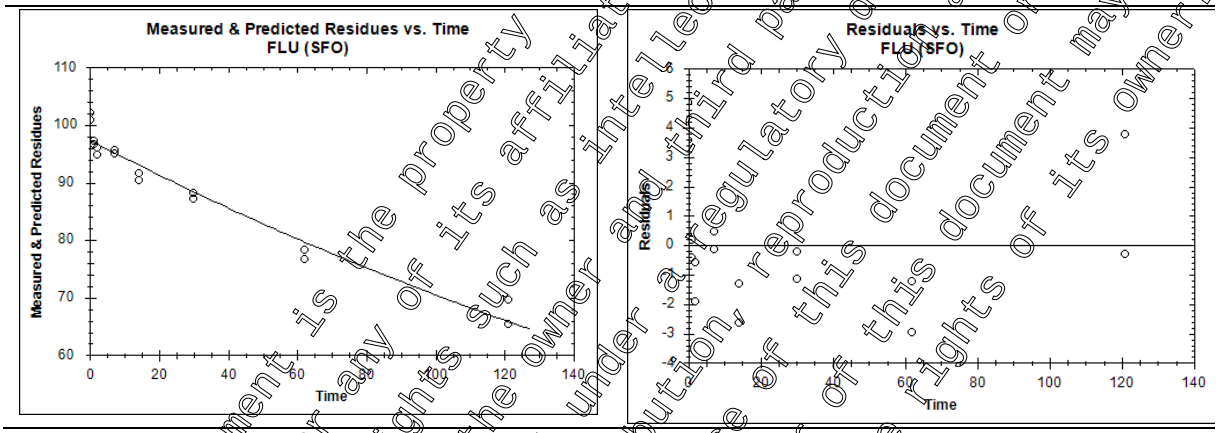


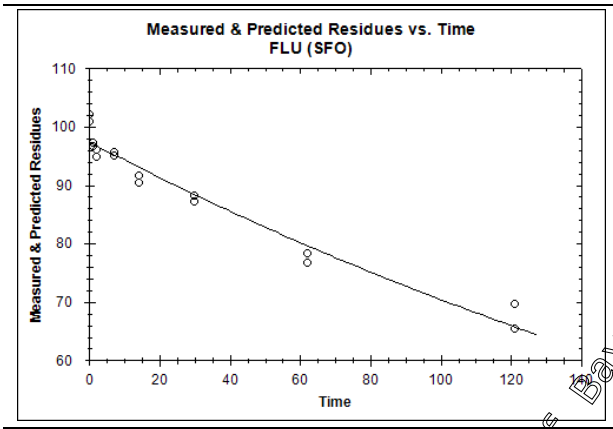
Table 7.1.2.1.1-8: Fluopyram (M-298296-01-1): kinetic and statistical results of degradation in soil Hoefchen am Hohensch for trigger endpoints, parent only fit

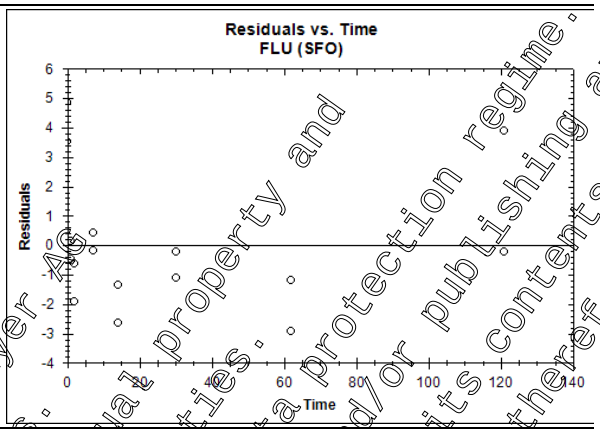
Kinetic model	DT_{50} actual	DT_{90} actual	VA	χ^2err / SWARC	k_1 / α	k_2 / β	g / t_b	t-test k_1 / k_2	95th CI of k_1	95th CI of k_2
	(d)	(d)		(% / -)	(1/d / -)	(1/d / d)	(- / d)	(-)	(1/d)	(1/d)
SFO	213.4	709	-	1.77 / 4.22	0.003248	-	-	<0.001 / -	0.00286 to 0.004	-
DFOP	209.9	747	+	1.01 / 0	1.459	0.003025	0.0566 / -	0.072 / <0.001	-0.36670 to 3.284	0.00273 to 0.003
FOMC	364.2	>1000	+	1.42 / 0.350	0.39320	75.4122	-	-	-	-
HS	**209.3**	**739**	+	1.01 / 0.127	0.04687	0.003038	- / 1.31	0.005 / <0.001	0.01643 to 0.077	0.00276 to 0.003

VA = visual assessment, + = good, o = acceptable, - = poor
SWARC = Scaled Weighted Area under Residue Curve
CI = confidence intervall

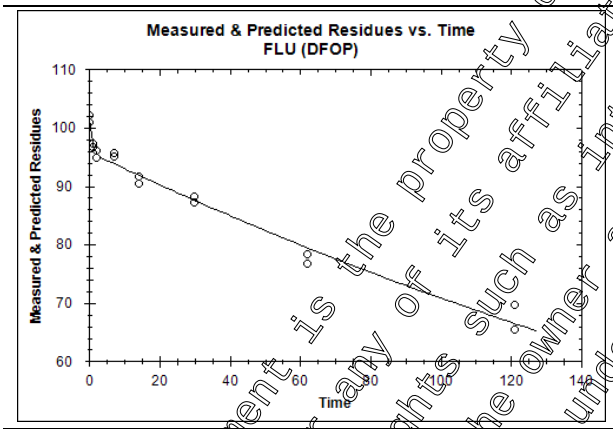
Trigger Endpoints: SFO fit (parent only) is statistically and visually (χ^2err, t-test) good. DFOP, FOMC and HS fits were alternatively tested. For DFOP, t-test of k_{fast} failed in combination with DT_{50} and DT_{90} extrapolated beyond study end. For FOMC, DT_{50} and DT_{90} are extrapolated beyond study end. Both fits are therefore not suitable, especially for accumulation assessments. HS fit is statistically (χ^2err, t-test) and visually good. Consequently, **HS** degradation model is appropriate for trigger endpoints, as it shows lowest χ^2err of all suitable models (SFO, HS).

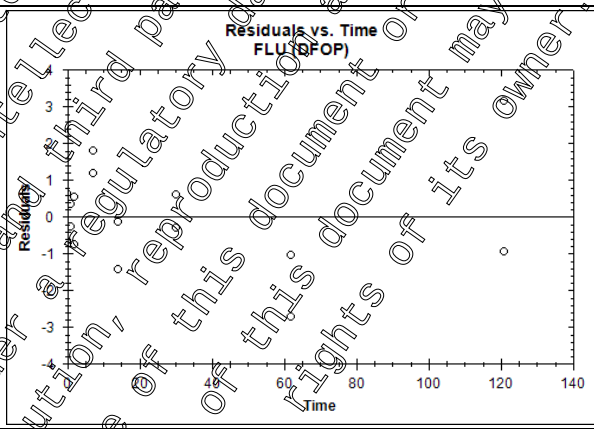
SFO



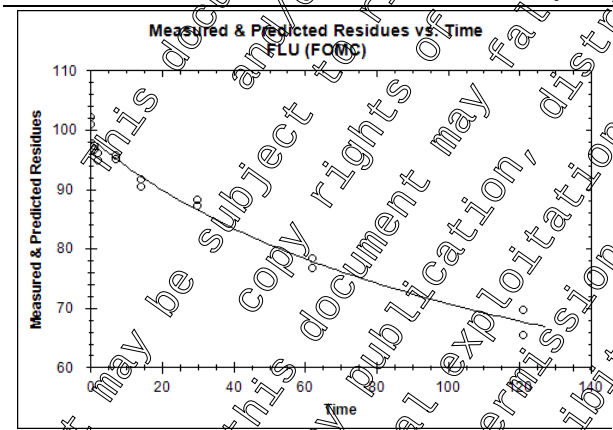


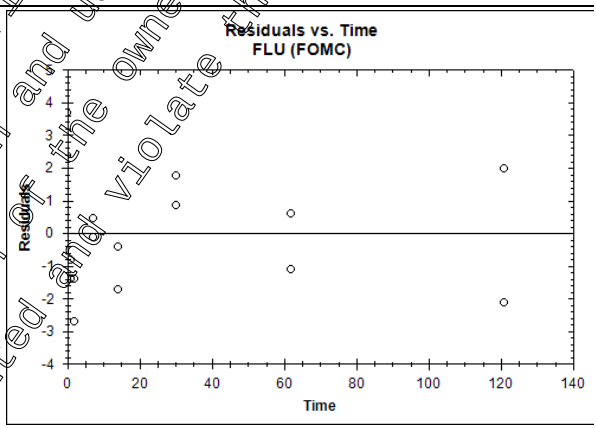
DFOP



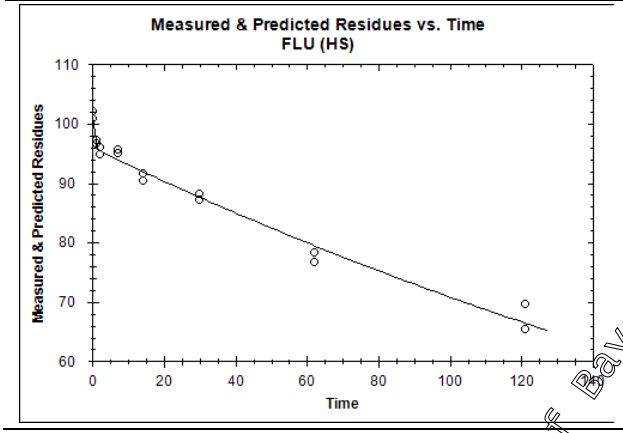


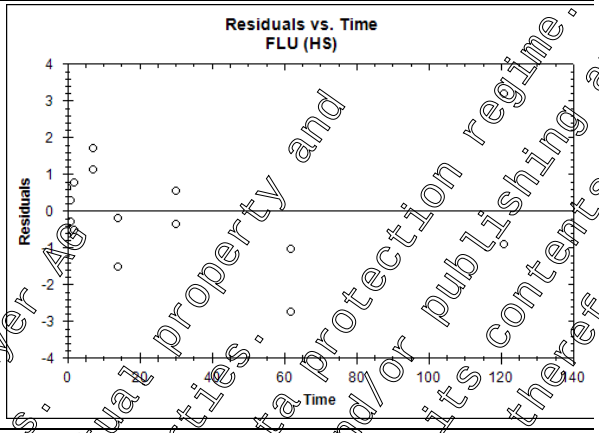
FOMC





HS





Laacherhof AXXa

Table 7.1.2.1.1-9: Fluopyram (M-298296-01-1): kinetic and statistical results of degradation in soil Laacherhof AXXa for modelling endpoints

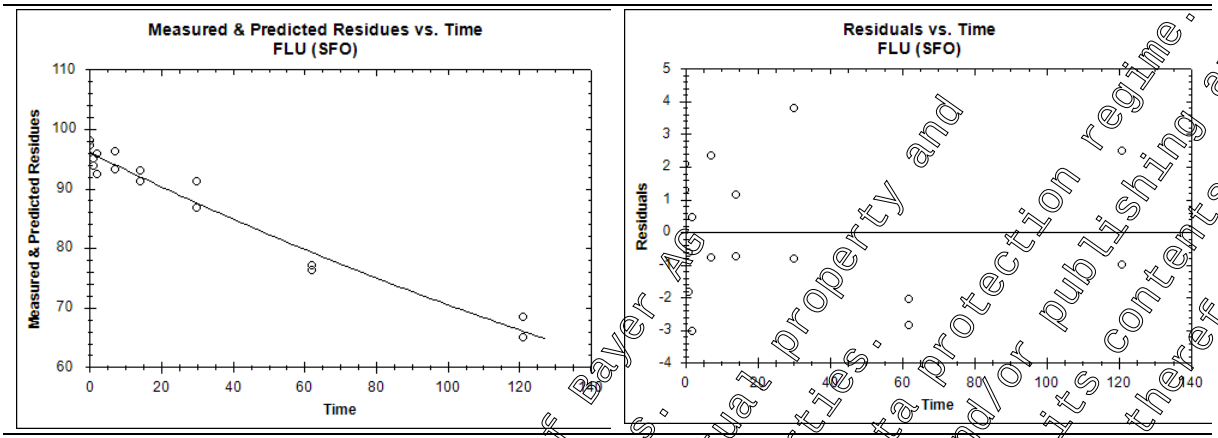
Kinetic model	DT_{50} actual	DT_{90} actual	DT_{50} fast / slow	VA	χ^2err / SWARC	k_1	k_2	g	t-test k_1 / k_2	95th CI of k_1	95th CI of k_2
	(d)	(d)	(d)		(% / -)	(1/d)	(1/d)	(-)	(-)	(1/d)	(1/d)
SFO, free fit	223.8	743.3			1.25 / 1.20	0.003098	-	-	<0.001	0.00275 to 0.003	-
DFOP	223.3	741.9	223.3 / 223.4	+	1.44 / 1.19	0.003104	0.003103	0	<0.001 / <0.001	0.00310 to 0.003	0.00280 to 0.003
SFO, fixed fit	**223.7** fix	743.3 fix	-	+	1.19 / 1.20	0.003098		-	-	-	-

VA = visual assessment, + = good, o = acceptable, - = poor
SWARC = Scaled Weighted Area under Residue Curve
CI = confidence interval
fixed fit: parent parameters fixed to free fit values; DT50 FLU-7-OH fixed to 95th CI rate of free fit.

Modelling Endpoints: SFO fit is statistically and visually good (χ^2err <15%, t-test <0.05). SWARC value is < 40, not indicating a biphasic decline. Consequently, **SFO** degradation model is appropriate for modelling endpoints.

However, metabolite FLU-7-OH is rising until the end of study. The pathway fit (free fit) was therefore modified with a fixed DT_{50} value for FLU-7-OH (fixed fit). The DT_{50} value of FLU-7-OH was fixed to a conservative value (95% confidence interval k of free fit), formation fractions were fitted and parent parameters were fixed to values derived from the free fit. Finally, this **fixed SFO fit** was considered appropriate.

SFO free



SFO fixed

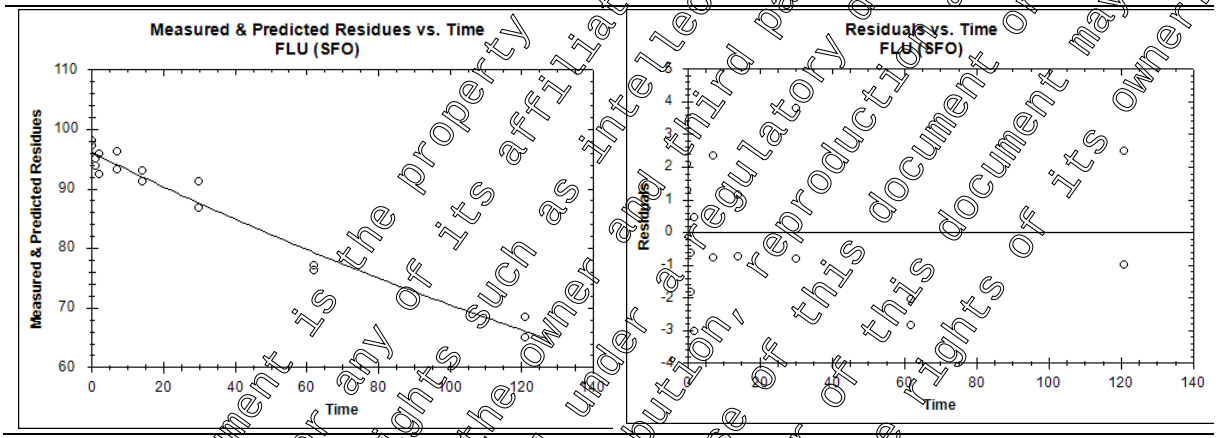


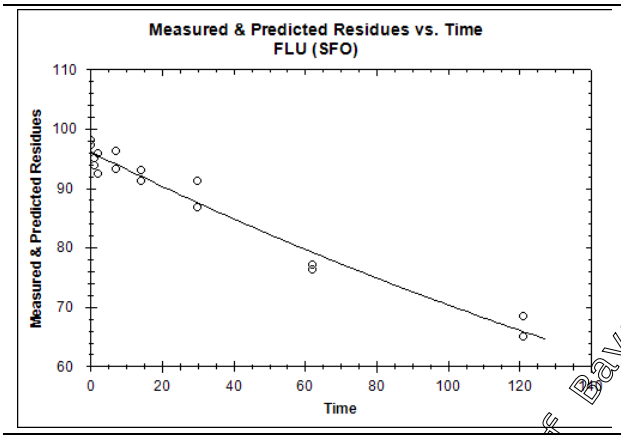
Table 7.1.2.1.1-10: Fluopyram (M-298296-01-1): kinetic and statistical results of degradation in soil Laacherhof AXXa for trigger endpoints, parent only fit

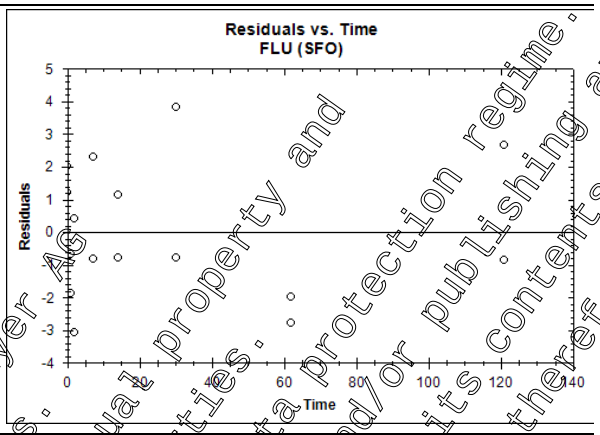
Kinetic model	DT_{50} actual	DT_{90} actual	VA	χ^2err / SWARC	k_1 / α	k_2 / β	g / t_b	t-test k_1 / k_2	95th CI of k_1	95th CI of k_2
	(d)	(d)		(% / -)	(1/d / -)	(1/d / d)	(- / d)	(-)	(1/d)	(1/d)
SFO	**221.9**	**737**	+	1.23 / 1.19	0.003123	-	-	<0.001 / -	0.00277 to 0.003	-
DFOP	267.7	>1000	+	1.39 / 1.55	0.005235	<0.000001	0.6633 / -	0.476 / 0.500	-0.16170 to 0.172	-0.24480 to 0.245
FOMC	247.8	>1000	+	1.30 / 1.52	1.69850	491.669	-	-	-	-
HS	219.5	745	+	1.28 / 1.70	0.03711	0.003061	- / 0.623	0.007 / <0.001	0.01191 to 0.062	0.00269 to 0.003

VA = visual assessment, + = good, o = acceptable, - = poor
SWARC = Scaled Weighted Area under Residue Curve
CI = confidence intervall

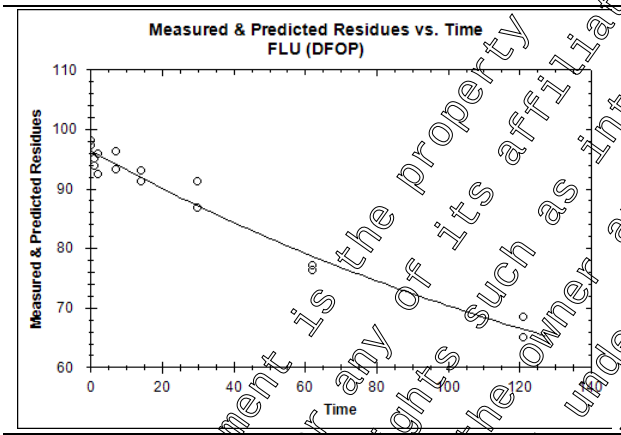
Trigger Endpoints: SFO fit (parent only) is statistically (χ^2err, t-test) and visually good. DFOP, FOMC and HS fits were alternatively tested. For DFOP, t-tests of k_{fast} and k_{slow} failed in combination with DT_{50} and DT_{90} extrapolated beyond study end. For FOMC, DT_{50} and DT_{90} are extrapolated beyond study end. Both fits are therefore not suitable, especially for accumulation assessments. HS fit is statistically (χ^2err, t-test) and visually good, but not better than SFO. Consequently, **SFO** degradation model is appropriate for trigger endpoints, as it shows lowest χ^2err of all suitable models (SFO, HS).

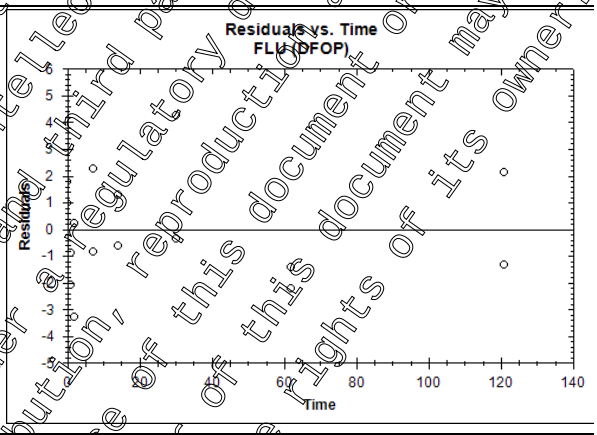
SFO



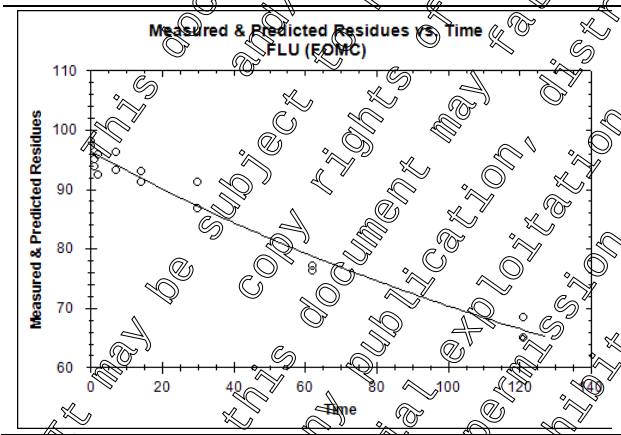


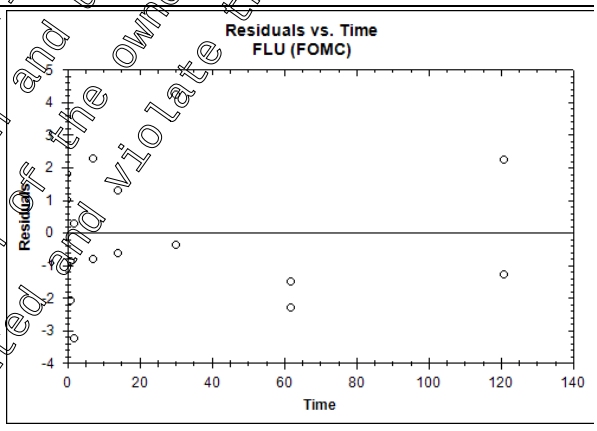
DFOP



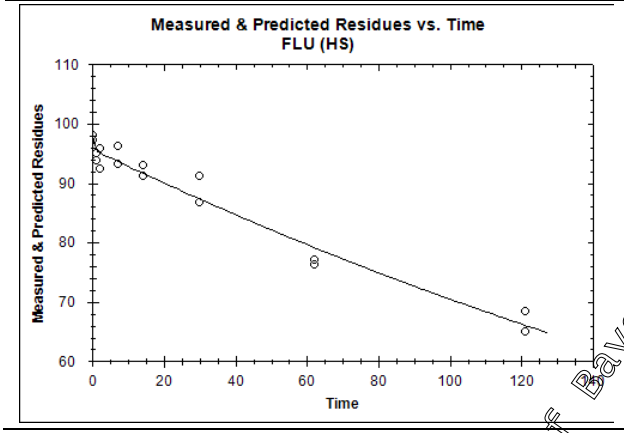


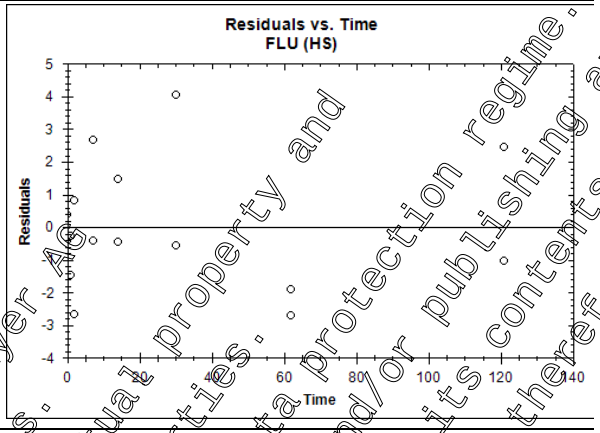
FOMC





HS





Laacherhof Wurmwiese

Table 7.1.2.1.1-11: Fluopyram (M-298296-01-1): kinetic and statistical results of degradation in soil Laacherhof Wurmwiese for modelling endpoints

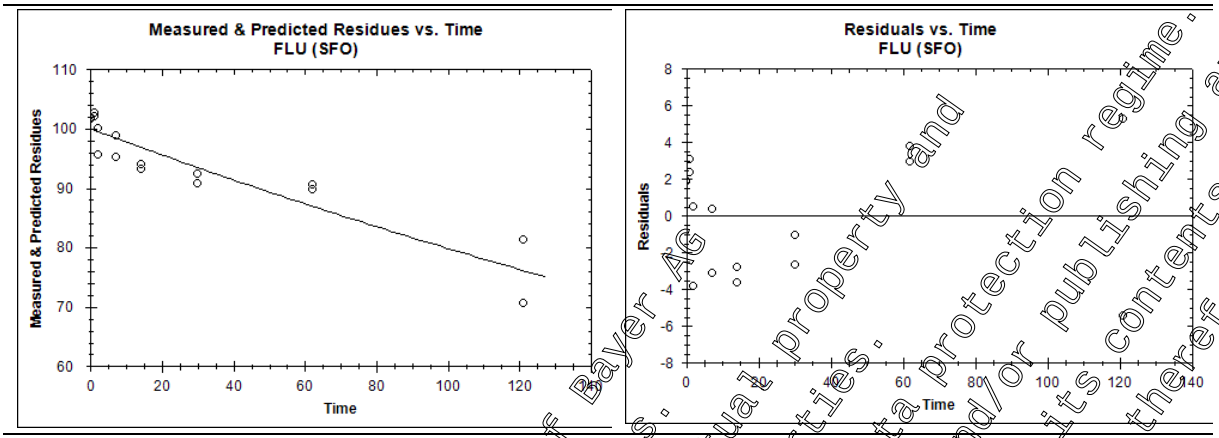
Kinetic model	DT_{50} actual	DT_{90} actual	DT_{50} fast / slow	VA	χ^2err / SWARC	k_1	k_2	g	t-test k_1 / k_2	95th CI of k_1	95th CI of k_2
	(d)	(d)	(d)		(% / -)	(1/d)	(1/d)	(-)	(-)	(1/d)	(1/d)
SFO, free fit	307.7	1022		-	1.91 / 6.23	0.002253	-	-	< 0.001	0.00176 to 0.003	-
DFOP	349.1	1000	8.06 / 367	+	1.94 / 3.93	0.08597	0.001888	0.0336	0.009 / <0.001	0.01881 to 0.153	0.00111 to 0.003
SFO, fixed fit	**307.7** fix	1022 fix	-	+	1.81 / 6.13	0.002253	-	-	- / -	-	-

VA = visual assessment, + = good, o = acceptable, - = poor
SWARC = Scaled Weighted Area under Residue Curve
CI = confidence interval
fixed fit: parent parameters fixed to free fit values, DT50 FLU-7-OH fixed to 95th CI rate of free fit.

Modelling Endpoints: SFO fit is statistically and visually good (χ^2err <15%, t-test <0.05). SWARC value is < 40, not indicating a biphasic decline. Consequently, **SFO** degradation model is appropriate for modelling endpoints.

However, metabolite FLU-7-OH is rising until the end of study. The pathway fit (free fit) was therefore modified with a fixed DT_{50} value for FLU-7-OH (fixed fit). The DT_{50} value of FLU-7-OH was fixed to a conservative value (95% confidence interval k of free fit), formation fractions were fitted and parent parameters were fixed to values derived from the free fit. Finally, this **fixed SFO fit** was considered appropriate.

SFO free



SFO fixed

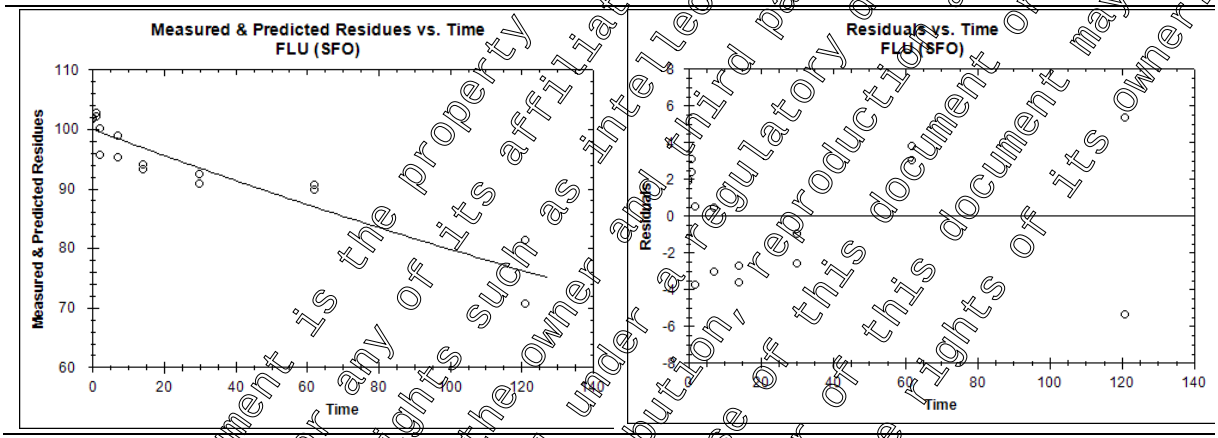


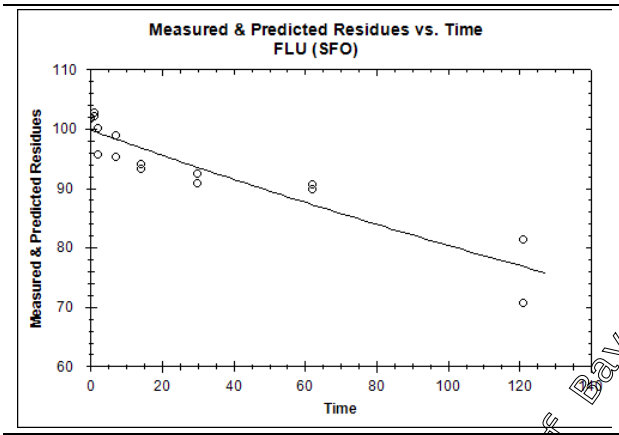
Table 7.1.2.1.1-12: Fluopyram (M-298296-01-1): kinetic and statistical results of degradation in soil Laacherhof Wurmwiese for trigger endpoints, parent only fit

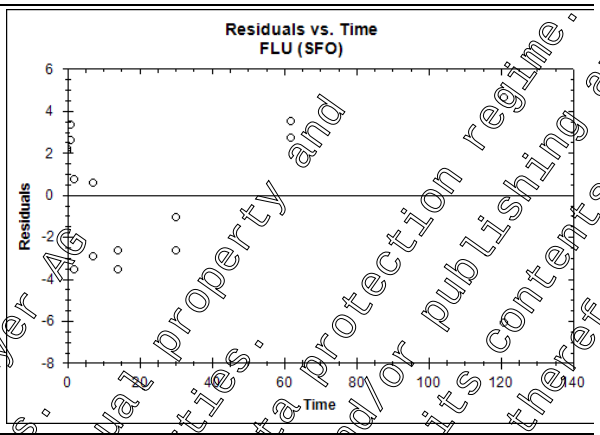
Kinetic model	DT_{50} actual	DT_{90} actual	VA	χ^2err / SWARC	k_1 / α	k_2 / β	g / t_b	t-test k_1 / k_2	95th CI of k_1	95th CI of k_2
	(d)	(d)		(% / -)	(1/d / -)	(1/d / d)	(- / d)	(-)	(1/d)	(1/d)
SFO	**320.8**	**1066**	+	1.89 / 5.95	0.002161	-	- / -	<0.001	0.00167 to 0.003	-
DFOP	341.5	>1000	+	1.67 / 0.534	0.4108	0.001889	0.0469 / -	0.248 / <0.001	-0.73800 to 1.560	0.00128 to 0.003
FOMC	331.4	>1000	+	2.02 / 5.99	7.02800	3197.00	- / -	- / -	-	-
HS	336.1	>1000	+	1.63 / 0.618	0.01969	0.001918	- / 2.72	0.116 / <0.001	-0.01096 to 0.050	0.00136 to 0.002

VA = visual assessment, + = good, o = acceptable, - = poor
SWARC = Scaled Weighted Area under Residue Curve
CI = confidence intervall

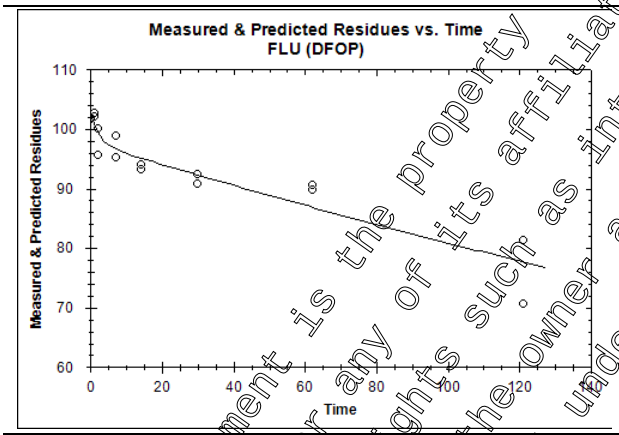
Trigger Endpoints: SFO fit (parent only) is statistically (χ^2err, t-test) and visually good. DFOP, FOMC and HS fits were alternatively tested. For DFOP and HS, t-test of k_{fast} failed in combination with DT_{50} and DT_{90} extrapolated beyond study end. For FOMC, DT_{50} and DT_{90} are extrapolated beyond study end. These fits are therefore not suitable, especially for accumulation assessments. Consequently, **SFO** degradation model is appropriate for trigger endpoints.

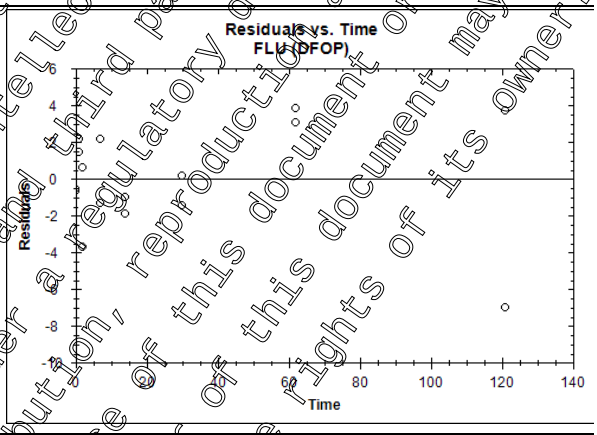
SFO



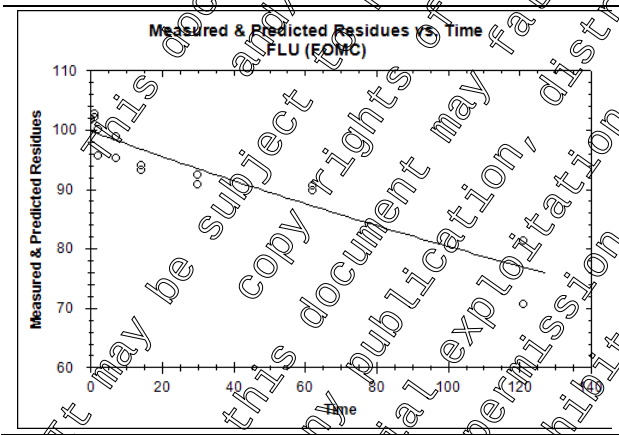


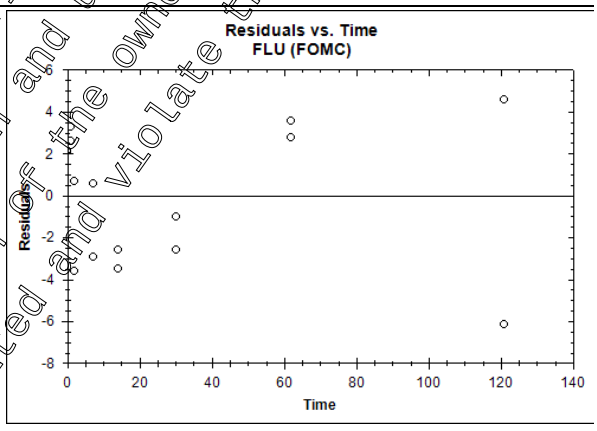
DFOP



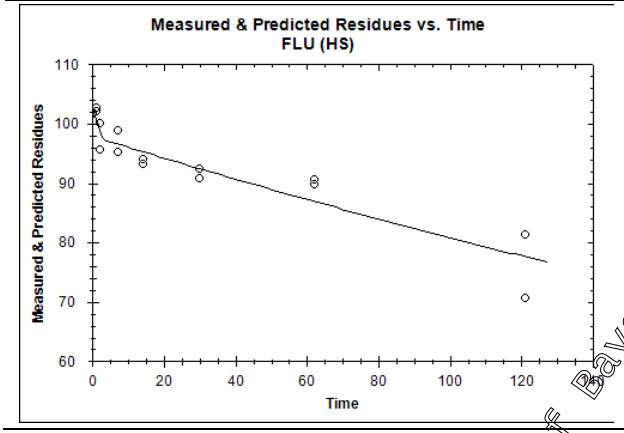


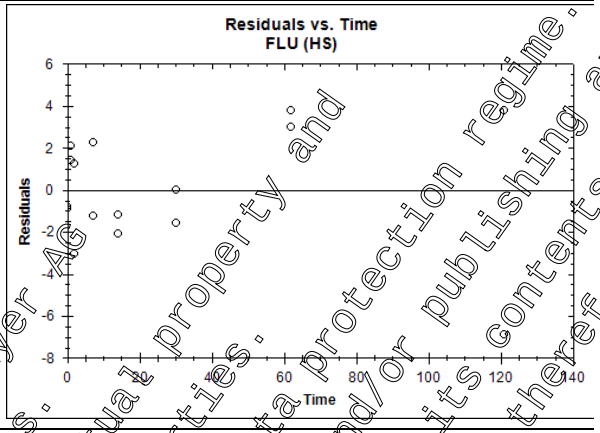
FOMC





HS





Laacherhof AIIIa

Table 7.1.2.1.1-13: Fluopyram (M-298296-01-1): kinetic and statistical results of degradation in soil Laacherhof AIIIa for modelling endpoints

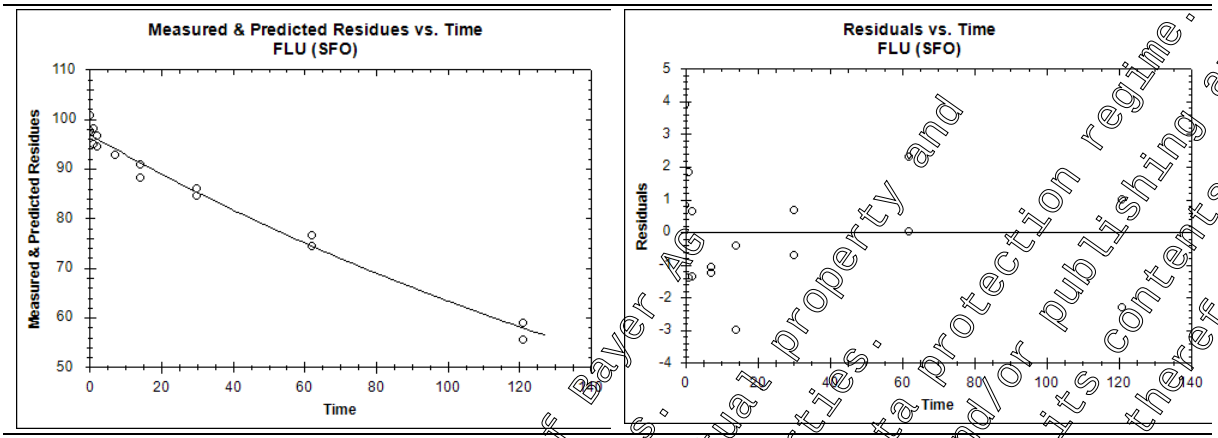
Kinetic model	DT_{50} actual	DT_{90} actual	DT_{50} fast / slow	VA	χ^2err / SWARC	k_1	k_2	g	t-test k_1 / k_2	95th CI of k_1	95th CI of k_2
	(d)	(d)	(d)		(% / -)	(1/d)	(1/d)	(-)	(-)	(1/d)	(1/d)
SFO, free fit	163.2	542.0		-	1.12 / 2.79	0.004248	-	-	<0.001	0.00390 to 0.005	-
DFOP	164.7	568.9	3.305 / 174.1	+	0.994 / 1.90	0.2097	0.003982	0.0366	0.002 / <0.001	0.078 to 0.341	0.00362 to 0.004
SFO, fixed fit	**163.2** fix	542.0 fix	-	+	1.06 / 2.79	0.004248		-	-	-	-

VA = visual assessment, + = good, o = acceptable, - = poor
SWARC = Scaled Weighted Area under Residue Curve
CI = confidence interval
fixed fit: parent parameters fixed to free fit values, DT50 FLU-7-OH fixed to 95th CI rate of free fit.

Modelling Endpoints: SFO fit is statistically and visually good (χ^2err <15%, t-test <0.05). SWARC value is < 40, not indicating a biphasic decline. Consequently, **SFO** degradation model is appropriate for modelling endpoints.

However, metabolite FLU-7-OH is rising until the end of study. The pathway fit (free fit) was therefore modified with a fixed DT_{50} value for FLU-7-OH (fixed fit). The DT_{50} value of FLU-7-OH was fixed to a conservative value (95% confidence interval k of free fit), formation fractions were fitted and parent parameters were fixed to values derived from the free fit. Finally, this **fixed SFO fit** was considered appropriate.

SFO free



SFO fixed

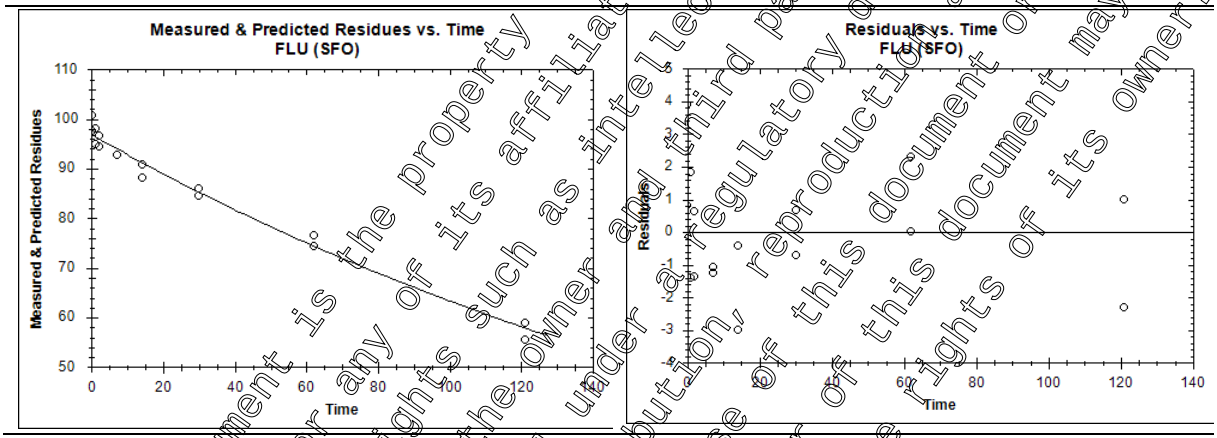


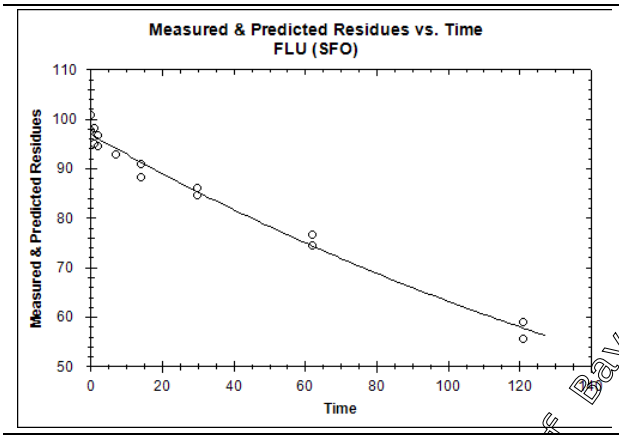
Table 7.1.2.1.1-14: Fluopyram (M-298296-01-1): kinetic and statistical results of degradation in soil Laacherhof AIIa for trigger endpoints, parent only fit

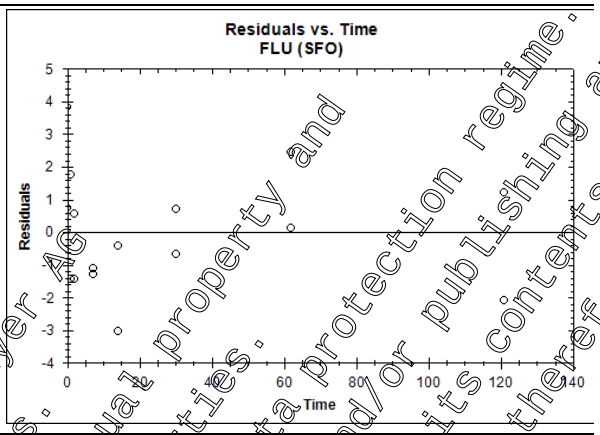
Kinetic model	DT_{50} actual	DT_{90} actual	VA	χ^2err / SWARC	k_1 / α	k_2 / β	g / t_b	t-test k_1 / k_2	95th CI of k_1	95th CI of k_2
	(d)	(d)		(%, -)	(1/d / -)	(1/d / d)	(- / d)	(-)	(1/d)	(1/d)
SFO	161.8	537	+	1.11 / 1.69	0.004285	-	-	<0.001	0.00394 to 0.0050	-
DFOP	159.9	551	+	0.746 / 1.17	0.9335886	0.0041172	0.0342 / -	0.158 / <0.001	-0.81680 to 2.6840	0.00376 to 0.0040
FOMC	161.8	538	+	1.09 / 1.69	144400	336900	-	-	-	-
HS	**160.5**	**552**	+	0.779 / 1.17	0.01833	0.004114	- / 2.30	0.027 / <0.001	0.00159 to 0.0350	0.00375 to 0.0040

VA = visual assessment, + = good, o = acceptable, - = poor
SWARC = Scaled Weighted Area under Residue Curve
CI = confidence intervall

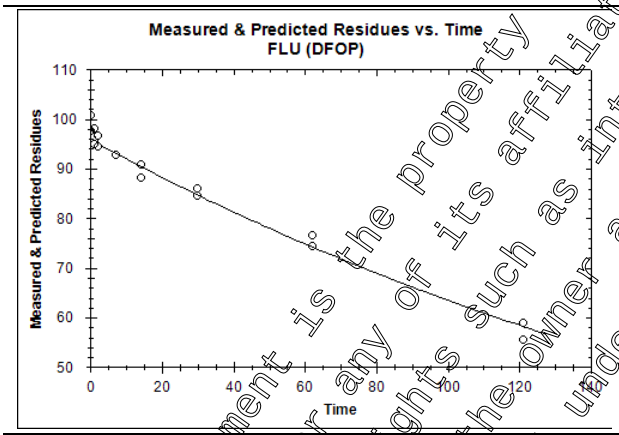
Trigger Endpoints: SFO fit (parent only) is statistically (χ^2err, t-test) and visually good. DFOP, FOMC and HS fits were alternatively tested. For DFOP, t-test of k_{fast} failed in combination with DT_{50} and DT_{90} extrapolated beyond studyend. For FOMC, DT_{50} and DT_{90} are extrapolated beyond study end. Both fits are therefore not suitable, especially for accumulation assessments. HS fit is statistically (χ^2err, t-test) and visually good. Consequently, **HS** degradation model is appropriate for trigger endpoints, as it shows lowest χ^2err of all suitable models (SFO, HS).

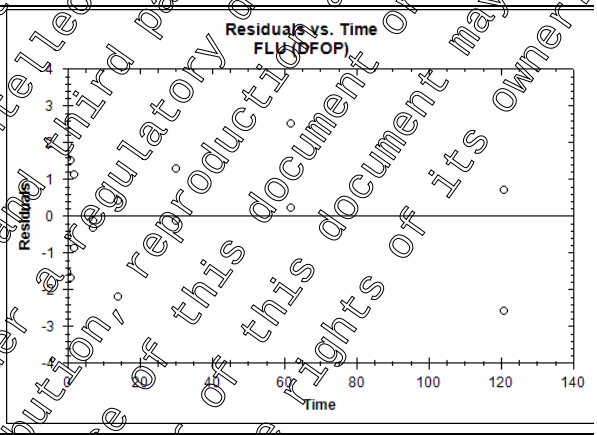
SFO



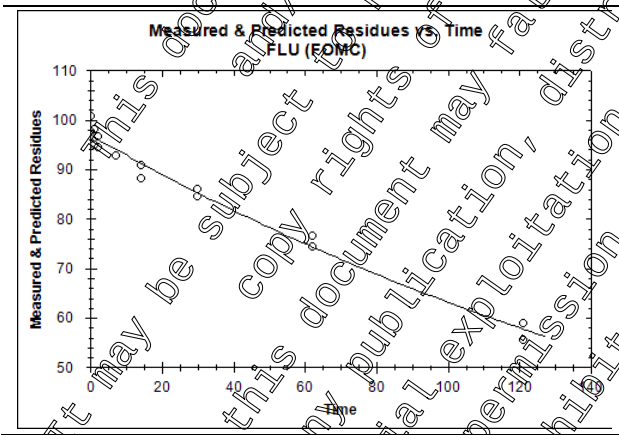


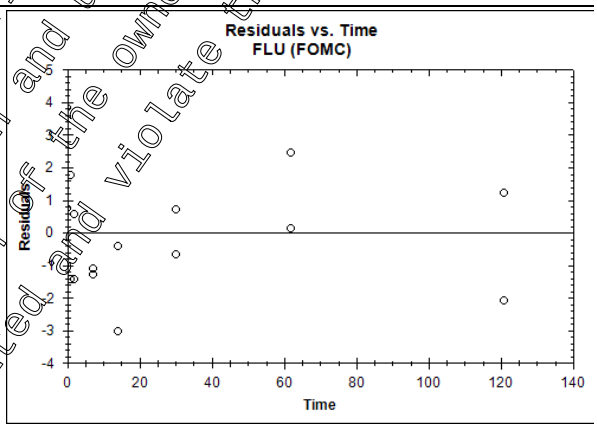
DFOP



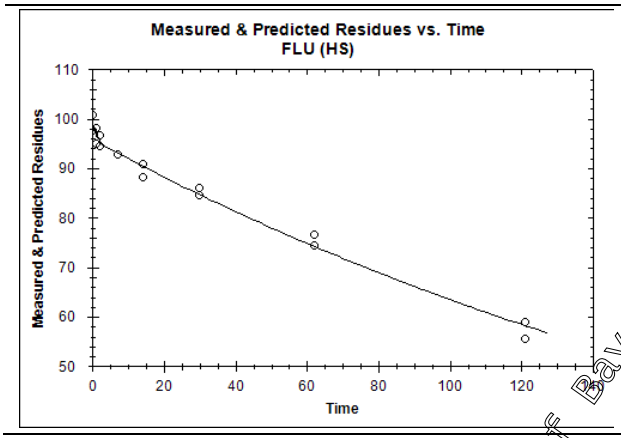


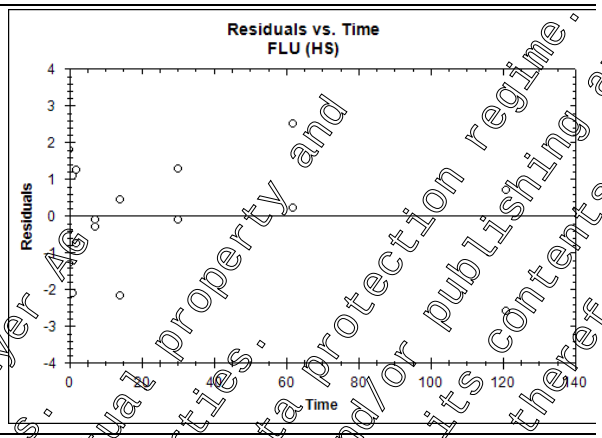
FOMC





HS





Hoefchen am Hohenseh

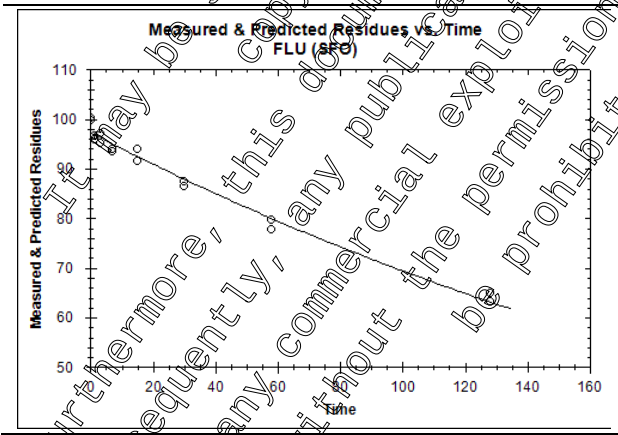
Table 7.1.2.1.1-15: Fluopyram (M-298413-01-1): kinetic and statistical results of degradation in soil Hoefchen am Hohenseh for modelling endpoints

Kinetic model	DT_{50} actual	DT_{90} actual	DT_{50} fast / slow	VA	χ^2err / SWARC	k_1	k_2	g	t-test k_1 / k_2	95th CI of k_1	95th CI of k_2
	(d)	(d)	(d)		(% / -)	(1/d)	(1/d)	(-)	(-)	(1/d)	(1/d)
SFO	**205.2**	682			1.15 / 1.12	0.003378	-	-	<0.001	0.00311 to 0.004	-
DFOP	206.8	705	2.69 / 215	+	0.982 / 0.671	0.2575	0.00323	0.0248	0.012 / <0.001	0.04658 to 0.468	0.00295 to 0.004

VA = visual assessment, + = good, o = acceptable, - = poor
SWARC = Scaled Weighted Area under Residue Curve
CI = confidence interval

Modelling Endpoints: SFO fit is statistically and visually good (χ^2err <15%, t-test <0.05). SWARC value is < 40, not indicating a biphasic decline. Consequently, **SFO** degradation model is appropriate for modelling endpoints.

SFO



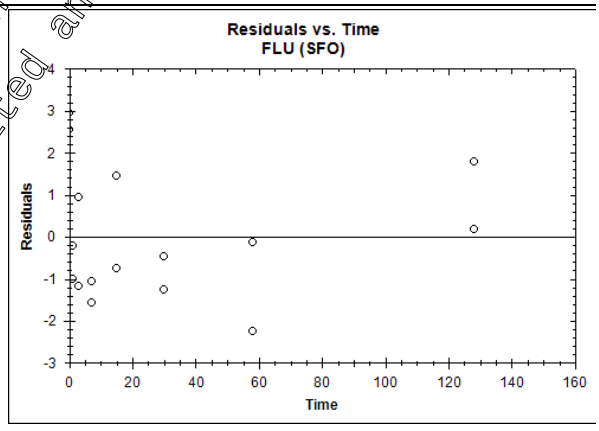


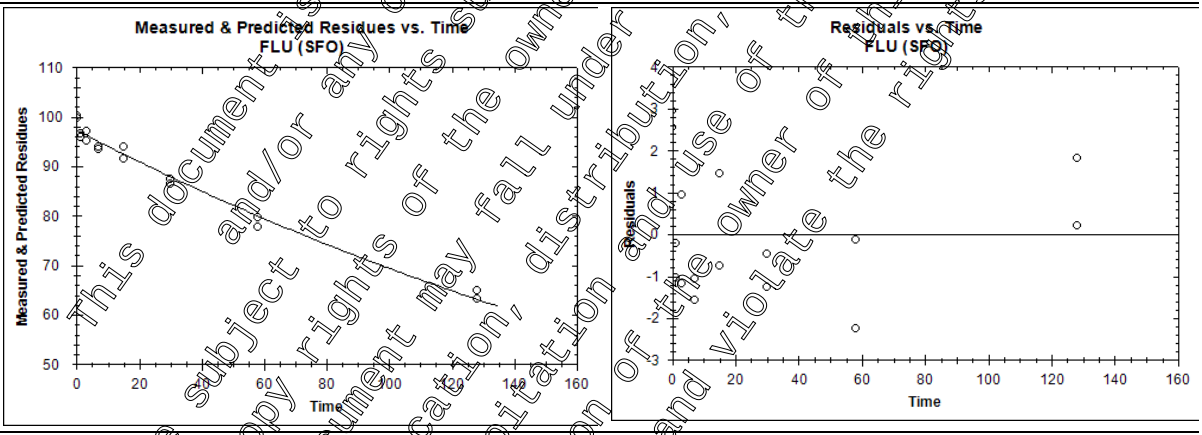
Table 7.1.2.1.1-16: Fluopyram (M-298413-01-1): kinetic and statistical results of degradation in soil Hoefchen am Hohenseh for trigger endpoints, parent only fit

Kinetic model	DT_{50} actual	DT_{90} actual	VA	χ^2err / SWARC	k_1 / α	k_2 / β	g / t_b	t-test k_1 / k_2	95th CI of k_1	95th CI of k_2
	(d)	(d)		(% / -)	(1/d / -)	(1/d / d)	(- / d)	(-)	(1/d)	(1/d)
SFO	205	681	+	1.15 / 1.12	0.003381		-	<0.001	0.00312 to 0.004	-
DFOP	201	693	+	0.68 / 0.66	3.194	0.00327	0.0363 / -	0.314 / <0.001	9.42700 to 15.815	0.00306 to 0.003
FOMC	249.6	>1000	+	0.99 / 0.59	0.86504	203.152	-	-	-	-
HS	**213.9**	**732**	+	1.13 / 0.63	0.004143	0.003104	- / 28.0	<0.001 / <0.001	0.00230 to 0.006	0.00269 to 0.004

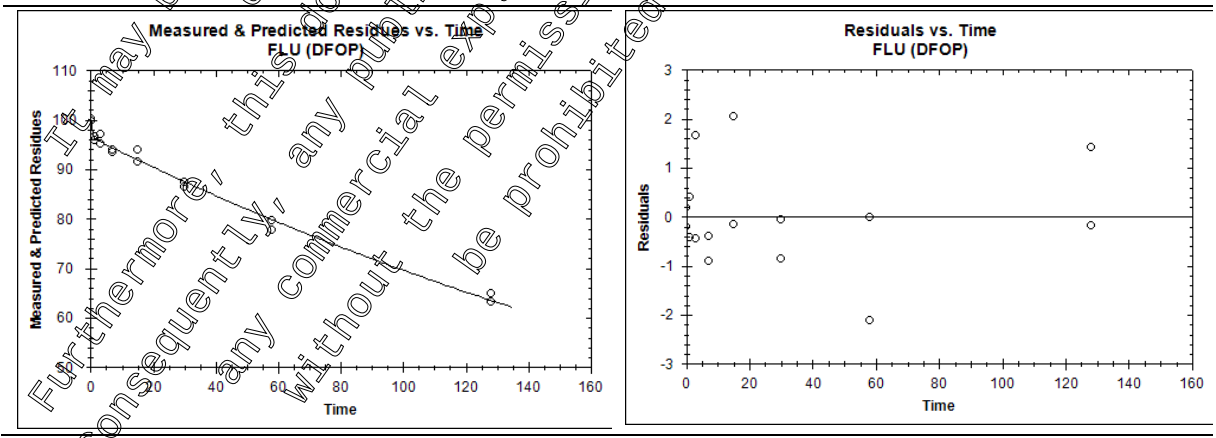
VA = visual assessment, + = good, o = acceptable, - = poor
SWARC = Scaled Weighted Area under Residue Curve
CI = confidence intervall

Trigger Endpoints: SFO fit (parent only) is statistically (χ^2err, t-test) and visually good. DFOP, FOMC and HS fits were alternatively tested. For DFOP, t-test of k_{ast} failed in combination with DT_{50} and DT_{90} extrapolated beyond study end. For FOMC, DT_{50} and DT_{90} are extrapolated beyond study end. Both fits are therefore not suitable, especially for accumulation assessments. HS fit is statistically (χ^2err, t-test) and visually good. Consequently, **HS** degradation model is appropriate for trigger endpoints, as it shows lowest χ^2err of all suitable models (SFO, HS).

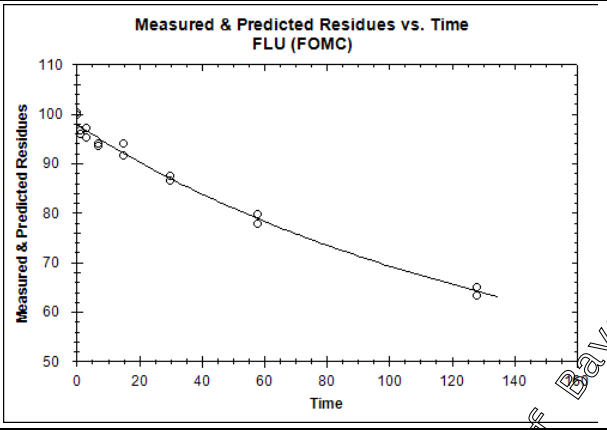
SFO

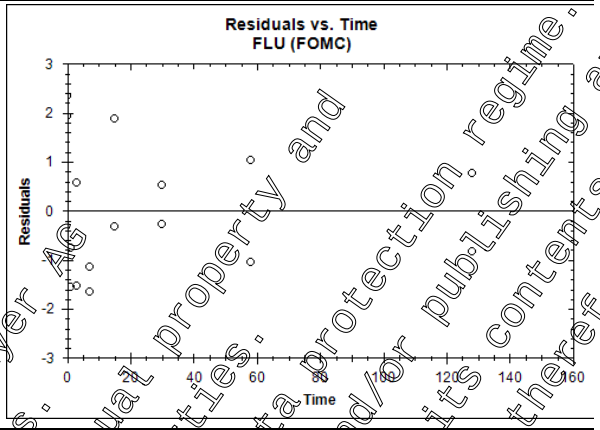


DFOP

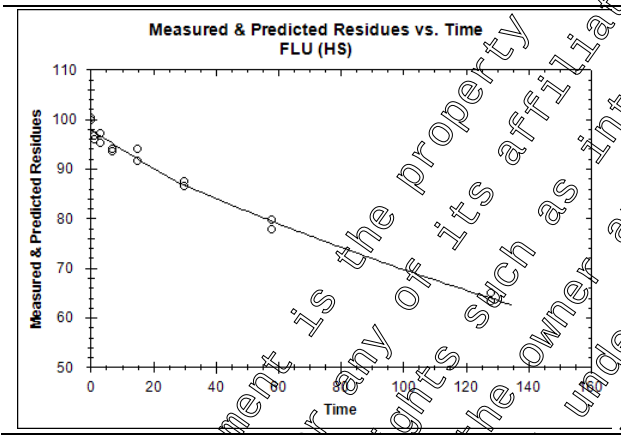


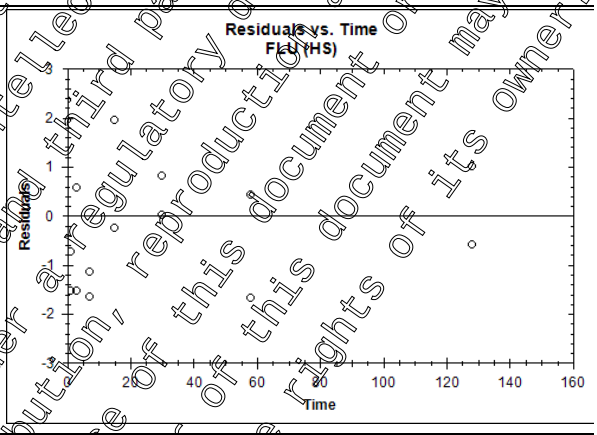
FOMC





HS





Laacherhof AXXa

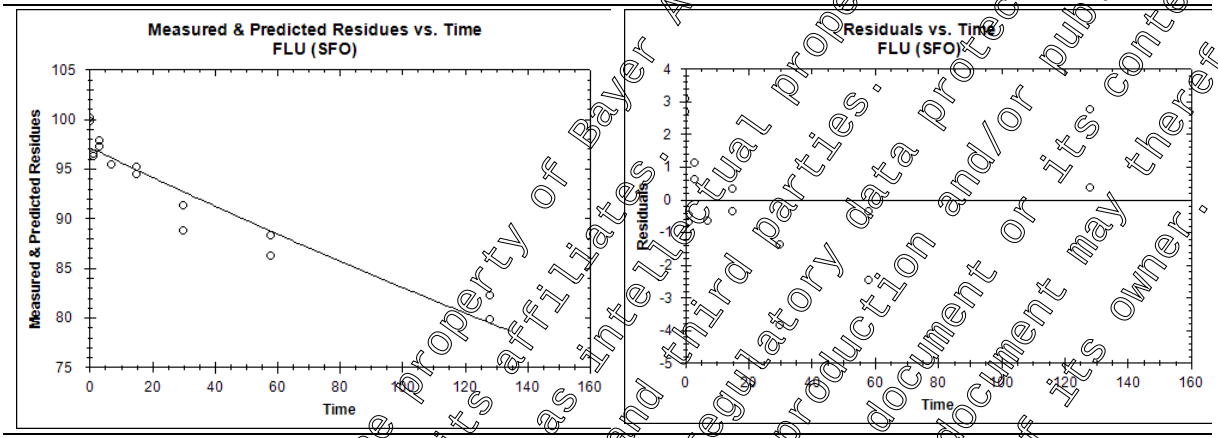
Table 7.1.2.1.1-17: Fluopyram (M-298413-01-1): kinetic and statistical results of degradation in soil Laacherhof AXXa for modelling endpoints

Kinetic model	DT_{50} actual	DT_{90} actual	DT_{50} fast / slow	VA	χ^2err / SWARC	k_1	k_2	g	t-test k_1 / k_2	95th CI of k_1	95th CI of k_2
	(d)	(d)	(d)		(% / -)	(1/d)	(1/d)	(-)	(-)	(1/d)	(1/d)
SFO, free fit	441.5	>1000		+	1.39 / 7.40	0.00157	-	-	<0.001	0.00130 to 0.002	-
DFOP	588.2	2085	10.6 / 644	+	0.953 / 0.346	0.06512	0.001076	0.0587	0.014 / <0.001	0.01062 to 0.120	0.00069 to 0.001
SFO, fixed fit	**441.5** ^{fix}	>1000 ^{fix}	-	+	1.32 / 7.38	0.00157	-	-	- / -	-	-

VA = visual assessment, + = good, o = acceptable, - = poor
SWARC = Scaled Weighted Area under Residue Curve
CI = confidence intervall
fixed fit: parent parameters fixed to free fit values, DT50 FLU-7-OH fixed to 95th CI rate of free fit.

Modelling Endpoints:	SFO fit is statistically and visually good (χ^2err <15%, t-test <0.05). SWARC value is < 40, not indicating a biphasic decline. Consequently, **SFO** degradation model is appropriate for modelling endpoints. However, metabolite FLU-7-OH is rising until the end of study. The pathway fit (free fit) was therefore modified with a fixed DT_{50} value for FLU-7-OH (fixed fit). The DT_{50} value of FLU-7-OH was fixed to a conservative value (95% confidence interval k of free fit), formation fractions were fitted and parent parameters were fixed to values derived from the free fit. Finally, this **fixed SFO fit** was considered appropriate.

SFO free



SFO fixed

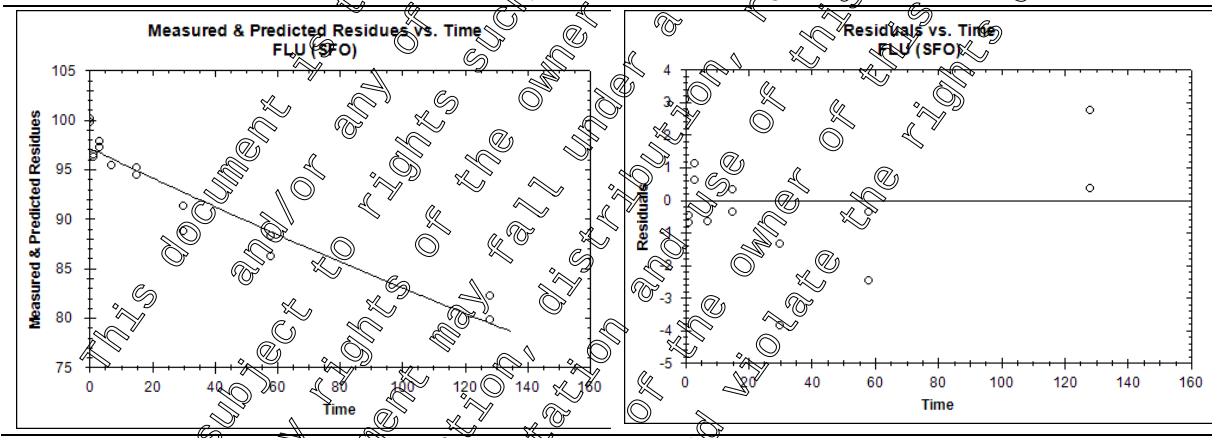


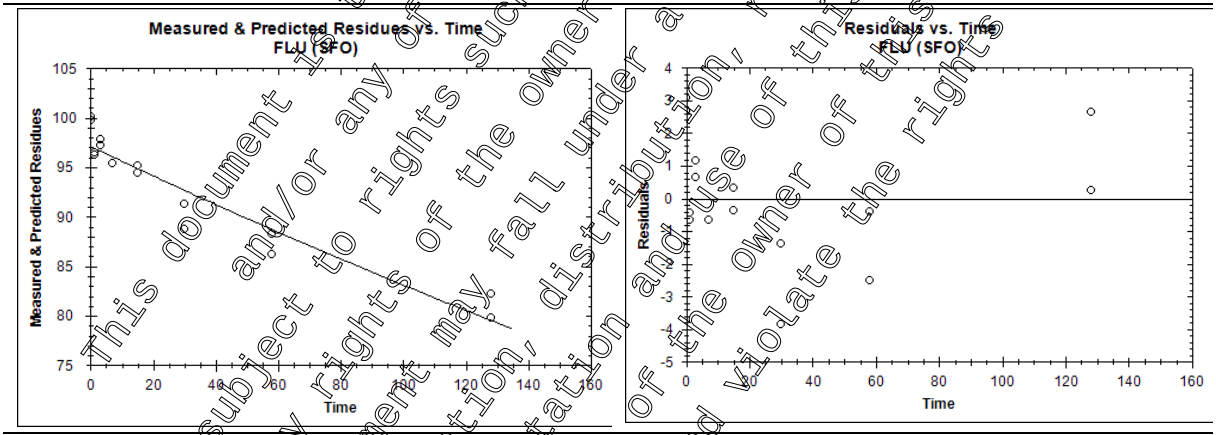
Table 7.1.2.1.1-18: Fluopyram (M-298413-01-1): kinetic and statistical results of degradation in soil Laacherhof AXXa for trigger endpoints, parent only fit

Kinetic model	DT_{50} actual	DT_{90} actual	VA	χ^2err / SWARC	k_1 / α	k_2 / β	g / t_b	t-test k_1 / k_2	95th CI of k_1	95th CI of k_2
	(d)	(d)		(% / -)	(1/d / -)	(1/d / d)	(- / d)	(-)	(1/d)	(1/d)
SFO	**444.5**	**>1000**	+	1.39 / 7.42	0.001559		-	0.001 -	0.00129 to 0.002	-
DFOP	653.3	>1000	+	0.940 / 0	0.0450724	0.0009469	0.0718 / -	0.141 / 0.020	0.03343 to 0.124	0.00014 to 0.002
FOMC	>1000	>1000	+	0.877 / 0	0.11451	28.9430	-	-	-	-
HS	483.5	>1000	+	1.19 / 1.85	0.0063654	0.0013642	- / 6.70	0.132 / 0.001	0.00430 to 0.017	0.00109 to 0.002

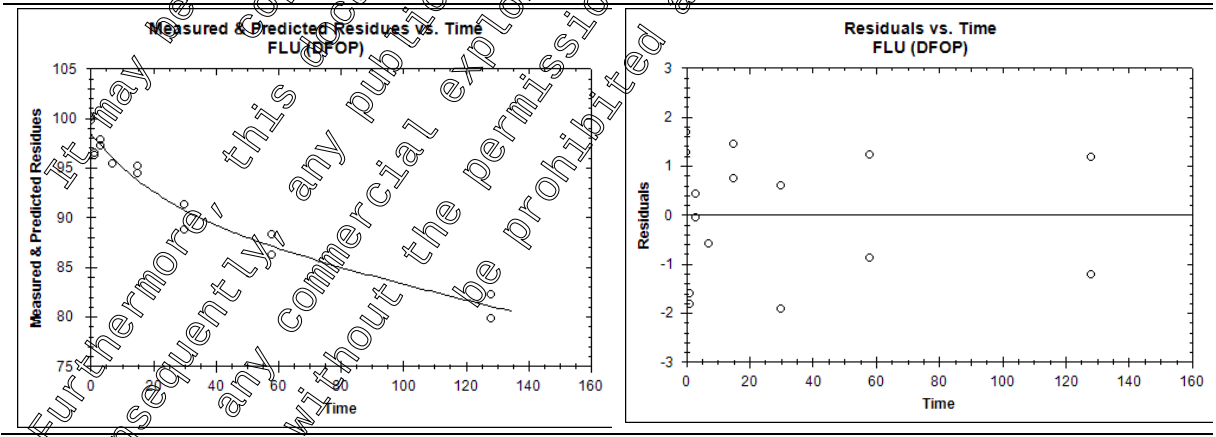
VA = visual assessment, + = good, o = acceptable, - = poor
SWARC = Scaled Weighted Area under Residue Curve
CI = confidence intervall

Trigger Endpoints: SFO fit is statistically (χ^2err, t-test) and visually good. DFOP, FOMC and HS fits were alternatively tested. For DFOP and HS, t-test of k_{fast} failed in combination with DT_{50} and DT_{90} extrapolated beyond study end. For FOMC, DT_{50} and DT_{90} are extrapolated beyond study end. These fits are therefore not suitable, especially for accumulation assessments. Consequently, **SFO** degradation model is appropriate for trigger endpoints.

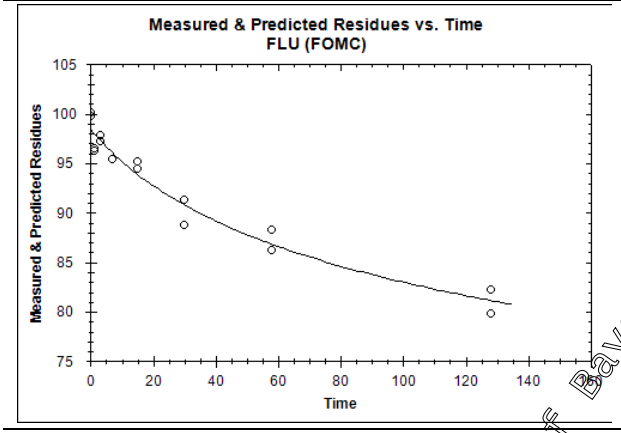
SFO

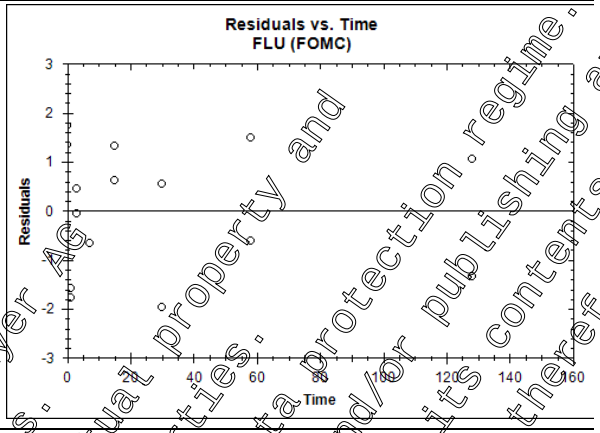


DFOP

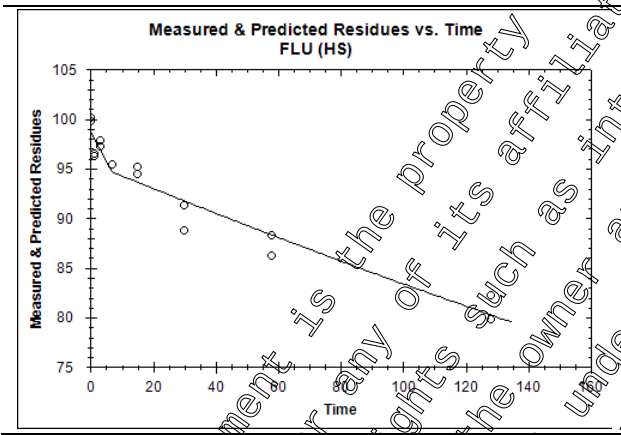


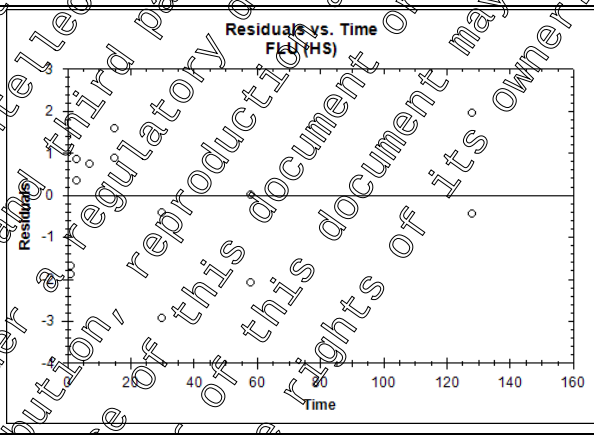
FOMC





HS





Laacherhof Wurmwiese

Table 7.1.2.1.1-19: Fluopyram (M-298413-01-1): kinetic and statistical results of degradation in soil Laacherhof Wurmwiese for modelling endpoints

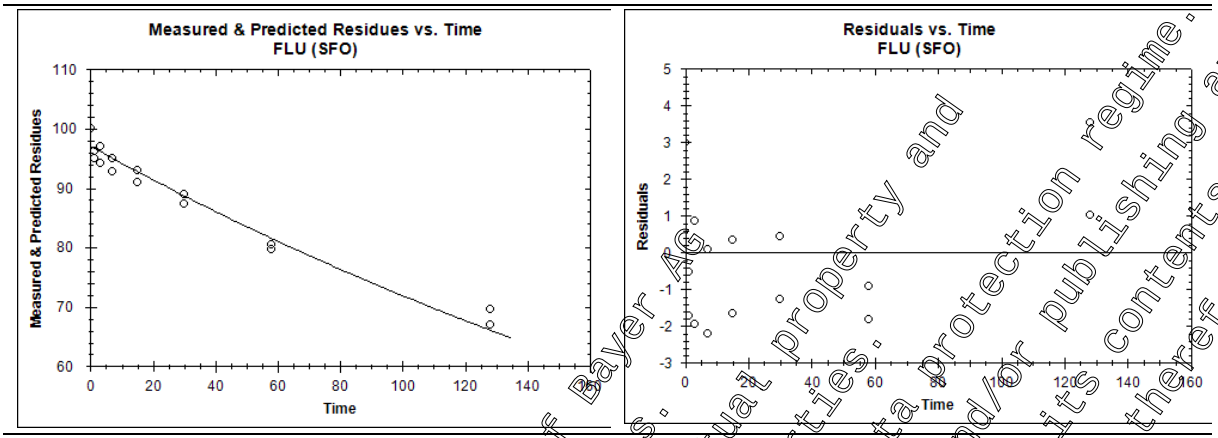
Kinetic model	DT_{50} actual	DT_{90} actual	DT_{50} fast / slow	VA	χ^2err / SWARC	k_1	k_2	g	t-test k_1 / k_2	95th CI of k_1	95th CI of k_2
	(d)	(d)	(d)		(% / -)	(1/d)	(1/d)	(-)	(-)	(1/d)	(1/d)
SFO	**230.97**	767		+	1.38 / 6.94	0.003001	-	-	<0.001	0.00266 to 0.003	-
DFOP	247.4	855	1.74 / 262	+	1.00 / 1.19	0.399	0.002648	0.0374	<0.001 / <0.001	0.20150 to 0.596	0.00237 to 0.003

VA = visual assessment, + = good, o = acceptable, - = poor
SWARC = Scaled Weighted Area under Residue Curve
CI = confidence interval

Modelling Endpoints: SFO fit is statistically and visually good (χ^2err <15%, t-test <0.05). SWARC value is < 40, not indicating a biphasic decline. Consequently, SFO degradation model would be appropriate for modelling endpoints.

Based on metabolite FLU-7-OH fit results, DFOP parent fit was tested. However, DFOP fit shows no significant improvement and weight of evidence still supports parent SFO. Even more, the ratio of DFOP DT_{90}/DT_{50} (855 d / 247 d) is 3.46, showing that the fit is very close to the SFO, where this ratio is 3.32. Consequently, **SFO** degradation model is indeed appropriate for modelling endpoints.

SFO



DFOP

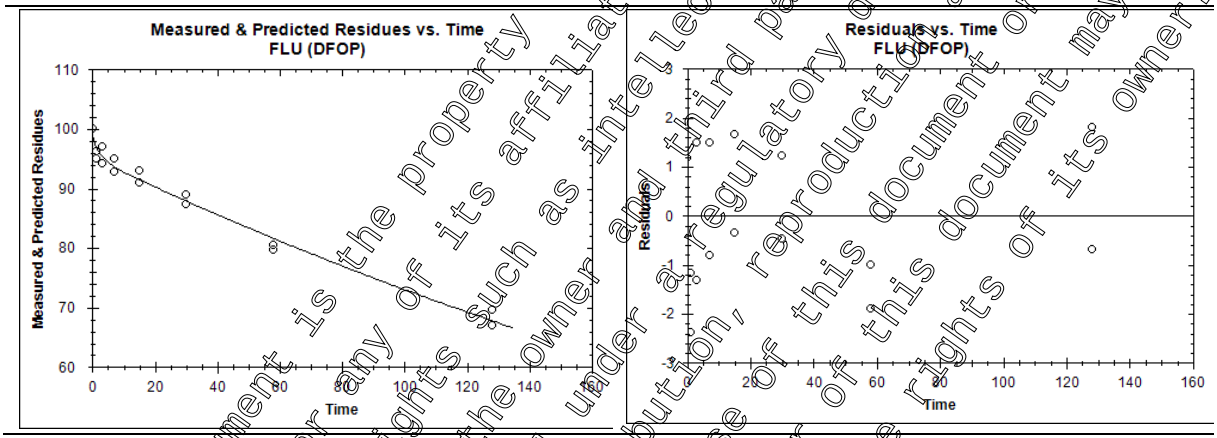


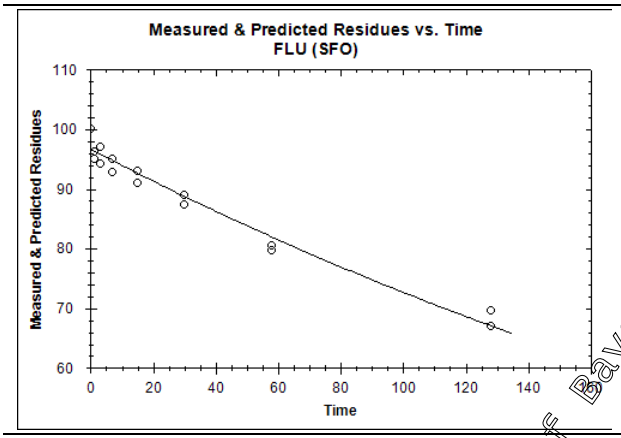
Table 7.1.2.1.1-20: Fluopyram (M-298413-01-1): kinetic and statistical results of degradation in soil Laacherhof Wurmwiese for trigger endpoints, parent only fit

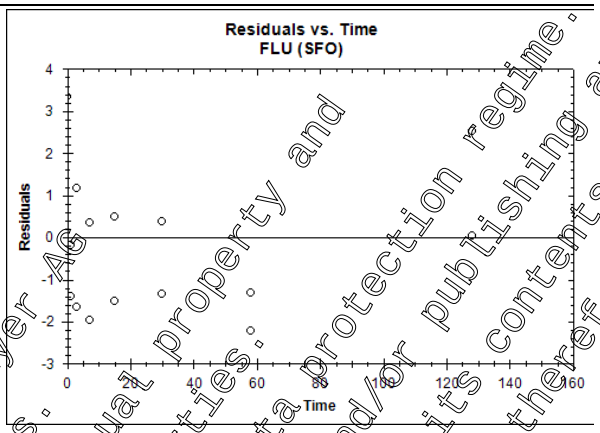
Kinetic model	DT_{50} actual	DT_{90} actual	VA	χ^2err / SWARC	k_1 / α	k_2 / β	g / t_b	t-test k_1 / k_2	95th CI of k_1	95th CI of k_2
	(d)	(d)		(%) / -	(1/d / -)	(1/d / d)	(- / d)	(-)	(1/d)	(1/d)
SFO	242.7	806	+	4.33 / 7.35	0.002856	-	-	<0.001 -	0.00255 to 0.003	-
DFOP	238.1	828	+	0.69 / 0.044	3.806	0.00273	0.0423 / -	0.374 / <0.001	-18.870 to 26.483	0.00249 to 0.003
FOMC	372.7	>1000	+	1.10 / 0.838	0.49578	122.302	-	-	-	-
HS	**245**	**843**		1.06 / 0.832	0.0131	0.002691	- / 3.26	0.017 / <0.001	0.00235 to 0.024	0.00238 to 0.003

VA = visual assessment, + = good, o = acceptable, - = poor
SWARC = Scaled Weighted Area under Residue Curve
CI = confidence intervall

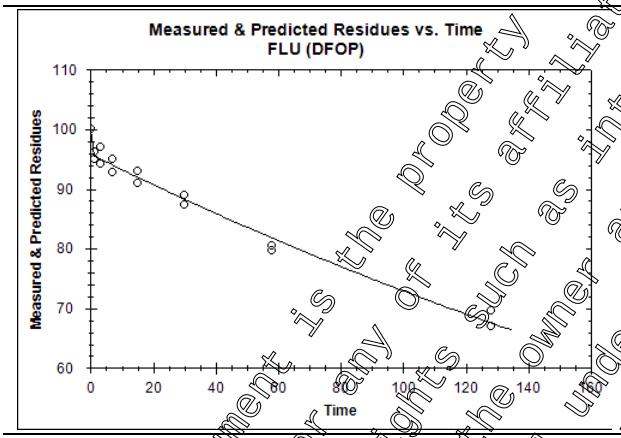
Trigger Endpoints: SFO fit is statistically (χ^2err, t-test) and visually good. DFOP, FOMC and HS fits were alternatively tested. For DFOP, t-test of k_{fast} failed in combination with DT_{50} and DT_{90} extrapolated beyond study end. For FOMC, DT_{50} and DT_{90} are extrapolated beyond study end. Both fits are therefore not suitable, especially for accumulation assessments. HS fit is statistically (χ^2err, t-test) and visually good. Consequently, **HS** degradation model is appropriate for trigger endpoints, as it shows lowest χ^2err of all suitable models (SFO, HS).

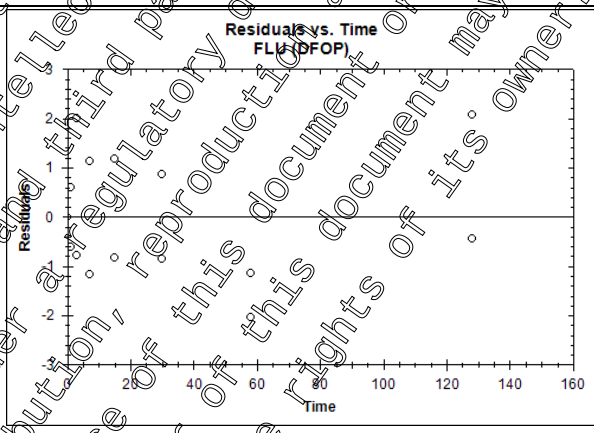
SFO



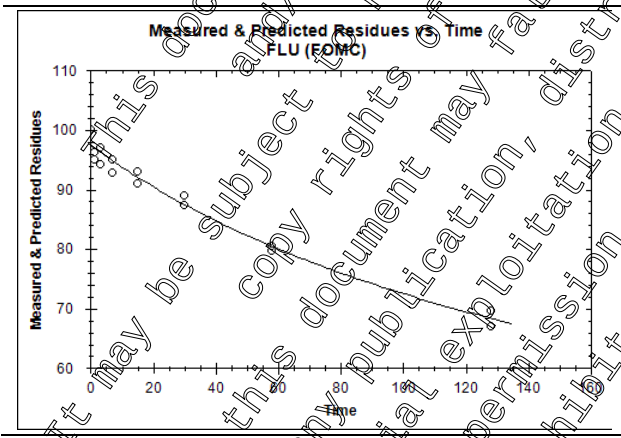


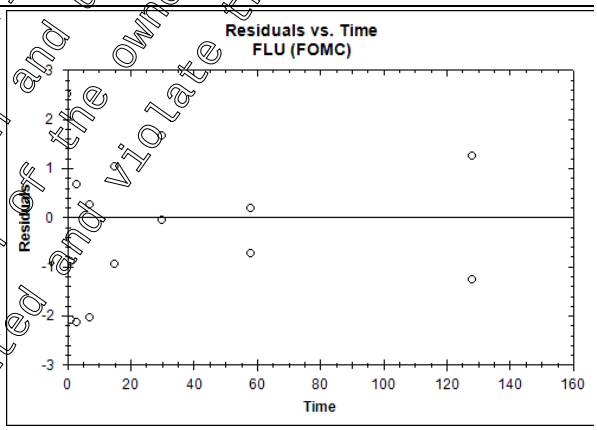
DFOP



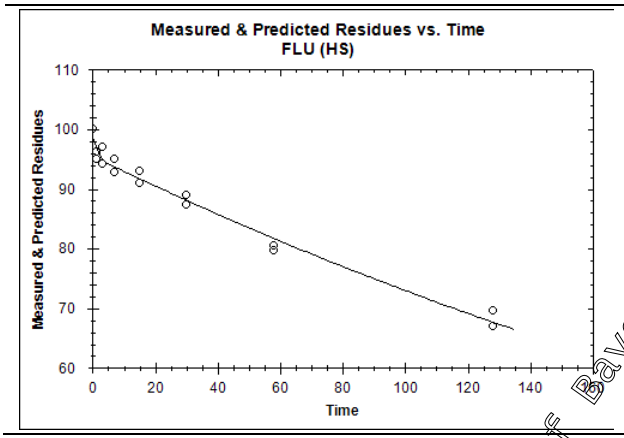


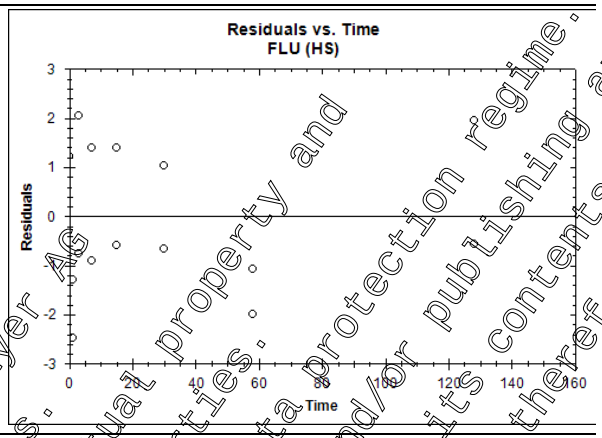
FOMC





HS





Dollendorf II

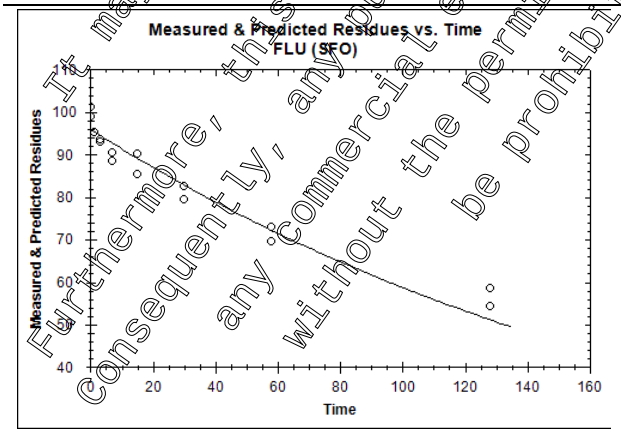
Table 7.1.2.1.1-21: Fluopyram (M-298413-01-1): kinetic and statistical results of degradation in soil Dollendorf II for modelling endpoints

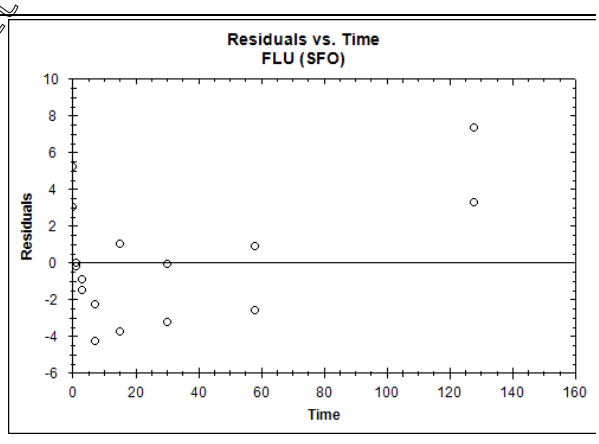
Kinetic model	DT_{50} actual	DT_{90} actual	DT_{50} fast / slow	VA	χ^2err / SWARC	k_1	k_2	g	t-test k_1 / k_2	95th CI of k_1	95th CI of k_2
	(d)	(d)	(d)		(% / -)	(1/d)	(1/d)	(-)	(-)	(1/d)	(1/d)
SFO	**141.1**	469		o	2.64 / 18.0	0.004912	-	-	<0.001	0.00424 to 0.006	-
DFOP	159.7	585	3.15 / 183	+	1.24 / 0.769	0.22	0.003788	0.0844	<0.001 / <0.001	0.09665 to 0.343	0.00329 to 0.004

VA = visual assessment, + = good, o = acceptable, - = poor
SWARC = Scaled Weighted Area under Residue Curve
CI = confidence interval

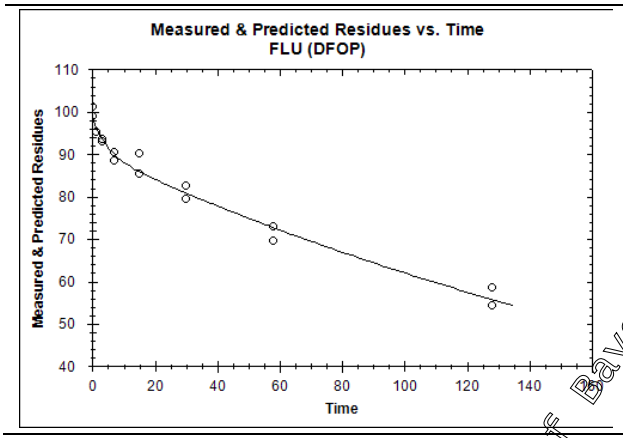
Modelling Endpoints: SFO fit is statistically and visually good (χ^2err <15%, t-test <0.05). SWARC value is < 40, not indicating a biphasic decline (please note, y-scale at figure is zoomed, not starting at 0 %). Consequently, SFO degradation model would be appropriate for modelling endpoints.
Based on metabolite FLU-7-OH fit results, DFOP parent fit was tested. However, DFOP fit shows no significant improvement and weight of evidence still supports parent SFO. Even more, the ratio of DFOP DT_{90}/DT_{50} (585 d / 160 d) is 3.65, showing that the fit is very close to the SFO, where this ratio is 3.32. Consequently, **SFO** degradation model is indeed appropriate for modelling endpoints.

SFO





DFOP



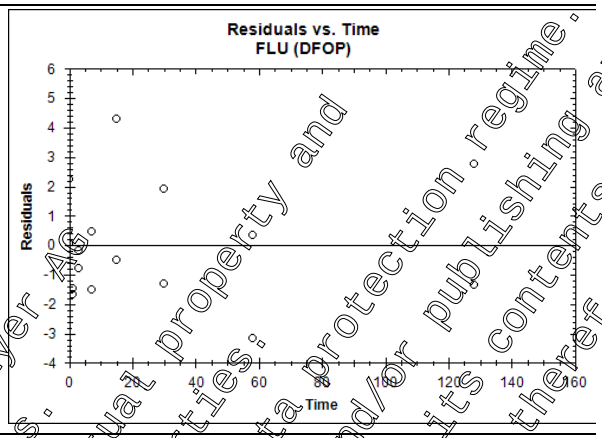


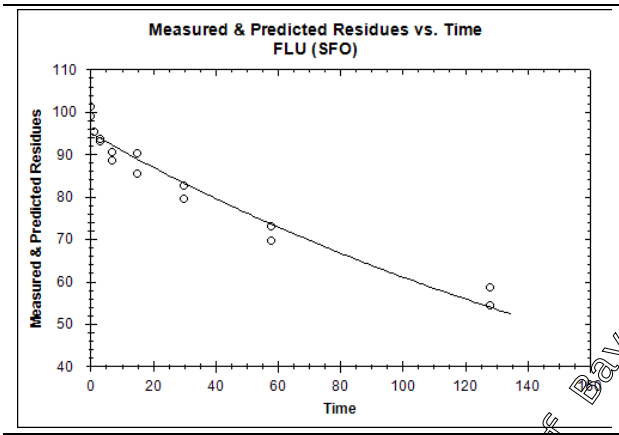
Table 7.1.2.1.1-22: Fluopyram (M-298413-01-1): kinetic and statistical results of degradation in soil Dollendorf II for trigger endpoints, parent only fit

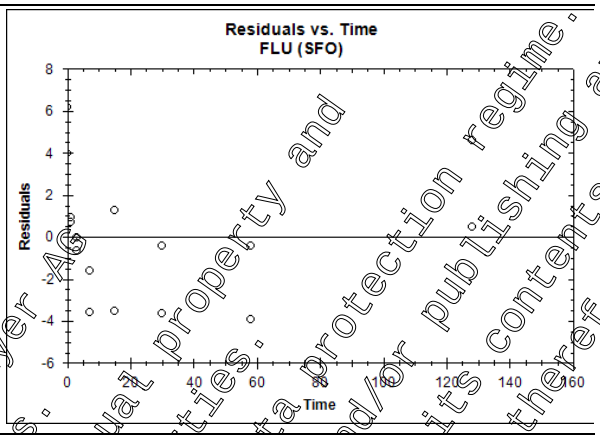
Kinetic model	DT_{50} actual	DT_{90} actual	VA	χ^2err / SWARC	k_1 / α	k_2 / β	g / t_B	t-test k_1 / k_2	95th CI of k_1	95th CI of k_2
	(d)	(d)		(%) / -	(1/d / -)	(1/d / d)	- / d)	(-)	(1/d)	(1/d)
SFO	**156.9**	**521**	+	2.37 / 13.0	0.004418	-	- / -	0.001	0.00383 to 0.005	-
DFOP	155	563	+	1.05 / 1.00	0.3057799	0.0039436	0.0785 / -	0.052 / <0.001	-0.05628 to 1.068	0.00347 to 0.004
FOMC	204.9	1000	+	1.62 / 2.39	0.47660	62.4134	- / -	- / -	-	-
HS	156.9	566	+	1.19 / 1.39	0.021651	0.003937	4.26	0.006 / <0.001	0.00721 to 0.036	0.00346 to 0.004

VA = visual assessment, + = good, o = acceptable, - = poor
SWARC = Scaled Weighted Area under Residue Curve
CI = confidence intervall

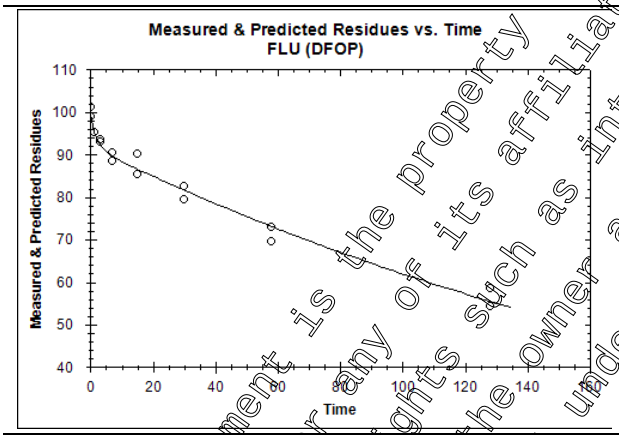
Trigger Endpoints: SFO fit is statistically (χ^2err, t-test) and visually good. DFOP, FOMC and HS fits were alternatively tested. For DFOP, t-test of k_{fast} failed in combination with DT_{50} and DT_{90} extrapolated beyond study end. For FOMC, DT_{50} and DT_{90} are extrapolated beyond study end. Both fits are therefore not suitable, especially for accumulation assessments.
HS fit is statistically (χ^2err, t-test) and visually good. However, pathway fit for metabolite FLU-7-OH is visually better with parent SFO compared to parent HS. Consequently, **SFO** degradation model is appropriate for trigger endpoints, as it shows a similarly good fit as HS model and is visually most suitable for metabolite FLU-7-OH.

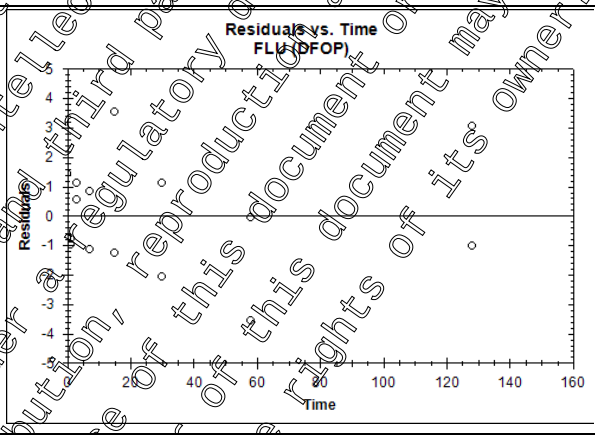
SFO



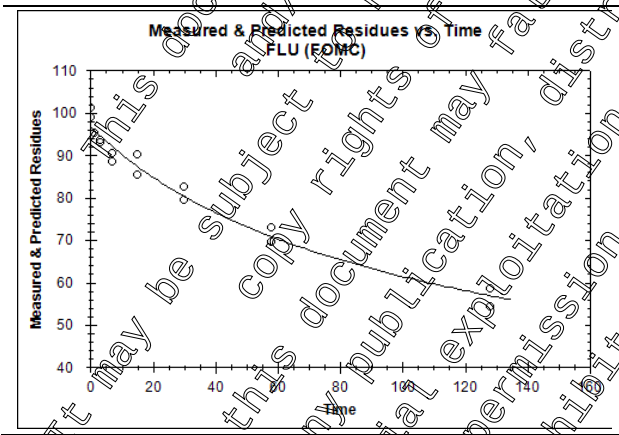


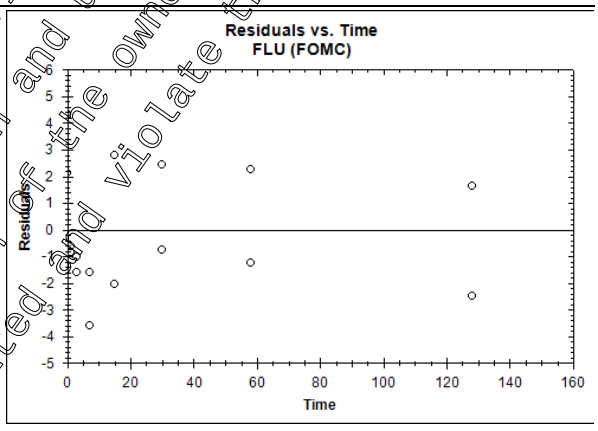
DFOP



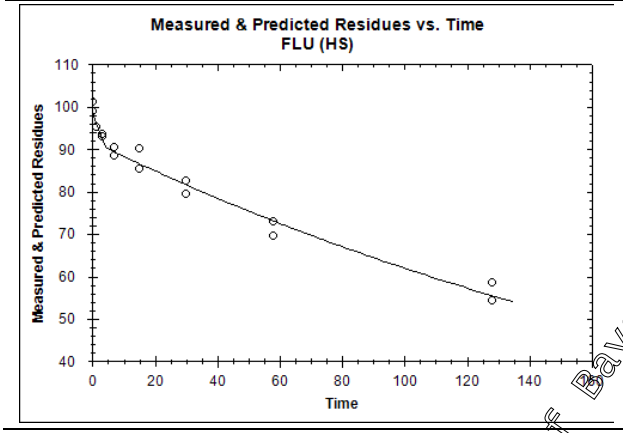


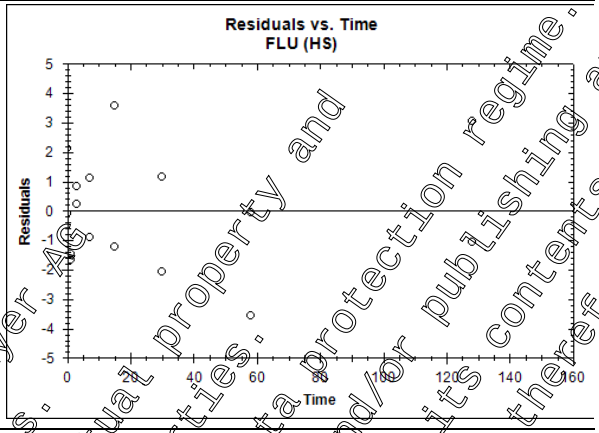
FOMC





HS





Degradation of fluopyram-7-hydroxy

Hoefchen am Hohensch

Table 7.1.2.1.1-23: FLU-7-OH (M-298296-01-1): kinetic and statistical results of degradation in soil Hoefchen am Hohensch for modelling endpoints

Kinetic model, Parent - metabolite	DT_{50} actual	DT_{90} actual	VA	χ^2err	SWARC	k	t-test k	95th CI of k	ff (FLU)
	(d)	(d)		(%)	(-)	(1/d)	(-)	(1/d)	(-)
SFO - SFO, free fit	13.14	43.65	+	8.05	3.05	0.05276	<0.001	0.03842 to 0.067	0.6126
DFOP - SFO	31.20	103.7	+	7.41	0.243	0.02221	<0.001	0.01004 to 0.034	0.3050
SFO - SFO, fixed fit	**18.04** fix	59.93 fix	+	10.3	30.6	0.03842	-	-	**0.4837**

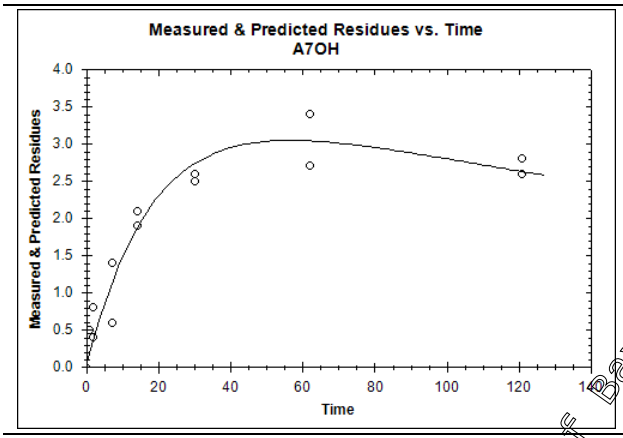
VA = visual assessment, + = good, o = acceptable, - = poor
SWARC = Scaled Weighted Area under Residue Curve
CI = confidence interval
fixed fit: parent parameters fixed to free fit values, DT50 FLU-7-OH fixed to 95th CI rate of free fit.

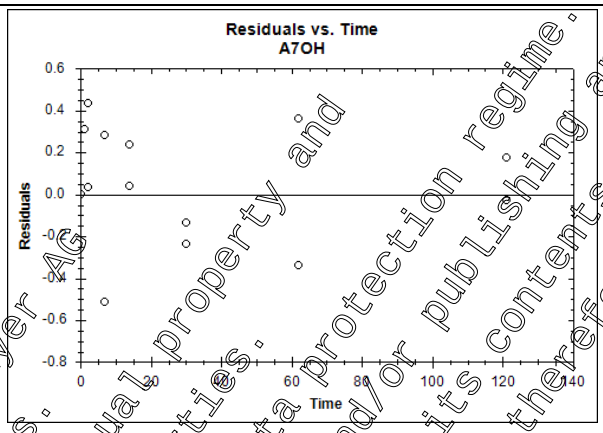
Modelling Endpoints: SFO fit (parent SFO) is statistically and visually good (χ^2err <25%, t-test < 0.1, formation fraction ff is 1, SWARC <40). Consequently, SFO degradation model (parent SFO) is appropriate for modelling endpoints.

However, metabolite FLU-7-OH is rising until the end of study (last 4 time points). The pathway fit (free fit) was therefore modified with a fixed DT_{50} value for FLU-7-OH (fixed fit). The DT_{50} of FLU-7-OH was fixed to a conservative value (95% confidence interval k of free fit), formation fractions were fitted and parent parameters were fixed to values derived from the free fit. Finally, this **fixed SFO** degradation model (**parent SFO**) is considered conservatively appropriate for modelling endpoints.

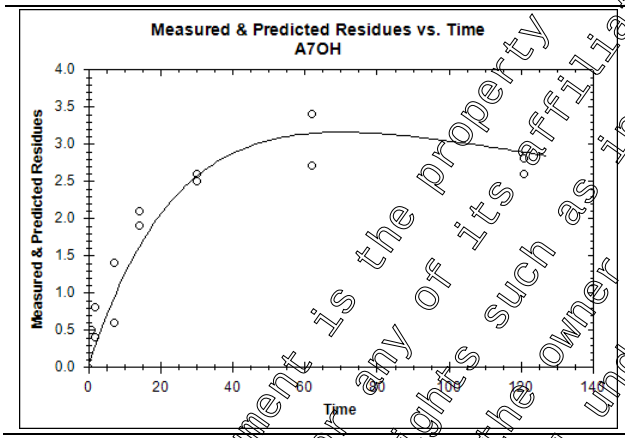
In addition, a more conservative fixed DT_{50} of 1000 d for FLU-7-OH was checked, which clearly shows an over-prediction of the metabolite residues and is therefore not appropriate.

SFO free/SFO free





SFO fixed/SFO fixed



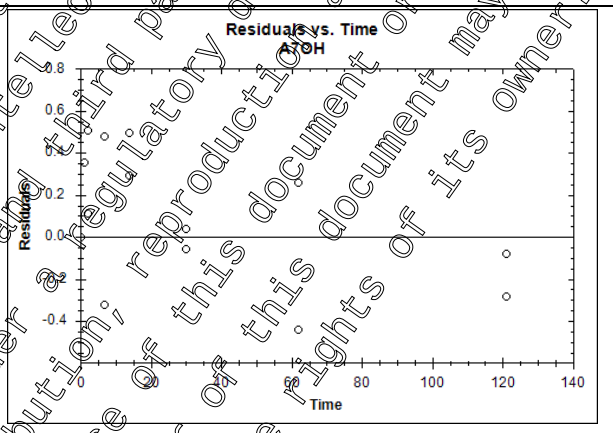


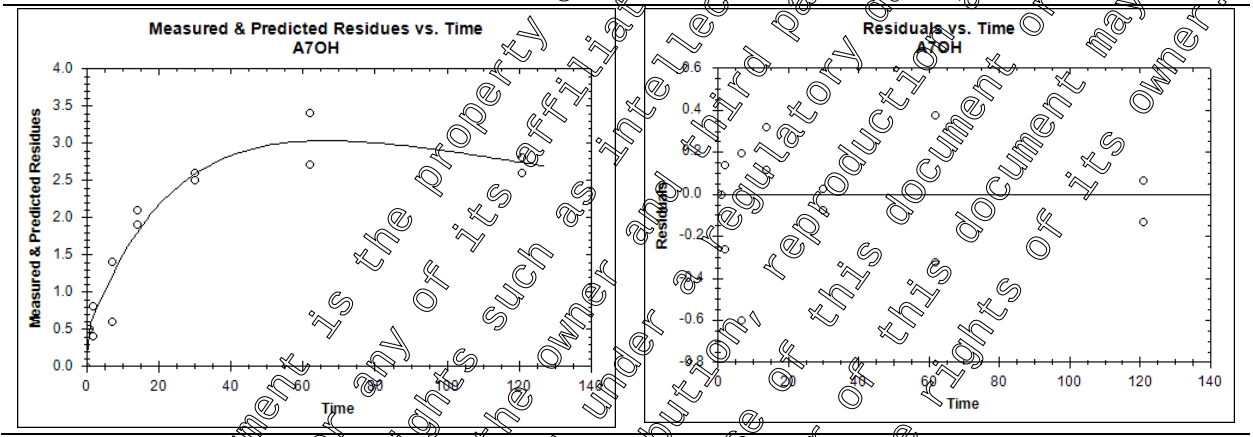
Table 7.1.2.1.1-24: FLU-7-OH (M-298296-01-1): kinetic and statistical results of degradation in soil Hoefchen am Hohenseh for trigger endpoints, pathway fit

Kinetic model, Parent - metabolite	DT_{50} actual	DT_{90} actual	VA	χ^2err	SWARC	k	t-test k	95th CI of k	FF (FLU)
	(d)	(d)		(%)	(-)	(1/d)	(-)	(1/d)	(-)
HS - SFO	**17.71**	**58.82**	+	5.23	1.54	0.039145	<0.001	0.02459 to 0.054	0.4669

VA = visual assessment, + = good, o = acceptable, - = poor
SWARC = Scaled Weighted Area under Residue Curve
CI = confidence intervall

Trigger Endpoints: SFO fit (parent HS) is statistically (χ^2err, t-test) and visually good. Consequently, **SFO** degradation model (**parent HS**) is appropriate for trigger endpoints.

HS/SFO



Laacherhof AXXa

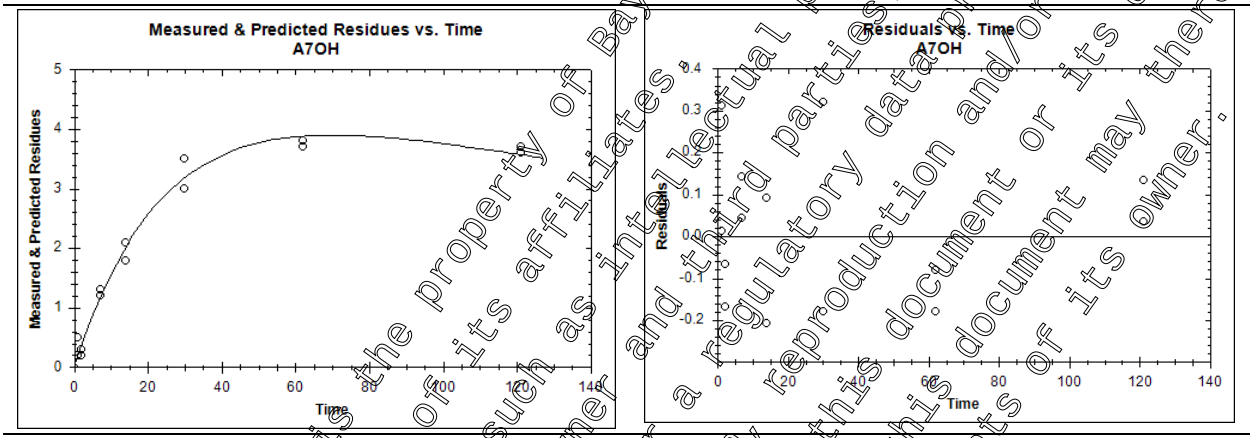
Table 7.1.2.1.1-25: FLU-7-OH (M-298296-01-1): kinetic and statistical results of degradation in soil Laacherhof AXXa for modelling endpoints

Kinetic model, Parent - metabolite	DT_{50} actual	DT_{90} actual	VA	χ^2err	SWARC	k	t-test k	95th CI of k	ff (FLU)
	(d)	(d)		(%)	(-)	(1/d)	(-)	(1/d)	(-)
SFO - SFO, free fit	17.54	58.26	+	4.15	0	0.03952	<0.001	0.03419 to 0.045	0.6430
DFOP - SFO	17.55	58.30	+	4.15	0	0.03949	<0.001	0.03403 to 0.045	0.6415
SFO - SFO, fixed fit	**20.27** [fix]	67.35 [fix]	+	5.22	11.4	0.03419	-	-	**0.5798**

VA = visual assessment, + = good, o = acceptable, - = poor
SWARC = Scaled Weighted Area under Residue Curve
CI = confidence intervall
fixed fit: parent parameters fixed to free fit values, DT50 FLU-7-OH fixed to 95th CI rate of free fit.

Modelling Endpoints: SFO fit (parent SFO) is statistically and visually good (χ^2err <25%, t-test < 0.1, formation fraction ff is <1, SWARC <40). Consequently, SFO degradation model (parent SFO) is appropriate for modelling endpoints.
However, metabolite FLU-7-OH is rising until the end of study (last 4 time points). The pathway fit (free fit) was therefore modified with a fixed DT_{50} value for FLU-7-OH (fixed fit). The DT_{50} of FLU-7-OH was fixed to a conservative value (95% confidence interval k of free fit), formation fractions were fitted and parent parameters were fixed to values derived from the free fit. Finally, this **fixed SFO** degradation model (**parent SFO**) is considered conservatively appropriate for modelling endpoints.
In addition, a more conservative fixed DT_{50} of 1000 d for FLU-7-OH was checked, which clearly shows an over-prediction of the metabolite residues and is therefore not appropriate.

SFO free/SFO free



SFO fixed/SFO fixed

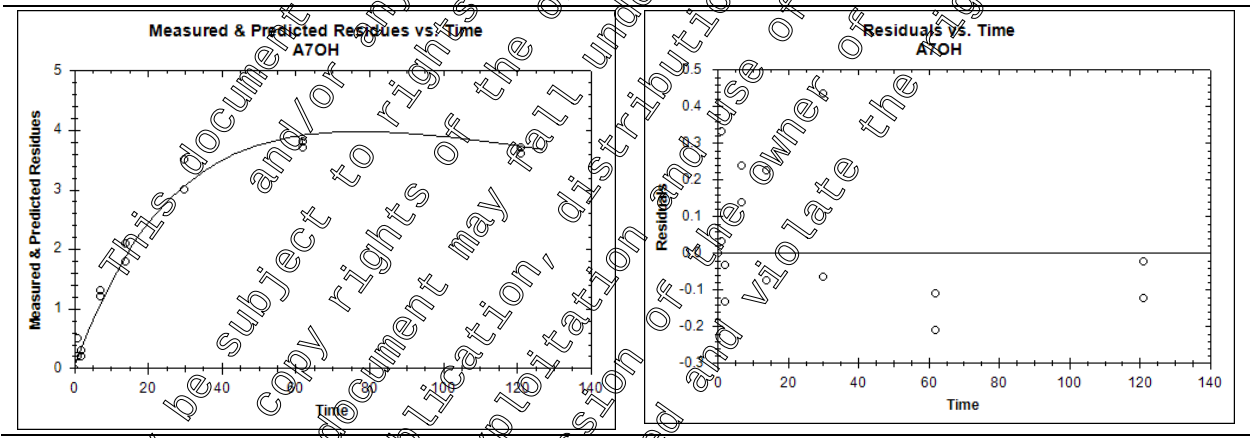


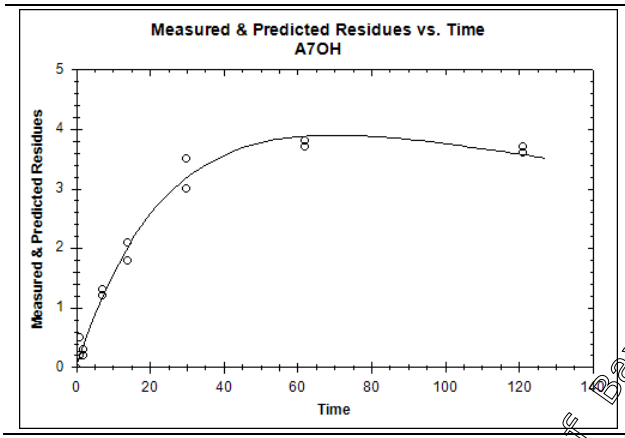
Table 7.1.2.1.1-26: FLU-7-OH (M-298296-01-1): kinetic and statistical results of degradation in soil Laacherhof AXXa for trigger endpoints, pathway fit

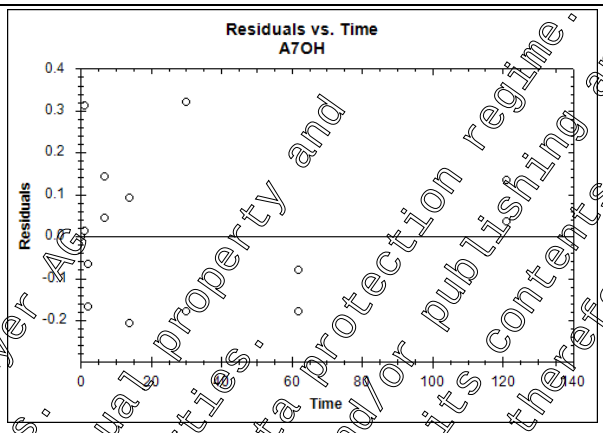
Kinetic model, Parent - metabolite	DT_{50} actual	DT_{90} actual	VA	χ^2err	SWARC	k	t-test k	95th CI of k	FF (FLU)
	(d)	(d)		(%)	(-)	(1/d)	(-)	(1/d)	(-)
SFO - SFO	17.54	58.26	+	4.15	0	0.03952	<0.001	0.03419 to 0.045	0.6430

VA = visual assessment, + = good, o = acceptable, - = poor
SWARC = Scaled Weighted Area under Residue Curve
CI = confidence intervall

Trigger Endpoints: SFO fit (parent SFO) is statistically (χ^2err, t-test) and visually good. Consequently, **SFO** degradation model (**parent SFO**) is appropriate for trigger endpoints.

SFO/SFO





Laacherhof Wurmwiese

Table 7.1.2.1.1-27: FLU-7-OH (M-298296-01-1): kinetic and statistical results of degradation in soil Laacherhof Wurmwiese for modelling endpoints

Kinetic model, Parent - metabolite	DT_{50} actual	DT_{90} actual	VA	χ^2err	SWARC	k	t-test k	95th CI of k	ff (FLU)
	(d)	(d)		(%)	(-)	(1/d)	(-)	(1/d)	(-)
SFO - SFO, free fit	12.61	41.9	+	6.05	2.05	0.05495	<0.001	0.04555 to 0.064	1.0000
DFOP - SFO	27.42	91.1	+	5.46	2.20	0.02528	0.050	-0.00370 to 0.054	0.5499
SFO - SFO, fixed fit	**15.22** fix	50.6 fix	+	7.25	11.0	0.04555	-	-	**0.8690**

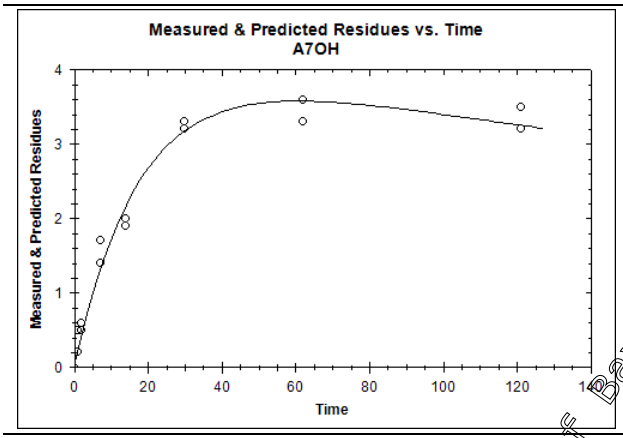
VA = visual assessment, + = good, o = acceptable, - = poor
SWARC = Scaled Weighted Area under Residue-Curve
CI = confidence intervall
fixed fit: parent parameters fixed to free fit values, DT50 FLU-7-OH fixed to 95th CI rate of free fit.

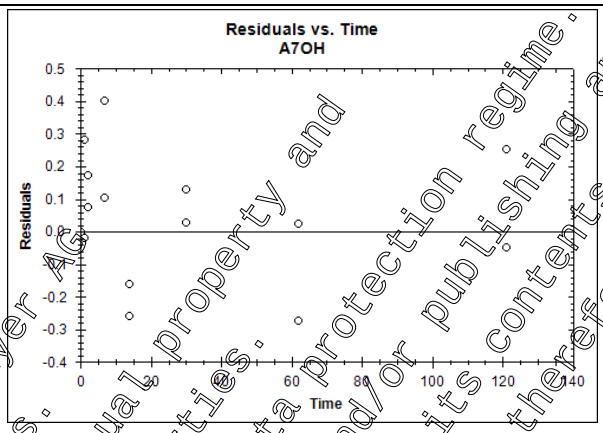
Modelling Endpoints: SFO fit (parent SFO) is statistically and visually good (χ^2err <25%, t-test < 0.1, SWARC <40). Formation fraction ff from fluopyram to FLU-7-OH = 1. Therefore, DFOP parent/SFO metabolite was tested. However, DFOP parent/SFO metabolite shows no significant improvement of the fit and weight of evidence still supports parent SFO, as χ^2err and SWARC values of parent and metabolite are very good, t-test is <0.1. Consequently, SFO degradation model (parent SFO) is appropriate for modelling endpoints.

However, metabolite FLU-7-OH is rising until the end of study (last 4 time points). The pathway fit (free fit) was therefore modified with a fixed DT_{50} value for FLU-7-OH (fixed fit). The DT_{50} of FLU-7-OH was fixed to a conservative value (95% confidence interval k of free fit), formation fractions were fitted and parent parameters were fixed to values derived from the free fit. Finally, this **fixed SFO** degradation model (**parent SFO**) is considered conservatively appropriate for modelling endpoints.

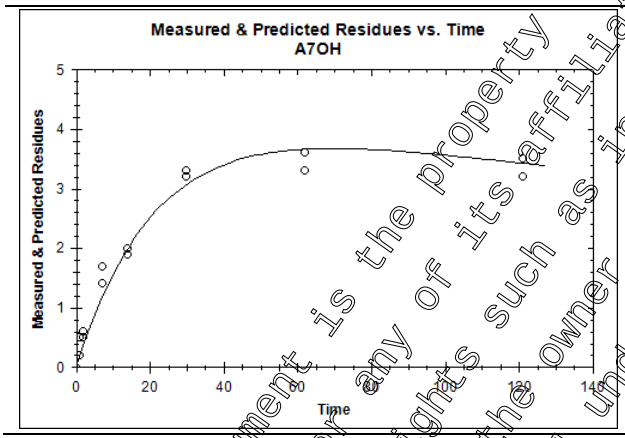
In addition, a more conservative fixed DT_{50} of 1000 d for FLU-7-OH was checked, which clearly shows an over-prediction of the metabolite residues and is therefore not appropriate

SFO free/SFO free





SFO fixed/SFO fixed



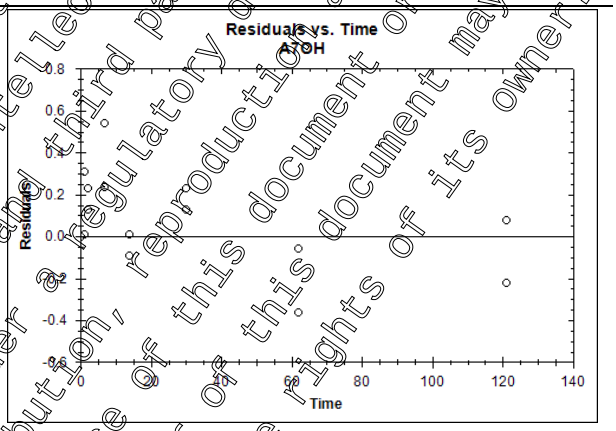


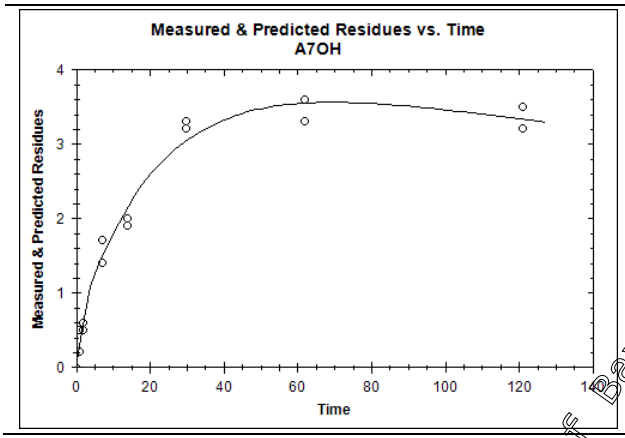
Table 7.1.2.1.1-28: FLU-7-OH (M-298296-01-1): kinetic and statistical results of degradation in soil Laacherhof Wurmwiese for trigger endpoints

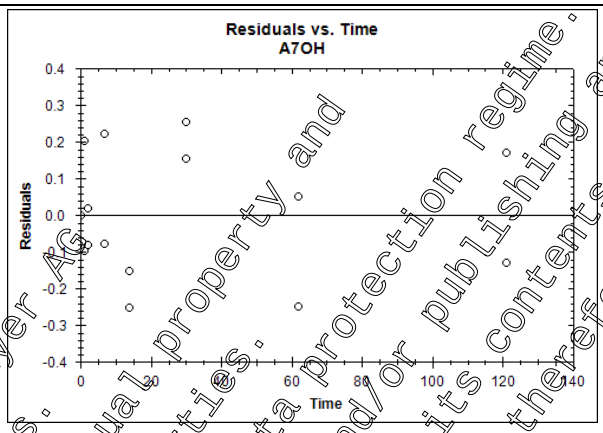
Kinetic model, Parent - metabolite	DT_{50} actual	DT_{90} actual	VA	χ^2 err	SWARC	k	t-test k	95th CI of k	FF (FLU)
	(d)	(d)		(%)	(-)	(1/d)	(-)	(1/d)	(-)
SFO - SFO	**12.61**	**41.9**	+	6.05	2.05	0.05495	<0.001	0.04555 to 0.064	1.0000

VA = visual assessment, + = good, o = acceptable, - = poor
SWARC = scaled Weighted Area under Residue Curve
CI = confidence intervall

Trigger Endpoints: SFO fit (parent SFO) is statistically (χ² err, t-test) and visually good. Consequently, **SFO** degradation model (**parent SFO**) is appropriate for trigger endpoints.

SFO/SFO





Laacherhof AIIIa

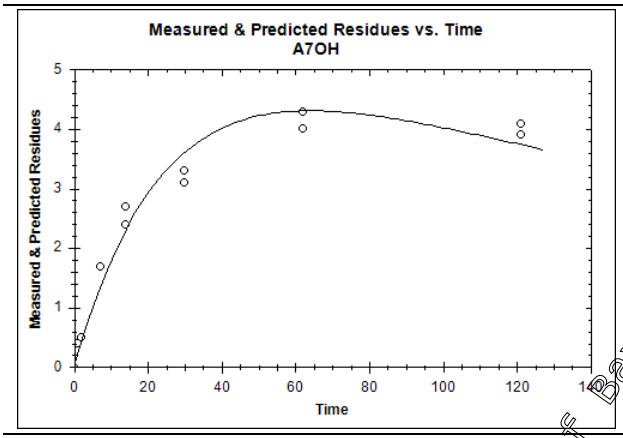
Table 7.1.2.1.1-29: FLU-7-OH (M-298296-01-1): kinetic and statistical results of degradation in soil Laacherhof AIIIa for modelling endpoints

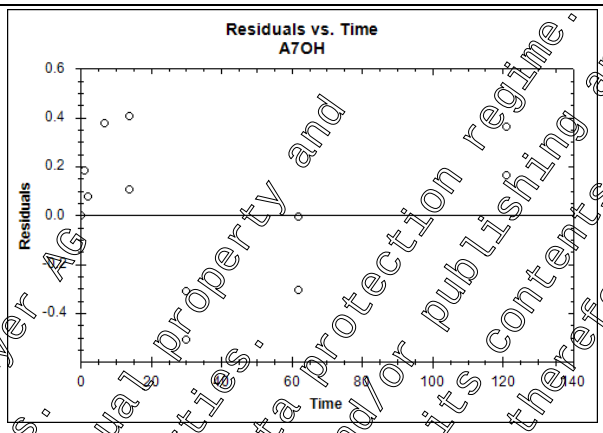
Kinetic model, Parent - metabolite	DT_{50} actual	DT_{90} actual	VA	χ^2err	SWARC	k	t-test k	95th CI of k	ff (FLU)
	(d)	(d)		(%)	(-)	(1/d)	(-)	(1/d)	(-)
SFO - SFO, free fit	17.83	59.23	+	9.06	24.6	0.03887	<0.001	0.03143 to 0.046	0.5342
DFOP - SFO	31.77	1055	+	3.25	0.420	0.02182	<0.001	0.01618 to 0.027	0.3384
SFO - SFO, fixed fit	**22.05** fix	73.26 fix	+	9.70	33.9	0.03143	-	-	**0.4603**

VA = visual assessment, + = good, o = acceptable, - = poor
SWARC = Scaled Weighted Area under Residue-Curve
CI = confidence intervall
fixed fit: parent parameters fixed to free fit values, DT50 FLU-7-OH fixed to 95th CI rate of free fit.

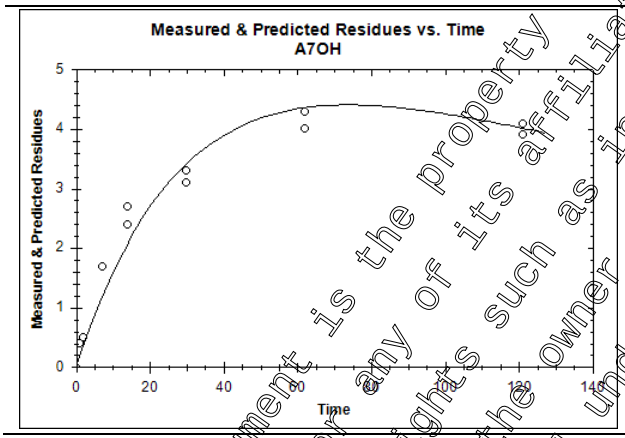
Modelling Endpoints: SFO fit (parent SFO) is statistically and visually good (χ^2err <25%, t-test < 0.1, formation fraction ff is <1, SWARC <40). Consequently, SFO degradation model (parent SFO) is appropriate for modelling endpoints.
However, metabolite FLU-7-OH is rising until the end of study (last 4 time points). The pathway fit (free fit) was therefore modified with a fixed DT_{50} value for FLU-7-OH (fixed fit). The DT_{50} of FLU-7-OH was fixed to a conservative value (95% confidence interval k of free fit), formation fractions were fitted and parent parameters were fixed to values derived from the free fit. Finally, this **fixed SFO** degradation model (**parent SFO**) is considered conservatively appropriate for modelling endpoints.
In addition, a more conservative fixed DT_{50} of 1000 d for FLU-7-OH was checked, which clearly shows an over-prediction of the metabolite residues and is therefore not appropriate.

SFO free/SFO free





SFO fixed/SFO fixed



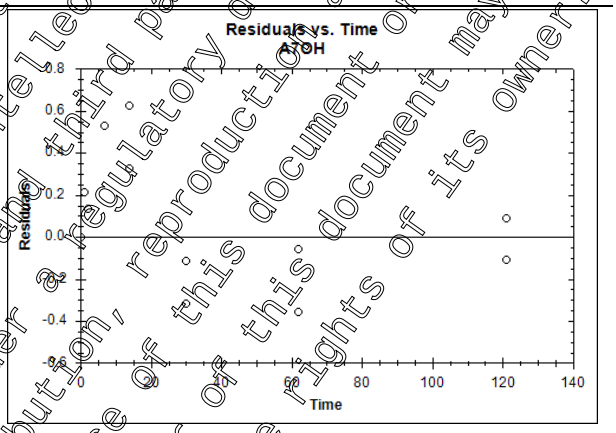


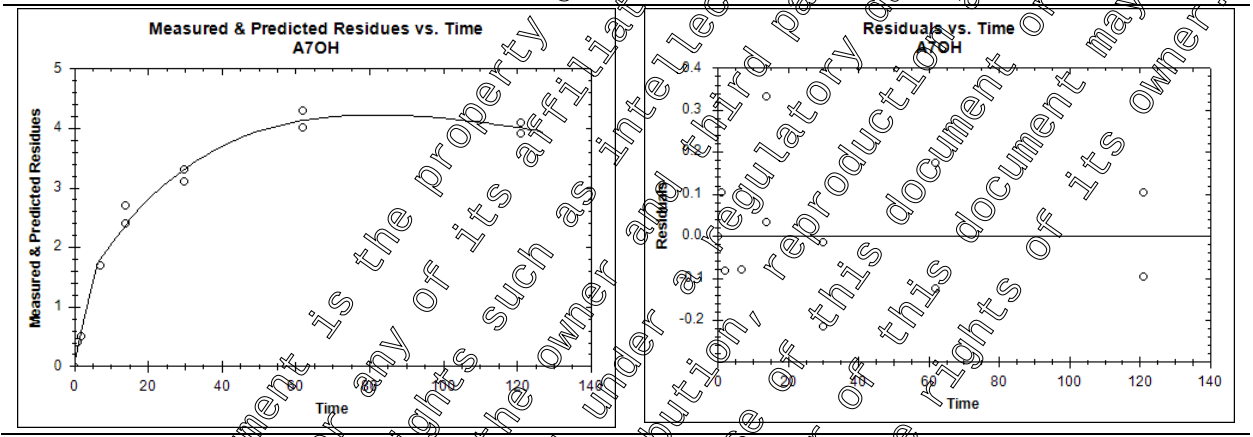
Table 7.1.2.1.1-30: FLU-7-OH (M-298296-01-1): kinetic and statistical results of degradation in soil Laacherhof AIIIa for trigger endpoints, pathway fit

Kinetic model, Parent - metabolite	DT_{50} actual	DT_{90} actual	VA	χ^2err	SWARC	k	t-test k	95th CI of k	FF (FLU)
	(d)	(d)		(%)	(-)	(1/d)	(-)	(1/d)	(-)
HS - SFO	**29.28**	**97.27**	+	3.39	0.929	0.02367	<0.001	0.0191 to 0.028	0.3589

VA = visual assessment, + = good, o = acceptable, - = poor
SWARC = Scaled Weighted Area under Residue Curve
CI = confidence intervall

Trigger Endpoints:	SFO fit (parent HS) is statistically (χ^2err, t-test) and visually good. Consequently, **SFO** degradation model (**parent HS**) is appropriate for trigger endpoints.

HS/SFO



Hoefchen am Hohenseh

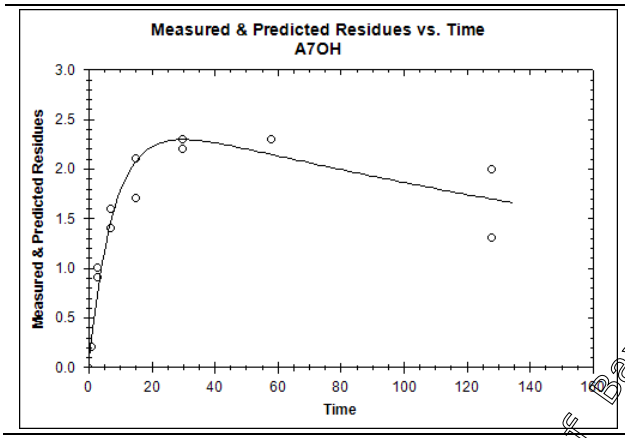
Table 7.1.2.1.1-31: FLU-7-OH (M-298413-01-1): kinetic and statistical results of degradation in soil Hoefchen am Hohenseh for modelling endpoints

Kinetic model, Parent - metabolite	DT_{50} actual	DT_{90} actual	VA	χ^2err	SWARC	k	t-test k	95th CI of k	ff (FLU)
	(d)	(d)		(%)	(-)	(1/d)	(-)	(1/d)	(-)
SFO - SFO	**5.618**	18.7	+	6.11	2.76	0.12340	<0.001	0.09225 to 0.154	**0.9528**
DFOP - SFO	12.98	43.1	+	5.16	3.32	0.05339	<0.001	0.02584 to 0.081	0.4392

VA = visual assessment, + = good, o = acceptable, - = poor
SWARC = Scaled Weighted Area under Residue Curve
CI = confidence intervall

Modelling Endpoints:	SFO fit (parent SFO) is statistically and visually good (χ^2err <25%, t-test < 0.1, formation fraction ff is <1, SWARC <40). Consequently, **SFO** degradation model (**parent SFO**) is appropriate for modelling endpoints. The metabolite FLU-7-OH is decreasing until the end of study (last 4 time points). Therefore, the free fitted **DT_{50} of 5.62 d is considered as a “reliable DT_{50}”.**

SFO/SFO



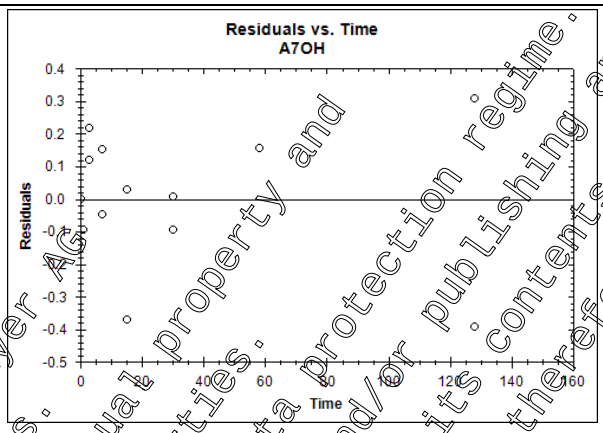


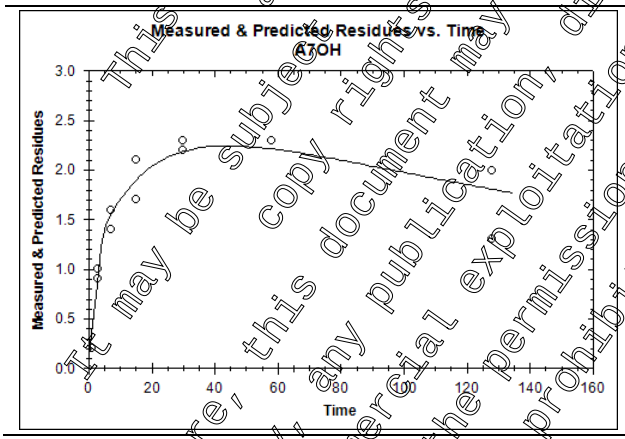
Table 7.1.2.1.1-32: FLU-7-OH (M-298413-01-1): kinetic and statistical results of degradation in soil Hoefchen am Hohensch for trigger endpoints, pathway fit

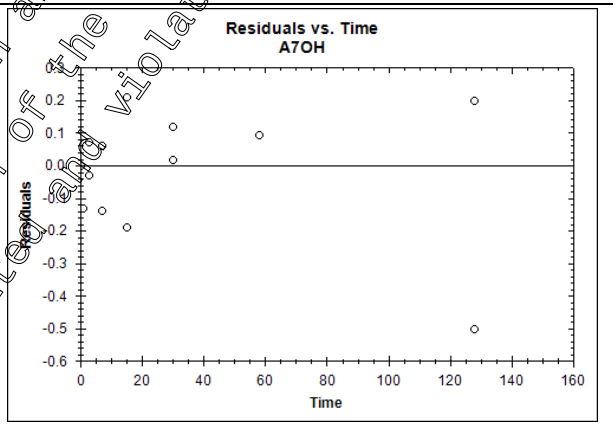
Kinetic model, Parent - metabolite	DT_{50} actual	DT_{90} actual	VA	χ^2err	SWARC	k	t-test k	95th CI of k	FF (FLU)
	(d)	(d)		(%)	(-)	(1/d)	(-)	(1/d)	(-)
HS - SFO	**12.07**	**40.1**		4.61	7.55	0.05742	<0.001	0.02910 to 0.086	0.4698

VA = visual assessment, + = good, o = acceptable, - = poor
SWARC = Scaled Weighted Area under Residue Curve
CI = confidence intervall

Trigger Endpoints: SFO fit (parent HS) is statistically (χ^2err, t-test) and visually good. Consequently, **SFO** degradation model (**parent HS**) is appropriate for trigger endpoints.

HS/SFO





Laacherhof AXXa

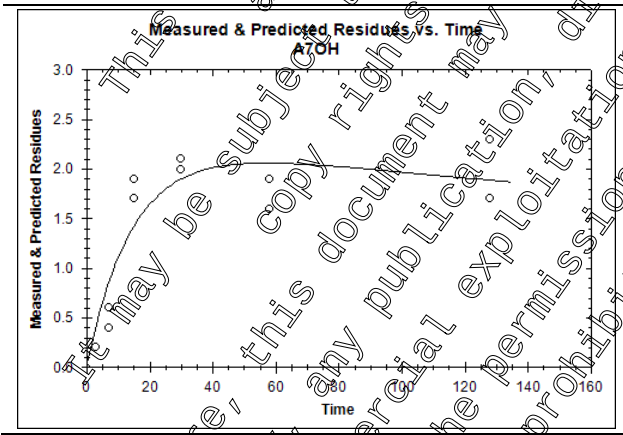
Table 7.1.2.1.1-33: FLU-7-OH (M-298413-01-1): kinetic and statistical results of degradation in soil Laacherhof AXXa for modelling endpoints

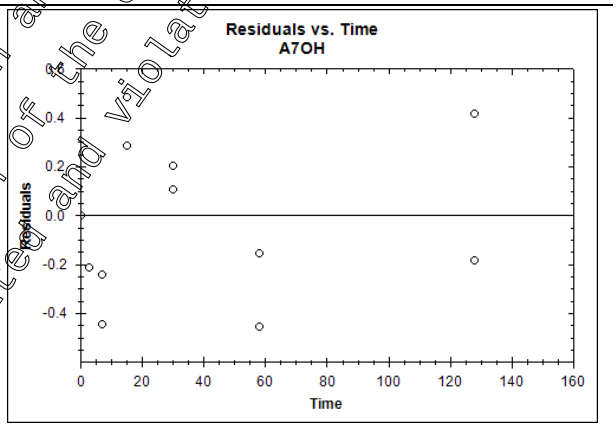
Kinetic model, Parent - metabolite	DT_{50} actual	DT_{90} actual	VA	χ^2err	SWARC	k	t-test k	95th CI of k	ff (FLU)
	(d)	(d)		(%)	(-)	(1/d)	(-)	(1/d)	(-)
SFO - SFO, free fit	10.22	34.0	+	15.6	11.3	0.06781	<0.001	0.03696 to 0.099	1.0000
DFOP - SFO	42.32	141	+	15.5	11.7	0.01638	0.004	0.00532 to 0.027	0.3209
SFO - SFO, fixed fit	**18.75** fix	62.3 fix	o	20.0	44.8	0.03696	-		**0.6294**

VA = visual assessment, + = good, o = acceptable, - = poor
SWARC = Scaled Weighted Area under Residue Curve
CI = confidence intervall
fixed fit: parent parameters fixed to free fit values, DT50 FLU-7-OH fixed to 95th CI rate of free fit.

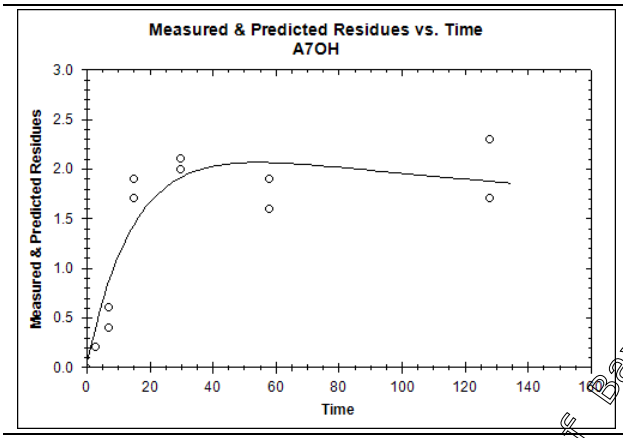
Modelling Endpoints: SFO fit (parent SFO) is statistically and visually good (χ^2err <25%, t-test < 0.1, SWARC <40). Formation fraction ff from fluopyram to FLU-7-OH = 1. Therefore, DFOP parent/SFO metabolite was tested. However, DFOP parent/SFO metabolite shows no significant improvement of the fit and weight of evidence still supports parent SFO as χ^2err and SWARC values of parent and metabolite are very good, t-test is <0.1. Consequently, SFO degradation model (parent SFO) is appropriate for modelling endpoints.
However, metabolite FLU-7-OH is rising until the end of study (last 4 time points). The pathway fit (free fit) was therefore modified with a fixed DT_{50} value for FLU-7-OH (fixed fit). The DT_{50} of FLU-7-OH was fixed to a conservative value (95% confidence interval k of free fit), formation fractions were fitted and parent parameters were fixed to values derived from the free fit. Finally, this **fixed SFO** degradation model (**parent SFO**) is considered conservatively appropriate for modelling endpoints.
In addition, a more conservative fixed DT_{50} of 1000 d for FLU-7-OH was checked, which clearly shows an overprediction of the metabolite residues and is therefore not appropriate

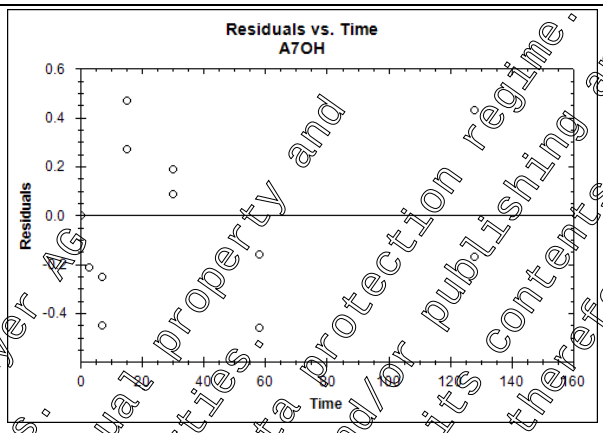
SFO free/SFO free



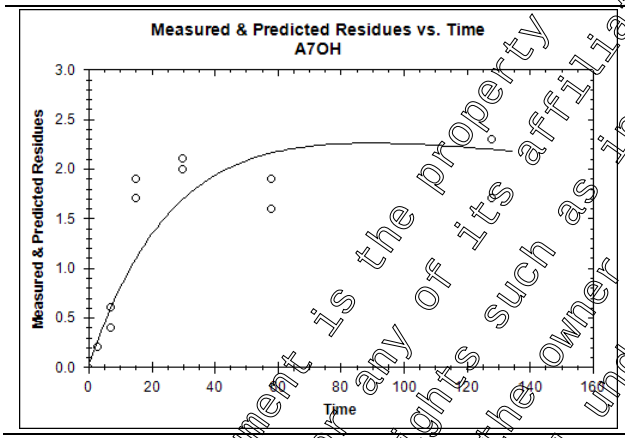


DFOP/SFO





SFO fixed/SFO fixed



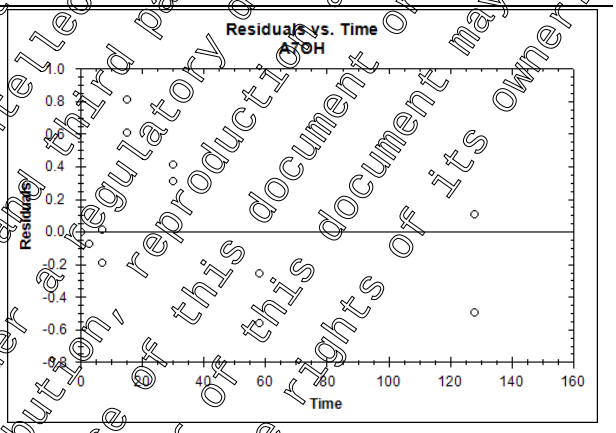


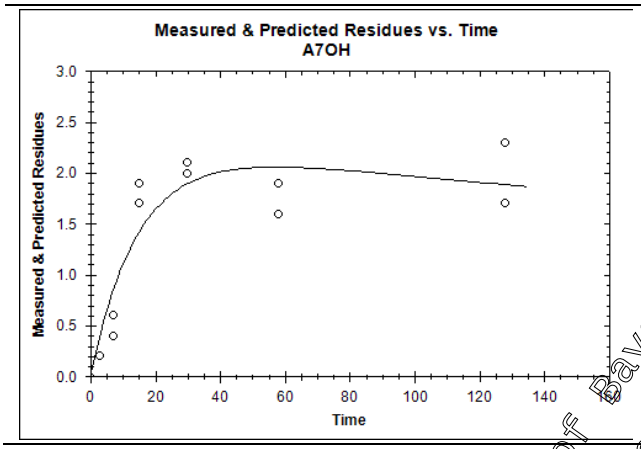
Table 7.1.2.1.1-34: FLU-7-OH (M-298413-01-1): kinetic and statistical results of degradation in soil Laacherhof AXXa for trigger endpoints, pathway fit

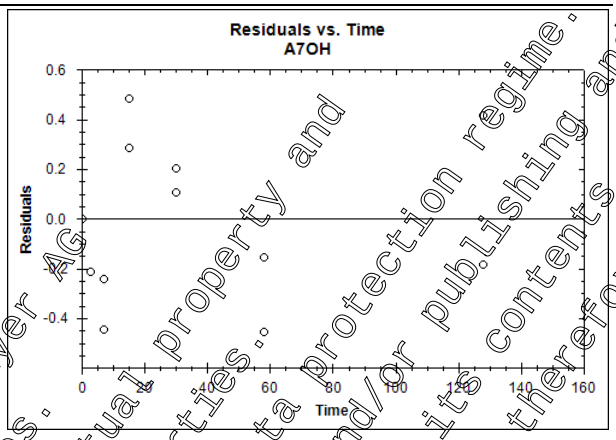
Kinetic model, Parent - metabolite	DT_{50} actual	DT_{90} actual	VA	χ^2 err	SWARC	k	t-test k	95th CI of k	FF (FLU)
	(d)	(d)		(%)	(-)	(1/d)	(-)	(1/d)	(-)
SFO - SFO	**10.22**	**34.0**	+	18.6	11.3	0.06781	<0.001	0.03696 to 0.099	1.0000

VA = visual assessment, + = good, o = acceptable, - = poor
SWARC = Scaled Weighted Area under Residue Curve
CI = confidence intervall

Trigger Endpoints: SFO fit (parent SFO) is statistically (χ² err, t-test) and visually good. Consequently, **SFO** degradation model (**parent SFO**) is appropriate for trigger endpoints.

HS/SFO





Laacherhof Wurmwiese

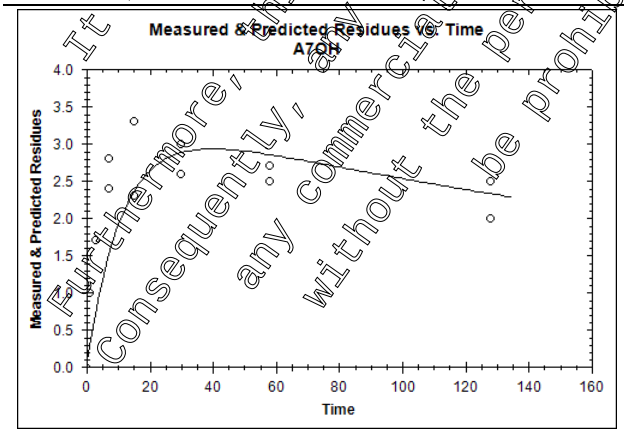
Table 7.1.2.1.1-35: FLU-7-OH (M-298413-01-1): kinetic and statistical results of degradation in soil Laacherhof Wurmwiese for modelling endpoints

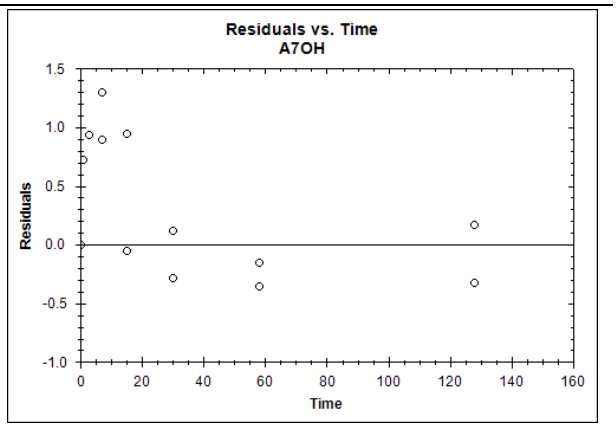
Kinetic model, Parent - metabolite	DT_{50} actual	DT_{90} actual	VA	χ^2err	SWARC	k	t-test k	95th CI of k	ff (FLU)
	(d)	(d)		(%)	(-)	(1/d)	(-)	(1/d)	(-)
SFO - SFO	**7.865**	26.1	o	22.6	76.2	0.08813	0.002	0.03305 to 0.143	**1.00**
DFOP - SFO	13.35	44.4	+	3.06	1.99	0.05190	0.001	0.02134 to 0.082	0.6121

VA = visual assessment, + = good, o = acceptable, - = poor
SWARC = Scaled Weighted Area under Residue Curve
CI = confidence intervall

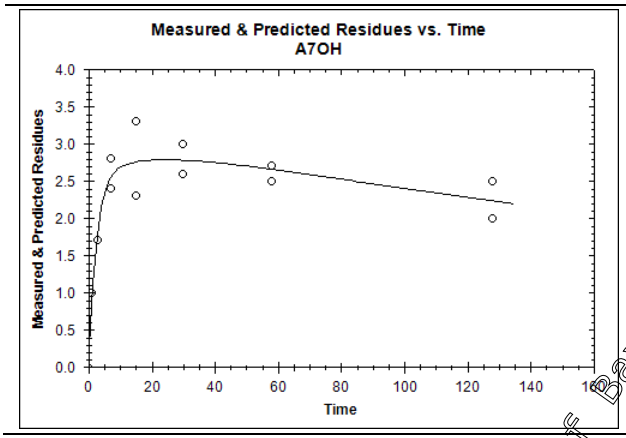
Modelling Endpoints: SFO fit (parent SFO) is statistically and visually acceptable (χ^2err <25%, t-test < 0.1). Only the SWARC value is > 40 for FLU-7-OH. Formation fraction ff from fluopyram to FLU -7-OH = 1. Therefore, DFOP parent/SFO metabolite was tested. However, DFOP parent/SFO metabolite shows no significant improvement of the fit and weight of evidence still supports parent SFO, as χ^2err and SWARC values of parent are very good. T-test of FLU-7-OH is <0.1. Consequently, **SFO** degradation model (**parent SFO**) is appropriate for modelling endpoints.
The metabolite FLU-7-OH is decreasing until the end of study (last 4 time points). Therefore, the **DT_{50} of 7.87 d is considered as a "reliable DT_{50}".**

SFO/SFO





DFOP/SFO



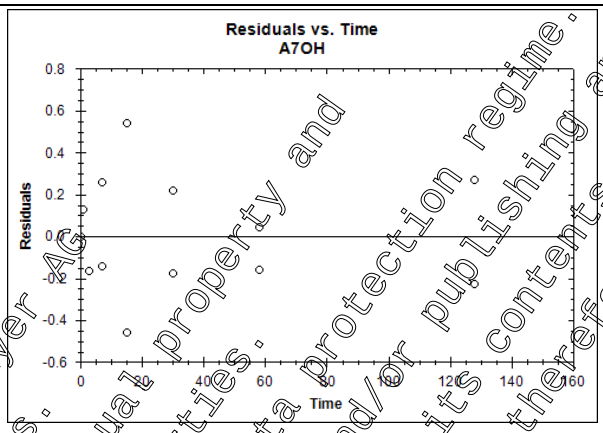


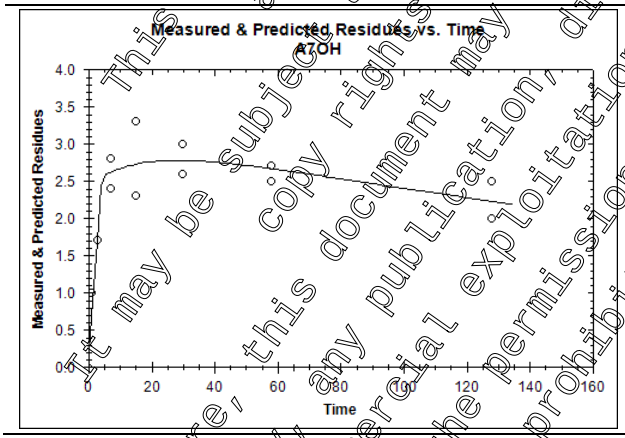
Table 7.1.2.1.1-36: FLU-7-OH (M-298413-01-1): kinetic and statistical results of degradation in soil Laacherhof Wurmwiese for trigger endpoints

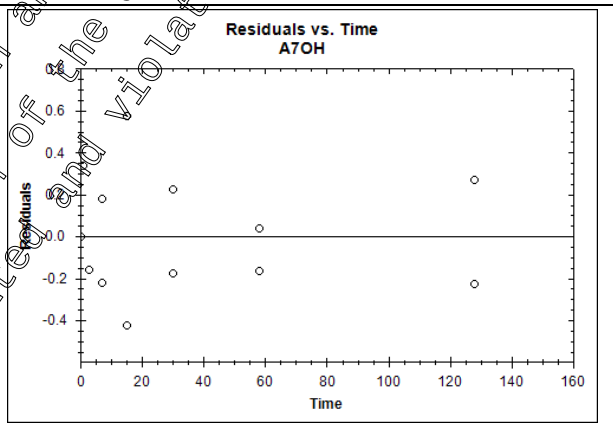
Kinetic model, Parent - metabolite	DT_{50} actual	DT_{90} actual	VA	χ^2 err	SWARC	k	t-test k	95th CI of k	FF (FLU)
	(d)	(d)		(%)	(-)	(1/d)	(-)	(1/d)	(-)
HS - SFO	**11.92**	**39.6**		5.17	1.20	0.05816	0.003	0.02009 to 0.096	0.6829

VA = visual assessment, + = good, o = acceptable, - = poor
SWARC = Scaled Weighted Area under Residue Curve
CI = confidence intervall

Trigger Endpoints: SFO fit (parent HS) is statistically (χ^2 err, t-test) and visually good. Consequently, **SFO** degradation model (**parent HS**) is appropriate for trigger endpoints.

HS/SFO





Dollendorf II

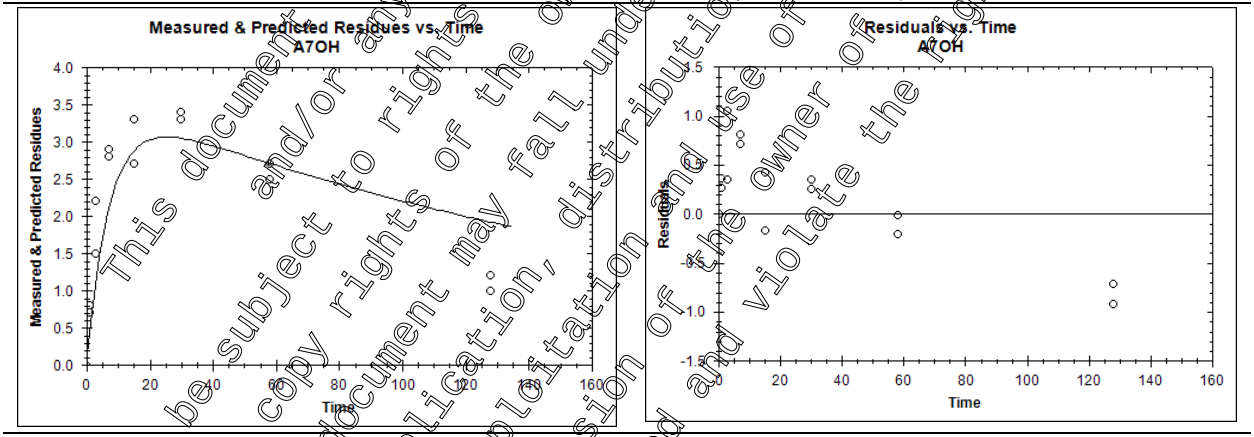
Table 7.1.2.1.1-37: FLU-7-OH (M-298413-01-1): kinetic and statistical results of degradation in soil Dollendorf II for modelling endpoints

Kinetic model, Parent - metabolite	DT_{50} actual	DT_{90} actual	VA	χ^2err	SWARC	k	t-test k	95th CI of k	ff (FLU)
	(d)	(d)		(%)	(-)	(1/d)	(-)	(1/d)	(-)
SFO - SFO	**5.109**	17.0	o	19.0	70.2	0.13570	<0.001	0.06540 to 0.206	**1.00**
DFOP - SFO	13.75	45.7	o	12.0	9.81	0.05042	<0.001	0.02496 to 0.076	0.3927

VA = visual assessment, + = good, o = acceptable, - = poor
SWARC = Scaled Weighted Area under Residue Curve
CI = confidence intervall

Modelling Endpoints: SFO fit (parent SFO) is statistically and visually acceptable (χ^2err < 25%, t-test < 0.1). Only the SWARC value is > 40 for FLU-7-OH. Formation fraction ff from fluopyram to FLU-7-OH = 1. Therefore, DFOP parent/SFO metabolite was tested. However, DFOP parent/SFO metabolite shows no significant improvement of the fit. Quite the contrary, the visual fit of FLU-7-OH is worse than SFO parent/SFO metabolite and weight of evidence still supports parent SFO as χ^2err and SWARC values of parent are very good. T-test of FLU-7-OH is <0.1. Consequently, **SFO** degradation model (**parent SFO**) is appropriate for modelling endpoints.
The metabolite FLU-7-OH is decreasing until the end of study (last 4 time points). Therefore, the **DT_{50} of 5.11 d is considered as a "reliable DT_{50}".**

SFO/SFO



DFOP/SFO

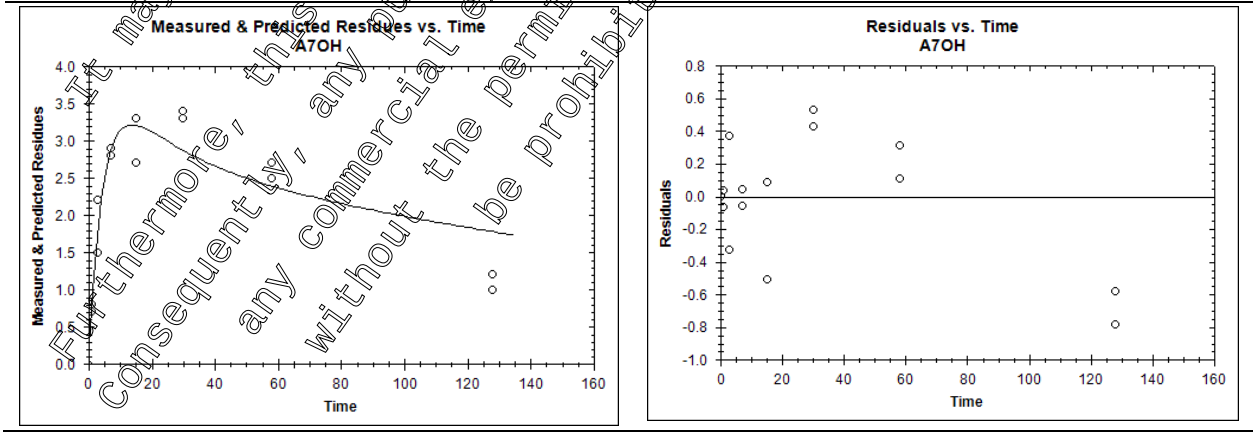


Table 7.1.2.1.1-38: FLU-7-OH (M-298413-01-1): kinetic and statistical results of degradation in soil Dollendorf II for trigger endpoints

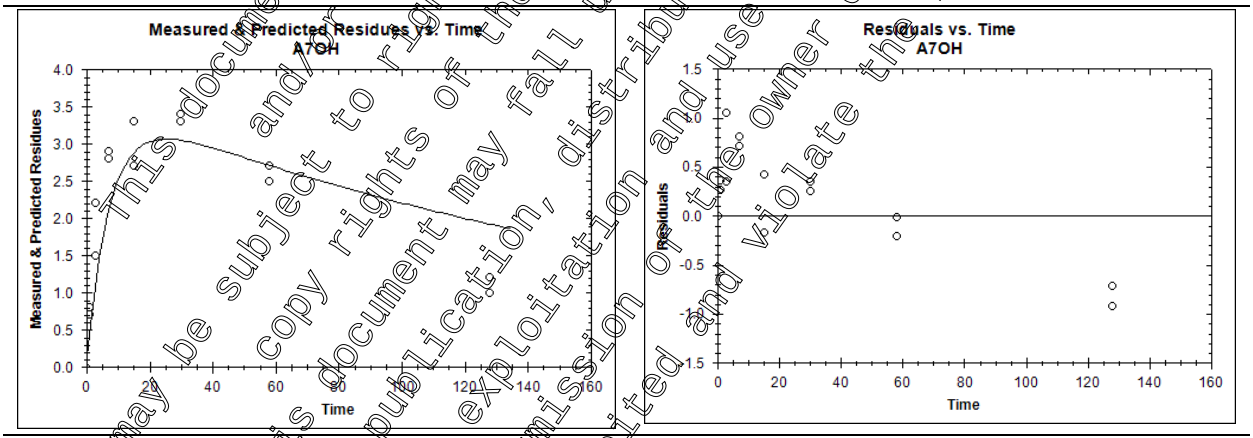
Kinetic model, Parent - metabolite	DT_{50} actual	DT_{90} actual	VA	χ^2err	SWARC	k	t-test k	95th CI of k	FF (FLU)
	(d)	(d)		(%)	(-)	(1/d)	(-)	(1/d)	(-)
SFO - SFO (pathway fit)	**5.109**	**17.0**	o	19.0	70.2	0.13570	<0.001	0.00546 to 0.206	1.00
HS - SFO (pathway fit)	13.84	46.0	-	13.6	28.4	0.05009	<0.001	0.02405 to 0.076	0.3941
SFO (decline fit)	63.2	210	+	2.74	0	0.01097	<0.001	0.00928 to 0.013	

VA = visual assessment, + = good, o = acceptable, - = poor
SWARC = Scaled Weighted Area under Residue Curve
CI = confidence intervall

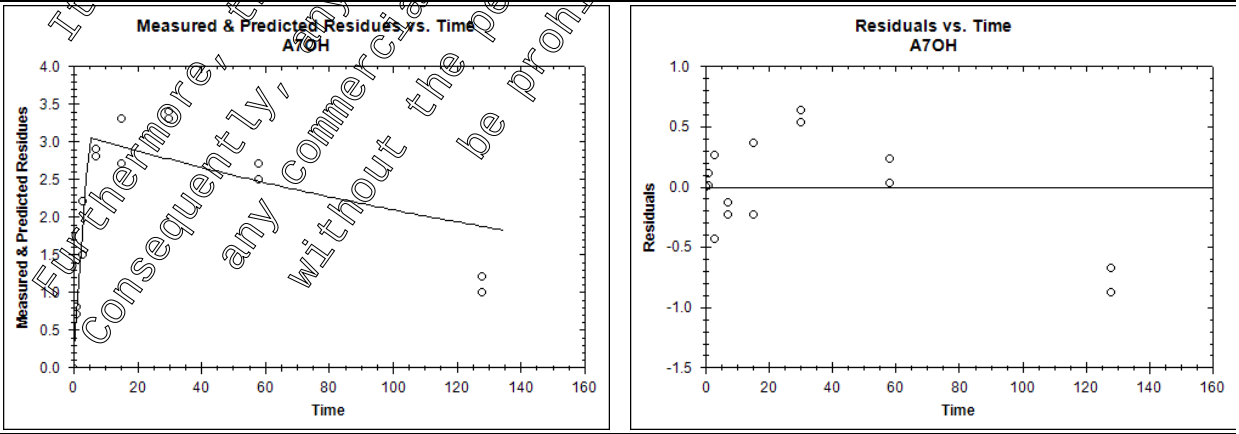
Trigger Endpoints: SFO fit (parent SFO) is statistically (χ^2err, t-test) and visually acceptable.
For parent, also HS is statistically and visually good. However, the pathway fit for the metabolite FLU-7-OH is visually very poor assuming parent HS, but significantly better with parent SFO. Consequently, **SFO** degradation model (**parent SFO**) is considered appropriate for trigger endpoints.

Alternatively, a decline SFO fit was tested and is statistically (χ^2err, t-test) and visually good. However, the decline fit delivers only a dissipation $DisT_{50}$ and not a description of the simultaneous formation and degradation of the metabolite. Therefore, a conservative $DisT_{50}$ is not perfectly appropriate for trigger purpose and should not be over-interpreted.
Consequently, **SFO** degradation model (**parent SFO**) $DegT_{50}$ is considered most appropriate here for the fast degrading metabolite FLU-7-OH.

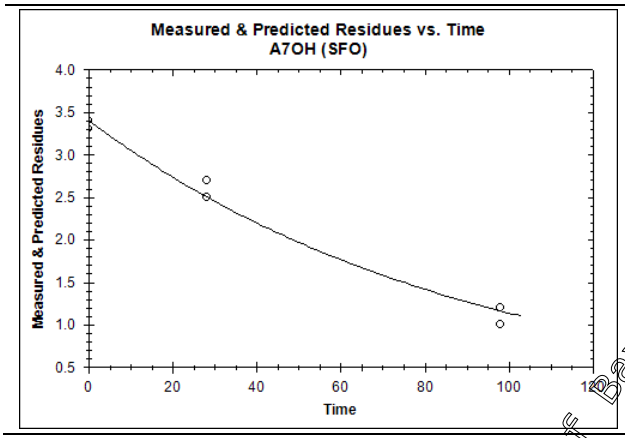
SFO/SFO

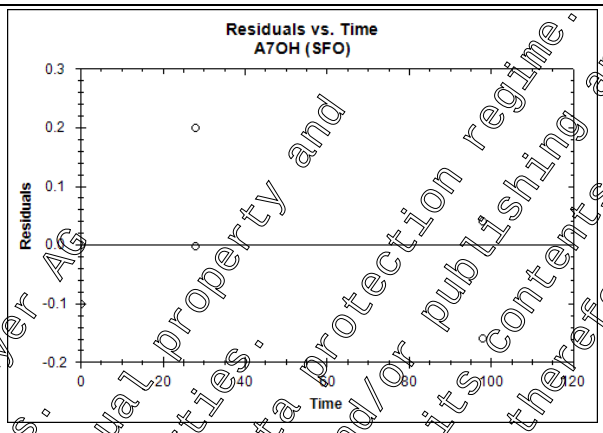


HS/SFO



SFO decline





III. CONCLUSIONS

Moisture and temperature correction factors to normalise DT_{50} values to a moisture of pF2 and 20°C are summarised in the following.

Table 7.1.2.1.1-39: Moisture and temperature correction factors $f_\theta \cdot f_T$ for DT_{50} normalisation (reference moisture at pF 2, 20°C), (FOCUS field capacity, θ_{ref}: default of reference soil moisture, pF2, as in FOCUS, 2014b; MWHC: maximum water holding capacity)

Soil	Soil texture (USDA)	Study moist. (% MWHC)	MWHC (g/100 g)	Study moist. θ (g/100 g)	Study temp. T (°C)	FOCUS field capacity θ_{ref} (g/100 g)	f_θ (-)	f_T (-)	$f_\theta \cdot f_T$ (-)
Hoefchen am Hohenseh [1]	Silt loam	55	63.2	34.8	20	26	1	1	1
Laacherhof AXXa [1]	Sandy loam	55	48.6	26.7	20	19	1	1	1
Laacherhof Wurmwiese [1]	Loam	55	68.5	37.7	20	25	1	1	1
Laacherhof AHla [1]	Loam	55	51.6	28.4	20	25	1	1	1
Hoefchen am Hohenseh [2]	Silt loam	55	59.4	32.7	20	26	1	1	1
Laacherhof AXXa [2]	Sandy loam	55	48.4	26.6	20	19	1	1	1
Laacherhof Wurmwiese [2]	Sandy loam	55	55.5	30.5	20	19	1	1	1
Dollendorf II [2]	Clay loam	55	84.6	46.5	20	28	1	1	1

[1] M-298296-01-1
[2] M-298413-01-1

Kinetic parameters

Table 7.1.2.1.1-40: Laboratory soil $DegT_{50}$ parameters of fluopyram for modelling purpose (normalised: pF2, 20°C, Q10 2.58)

Fluopyram (FLU)	Dark aerobic conditions						
Soil type (USDA)		**pH ($CaCl_2$)**	**T (C°) / % MWHC**	**$DegT_{50\ actual}$ / $DT_{90\ actual}$ (d)**	**$DegT_{50\ mod}$ (d) 20°C, pF2 / 10 kPa [3]**	**St. (χ^2)**	**Method of calculation**
Silt loam, Hoefchen am Hohenseh [1]		6.6	20 / 55	214.3 / 712.0	214.3	1.67	SFO
Sandy loam, Laacherhof AXXa [1]		6.6	20 / 55	223.7 / 743.3	223.7	1.19	SFO
Loam, Laacherhof Wurmwiese [1]		5.5	20 / 55	307.7 / >1000	307.7	1.81	SFO
Loam, Laacherhof AIIIa [1]		6.6	20 / 55	163.2 / 542.0	163.2	1.06	SFO
Silt loam, Hoefchen am Hohenseh [2]		6.7	20 / 55	205.2 / 682	205.2	1.15	SFO
Sandy loam, Laacherhof AXXa [2]		6.2	20 / 55	441.5 / >1000	441.5	1.32	SFO
Sandy loam, Laacherhof Wurmwiese [2]		5.2	20 / 55	230.97 / 767	230.97	1.38	SFO
Clay loam, Dollendorf II [2]		7.5	20 / 55	141.1 / 469	141.1	2.64	SFO

[1] M-298296-01-1
[2] M-298413-01-1
[3] Normalised using a Q10 of 2.58 and Walker equation coefficient of 0.7

Table 7.1.2.1.1-41: Laboratory soil $DegT_{50}$ parameters of fluopyram for trigger purpose

Fluopyram (FLU)	**Dark aerobic conditions**						
Soil type (USDA)		**pH ($CaCl_2$)**	**T (C°) / % MWHC**	**$DegT_{50\ actual}$ / $DT_{90\ actual}$ (d)**	**$DegT_{50\ mod}$ (d) 20°C pF2 / 10 kPa [3]**	**St. (χ^2)**	**Method of calculation**
Silt loam, Hoefchen am Hohenseh [1]		6.6	20 / 55	209.3 / 739		1.01	HS
Sandy loam, Laacherhof AXXa [1]		6.6	20 / 55	221.9 / 737		1.25	SFO
Loam, Laacherhof Wurmwiese [1]		5.5	20 / 55	320.8 / >1000		1.89	SFO
Loam, Laacherhof AIIIa [1]		6.6	20 / 55	160.5 / 552		0.779	HS
Silt loam, Hoefchen am Hohenseh [2]		6.7	20 / 55	213.9 / 732		1.13	HS
Sandy loam, Laacherhof AXXa [2]		6.2	20 / 55	444.5 / >1000		1.39	SFO
Sandy loam, Laacherhof Wurmwiese [2]		5.2	20 / 55	245 / 843		1.06	HS
Clay loam, Dollendorf II [2]		7.3	20 / 55	156.9 / 526		2.37	SFO

[1] M-298296-01-1
[2] M-298413-01-1
[3] Normalised using a Q10 of 2.58 and Walker equation coefficient of 0.7

Table 7.1.2.1.1-42: Laboratory soil $DegT_{50}$ parameters of fluopyram-7-hydroxy for modelling purpose (normalised: pF2, 20°C, Q10 2.58)

fluopyram-7-hydroxy (FLU-7-OH)	Dark aerobic conditions Formation from parent fluopyram in pathway fit							
Soil type (USDA)		**pH ($CaCl_2$)**	**T (C°) / % MWHC**	**$DegT_{50}$ actual / DT_{90} actual (d)**	**$DegT_{50}$ mod (d) 20°C pF2 / 10 kPa [3]**	**ff (FLU-7-OH)**	**St. (χ^2)**	**Method of calculation parent - metabolite**
Silt loam, Hoefchen am Hohenseh [1]		6.6	20 / 55	18.04 / 59.93	18.04	0.4837	10.3	SFO-SFO (95th CI rate fixed)
Sandy loam, Laacherhof AXXa [1]		6.6	20 / 55	20.27 / 67.35	20.27	0.5798	5.22	SFO-SFO (95th CI rate fixed)
Loam, Laacherhof Wurmwiese [1]		5.5	20 / 55	15.22 / 50.6	15.22	0.8690	7.35	SFO-SFO (95th CI rate fixed)
Loam, Laacherhof AIIIa [1]		6.6	20 / 55	22.05 / 73.26	22.05	0.4693	9.70	SFO-SFO (95th CI rate fixed)
Silt loam, Hoefchen am Hohenseh [2]		6.7	20 / 55	5.618 / 18.7	5.618	0.9528	6.14	SFO-SFO
Sandy loam, Laacherhof AXXa [2]		6.2	20 / 55	18.75 / 62.3	18.75	0.6294	20.0	SFO-SFO (95th CI rate fixed)
Sandy loam, Laacherhof Wurmwiese [2]		5.2	20 / 55	7.865 / 26.1	7.865	1.0000	22.6	SFO-SFO
Clay loam, Dollendorf II [2]		7.3	20 / 55	5.109 / 17.0	5.109	1.0000	19.0	SFO-SFO

[1] M-298296-01-1
[2] M-298413-01-1
[3] Normalised using a Q10 of 2.58 and Walker equation coefficient of 0.7

Table 7.1.2.1.1-43: Laboratory soil $DegT_{50}$ parameters of fluopyram-7-hydroxy for trigger purpose

fluopyram-7-hydroxy (FLU-7-OH)	Dark aerobic conditions Formation from parent fluopyram in pathway fit							
Soil type (USDA)		**pH ($CaCl_2$)**	**T (C°) / % MWHC**	**$DegT_{50}$ actual / DT_{90} actual (d)**	**$DegT_{50}$ mod (d) 20°C pF2 / 10 kPa [3]**	**ff (FLU-7-OH)**	**St. (χ^2)**	**Method of calculation parent - metabolite**
Silt loam, Hoefchen am Hohenseh [1]		6.6	20 / 55	17.71 / 58.82		0.4669	5.23	HS-SFO
Sandy loam, Laacherhof AXXa [1]		6.6	20 / 55	17.54 / 58.26		0.6430	4.15	SFO-SFO
Loam, Laacherhof Wurmwiese [1]		5.5	20 / 55	12.61 / 41.9		1.0000	6.05	SFO-SFO
Loam, Laacherhof AIIIa [1]		6.6	20 / 55	29.28 / 97.27		0.3589	3.39	HS-SFO
Silt loam, Hoefchen am Hohenseh [2]		6.7	20 / 55	12.07 / 40.1		0.4698	4.61	HS-SFO
Sandy loam, Laacherhof AXXa [2]		6.2	20 / 55	10.22 / 34.0		1.0000	15.6	SFO-SFO
Sandy loam, Laacherhof Wurmwiese [2]		5.2	20 / 55	11.92 / 39.6		0.6829	5.17	HS-SFO
Clay loam, Dollendorf II [2]		7.3	20 / 55	5.109 / 17.0		1.0000	19.0	SFO-SFO

[1] M-298296-01-1
[2] M-298413-01-1
[3] Normalized using a Q10 of 2.58 and Walker equation coefficient of 0.7

3. Assessment and conclusion

Assessment and conclusion by applicant:
The kinetic evaluation followed FOCUS guidances and is considered valid and reliable.

Assessment and conclusion by RMS:
Outcome and conclusion of the study: RMS should indicate if they agree to the results and conclusions of the APPL.

1. Information on the study

Data Point:	KCA 7.1.2.1.1/10
Report Author:	[redacted]
Report Year:	2020
Report Title:	Fluopyram (FLU): Kinetic evaluation of aerobic laboratory soil degradation in US soils according to FOCUS Kinetics using KinGUI 2.1
Report No:	EnSa-20-0427
Document No:	M-761880-01-1
Guideline(s) followed in study:	not applicable
Deviations from current test guideline:	Current Guideline: not applicable (kinetic evaluation)
Previous evaluation:	No, not previously submitted
GLP/Officially recognised testing facilities:	No, not conducted under GLP/Officially recognised testing facilities
Acceptability/Reliability:	Yes

2. Full summary of KCA 7.1.2.1.1/10

Executive Summary

The residue data of study M-299548-02-1 (see KCA 7.1.1.1/03) was evaluated for calculation of trigger and modelling endpoints following the recommendations given by FOCUS Kinetics.

The non-normalized DT_{50} values for fluopyram (trigger endpoints) were between 483 and 865 days in the tested soils. The normalized (20 °C, pH 2) DT_{50} values for fluopyram (modelling endpoints) were between 490 and 789 days in the tested soils.

I. METHODS

A kinetic modelling analysis of aerobic laboratory soil residue data of fluopyram (FLU) was conducted in order to derive kinetic parameters suitable for modelling and for trigger purpose, using the software tool KinGUI 2.1. The identification of the appropriate kinetic model followed the recommendations given by FOCUS Kinetics (FOCUS, 2006, 2014a) based on a detailed statistical analysis including visual assessment, χ^2 statistic, significance t-test and correlation analysis. Additionally, the Scaled Weighted Area under Residue Curve (SWARC) was used as a further indicator for the visual assessment and to choose the appropriate model.

The modelling analysis is based on residue data from an aerobic laboratory soil degradation study in US soils (KCA 7.1.1.1/03, M-299548-02-1). For both labels the same soil names are reported. The soils with the same name are similar in terms of soil properties and have been collected in the same year. They are considered as the same soil and were therefore combined (EFSA, 2018). Thus, the two labels with the same soil name are evaluated together.

The experimental study duration has been 365 days, longer than the recommended standard duration of 120 d (OECD 307). The full study period was considered for the kinetic evaluation. Nevertheless, in soil Springfield, a reduced microbial carbon content was observed at day 365. Therefore, late sampling points should be considered with caution.

Extraction methods during the experimental study have been changed. At the beginning of the study no aggressive extract was taken. Therefore, residues of sample days without aggressive extract (with the exception of day 0) were omitted to ensure consistency of the dataset (Springfield: 3-7 d, Porterville: 3-

30 d). The day 0 samples were not omitted, because all radioactivity is supposed to be parent (FOCUS, 2006, 2014a). Moreover, the aggressive extract was analysed only partly for Springfield soil (133-365 d). In this soil, it turned out to be almost entirely fluopyram. Thus, the aggressive extracts of all other samples were conservatively added to fluopyram, in this evaluation.

No relevant metabolites have been identified in the experimental study.

It was assumed the parent directly degraded in the sink.

II. RESULTS

Degradation of Fluopyram

Results of the kinetic evaluation for modelling and trigger purpose based on residue data from an aerobic laboratory soil degradation study in US soils (M-299548-02-1) are summarised in the tables below.

Table 7.1.2.1.1-44: Fluopyram: kinetic and statistical results of degradation in soil Springfield, Nebraska for modelling endpoints

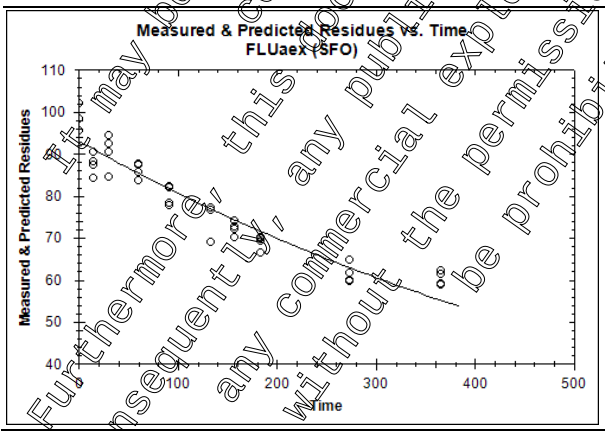
Kinetic model	DT_{50} actual	DT_{90} actual	DT_{50} fast / slow	VA	χ^2err / SWARC	k_1	k_2	g	t-test k_1 / k_2	95th CI of k_1	95th CI of k_2
	(d)	(d)	(d)		(% / -)	(1/d)	(1/d)	(-)	(-)	(1/d)	(1/d)
SFO	**483.4**	>1000		o	3.18 / 22.4	0.001434			<0.001	0.00128 to 0.002	-
DFOP	>1000	>1000	136 / >1000	+	2.43 / 5.50	0.005107 [1]	2.3E-14 [1]	0.4512 [1]	0.212 / 0.500	-0.00727 to 0.017	-0.00440 to 0.004

VA = visual assessment, + = good, o = acceptable, - = poor
SWARC = Scaled Weighted Area under Residue Curve
CI = confidence interval
[1] = fast and slow rate k1, k2 were exchanged here, compared to KinGui output, to deliver the correct g, which has to be related to the fast phase (g fast = 1 - g slow)

Modelling Endpoints: SFO fit is statistically (χ^2err <15%, t-test <0.05) good and visually acceptable. SWARC value is < 40, not indicating a biphasic decline. Consequently, **SFO** degradation model is appropriate for modelling endpoints.

In addition, a significantly reduced biomass (< 50 % of d 0 value; 0.93 % of TOC) was observed at day 365. Therefore, this sampling point should be considered with caution and not overinterpreted.

SFO



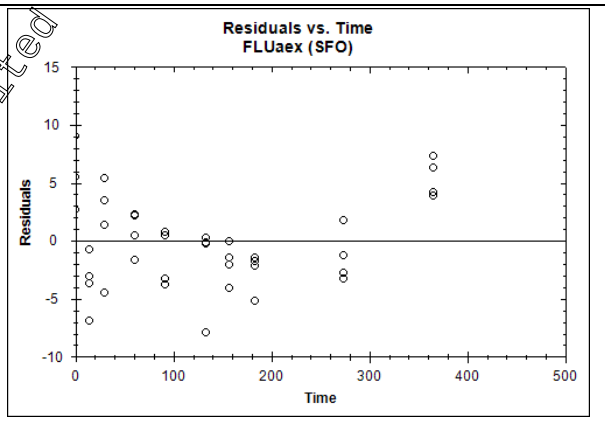


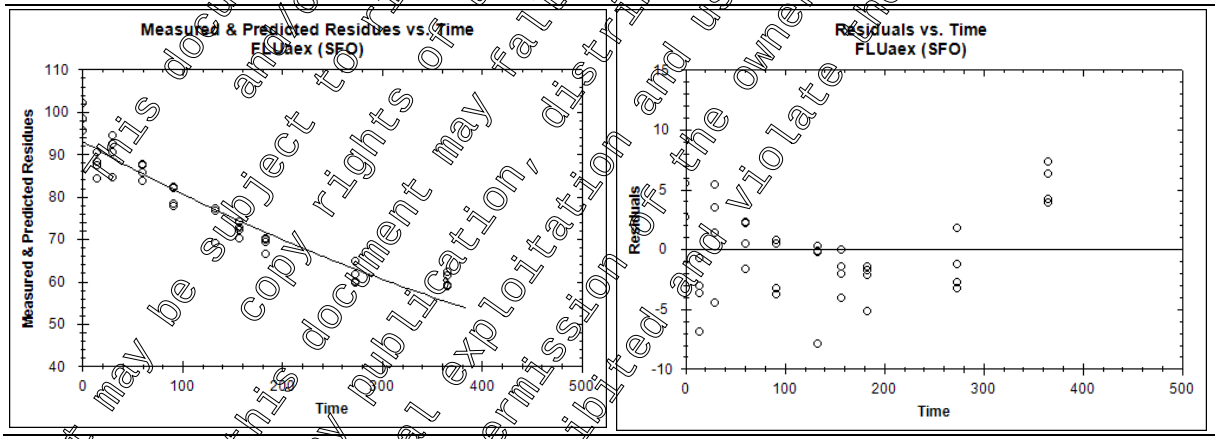
Table 7.1.2.1.1-45: Fluopyram: kinetic and statistical results of degradation in soil Springfield, Nebraska for trigger endpoints

Kinetic model	DT_{50} actual	DT_{90} actual	VA	χ^2err / SWARC	k_1 / α	k_2 / β	g / t_b	t-test k_1 / k_2	95th CI of k_1	95th CI of k_2
	(d)	(d)		(% / -)	(1/d / -)	(1/d / d)	(- / -)	(-)	(1/d)	(1/d)
SFO	**483.4**	>1000	o	3.18 / 22.4	0.001434		- / -	<0.001	0.00128 to 0.002	-
DFOP	>1000	>1000	+	2.43 / 5.50	0.005107 [1]	2.3 E-14 [1]	0.4512 [1]	0.212 / 0.500	-0.00727 to 0.017	-0.00440 to 0.004
FOMC	704.1	>1000	+	2.37 / 6.47	0.39760	149.285	- / -	-	-	-
HS	466.2	>1000	o	2.57 / 16.7	36.47	0.001308	- / 0.092	<0.001 / <0.001	36.47 to 36.47	0.001 to 0.001

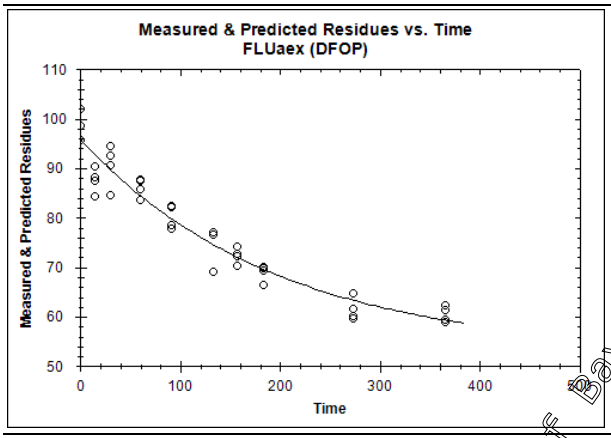
VA = visual assessment, + = good, o = acceptable, - = poor
SWARC = Scaled Weighted Area under Residue Curve
[1] = fast and slow rate k1, k2 were exchanged here, compared to KinGui output, to deliver the correct g, which has to be related to the fast phase (g fast = 1 – g slow).

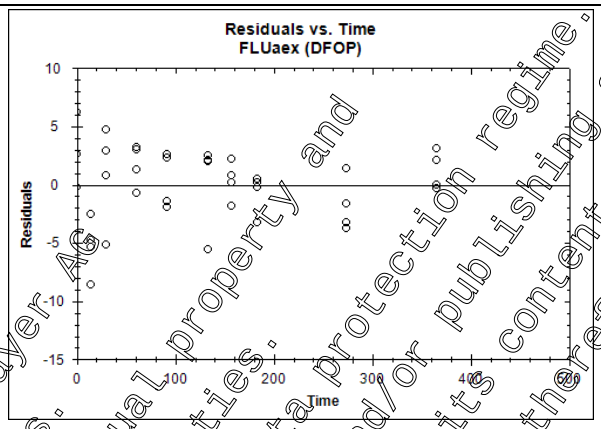
Trigger Endpoints: SFO fit is statistically (χ^2err, t-test) good and visually acceptable. DFOP, FOMC and HS fits were alternatively tested. For DFOP, t-test of k_{fast} and k_{slow} failed in combination with DT_{50} and DT_{90} extrapolated beyond study end. For FOMC, DT_{50} and DT_{90} are extrapolated beyond study end. Both fits are therefore not suitable, especially for accumulation assessments. HS fit is statistically (χ^2err, t-test) good and visually acceptable. However, the visual HS fit is not clearly an improvement towards SFO and featuring an unrelibale breakpoint t_b, very close to the starting time. Consequently, **SFO** degradation model is appropriate for trigger endpoints.
In addition, a significantly reduced biomass (< 50 % of d 0 value; 0.93 % of TOC) was observed at day 365. Therefore, this sampling point should be considered with caution and not overinterpreted.

SFO

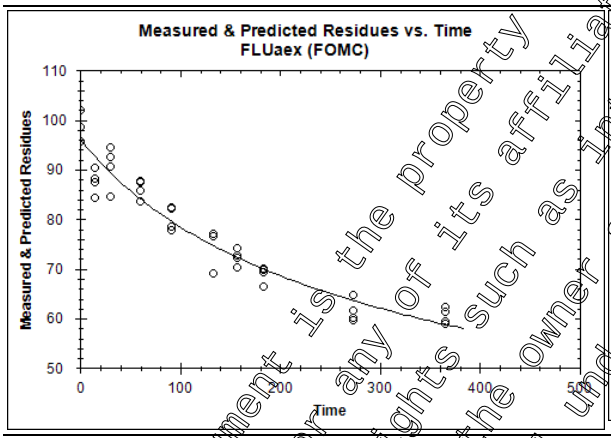


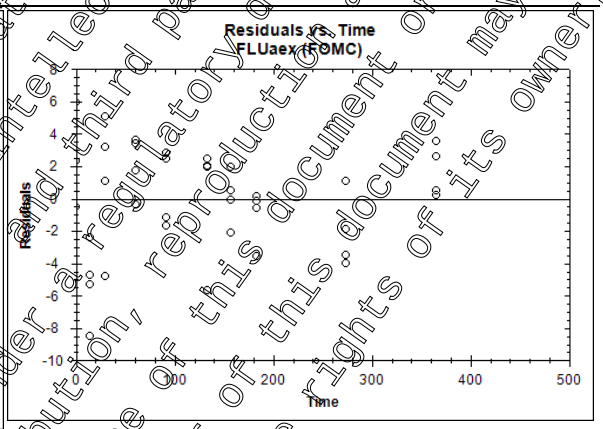
DFOP



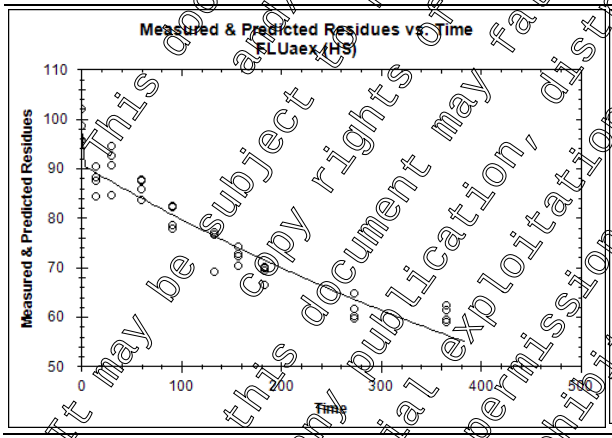


FOMC





HS



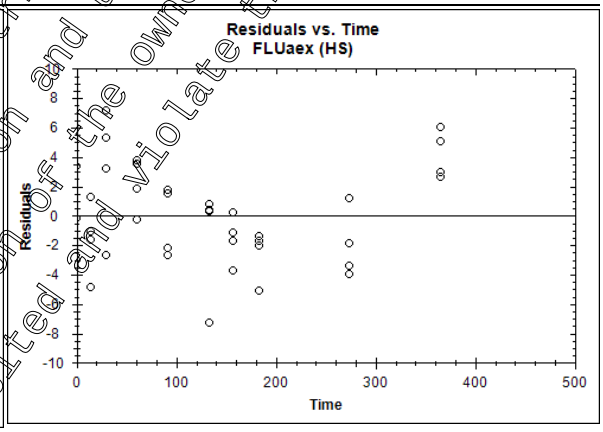


Table 7.1.2.1.1-46: Fluopyram: kinetic and statistical results of degradation in soil Porterville, California for modelling endpoints

Kinetic model	DT_{50} actual	DT_{90} actual	DT_{50} fast / slow	VA	χ^2err / SWARC	k_1	k_2	g	t-test k_1 / k_2	95th CI of k_1	95th CI of k_2
	(d)	(d)	(d)		(% / -)	(1/d)	(1/d)	(-)	(-)	(1/d)	(1/d)
SFO	**864.5**	>1000	-	+	2.00 / 6.71	0.0008018	-		<0.001	0.00061 to 0.001	-
DFOP	>1000	>1000	154 / >1000	+	1.50 / 0.600	0.004503	<0.00001	0.3107	0.386 / 0.500	-0.02555 to 0.035	-0.00646 to 0.006

VA = visual assessment, + = good, o = acceptable, - = poor
SWARC = Scaled Weighted Area under Residue Curve
CI = confidence intervall

Modelling Endpoints: SFO fit is statistically and visually good (χ^2err <15%, t-test <0.05). SWARC value is < 40, not indicating a biphasic decline. Consequently, **SFO** degradation model is appropriate for modelling endpoints.

SFO

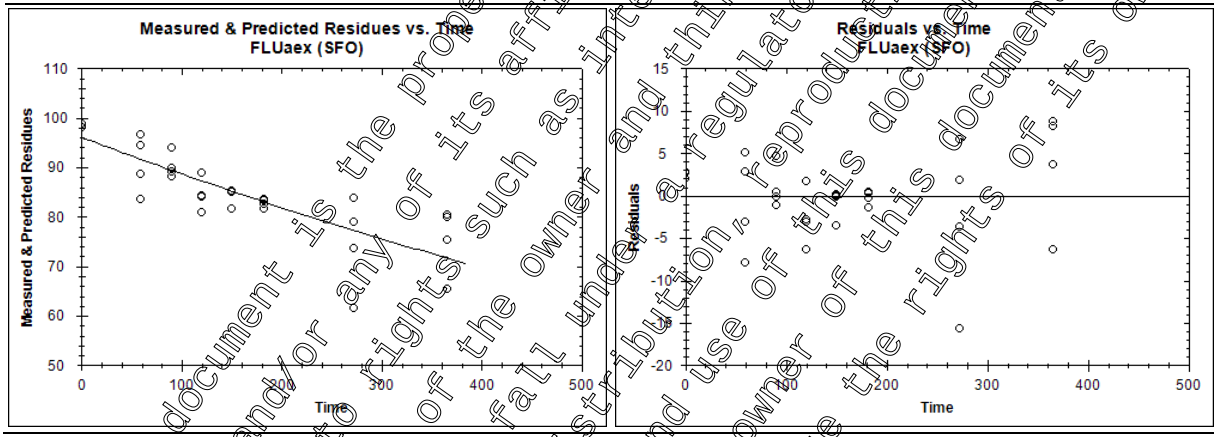


Table 7.1.2.1.1-47: Fluopyram: kinetic and statistical results of degradation in soil Porterville, California for trigger endpoints

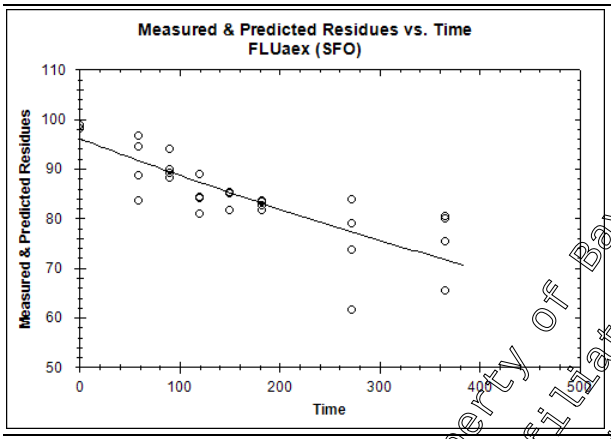
Kinetic model	DT_{50} actual	DT_{90} actual	VA	χ^2err / SWARC	k_1 / α	k_2 / β	g / t_b	t-test k_1 / k_2	95th CI of k_1	95th CI of k_2
	(d)	(d)		(% / -)	(1/d / -)	(1/d / d)	(- / -)	(-)	(1/d)	(1/d)
SFO	**864.5**	>1000	+	2.00 / 6.71	0.0008018	-	- / -	<0.001	0.00061 to 0.001	-
DFOP	>1000	>1000	+	1.50 / 0.600	0.004503	<0.00001	0.3107 / -	0.386 / 0.500	-0.02555 to 0.035	-0.00646 to 0.006
FOMC	>1000	>1000		1.46 / 0.456	0.24259	155.504	- / -	- / -	-	-
HS	864.5	>1000	+	2.30 / 6.71	0.0008017	<0.00001	- / 1719	<0.001 / <0.001	0.00068 to 0.001	<0.00001 to <0.00001

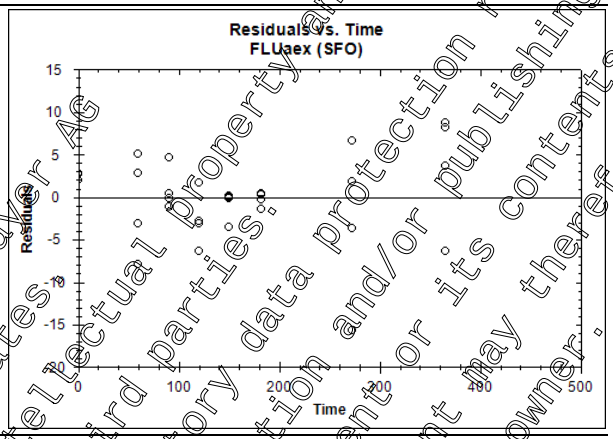
VA = visual assessment, + = good, o = acceptable, - = poor
SWARC = Scaled Weighted Area under Residue Curve
CI = confidence intervall

Trigger Endpoints: SFO fit is statistically (χ^2err, t-test) and visually good. DFOP, FOMC and HS fits were alternatively tested. For DFOP, t-test of k_{fast} and k_{slow} failed in combination with DT_{50} and DT_{90} extrapolated beyond study end. For FOMC, DT_{50} and DT_{90} are extrapolated beyond study end. Both fits are

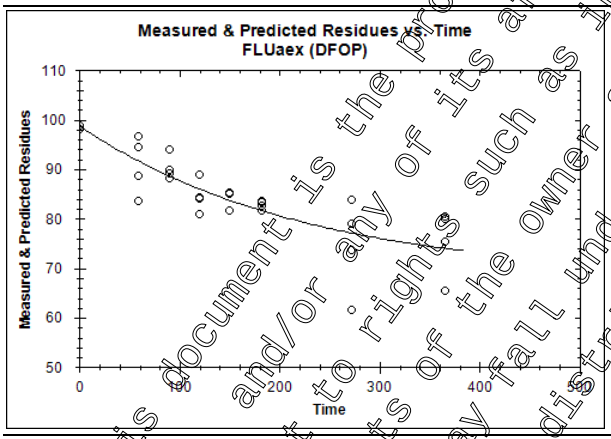
therefore not suitable, especially for accumulation assessments. HS fit is statistically (χ^2err, t-test) and visually good, but not better than SFO. Moreover, breakpoint t_b is extraploated far beyond study end, resulting in a pseudo-SFO. Consequently, **SFO** degradation model is appropriate for trigger endpoints.

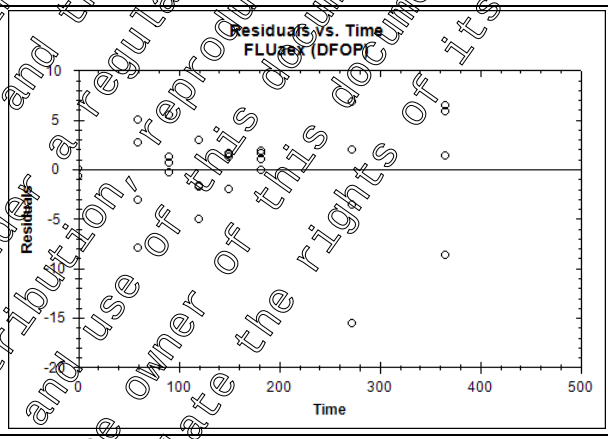
SFO



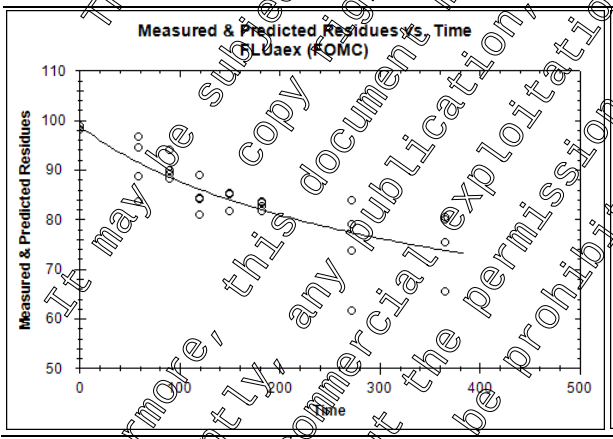


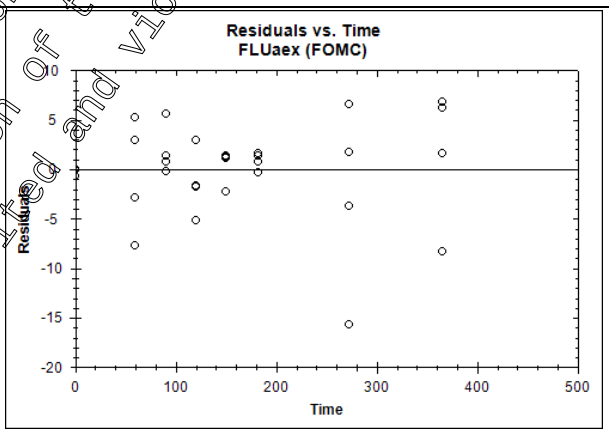
DFOP



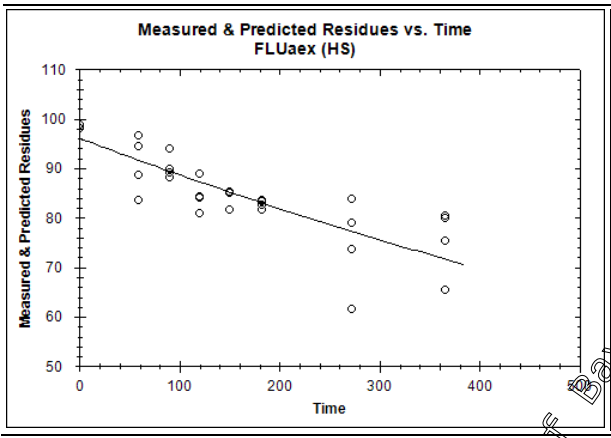


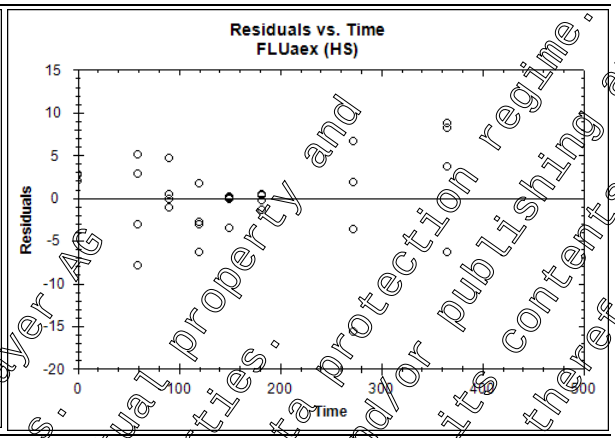
FOMC





HS





Moisture and temperature correction factors to normalise DT_{50} values to a moisture of pF2 and 20°C are summarised in the following table.

Table 7.1.2.1.1-48: Moisture and temperature correction factors $f_\theta \cdot f_T$ for DT_{50} normalisation (reference moisture at pF2, 20°C), (FOCUS field capacity, θ_{ref}: default of reference soil moisture, pF2, as in FOCUS, 2014b; MWHC: maximum water holding capacity)

Soil	Soil texture (USDA)	Study moist. (% WHC 0.33 bar)	WHC 0.33 bar, pF 2.5 (g/100 g)	WHC 0.1 bar, pF 2, field capacity θ_{ref} (g/100 g)	Study moist. θ (g/100 g)	Study temp. T (°C)	f_θ (-)	f_T (-)	$f_\theta \cdot f_T$ (-)
Springfield, Nebraska	Silty clay loam	75	28.3	41.3	21.4 [1]	25	0.6311	1.6062	1.0138
Porterville, California	Sandy loam	75	14.6	25.1	11.2 [1]	25	0.5684	1.6062	0.9130

[1] The moisture content stated directly in the experimental study (M-299548-02-1, page 19) was used.

III. CONCLUSIONS

The laboratory soil Deg T_{50} parameters of fluopyram for modelling and trigger purpose based on residue data from an aerobic laboratory soil degradation study in US soils are summarised in the tables below.

Table 7.1.2.1.1-49: Laboratory soil $DegT_{50}$ parameters of fluopyram for modelling purpose (normalised: pF2, 20°C, Q10 2.58)

Fluopyram	Dark aerobic conditions					
Soil type (USDA) [2]	**pH ($CaCl_2$)**	**T (C°) / % MWHC**	**$DegT_{50\ actual}$ / $DT_{90\ actual}$ (d)**	**$DegT_{50\ mod}$ (d) 20°C pF2 / 10 kPa [1]**	**St. (χ^2)**	**Method of calculation**
Silty clay loam, Springfield, USA	6.5	25 / 49.7	483.4 / >1000	490.0	3.18	SFO
Sandy loam, Porterville, USA	7.9	25 / 36.0	864.5 / >1000	789.3	2.00	SFO

[1] Normalised using a Q_{10} of 2.58 and Walker equation coefficient of 0.7
[2] M-299548-02-1

Table 7.1.2.1.1-50: Laboratory soil $DegT_{50}$ parameters of fluopyram for trigger purpose

Fluopyram	Dark aerobic conditions					
Soil type (USDA) [2]	**pH ($CaCl_2$)**	**T (C°) / % MWHC**	**$DegT_{50\ actual}$ / $DT_{90\ actual}$ (d)**	**$DegT_{50\ mod}$ (d) 20°C pF2 / 10 kPa [1]**	**St. (χ^2)**	**Method of calculation**
Silty clay loam, Springfield, USA M	6.5	25 / 49.7	483.4 / >1000	-	3.18	SFO
Sandy loam, Porterville, USA M	7.9	25 / 36.0	864.5 / >1000	-	2.00	SFO

[1] Normalised using a Q_{10} of 2.58 and Walker equation coefficient of 0.7
[2] M-299548-02-1

3. Assessment and conclusion

Assessment and conclusion by applicant:
The kinetic evaluation followed FOCUS guidances and is considered valid and reliable.

Assessment and conclusion by RMS:
Outcome and conclusion of the study: RMS should indicate if they agree to the results and conclusions of the APPL.

1. Information on the study

Data Point:	KCA 7.1.2.1.1/11
Report Author:	[redacted]
Report Year:	2021
Report Title:	Fluopyram (FLU): Kinetic evaluation of aerobic laboratory soil degradation in Brazilian soil according to FOCUS kinetics using KinGUI 2.1
Report No:	EnSa-20-0606
Document No:	M-761965-01-1
Guideline(s) followed in study:	not applicable
Deviations from current test guideline:	Current Guideline: not applicable (kinetic evaluation)
Previous evaluation:	No, not previously submitted
GLP/Officially recognised testing facilities:	No, not conducted under GLP/Officially recognised testing facilities
Acceptability/Reliability:	Yes

2. Full summary of KCA 7.1.2.1.1/11

Executive Summary

A kinetic modelling analysis of aerobic laboratory soil residue data of fluopyram (FLU) and fluopyram-7-hydroxy (FLU-7-OH) was conducted in order to derive kinetic parameters suitable for modelling and for trigger purpose, using the software tool KinGUI 2.1. The identification of the appropriate kinetic model followed the recommendations given by FOCUS Kinetics. The modelling analysis is based on residue data from an aerobic laboratory soil degradation study on Brazilian soils.

The normalised modelling $DegT_{50}$ value for fluopyram (modelling endpoints) was calculated to be 440.3 days while the non-normalised trigger $DegT_{50}$ value was 1000 days. The normalised modelling $DegT_{50}$ value for fluopyram-7-hydroxy (modelling endpoints) was calculated to be 8.24 days while the non-normalised trigger $DegT_{50}$ value was 13.23 days.

I. METHODS

A kinetic modelling analysis of aerobic laboratory soil residue data of fluopyram (FLU) and fluopyram-7-hydroxy (FLU-7-OH) was conducted in order to derive kinetic parameters suitable for modelling and for trigger purpose, using the software tool KinGUI 2.1. The identification of the appropriate kinetic model followed the recommendations given by FOCUS Kinetics (FOCUS, 2006, 2014a) based on a detailed statistical analysis including visual assessment, χ^2 statistic, significance t-test and correlation analysis, using correspondingly pre-processed residue data. Additionally, the Scaled Weighted Area under Residue Curve (SWARC) was used as a further indicator for the visual assessment and to choose the appropriate model.

The modelling analysis is based on residue data from an aerobic laboratory soil degradation study on Brazilian soils (KCA 7.1.1.1/04, M-349303-02-1).

The soil metabolite fluopyram-7-hydroxy was found at relevant amounts in soils, in general (> 5% of applied radioactivity), and with sufficient data points above the limit of detection (LOD) in these soils here. Therefore, the metabolite degradation was included in the pathway.

Finally, the following degradation pathway was considered in the compartment model.

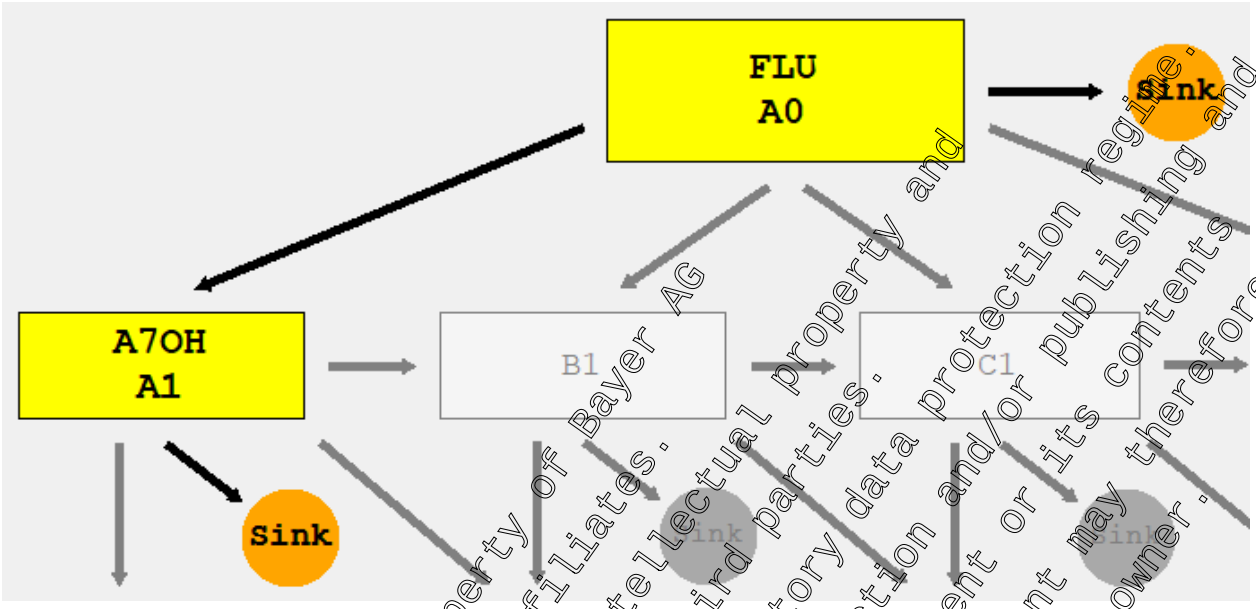


Figure 7.1.2.1.1-7: Compartment model of aerobic soil degradation of fluopyram (FLU = fluopyram, A7OH = FLU-7-OH)

The representativity of the examined Brazilian soils for European agricultural conditions was evaluated in a separate report (KCA 7.1.2.1.1/05, M-759268-01-1). The kinetic evaluation of fluopyram is summarised here for the representative soil only.

For the evaluation of trigger endpoints, a two-step-process was followed. Initially, the parent was fitted alone and its trigger endpoints were derived from this fit. Secondly, for metabolite evaluation, the appropriate pathway scheme was chosen in combination with the best-fit kinetic model selected for parent only. Trigger endpoints for the metabolites were derived from this free fitted pathway fit, if appropriate.

II. RESULTS

Degradation of fluopyram

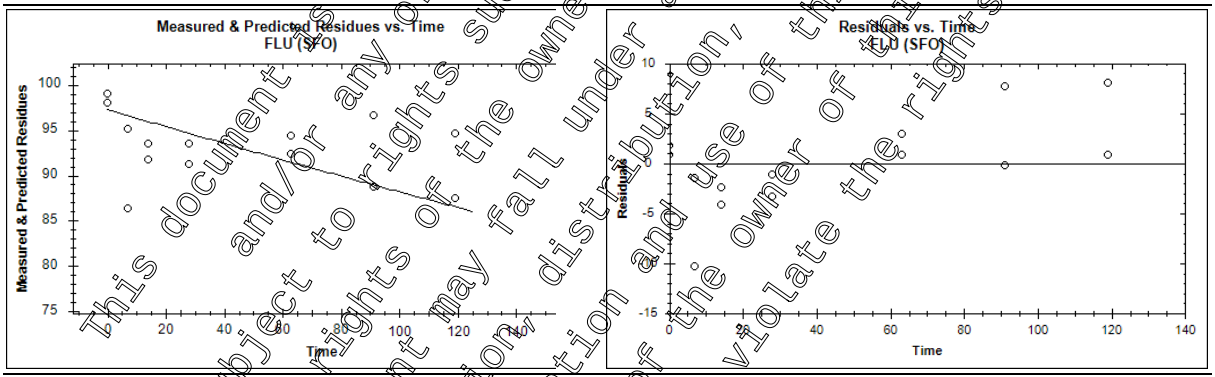
Table 7.1.2.1.1-51: Fluopyram: kinetic and statistical results of degradation in soil Argissolo for modelling endpoints, pathway fit

Kinetic model	DT_{50} actual	DT_{90} actual	DT_{50} fast / slow	VA	χ^2err / SWARC	k_1	k_2	g	t-test k_1 / k_2	95% CI of k_1	95% CI of k_2
	(d)	(d)	(d)		(% / -)	(1/d)	(1/d)	(-)	(-)	(1/d)	(1/d)
SFO	**707.1**	>1000	-	o	3.05 / 20.4	0.0009802	-		0.004	0.00031 to 0.002	-
DFOP	>1000	>1000	0.00012 / >1000	o	0.90 / 5.94	5717	0.00002258	0.0642	<0.001 / 0.463	5717.00 to 5717.01	0.00045 to <0.0005

VA = visual assessment, + = good, o = acceptable, - = poor
SWARC = Scaled Weighted Area under Residue Curve
CI = confidence intervall

Modelling Endpoints: SFO fit is statistically (χ^2err <15%, t-test <0.05) good and visually acceptable. SWARC value is < 40, not indicating a biphasic decline. Consequently, **SFO** degradation model is appropriate for modelling endpoints.

SFO



DFOP

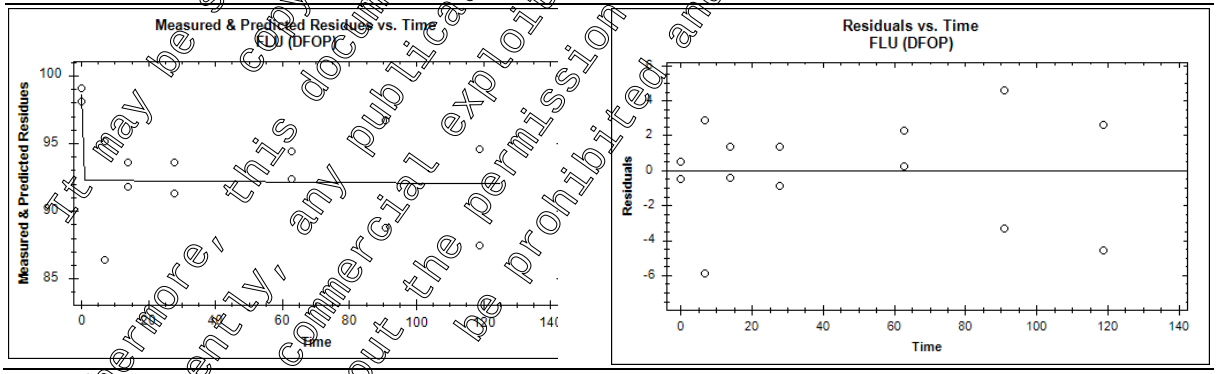


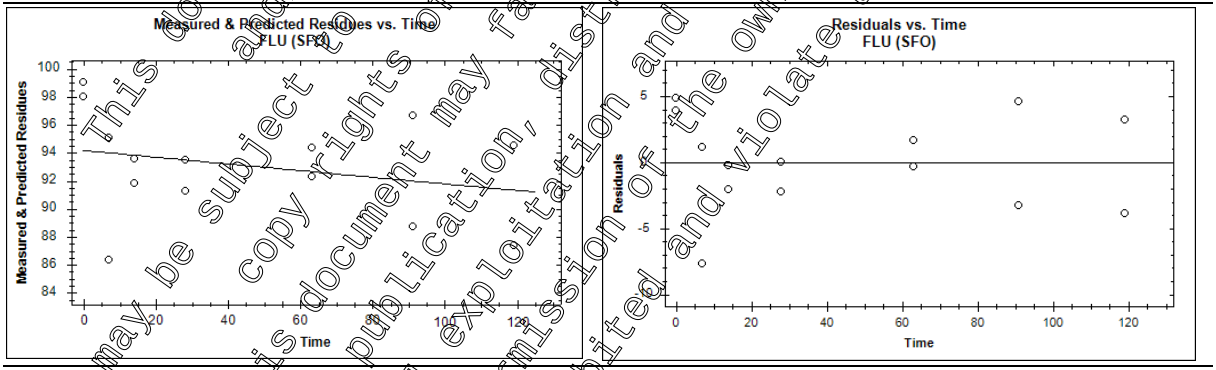
Table 7.1.2.1.1-52: Fluopyram: kinetic and statistical results of degradation in soil Argissolo for trigger endpoints, parent only fit

Kinetic model	DT_{50} actual	DT_{90} actual	VA	χ^2err / SWARC	k_1 / α	k_2 / β	g / t_b	t-test k_1 / k_2	95th CI of k_1	95th CI of k_2
	(d)	(d)		(% / -)	(1/d / -)	(1/d / d)	(- / d)	(-)	(1/d)	(1/d)
SFO, free fit	**>1000**	**>1000**	o	1.87 / 2.77	0.0002565	-	-	0.167	-0.00024 to 0.001	-
DFOP	>1000	>1000	o	0.89 / 5.71	2.807	5.188E-6	0.0648 -	<0.001 / 0.492	2.807 to 2.807	-0.00050 to 0.001
FOMC	>1000	>1000	o	na	0.0005783	1.202E-49	-	-	-	-
HS	>1000	>1000	o	0.89 / 5.71	32.880	5.189E-6	0.00204	<0.001 / 0.492	32.88 to 32.882	-0.00050 to 0.001
SFO, fixed fit	863.4	>1000	o	2.95 / 19.46	0.0008028	-	-	0.0016	0.00037 to 0.001	-

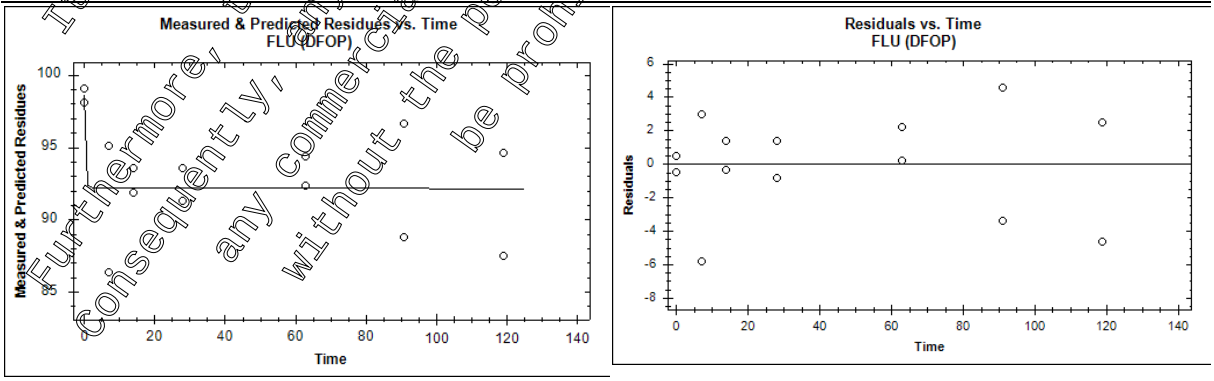
VA = visual assessment, + = good, o = acceptable, - = poor
SWARC = Scaled Weighted Area under Residue Curve
CI = confidence intervall
na = not available
fixed fit: M_0 fixed to mean amount at time t=0 d

Trigger Endpoints: SFO fit (parent only) is visually acceptable, only t-test fails. DFOP, FOMC and HS fits were alternatively tested. For DFOP and HS, t-test of k_2 failed in combination with DT_{50} and DT_{90} extrapolated beyond study end. For FOMC, DT_{50} and DT_{90} are extrapolated far beyond study end. FOMC is therefore not suitable, especially for accumulation assessments.
To account for the failed t-test of SFO, a modified SFO fit was tested with fixed M_0. The modfied SFO fit passes the t-test, but is statistically (χ^2err, SWARC) and visually worse than free SFO fit. Consequently, the **free fitted SFO** model is considered appropriate for trigger endpoints, as it shows lowest χ^2err, lowest SWARC and best visual fit of all suitable models (SFO free, SFO fixed).

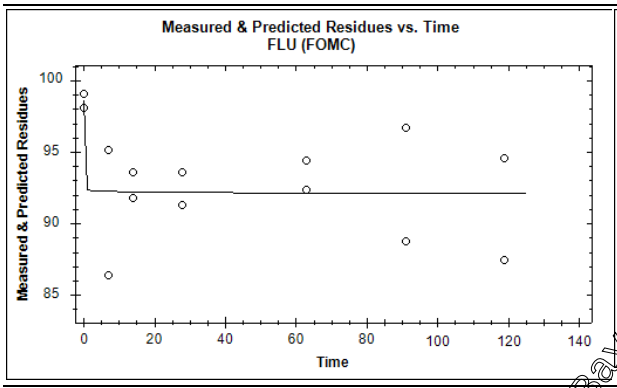
SFO free

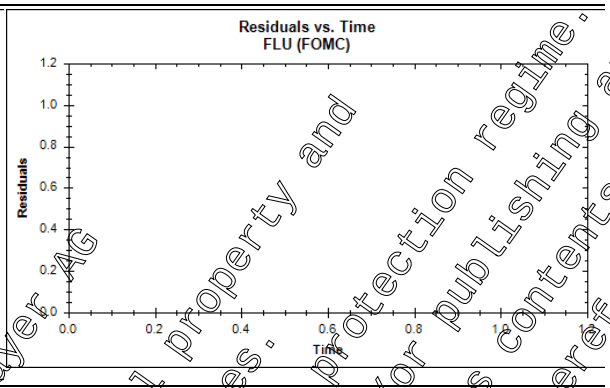


DFOP

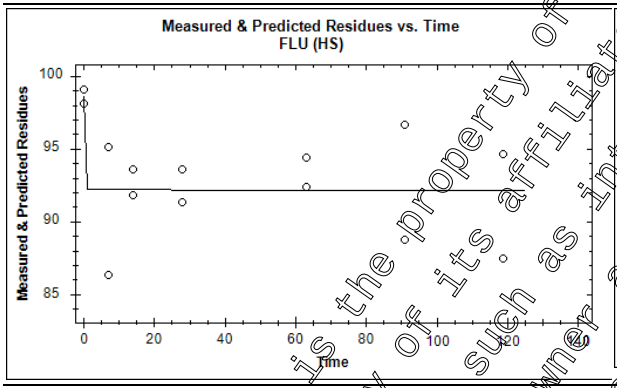


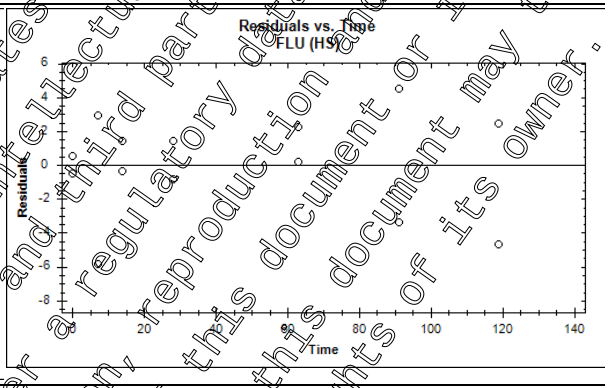
FOMC



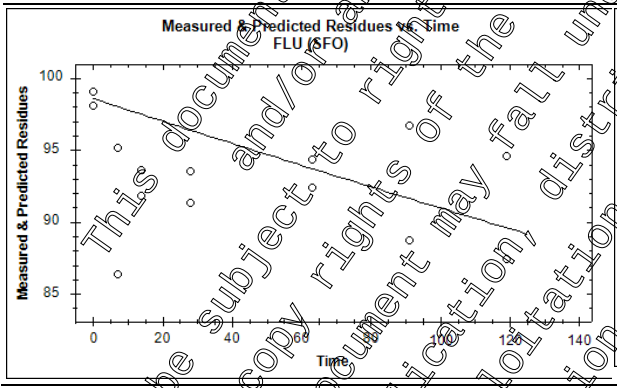


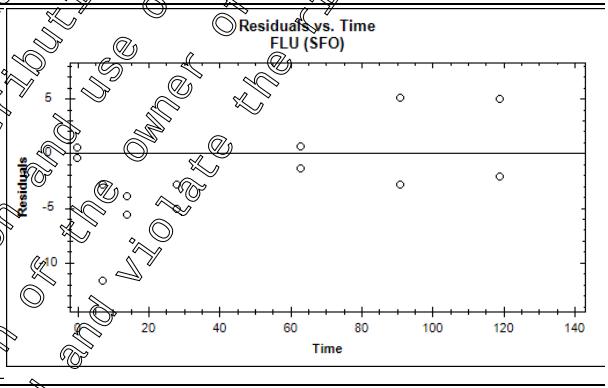
HS





SFO fixed





Degradation of fluopyram-7-hydroxy

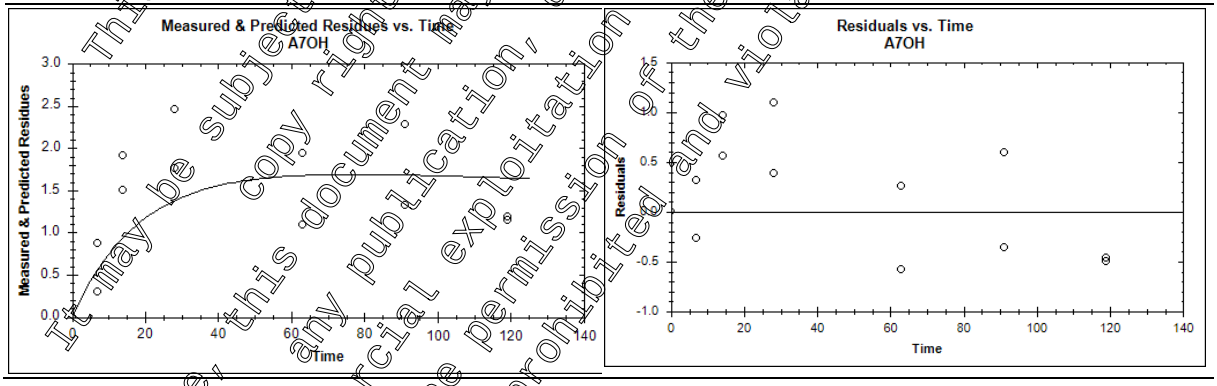
Table 7.1.2.1.1-53: FLU-7-OH: kinetic and statistical results of degradation in soil Argissolo for modelling endpoints

Kinetic model, Parent - metabolite	DT_{50} actual	DT_{90} actual	VA	χ^2err	SWARC	k	t-test k	95th CI of k	ff (FLU)
	(d)	(d)		(%)	(-)	(1/d)	(-)	(1/d)	(-)
SFO - SFO	**13.23**	43.9	o	26.0	42.3	0.0524094	0.030	0.00021 to 0.105	**1.00**
DFOP - SFO	>1000	>1000	-	26.5	108	3.075E-00	0.5	-0.00905 to 0.009	0.2303
SFO decline fit	135 decl	448 decl	o	9.78	0	0.0051358	0.071	-0.00081 to 0.011	-

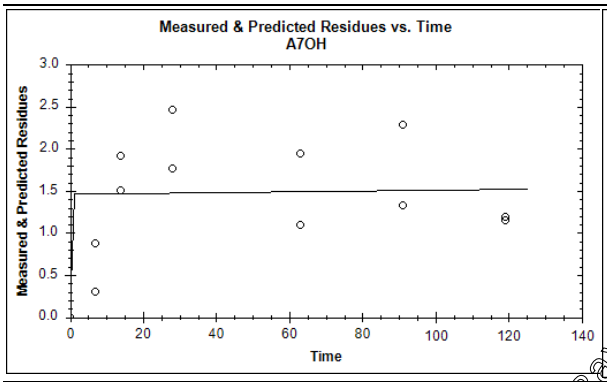
VA = visual assessment, + = good, o = acceptable, - = poor
SWARC = Scaled Weighted Area under Residue Curve
CI = confidence intervall
decline fit: starting at maximum FLU-7-OH mean values at t0 = 28 d after parent application

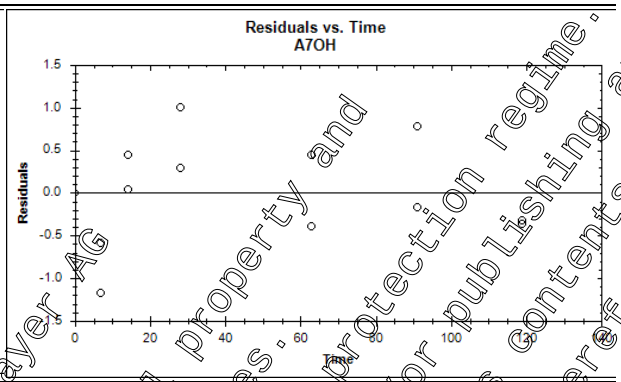
Modelling Endpoints: SFO fit (parent SFO) is statistically and visually acceptable (χ^2err ~25%, t-test < 0.1). Only the SWARC value is slightly > 40 for FLU-7-OH. Formation fraction ff from fluopyram to FLU -7-OH = 1.
Therefore, DFOP parent/SFO metabolite was tested. However, DFOP parent/SFO metabolite shows no improvement of the fit, is statistically not reliable (t-test) and weight of evidence still supports parent SFO, as χ^2err and SWARC values of parent are good.
Consequently, **SFO** degradation model (**parent SFO**) is appropriate for modelling endpoints.
The metabolite FLU-7-OH is decreasing until the end of study (last 4 time points), with maximum levels < 5% of applied parent.
In addition, a decline SFO fit was tested, starting at day 28. It is statistically (χ^2err, t-test) and visually acceptable. However, it is based on 4 time points with scattering data. Furthermore, it does not reflect the formation and degradation of the metabolite in parallel, and it is therefore not preferred for modelling purpose.

SFO/SFO

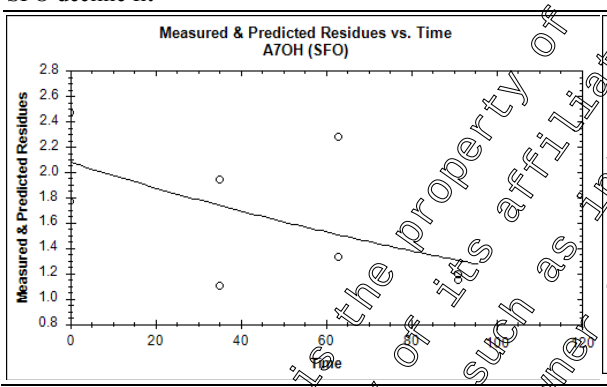


DFOP/SFO





SFO decline fit



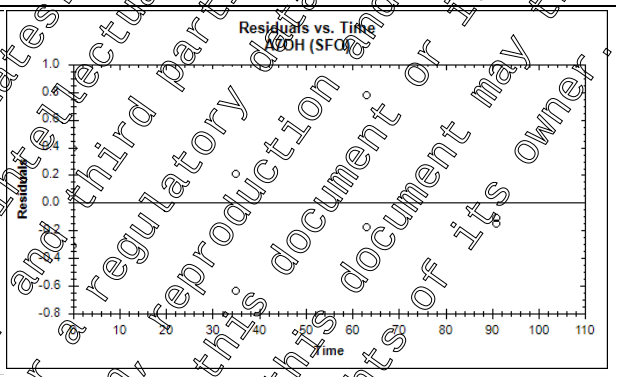


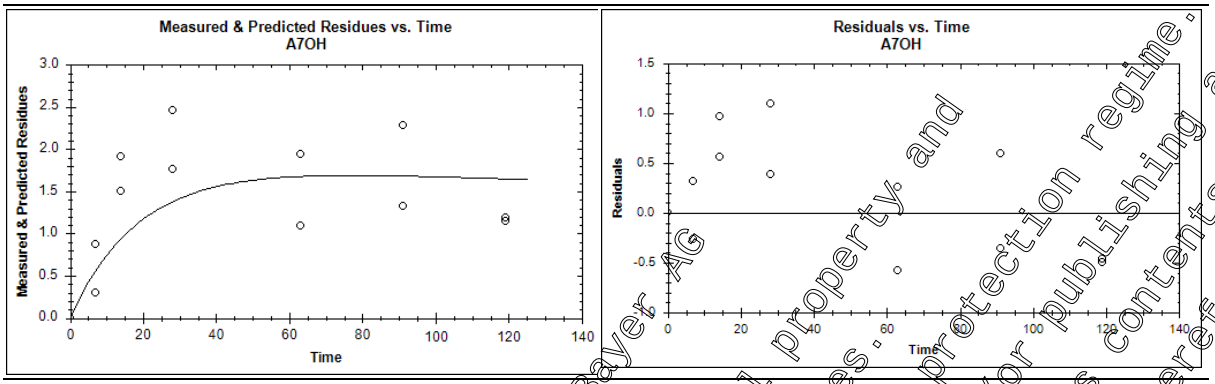
Table 7.1.2.1.1-54: FLU-7-OH: kinetic and statistical results of degradation in soil Argissolo for trigger endpoints, pathway fit

Kinetic model, parent - metabolite	DT_{50} actual	DT_{90} actual	VA	χ^2err	SWARC	k	t-test k	95th CI of k	ff (FLU)
	(d)	(d)		(%)	(-)	(1/d)	(-)	(1/d)	(-)
SFO - SFO, free fit	**13.23**	**43.9**	o	26.0	42.3	0.0524094	0.030	0.00021 to 0.105	**1.00**
SFO decline fit	133 decl	448 decl	o	9.78	0	0.0051358	0.071	-0.00081 to 0.011	-

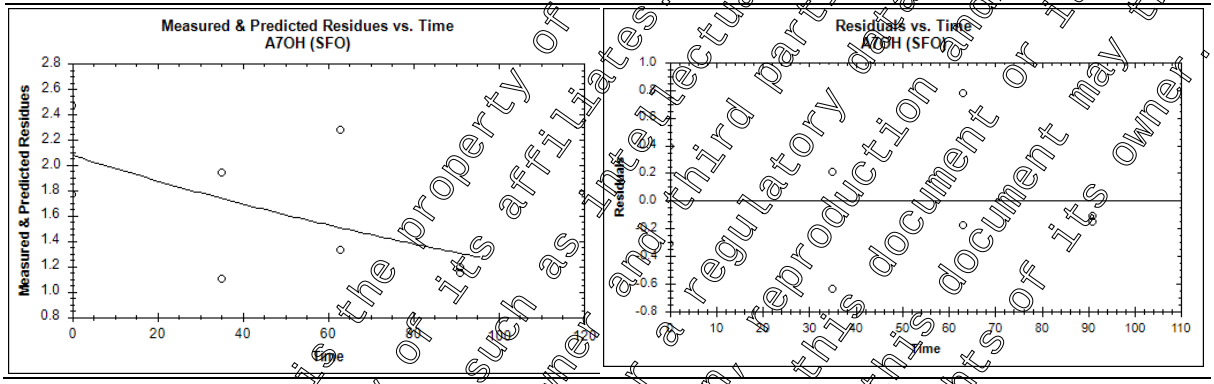
VA = visual assessment, + = good, o = acceptable, - = poor
SWARC = Scaled Weighted Area under Residue Curve
CI = confidence interval
decline fit: starting at maximum FLU-7-OH mean values at t_0 = 28 d after parent application

Trigger Endpoints: SFO fit (parent SFO) is statistically (χ^2err, t-test) and visually acceptable. Consequently, **SFO** degradation model (**parent SFO**) is appropriate for trigger endpoints.
In addition, a decline SFO fit was tested, starting at day 28. It is statistically (χ^2err, t-test) and visually acceptable. However, it is based on 4 time points with scattering data, and its DT_{50} and DT_{90} are extrapolated beyond study end. Therefore, it is considered not suitable, especially for accumulation assessments.

SFO/SFO



SFO decline fit



III. CONCLUSIONS

Normalisation

Moisture and temperature correction factors to normalise DT_{50} values to a moisture of pF2 and 20°C are summarised in the following:

Table 7.1.2.1.1-55: Moisture and temperature correction factors $f_\theta \cdot f_T$ for DT_{50} normalisation (reference moisture at pF 2, 20°C), (FOCUS field capacity, θ_{ref}: default of reference soil moisture, pF2, as in FOCUS, 2014b; MWHC: maximum water holding capacity)

Soil	Soil texture (USDA)	Study moist. (% MWHC)	MWHC (g/100 g)	Study moist, θ (g/100 g)	Study temp., T (°C)	FOCUS field capacity, θ_{ref} (g/100 g)	f_θ (-)	f_T (-)	$f_\theta \cdot f_T$ (-)
Argissolo [1]	Clay	40	61	24.4	20	48	0.6227	1	0.6227

[1] M-349303-02-1

The normalised modelling and not normalised trigger endpoints of laboratory degradation studies of fluopyram and its metabolites based on data from Brazilian soils are summarised in the tables below.

Table 7.1.2.1.1-56: Laboratory soil $DegT_{50}$ parameters of fluopyram for modelling purpose (normalised: pF2, 20°C, Q10: 2.58)

Fluopyram	Dark aerobic lab conditions, pathway fit						
Soil type (USDA)	pH (H_2O) (pH($CaCl_2$))	T. °C / % MWHC	$DegT_{50\ actual}$ / $DT_{90\ actual}$ (d)	$DegT_{50\ mod}$ (d) 20 °C pF2 / 10 kPa[2]	St. (χ^2)	Method of calculation
Clay, Argissolo [1]	5.9 (5.3) [3]	20 / 40	707.1 / >1000	440.3	3.05	SFO

[1] M-349303-02-1
[2] Normalised using a Q10 of 2.58 and Walker equation coefficient of 0.7
[3] pH $CaCl_2$ is calculated based on equation: pH H_2O = 0.953 pH $CaCl_2$ + 0.85; FOCUS, 2014b

Table 7.1.2.1.1-57: Laboratory soil $DegT_{50}$ parameters of fluopyram for trigger purpose

Fluopyram	Dark aerobic lab conditions, parent only fit						
Soil type (USDA)	pH (H_2O) (pH($CaCl_2$))	T. °C / % MWHC	$DT_{50\ actual}$ / $DT_{90\ actual}$ (d)	$DT_{50\ mod}$ (d) 20 °C pF2 / 10 kPa[2]	St. (χ^2)	Method of calculation
Clay, Argissolo [1]	5.9 (5.3) [3]	20 / 40	>1000 / >1000	-	1.87	SFO

[1] M-349303-02-1
[2] Normalised using a Q10 of 2.58 and Walker equation coefficient of 0.7
[3] pH $CaCl_2$ is calculated based on equation: pH H_2O = 0.953 pH $CaCl_2$ + 0.85; FOCUS, 2014b

Table 7.1.2.1.1-58: Laboratory soil $DegT_{50}$ parameters of fluopyram-7-hydroxy for modelling purpose (normalised: pF2, 20°C, Q10 2.58)

fluopyram-7-hydroxy	Dark aerobic lab conditions, formation from parent fluopyram in pathway fit						
Soil type (USDA)	pH (H_2O) (pH($CaCl_2$))	T. °C / % MWHC	$DegT_{50\ actual}$ / $DT_{90\ actual}$ (d)	$DegT_{50\ mod}$ (d) 20 °C pF2 / 10 kPa[2]	ff (FLU - 7-OH)	St. (χ^2)	Method of calculation parent - metabolite
Clay, Argissolo [1]	5.9 (5.3) [3]	20 / 40	13.23 / 43.9	8.24	1.00	26.0	SFO - SFO

[1] M-349303-02-1
[2] Normalised using a Q10 of 2.58 and Walker equation coefficient of 0.7
[3] pH $CaCl_2$ is calculated based on equation: pH H_2O = 0.953 pH $CaCl_2$ + 0.85; FOCUS, 2014b

Table 7.1.2.1.1-59: Laboratory soil DegT$_{50}$ parameters of fluopyram-7-hydroxy for trigger purpose

fluopyram-7-hydroxy	Dark aerobic lab conditions, formation from parent fluopyram in pathway fit							
Soil type (USDA)	pH (H_2O) (pH($CaCl_2$))	T. °C / % MWHC	DT$_{50\ actual}$ / DT$_{90\ actual}$ (d)	DT$_{50\ mod}$ (d) 20 °C pF2 / 10kPa[2]	ff (FLU - 7-OH)	St. (χ^2)	Method of calculation parent - metabolite
Clay, Argissolo [1]	5.9 (5.3) [3]	20 / 40	13.23 / 43.9	-	1.00	26.0	SFO - SFO

[1] M-349303-02-1
[2] Normalised using a Q10 of 2.58 and Walker equation coefficient of 0.7
[3] pH $CaCl_2$ is calculated based on equation: pH H_2O = 0.953 pH $CaCl_2$ + 0.85; FOCUS, 2014b

3. Assessment and conclusion

Assessment and conclusion by applicant:
The kinetic evaluation followed FOCUS guidances and is considered valid and reliable.

Assessment and conclusion by RMS:
Outcome and conclusion of the study. RMS should indicate if they agree to the results and conclusions of the APPL.

1. Information on the study

Data Point:	KCA 7.1.2.1.1/12
Report Author:	[redacted]
Report Year:	2020
Report Title:	Fluopyram (FLU): Kinetic evaluation of aerobic laboratory soil degradation in European soils (Hellpointner and Hennig, 2020) according to FOCUS Kinetics using KinGUI 2.1
Report No:	EnSa-20-0521
Document No:	M-761882-01-1
Guideline(s) followed in study:	not applicable
Deviations from current test guideline:	Current Guideline: not applicable (kinetic evaluation)
Previous evaluation:	No, not previously submitted
GLP/Officially recognised testing facilities:	No, not conducted under GLP/Officially recognised testing facilities
Acceptability/Reliability:	Yes

2. Full summary of KCA 7.1.2.1.1/12

Executive Summary

The residue data of an aerobic laboratory soil degradation study in European soils (KCA 7.1.1.1/05, M-681092-01-1, amended report M-681092-02-1) was evaluated for calculation of modelling endpoints following the recommendations given by FOCUS Kinetics.

The normalized (20 °C, pH 2) DT_{50} values for fluopyram (modelling endpoints) were between 247 and 1000 days in the tested soils.

I. METHODS

A kinetic modelling analysis of aerobic laboratory soil residue data of fluopyram (FLU) was conducted in order to derive kinetic parameters suitable for modelling purpose, using the software tool KinGUI 2.1. The identification of the appropriate kinetic model followed the recommendations given by FOCUS Kinetics (FOCUS, 2006, 2014a) based on a detailed statistical analysis including visual assessment, $\chi 2$ statistic, significance t-test and correlation analysis. Additionally, the Scaled Weighted Area under Residue Curve (SWARC) was used as a further indicator for the visual assessment and to choose the appropriate model.

The modelling analysis is based on residue data from an aerobic laboratory soil degradation study in European soils (KCA 7.1.1.1/05, M-681092-01-1, amended report M-681092-02-1). The soil metabolite fluopyram-7-hydroxy (FLU-7-OH) was detected only at one time point in one soil above the limit of detection (LOD). Therefore, no kinetic evaluation could be conducted for this metabolite.

It was assumed the parent directly degraded in the sink.

II. RESULTS

Degradation of Fluopyram

Results of the kinetic evaluation for modelling based on residue data from an aerobic laboratory soil degradation study in European soils (M-681092-01-1, amended report M-681092-02-1) are summarised in the tables below. Evaluation of trigger endpoints can be found in study(M-681092-01-1, amended report M-681092-02-1).

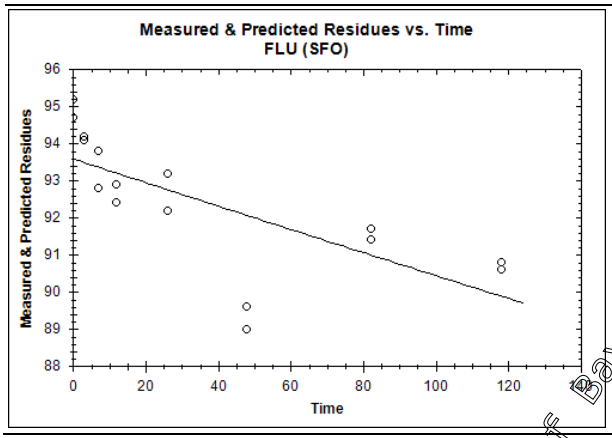
Table 7.1.2.1.1-60: Fluopyram: kinetic and statistical results of degradation in soil Little Oliver for modelling endpoints

Kinetic model	DT_{50} actual	DT_{90} actual	DT_{50} fast / slow	VA	χ^2err / SWARC	k_1	k_2	g	t-test k_1 / k_2	95th CI of k_1	95th CI of k_2
	(d)	(d)	(d)		(% / -)	(1/d)	(1/d)	(-)	(-)	(1/d)	(1/d)
SFO	**>1000**	>1000	-	+	1.02 / 4.91	0.0003411	-	-	<0.001	0.00017 to 0.001	-
DFOP	>1000	>1000	247 / 1000	+	0.756 / 0.643	0.05682	2.34 E-14	0.0441	0.117 / 0.5	-0.03210 to 0.146	-0.00044 to <0.0001

VA = visual assessment, + good, o acceptable, - poor
SWARC = Scaled Weighted Area under Residue Curve
CI = confidence interval

Modelling Endpoints: SFO fit is statistically and visually good (χ^2err <15%, t-test <0.05; please note, y-axis of left graph shows only a small range). SWARC value is < 40, not indicating a biphasic decline. Consequently, **SFO** degradation model is appropriate for modelling endpoints.

SFO



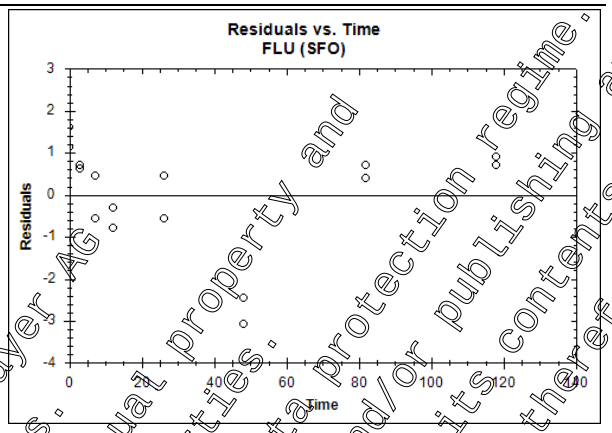


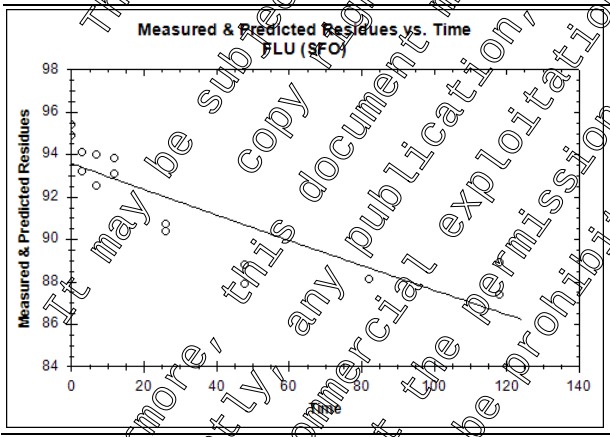
Table 7.1.2.1.1-61: Fluopyram: kinetic and statistical results of degradation in soil Auchy les Mines for modelling endpoints

Kinetic model	DT_{50} actual	DT_{90} actual	DT_{50} fast / slow	VA	χ^2err / SWARC	k_1	k_2	g	t-test k_1 / k_2	95th CI of k_1	95th CI of k_2
	(d)	(d)	(d)		(% / -)	(1/d)	(1/d)	(-)	(-)	(1/d)	(1/d)
SFO	**1051.3**	>1000		o	1.12 / 6.91	0.0006593			<0.001	0.00046 to 0.001	-
DFOP	>1000	>1000	19.1 / >1000	+	0.497 / 1.41	0.0362	6.25 E-12	0.0767	0.066 / 0.5	-0.00768 to 0.080	-0.00069 to 0.001

VA = visual assessment, + good, o acceptable, - poor
SWARC = Scaled Weighted Area under Residue Curve
CI = confidence interval

Modelling Endpoints: SFO fit is statistically good (χ^2err <15%, t-test <0.05) and visually acceptable (please note, y-axis of left graph shows only a small range). SWARC value is < 40, not indicating a biphasic decline. Consequently, **SFO** degradation model is appropriate for modelling endpoints.

SFO



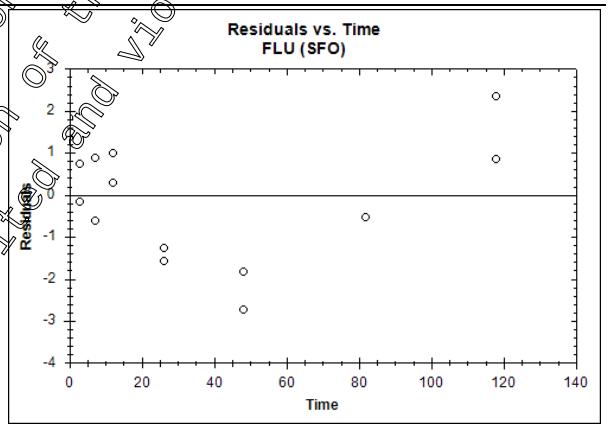


Table 7.1.2.1.1-62: Fluopyram: kinetic and statistical results of degradation in soil Urbanowice for modelling endpoints

Kinetic model	DT_{50} actual	DT_{90} actual	DT_{50} fast / slow	VA	χ^2err / SWARC	k_1	k_2	g	t-test k_1 / k_2	95th CI of k_1	95th CI of k_2
	(d)	(d)	(d)		(% / -)	(1/d)	(1/d)	(-)	(-)	(1/d)	(1/d)
SFO	**1348.8**	>1000	-	o	0.998 / 1.17	0.0005139	-	-	<0.001	0.00029 to 0.001	-
DFOP	>1000	>1000	19.8 / >1000	+	0.997 / 0.513	0.0350063	0.0001612	0.0413	0.352 / 0.419	-0.14136 to 0.211	-0.00135 to 0.002

VA = visual assessment, + good, o acceptable, - poor
SWARC = Scaled Weighted Area under Residue Curve
CI = confidence intervall

Modelling Endpoints: SFO fit is statistically good (χ^2err <15%, t-test <0.05) and visually acceptable (please note, y-axis of left graph shows only a small range). SWARC value is < 40, not indicating a biphasic decline. Consequently, **SFO** degradation model is appropriate for modelling endpoints.

SFO

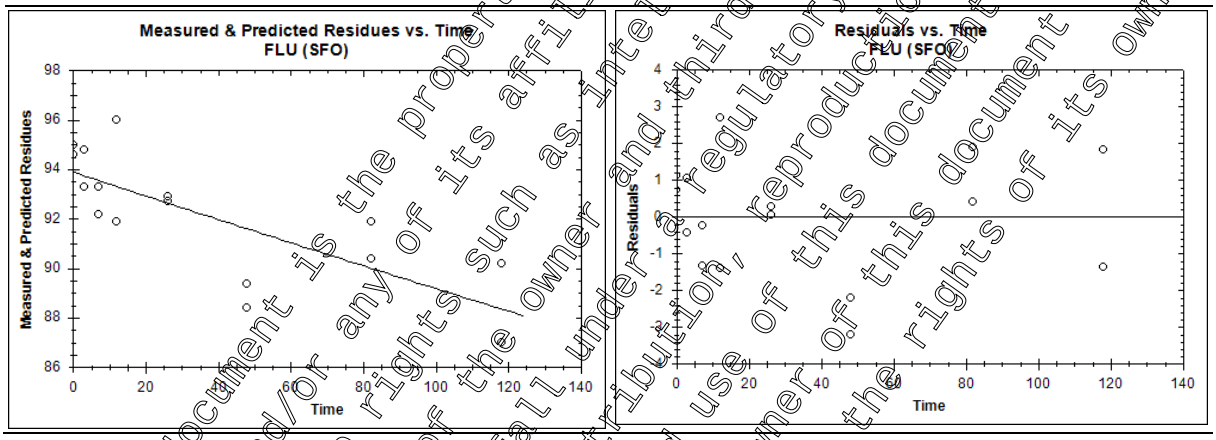


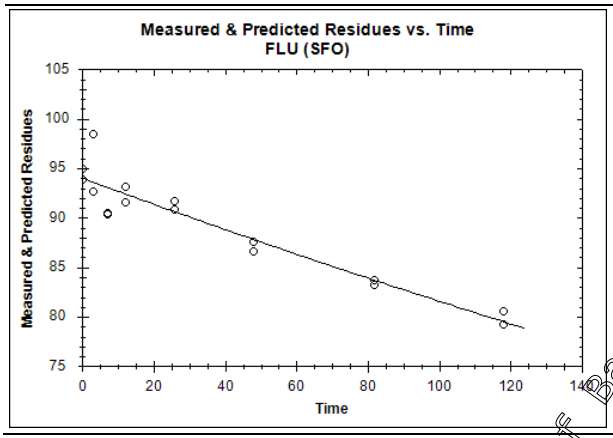
Table 7.1.2.1.1-63: Fluopyram: kinetic and statistical results of degradation in soil Charles River Farm for modelling endpoints

Kinetic model	DT_{50} actual	DT_{90} actual	DT_{50} fast / slow	VA	χ^2err / SWARC	k_1	k_2	g	t-test k_1 / k_2	95th CI of k_1	95th CI of k_2
	(d)	(d)	(d)		(% / -)	(1/d)	(1/d)	(-)	(-)	(1/d)	(1/d)
SFO	**489.17**	>1000	-	+	1.10 / 0.897	0.001417	-	-	<0.001	0.00116 to 0.002	-
DFOP	507.2	>1000	2.94 / 519	+	1.19 / 0.775	0.0358644	0.0013351	0.0159	0.364 / <0.001	-1.05856 to 1.530	0.00093 to 0.002

VA = visual assessment, + good, o acceptable, - poor
SWARC = Scaled Weighted Area under Residue Curve
CI = confidence intervall

Modelling Endpoints: SFO fit is statistically (χ^2err <15%, t-test <0.05) and visually good. SWARC value is < 40, not indicating a biphasic decline. Consequently, **SFO** degradation model is appropriate for modelling endpoints.

SFO



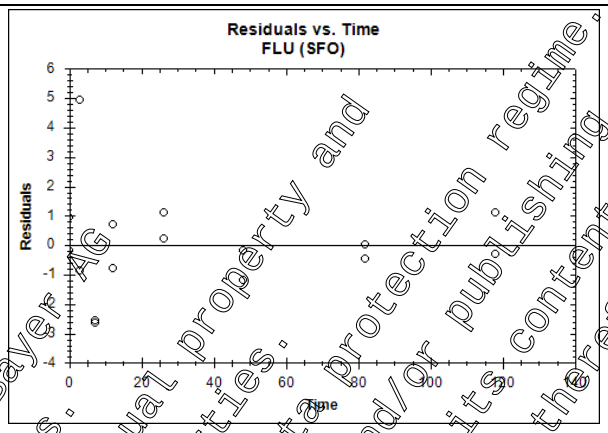


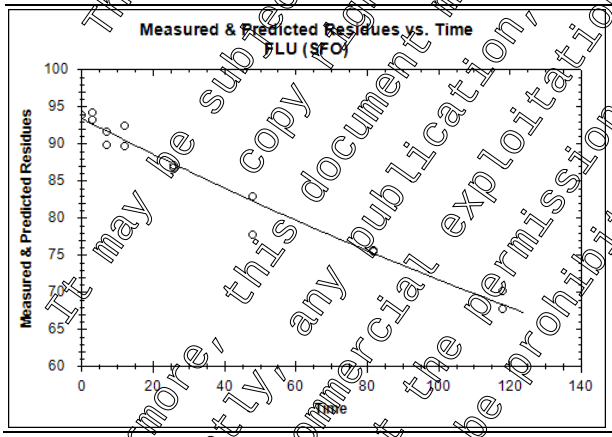
Table 7.1.2.1.1-64: Fluopyram: kinetic and statistical results of degradation in soil Sindos for modelling endpoints

Kinetic model	DT_{50} actual	DT_{90} actual	DT_{50} fast / slow	VA	χ^2err / SWARC	k_1	k_2	g	t-test k_1 / k_2	95th CI of k_1	95th CI of k_2
	(d)	(d)	(d)		(% / -)	(1/d)	(1/d)	(-)	(-)	(1/d)	(1/d)
SFO	**261.70**	869		+	0.858 / 1.61	0.002648			<0.001	0.00240 to 0.003	-
DFOP	314.8	>1000	32.8 / 362	+	0.740 / 0.312	0.021124	0.001913	0.0871	0.379 / 0.222	-0.11017 to 0.152	-0.00282 to 0.007

VA = visual assessment, + good, o acceptable, - poor
SWARC = Scaled Weighted Area under Residue Curve
CI = confidence interval

Modelling Endpoints: SFO fit is statistically (χ^2err <15%, t-test <0.05) and visually good. SWARC value is < 40, not indicating a biphasic decline. Consequently, **SFO** degradation model is appropriate for modelling endpoints.

SFO



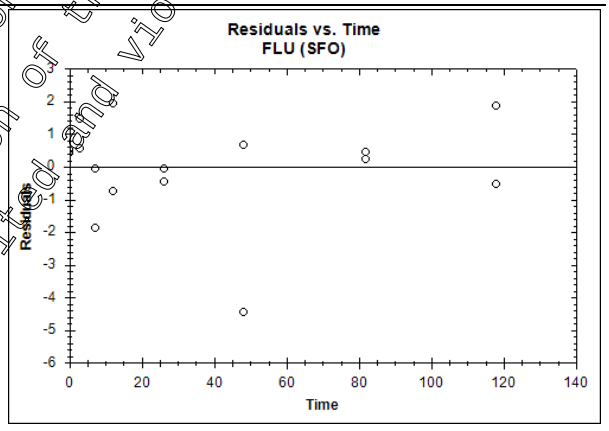


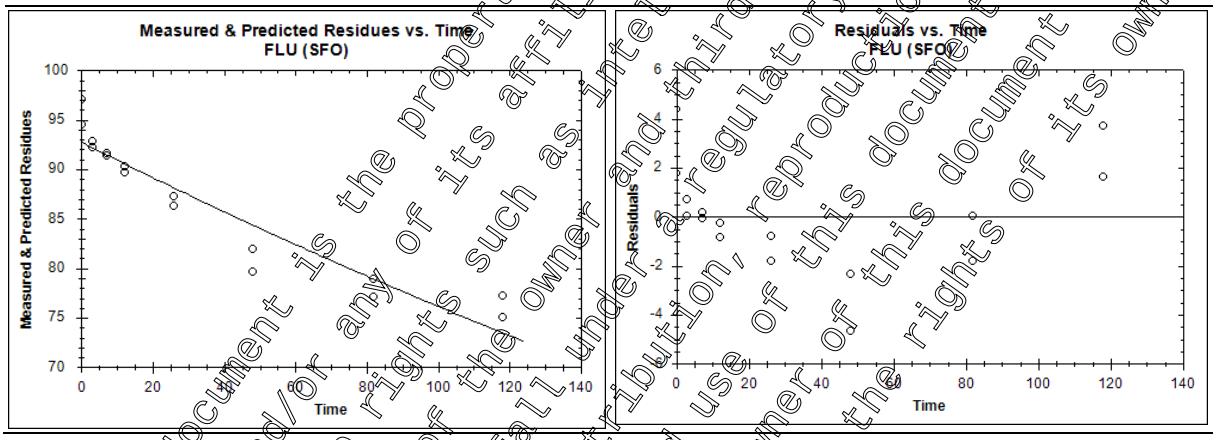
Table 7.1.2.1.1-65: Fluopyram: kinetic and statistical results of degradation in soil Paradiso San Zenone for modelling endpoints

Kinetic model	DT_{50} actual	DT_{90} actual	DT_{50} fast / slow	VA	χ^2err / SWARC	k_1	k_2	g	t-test k_1 / k_2	95th CI of k_1	95th CI of k_2
	(d)	(d)	(d)		(% / -)	(1/d)	(1/d)	(-)	(-)	(1/d)	(1/d)
SFO	**351.85**	>1000	-	o	1.84 / 15.2	0.00197	-	-	<0.001	0.00162 to 0.002	-
DFOP	>1000	>1000	30.2 / >1000	+	0.682 / 0.360	0.022944	< 5 E-7	0.2114	0.092 / 0.5	-0.0089 to 0.053	-0.0027 to 0.003

VA = visual assessment, + good, o acceptable, - poor
SWARC = Scaled Weighted Area under Residue Curve
CI = confidence intervall

Modelling Endpoints: SFO fit is statistically good (χ^2err <15%, t-test <0.05) and visually acceptable. SWARC value is < 40, not indicating a strong biphasic decline. Consequently, **SFO** degradation model is appropriate for modelling endpoints.

SFO



Data were normalised to standard conditions. Moisture and temperature correction factors to normalise DT_{50} values to a moisture of pF2 and 20°C are summarised in the following table.

Table 7.1.2.1.1-66: Moisture and temperature correction factors $f_\theta \cdot f_T$ for DT_{50} normalisation (reference moisture at pF2, 20°C; Q_{10} 2.58), (measured field capacity, θ_{ref}: measured moisture at pF 2; MWHC: maximum water holding capacity)

Soil	Soil texture (USDA)	Study moist. (% MWHC) [1]	MWHC (g/100 g)	Study moist. θ (g/100 g) [1]	Study temp. T (°C) [2]	measured field capacity θ_{ref} (g/100 g)	f_θ (-)	f_T (-)	$f_\theta \cdot f_T$ (-)
Little Oliver	Sandy loam	53.6	49.3	26.4	19.4	17.0	1.00	0.9447	0.9447
Auchy les Mines	Silt loam	54.0	53.2	28.7	19.4	27.2	1.00	0.9447	0.9447
Urbanowice	Silt loam	53.6	43.9	23.53	19.4	32.7	0.7942	0.9447	0.7503
Charles River Farm	Clay	54.0	55.4	29.9	19.4	29.2	1.00	0.9447	0.9447
Sindos	Loam	54.0	55.6	29.7	19.4	24.7	1.00	0.9447	0.9447
Paradiso San Zenone	Sandy loam	53.8	51.1	27.3	19.4	21.6	1.00	0.9447	0.9447

[1] mean measured values used (M-681092-02-1, p. 100), nominal 55 % MWHC
[2] mean recorded temperature (M-681092-02-1, p. 102)

III. CONCLUSIONS

The normalised laboratory soil $DegT_{50}$ parameters of fluopyram for modelling purpose based on residue data from an aerobic laboratory soil degradation study in European soils are summarised in the table below.

Table 7.1.2.1.1-67: Laboratory soil $DegT_{50}$ parameters of fluopyram for modelling purpose (normalised: pF2, 20°C, Q10 2.58)

Fluopyram	Dark aerobic conditions					
Soil type (USDA)	pH ($CaCl_2$)	T (C°) / % MWHC [2]	$DegT_{50\ actual}$ / $DT_{90\ actual}$ (d)	$DegT_{50\ mod}$ (d) 20°C pF2 / 10 kPa [1]	St. (χ^2)	Method of calculation
Sandy loam, Little Oliver, UK	5.5	19.4 / 53.6	>1000 / >1000	1000 (default)	1.02	SFO
Silt loam, Auchy les Mines, F	7.5	19.4 / 54.0	1051.3 / >1000	993.2	1.12	SFO
Silt loam Urbanowice, POL	4.9	19.4 / 53.6	>1000 / >1000	1000 (default)	0.998	SFO
Clay, Charles River Farm, Lleida, ES	7.7	19.4 / 54.0	489.17 / >1000	462.12	1.10	SFO
Loam, Sindos, GR	7.2	19.4 / 54.0	261.70 / 869	247.23	0.858	SFO
Sandy loam, Paradiso San Zenone, IT	5.4	19.4 / 53.8	351.85 / >1000	332.40	1.84	SFO

[1] Normalised to 20°C and pF 2 / 10 kPa, using Q_{10} of 2.58, Walker equation coefficient 0.7
[2] mean measured values used (M-681092-02-1, p. 100, p. 102)

3. Assessment and conclusion

Assessment and conclusion by applicant:
The kinetic evaluation followed FOCUS guidances and is considered valid and reliable.

Assessment and conclusion by RMS:
Outcome and conclusion of the study: RMS should indicate if they agree to the results and conclusions of the APPL.

1. Information on the study

Data Point:	KCA 7.1.2.1.1/13
Report Author:	[redacted]
Report Year:	2021
Report Title:	Fluopyram (FLU): Kinetic evaluation of aerobic laboratory soil degradation in European soils (Yuan and Kasel, 2020) according to FOCUS kinetics using KinGUI 2.1
Report No:	EnSa-20-0773
Document No:	M-761969-01-1
Guideline(s) followed in study:	not applicable
Deviations from current test guideline:	Current Guideline: not applicable (kinetic evaluation)
Previous evaluation:	No, not previously submitted
GLP/Officially recognised testing facilities:	No, not conducted under GLP/Officially recognised testing facilities
Acceptability/Reliability:	Yes

2. Full summary of KCA 7.1.2.1.1/13

Executive Summary

The residue data of aerobic laboratory soil residue data of fluopyram (FLU) and fluopyram-7-hydroxy (FLU-7-OH) of an aerobic soil degradation study with fluopyram the (KCA 7.1.1.1/06, M-753426-01-1) was evaluated for calculation of trigger and modelling endpoints following the recommendations given by FOCUS Kinetics.

The non-normalised DT_{50} values (trigger endpoints) were between 173.2 and <1000 days for fluopyram and between 18.67 and 74.68 days for fluopyram-7-hydroxy. The normalised (20 °C, pF 2) DT_{50} values (modelling endpoints) were between 163.2 and 995.9 days for fluopyram and between 17.64 and 88.19 days for fluopyram-7-hydroxy.

I. METHODS

A kinetic modelling analysis of aerobic laboratory soil residue data of fluopyram (FLU) and fluopyram-7-hydroxy (FLU-7-OH) was conducted in order to derive kinetic parameters suitable for modelling and for trigger purpose, using the software tool KinGUI 2.1. The identification of the appropriate kinetic model followed the recommendations given by FOCUS Kinetics (FOCUS, 2006, 2014a) based on a detailed statistical analysis including visual assessment, χ^2 statistic, significance t-test and correlation analysis. Additionally, the Scaled Weighted Area under Residue Curve (SWARC) was used as a further indicator for the visual assessment and to choose the appropriate model.

The modelling analysis is based on residue data from an aerobic laboratory soil degradation study in European soils (KCA 7.1.1.1/06, M-753426-01-1).

The soil metabolite fluopyram-7-hydroxy was found at relevant amounts in soils (> 5% of applied radioactivity), and with sufficient data points above the limit of detection (LOD), in 2 soils Le Thour and Brannens. Therefore, the metabolite degradation was included in the pathway, even when it was not found at relevant amounts (> 5 %).

For soils Hoeltinghausen, Hornton, Balbiano, Almayate East it was assumed the parent directly degraded in the sink. For soils Le Thour and Brannens, the following degradation pathway was considered in the compartment model.

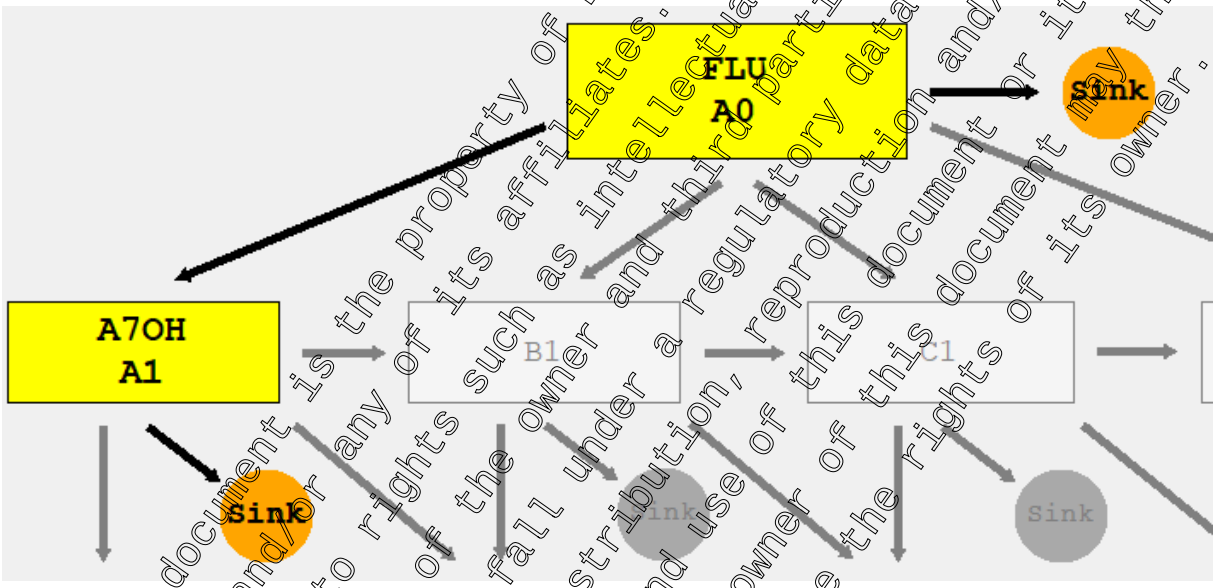


Figure 7.1.2.1.1-8: Compartment model of aerobic soil degradation of fluopyram (FLU = fluopyram, A7OH = FLU-7-OH) used for soils Le Thour and Brannens

II. RESULTS

Degradation of fluopyram

Results of the kinetic evaluation for modelling and trigger purpose based on residue data from an aerobic laboratory soil degradation study in EU soils are summarised in the tables below.

Table 7.1.2.1.1-68: Fluopyram: kinetic and statistical results of degradation in soil Hoeltinghausen for modelling endpoints, parent only fit

Kinetic model	DT_{50} actual	DT_{90} actual	DT_{50} fast / slow	VA	χ^2err / SWARC	k_1	k_2	g	t-test k_1 / k_2	95th CI of k_1	95th CI of k_2
	(d)	(d)	(d)		(% / -)	(1/d)	(1/d)	(-)	(-)	(1/d)	(1/d)
SFO	**1054.2**	>1000	-	+	0.668 / 4.86	0.0006575	-		<0.001	0.00047 to 0.001	-
DFOP	1054.2	>1000	14.2 / 1054.2	+	0.770 / 4.86	0.04866	0.0006575	2.56 E-14	na / 0.002	na	0.00029 to 0.001

VA = visual assessment, + good, o acceptable, - poor
SWARC = Scaled Weighted Area under Residue Curve
CI = confidence intervall
na = not available

Modelling Endpoints: SFO fit is statistically (χ^2err <15%, t-test <0.05) and visually good (please note, y-axis of left graph shows only a very small range). SWARC value is < 40, not indicating a biphasic decline. Consequently, **SFO** degradation model is appropriate for modelling endpoints.
However, it should be noted, that the microbial activity in this soil was always < 0.79% of TOC and thus probably significantly reduced compared to a standard trigger of 1 % TOC.

SFO

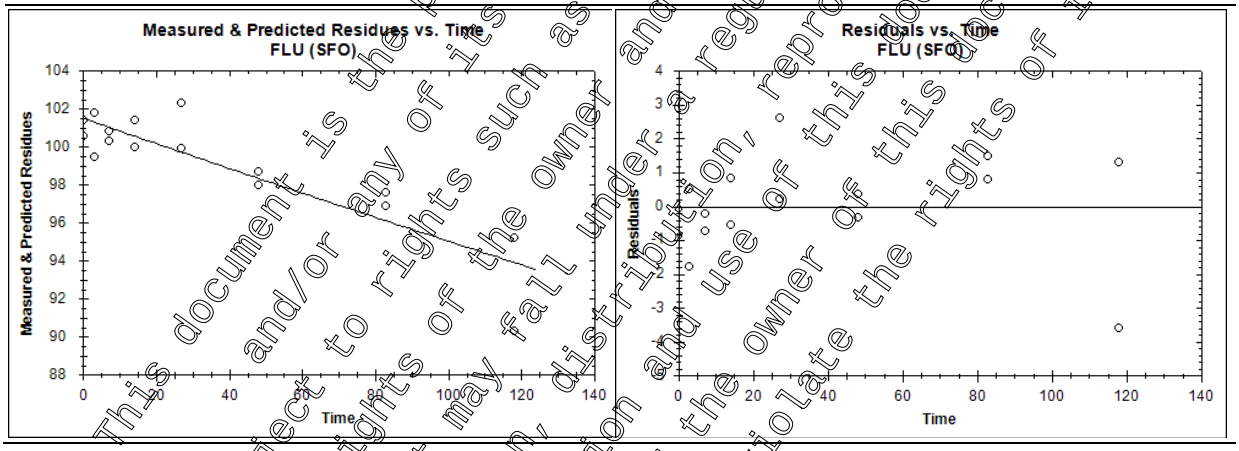


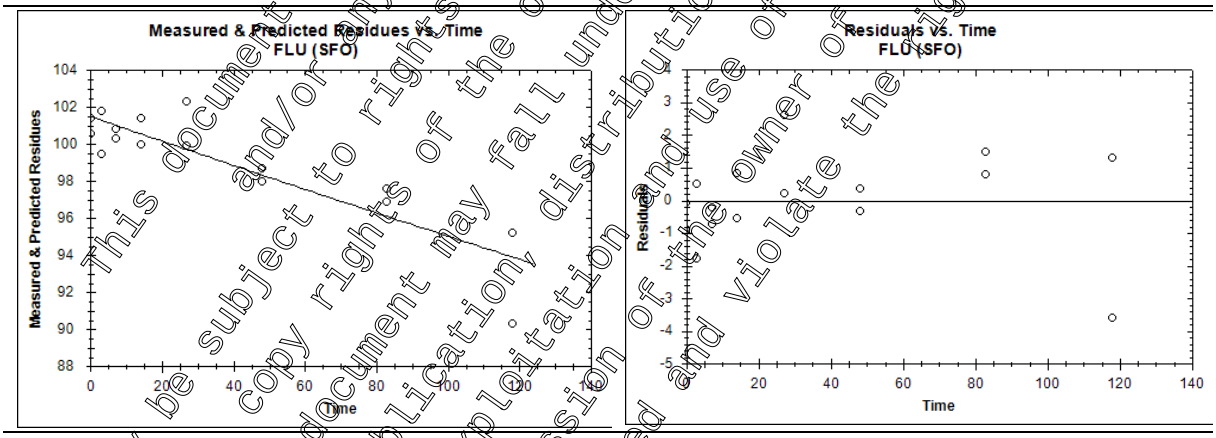
Table 7.1.2.1.1-69: Fluopyram: kinetic and statistical results of degradation in soil Hoeltinghausen for trigger endpoints, parent only fit

Kinetic model	DT_{50} actual	DT_{90} actual	VA	χ^2err / SWARC	k_1 / α	k_2 / β	g / t_b	t-test k_1 / k_2	95th CI of k_1	95th CI of k_2
	(d)	(d)		(% / -)	(1/d / -)	(1/d / d)	(- / d)	(-)	(1/d)	(1/d)
SFO	**1054.2**	**>1000**	+	0.668 / 4.86	0.0006575		-	<0.001 / -	0.00047 to 0.001	-
DFOP	1054.0	>1000	+	0.770 / 4.86	0.04866	0.0006575	2.56 E-14	na / 0.002	na	0.00029 to 0.001
FOMC	1055.0	>1000	+	0.713 / 4.86	313	476000	-	-	-	-
HS	847.0	>1000	+	0.493 / 0.12	0	0.0008452	- / 27.0	0.50 / <0.001	-0.00144 to 0.001	0.00046 to 0.001

VA = visual assessment, + = good, o = acceptable, - = poor
SWARC = Scaled Weighted Area under Residue Curve
CI = confidence intervall
na = not available

Trigger Endpoints: SFO fit (parent only) is statistically and visually (χ^2err, t-test) good, DFOP, FOMC and HS fits were alternatively tested. For DFOP and HS, t-test of k_1 failed in combination with DT_{50} and DT_{90} extrapolated beyond study end. Even, HS shows a lag phase, which is not considered appropriate for such a trigger evaluation. For FOMC, DT_{50} and DT_{90} are extrapolated beyond study end. All three fits are therefore not suitable, especially for accumulation assessments. Consequently, **SFO** degradation model is appropriate for trigger endpoints, as it shows lowest χ^2err of all suitable models (SFO).

SFO



HS

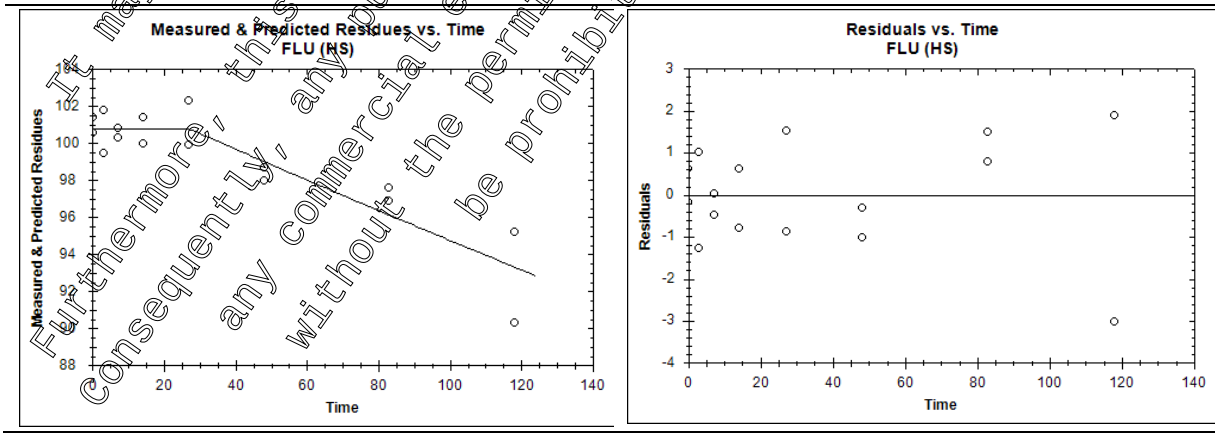


Table 7.1.2.1.1-70: Fluopyram: kinetic and statistical results of degradation in soil Hornton for modelling endpoints, parent only fit

Kinetic model	DT_{50} actual	DT_{90} actual	DT_{50} fast / slow	VA	χ^2err / SWARC	k_1	k_2	g	t-test k_1 / k_2	95th CI of k_1	95th CI of k_2
	(d)	(d)	(d)		(% / -)	(1/d)	(1/d)	(-)	(-)	(1/d)	(1/d)
SFO	**515.2**	>1000	-	o	2.27/ 17.91	0.0013453	-		<0.001	0.00083 to 0.002	-
DFOP	838	>1000	5.36 / 973.7	+	1.13 / 0.672	0.1292	0.0007119	0.0921	0.099 / 0.041	-0.05681 to 0.315	-0.00002 to 0.001

VA = visual assessment, + good, o acceptable, - poor
SWARC = Scaled Weighted Area under Residue Curve
CI = confidence intervall

Modelling Endpoints: SFO fit is statistically good (χ^2err <15%, t-test <0.05) and visually acceptable (please note, y-axis of left graph shows only a very small range). SWARC value is < 40 not indicating a biphasic decline. Consequently, **SFO** degradation model is appropriate for modelling endpoints.

SFO

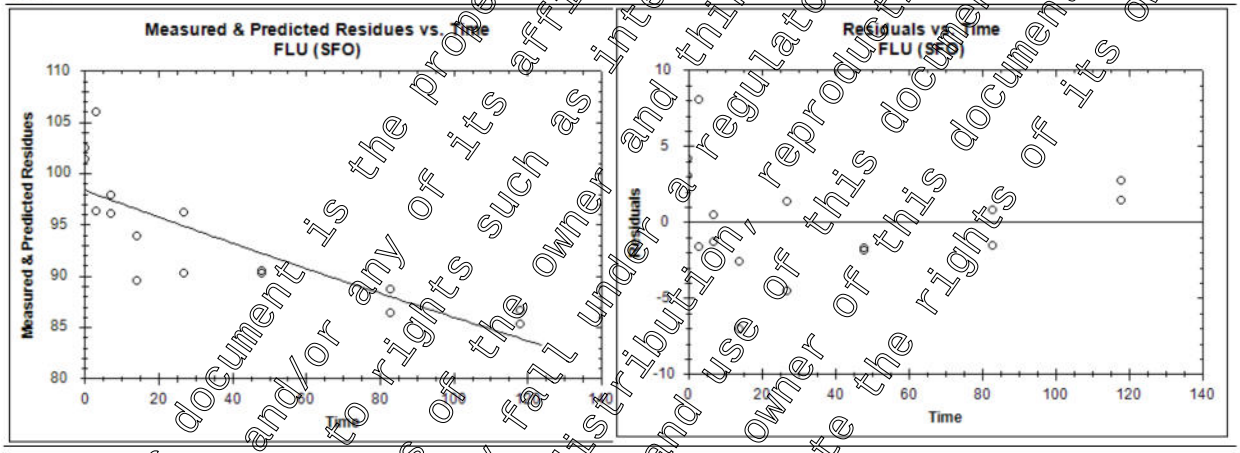


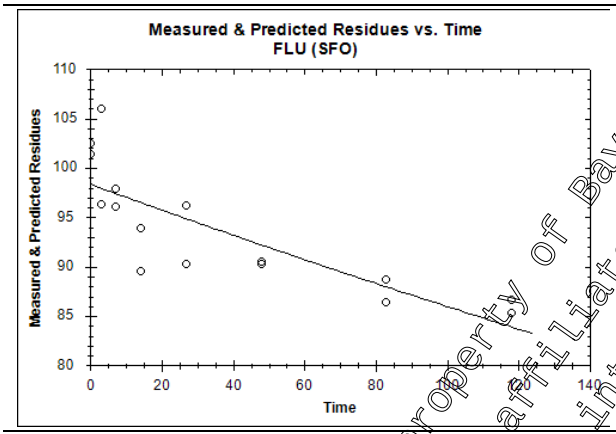
Table 7.1.2.1.1-71: Fluopyram: kinetic and statistical results of degradation in soil Hornton for trigger endpoints, parent only fit

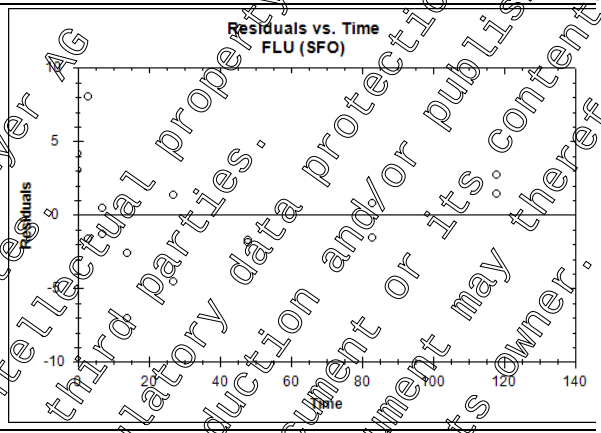
Kinetic model	DT_{50} actual	DT_{90} actual	VA	χ^2err / SWARC	k_1 / α	k_2 / β	g / t_b	t-test k_1 / k_2	95th CI of k_1	95th CI of k_2
	(d)	(d)		(% / -)	(1/d / -)	(1/d / d)	(- / d)	(-)	(1/d)	(1/d)
SFO	515.2	>1000	o	2.27/ 17.91	0.001345	-	-	<0.001	0.00083 to 0.002	-
DFOP	838.0	>1000	+	1.13 / 0.67	0.1292	0.0007119	0.0921 / -	0.099 / 0.041	-0.05681 to 0.315	-0.00002 to 0.001
FOMC	>1000	>1000		1.19 / 0.87	0.04787	3.19759	-	-	-	-
HS	**805.1**	**>1000**	+	0.742 / 0.47	0.00723	0.0007504	- / 13.74	0.044 / 0.006	-0.00040 to 0.015	0.00025 to 0.001

VA = visual assessment, + = good, o = acceptable, - = poor
SWARC = Scaled Weighted Area under Residue Curve
CI = confidence intervall

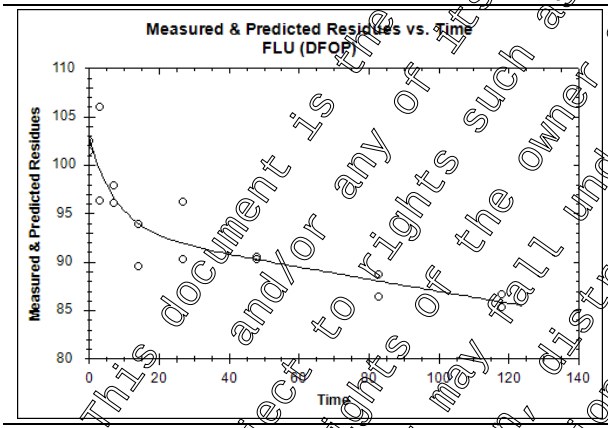
Trigger Endpoints:	SFO fit (parent only) is statistically (χ^2err, t-test) good and visually acceptable. DFOP, FOMC and HS fits were alternatively tested. For DFOP, t-test of k_{fast} failed in combination with DT_{50} and DT_{90} extrapolated beyond study end. For FOMC, DT_{50} and DT_{90} are extrapolated beyond study end. Both fits are therefore not suitable, especially for accumulation assessments. HS fit is statistically (χ^2err, t-test) good and visually acceptable. Consequently, **HS** degradation model is appropriate for trigger endpoints, as it shows lowest χ^2err of all suitable models (SFO, HS).

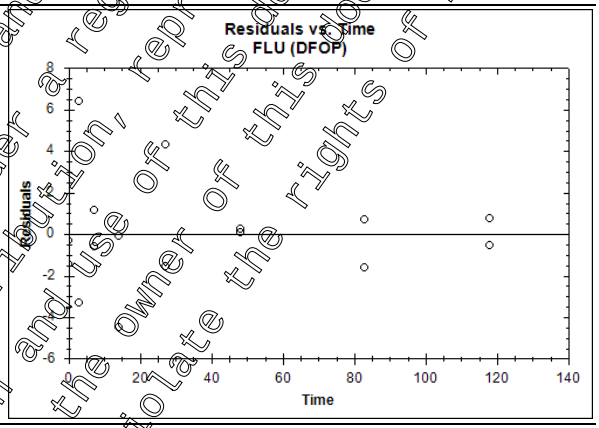
SFO



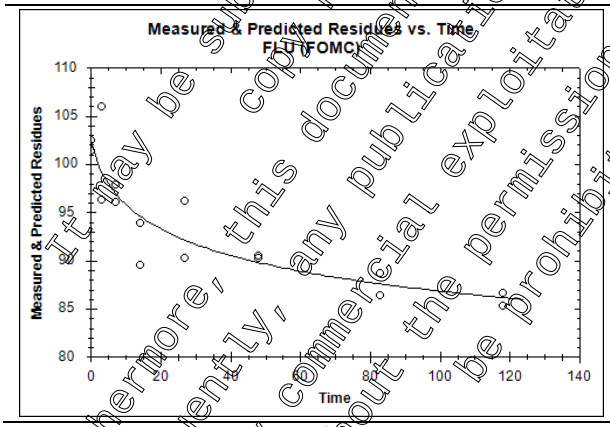


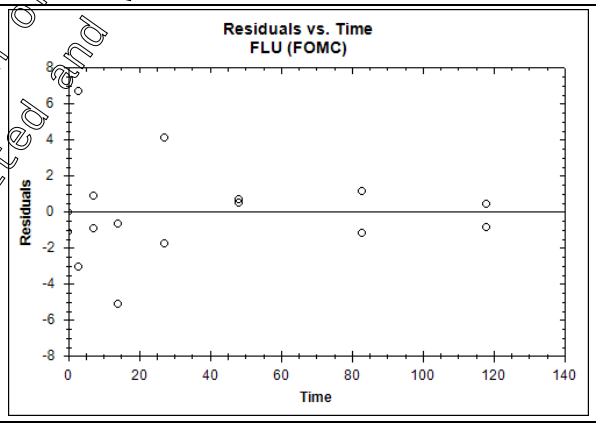
DFOP



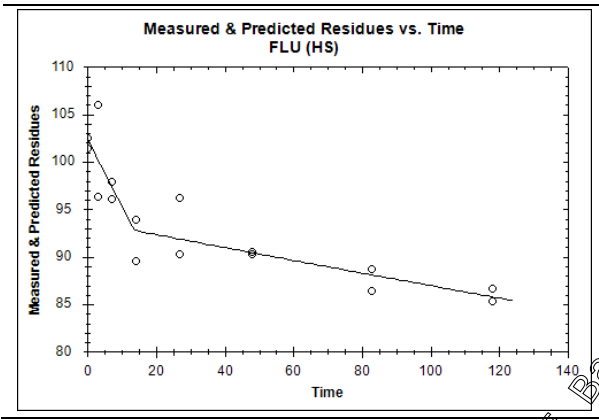


FOMC





HS



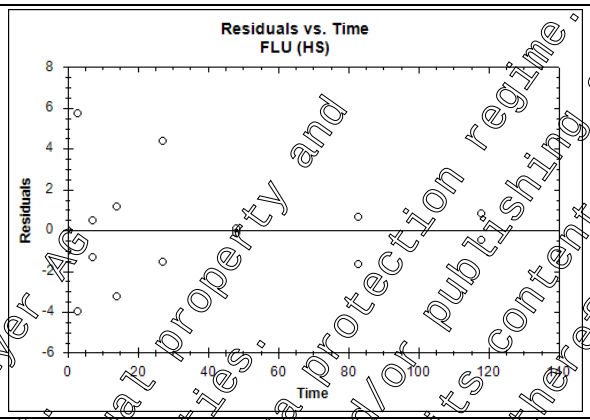


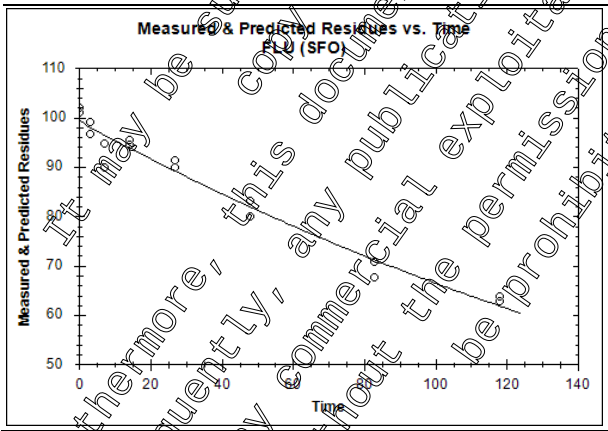
Table 7.1.2.1.1-72: Fluopyram: kinetic and statistical results of degradation in soil Le Thour for modelling endpoints, pathway fit

Kinetic model	DT_{50} actual	DT_{90} actual	DT_{50} fast / slow	VA	χ^2err / SWARC	k_1	k_2	g	t-test k_1 / k_2	95th CI of k_1	95th CI of k_2
	(d)	(d)	(d)		(% / -)	(1/d)	(1/d)	(-)	(-)	(1/d)	(1/d)
SFO	**172.8**	573.9	-	+	1.84 / 2.16	0.004012	-	-	0.001	0.00358 to 0.004	-
DFOP	173.9	627.6	166.7 / na	+	2.12 / 2.13	0.004158 [1]	1 E-6 [1]	0.9715 [1]	0.4684 / 0.5	-0.09765 to 0.106	-2.68888 to 2.689

VA = visual assessment: + good, o acceptable, - poor
SWARC = Scaled Weighted Area under Residue Curve
CI = confidence intervall
[1] = fast and slow rate k1, k2 were exchanged here, compared to KinGUI output, to deliver the correct g, which has to be related to the fast phase, g fast = 1 – g slow).

Modelling Endpoints: SFO fit is statistically (χ^2err <15%, t-test <0.05) and visually good. SWARC value is < 40, not indicating a biphasic decline.
Consequently, SFO degradation model is appropriate for modelling endpoints.

SFO



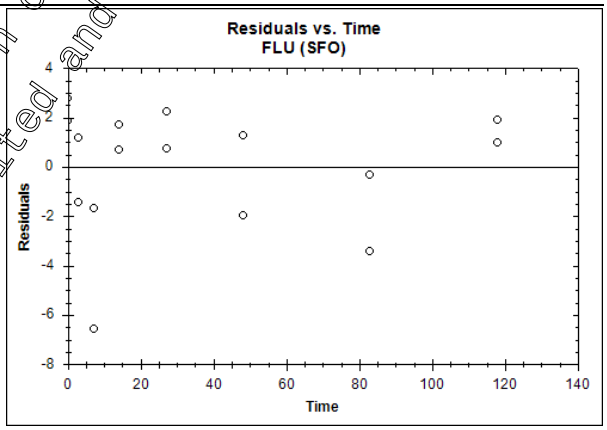


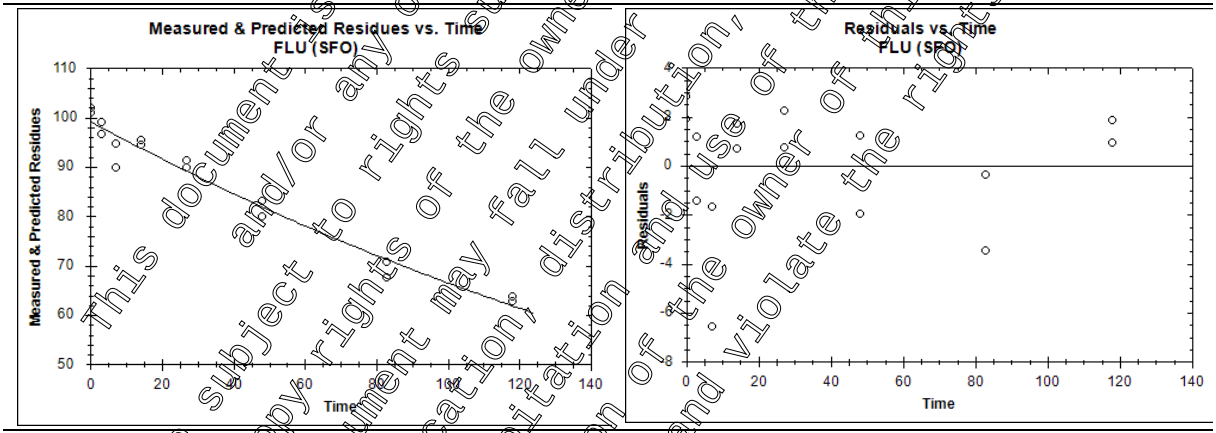
Table 7.1.2.1.1-73: Fluopyram: kinetic and statistical results of degradation in soil Le Thour for trigger endpoints, parent only fit

Kinetic model	DT_{50} actual	DT_{90} actual	VA	χ^2err / SWARC	k_1 / α	k_2 / β	g / t_b	t-test k_1 / k_2	95th CI of k_1	95th CI of k_2
	(d)	(d)		(% / -)	(1/d / -)	(1/d / d)	(- / d)	(-)	(1/d)	(1/d)
SFO	**173.2**	**575.4**	+	1.84 / 2.19	0.004002		-	<0.001	0.00357 to 0.004	-
DFOP	170.9	588.2	+	1.84 / 2.13	0.7127	0.003857	0.0337 / -	0.351 / <0.001	-2.855 to 4.28	0.00335 to 0.004
FOMC	185.3	936.7	+	1.93 / 3.18	2.138	483.901	-	-	-	-
HS	171.7	591.8	+	1.83 / 2.16	0.0122	0.003831	- / 4.24	0.085 / <0.001	-0.00418 to 0.029	0.00334 to 0.004

VA = visual assessment, + = good, o = acceptable, - = poor
SWARC = Scaled Weighted Area under Residue Curve
CI = confidence intervall

Trigger Endpoints: SFO fit (parent only) is statistically and visually (χ^2err, t-test) good, DFOP, FOMC and HS fits were alternatively tested. No visual nor statistical improvement could be reached with biphasic models. For DFOP and HS, t-test of k_{fast} failed in combination with DT_{50} and DT_{90} extrapolated beyond study end. For FOMC, DT_{50} and DT_{90} are extrapolated beyond study end. All three fits are therefore not suitable, especially for accumulation assessments. Consequently, **SFO** degradation model is appropriate for trigger endpoints, as it shows lowest χ^2err of all suitable models (SFO).

SFO



HS

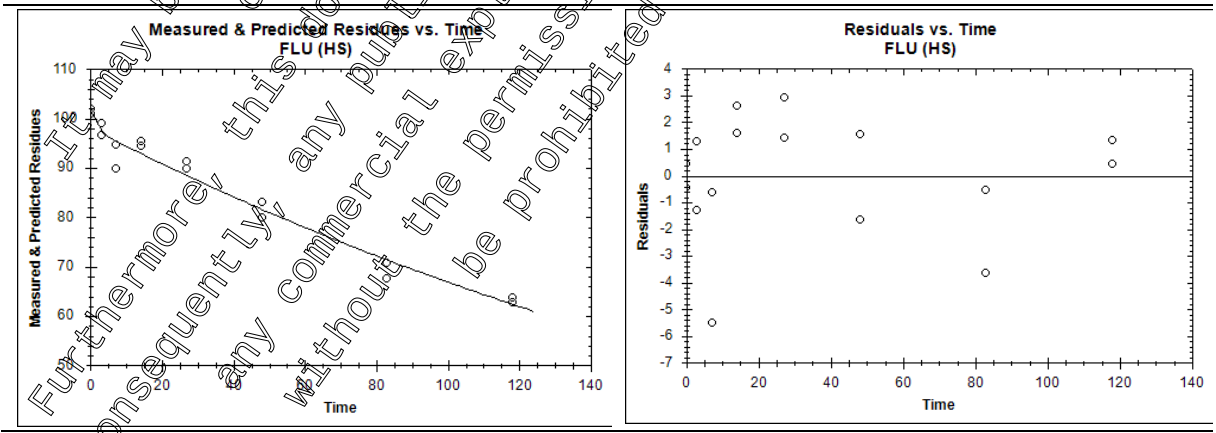


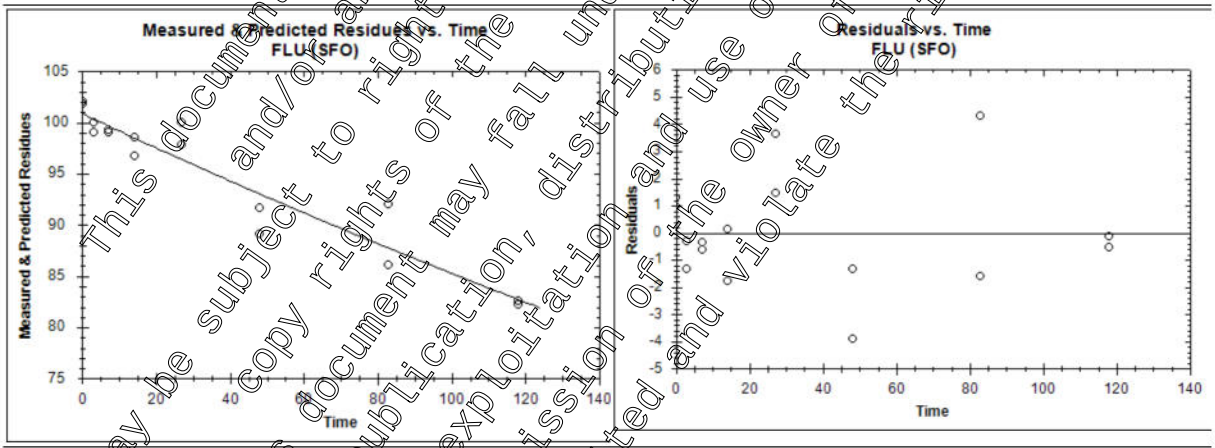
Table 7.1.2.1.1-74: Fluopyram: kinetic and statistical results of degradation in soil Brannens for modelling endpoints, pathway fit

Kinetic model	DT_{50} actual	DT_{90} actual	DT_{50} fast / slow	VA	χ^2err / SWARC	k_1	k_2	g	t-test k_1 / k_2	95th CI of k_1	95th CI of k_2
	(d)	(d)	(d)		(% / -)	(1/d)	(1/d)	(-)	(-)	(1/d)	(1/d)
SFO free fit	413.1	>1000	-	+	1.26 / 0.476	0.001678	-	-	<0.001	0.00139 to 0.002	-
DFOP	558.8	>1000	242.3 / >1000	+	1.46 / 0.493	0.002861	2.733 E-5	0.6195	0.4923 / 0.4999	-0.2851 to 0.291	-0.3982 to 0.3982
SFO fixed fit	**413.1** fix	>1000 fix	-	+	1.20 / 0.476	0.001678	-	-	-	-	-

VA = visual assessment, + good, o acceptable, - poor
SWARC = Scaled Weighted Area under Residue Curve
CI = confidence intervall
fixed fit: parent parameters fixed to free fit values, DT_{50} FLU-7-OH fixed to free fit values +25%

Modelling Endpoints: SFO fit is statistically (χ^2err <15%, t-test <0.05) and visually good. SWARC value is <40, not indicating a biphasic decline. Consequently, **SFO** degradation model is appropriate for modelling endpoints.
However, metabolite FLU-7-OH is rising until the end of study. The pathway fit (free fit) was therefore modified with a fixed DT_{50} value for FLU-7-OH (fixed fit). The DT_{50} value of FLU-7-OH was fixed to a conservative value: DT_{50} of free fit * 1.25, formation fractions were fitted and parent parameters were fixed to values derived from the free fit. Finally, this **fixed SFO fit** was considered appropriate.

SFO free fit



SFO fixed fit

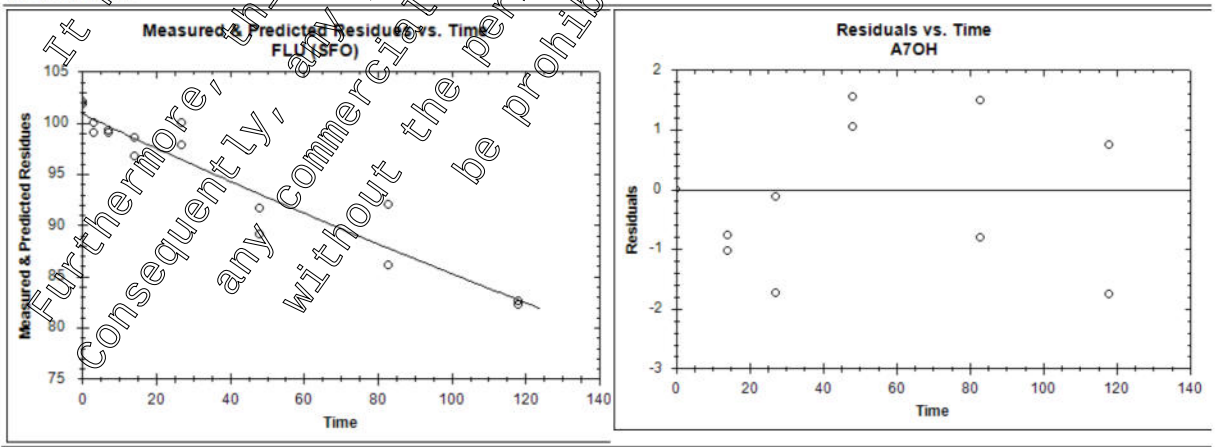


Table 7.1.2.1.1-75: Fluopyram: kinetic and statistical results of degradation in soil Brannens for trigger endpoints, parent only fit

Kinetic model	DT_{50} actual	DT_{90} actual	VA	χ^2err / SWARC	k_1 / α	k_2 / β	g / t_b	t-test k_1 / k_2	95th CI of k_1	95th CI of k_2
	(d)	(d)		(% / -)	(1/d / -)	(1/d / d)	(- / d)	(-)	(1/d)	(1/d)
SFO	**413.3**	**>1000**	+	1.26 / 0.475	0.001677	-	-	<0.001 / -	0.00139 to 0.002	-
DFOP	416.5	>1000	+	1.38 / 0.423	6.055	0.001628	0.0148 / -	<0.001 / <0.001	6.055 to 6.055	0.00130 to 0.002
FOMC	460.9	>1000	+	1.35 / 0.486	2.407	1381	-	-	-	-
HS	416.5	>1000	+	1.38 / 0.423	0.01009	0.001628	- / 1.77	0.031 / <0.001	0.00047 to 0.02	0.00130 to 0.002

VA = visual assessment, + = good, o = acceptable, - = poor
SWARC = Scaled Weighted Area under Residue Curve
CI = confidence intervall

Trigger Endpoints: SFO fit (parent only) is statistically and visually (χ²err, t-test) good. DFOP, FOMC and HS fits were alternatively tested. No visual nor statistical improvement could be reached with biphasic models. Consequently, **SFO** degradation model is appropriate for trigger endpoints, as it shows lowest χ^2err of all suitable models (SFO, DFOP, HS).

SFO

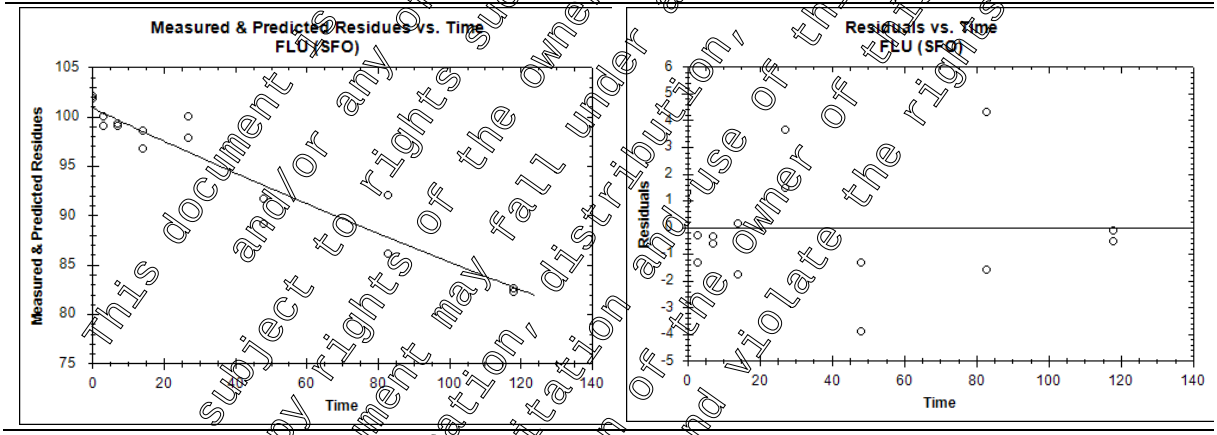


Table 7.1.2.1.1-76: Fluopyram: kinetic and statistical results of degradation in soil Balbiano for modelling endpoints, parent only fit

Kinetic model	DT_{50} actual	DT_{90} actual	DT_{50} fast / slow	VA	χ^2err / SWARC	k_1	k_2	g	t-test k_1 / k_2	95th CI of k_1	95th CI of k_2
	(d)	(d)	(d)		(% / -)	(1/d)	(1/d)	(-)	(-)	(1/d)	(1/d)
SFO	**366.5**	>1000	-	+	0.999 / 1.78	0.001891	-	-	<0.001	0.00167 to 0.002	-
DFOP	366.5	>1000	6.39 / 366.6	+	1.15 / 1.78	0.1085	0.001891	2.68 E-14	<0.001 / <0.001	0.1085 to 0.109	0.00156 to 0.002

VA = visual assessment, + good, o acceptable, - poor
SWARC = Scaled Weighted Area under Residue Curve
CI = confidence intervall

Modelling Endpoints: SFO fit is statistically (χ^2err <15%, t-test <0.05) and visually good. SWARC value is < 40, not indicating a biphasic decline. Consequently, **SFO** degradation model is appropriate for modelling endpoints.

SFO

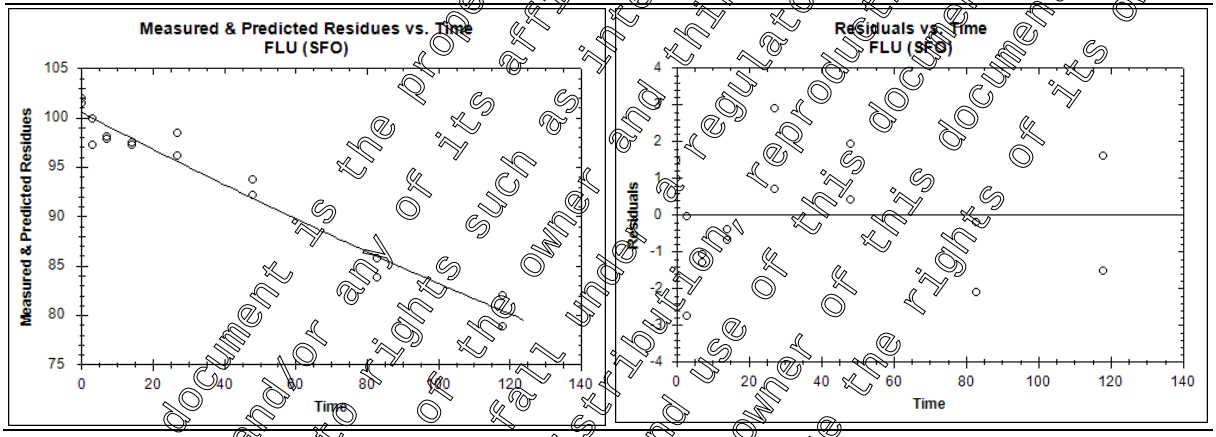


Table 7.1.2.1.1-77: Fluopyram: kinetic and statistical results of degradation in soil Balbiano for trigger endpoints, parent only fit

Kinetic model	DT_{50} actual	DT_{90} actual	VA	χ^2err / SWARC	k_1 / α	k_2 / β	g / t_b	t-test k_1 / k_2	95th CI of k_1	95th CI of k_2
	(d)	(d)		(% / -)	(1/d / -)	(1/d / d)	(- / d)	(-)	(1/d)	(1/d)
SFO	**366.5**	**>1000**	+	0.999 / 1.78	0.001891		-	<0.001 / -	0.00167 to 0.002	-
DFOP	366.5	>1000	+	1.15 / 1.78	0.1085	0.001891	<0.001 / -	<0.001 / <0.001	0.1085 to 0.109	0.00156 to 0.002
FOMC	366.6	>1000	+	1.07 / 1.78	1763	932300	-	-	-	-
HS	368.4	>1000	+	1.04 / 2.53	0.01098	0.001837	- / 1.79	0.005 / <0.001	0.00391 to 0.018	0.00159 to 0.002

VA = visual assessment, + = good, o = acceptable, - = poor
SWARC = Scaled Weighted Area under Residue Curve
CI = confidence intervall

Trigger Endpoints: SFO fit (parent only) is statistically and visually (χ^2err, t-test) good, DFOP, FOMC and HS fits were alternatively tested. No visual nor statistical improvement could be reached with biphasic models. Consequently, **SFO** degradation model is appropriate for trigger endpoints, as it shows lowest χ^2err of all suitable models (SFO, DFOP, HS).

SFO

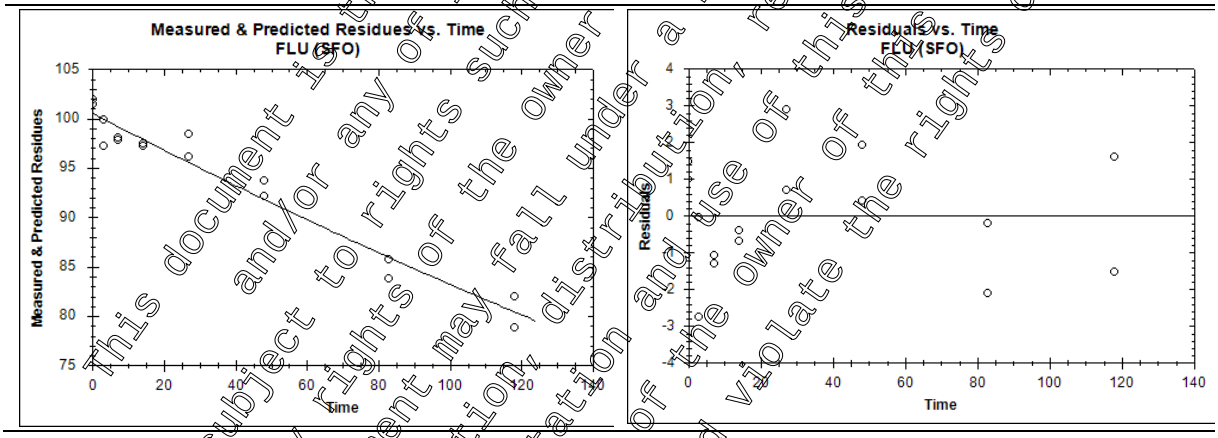


Table 7.1.2.1.1-78: Fluopyram: kinetic and statistical results of degradation in soil Almayate East for modelling endpoints, parent only fit

Kinetic model	DT_{50} actual	DT_{90} actual	DT_{50} fast / slow	VA	χ^2err / SWARC	k_1	k_2	g	t-test k_1 / k_2	95th CI of k_1	95th CI of k_2
	(d)	(d)	(d)		(% / -)	(1/d)	(1/d)	(-)	(-)	(1/d)	(1/d)
SFO	**292.9**	972.9	-	+	2.08 / 4.26	0.002367	-	-	<0.001	0.00196 to 0.003	-
DFOP	>1000	>1000	115.5 / >1000	+	2.35 / 3.80	0.006002	2.76 E-9	0.4724	0.477 / 0.5	-0.1911 to 0.203	-0.1259 to 0.126

VA = visual assessment, + good, o acceptable, - poor
SWARC = Scaled Weighted Area under Residue Curve
CI = confidence intervall

Modelling Endpoints: SFO fit is statistically (χ^2err <15% t-test <0.05) and visually good. SWARC value is < 40, not indicating a biphasic decline. Consequently, **SFO** degradation model is appropriate for modelling endpoints.

SFO

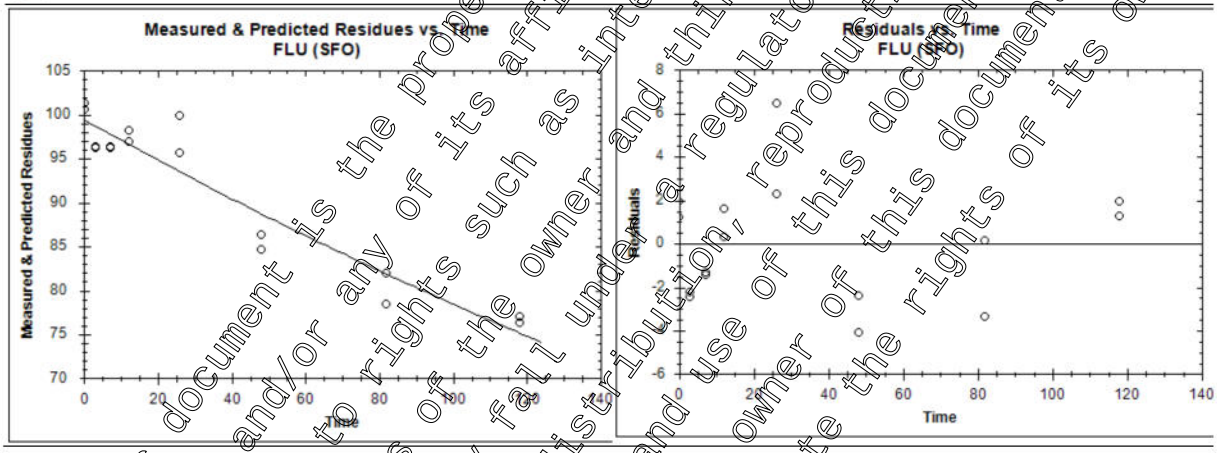


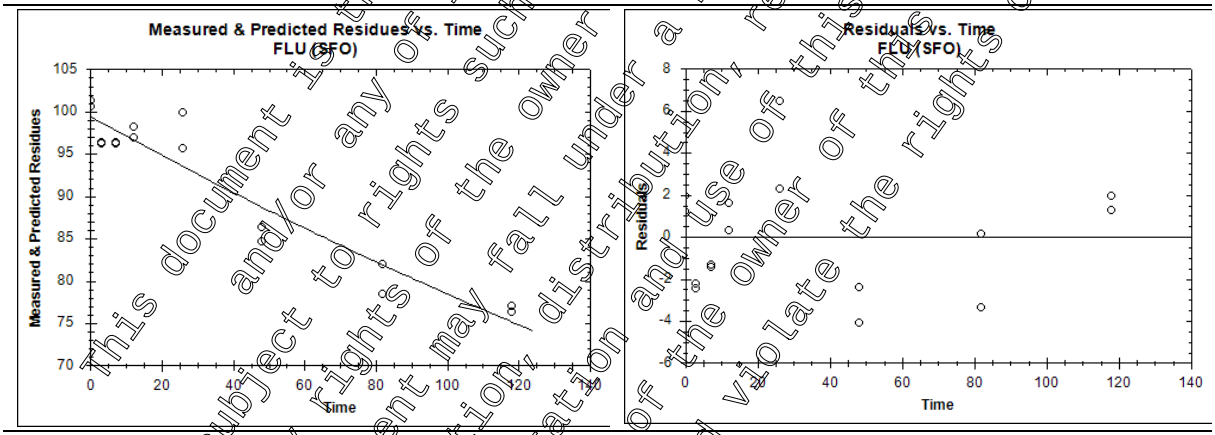
Table 7.1.2.1.1-79: Fluopyram: kinetic and statistical results of degradation in soil Almayete East for trigger endpoints, parent only fit

Kinetic model	DT_{50} actual	DT_{90} actual	VA	χ^2err / SWARC	k_1 / α	k_2 / β	g / t_b	t-test k_1 / k_2	95th CI of k_1	95th CI of k_2
	(d)	(d)		(% / -)	(1/d / -)	(1/d / d)	(- / d)	(-)	(1/d)	(1/d)
SFO	**292.9**	**972.9**	+	2.08 / 4.26	0.002367		-	<0.001	0.00196 to 0.002	-
DFOP	>1000	>1000	+	2.35 / 3.80	0.006002	2.76E-09	0.4724 / -	0.477 / 0.50	-0.1911 to 0.203	-0.1259 to 0.126
FOMC	396.6	>1000	+	2.18 / 3.91	0.7948	284.8919	-	-	-	-
HS	292.8	994.0	+	2.31 / 4.67	0.01936	0.002295	- / 1.23	0.032 / <0.001	0.00082 to 0.038	0.00184 to 0.003

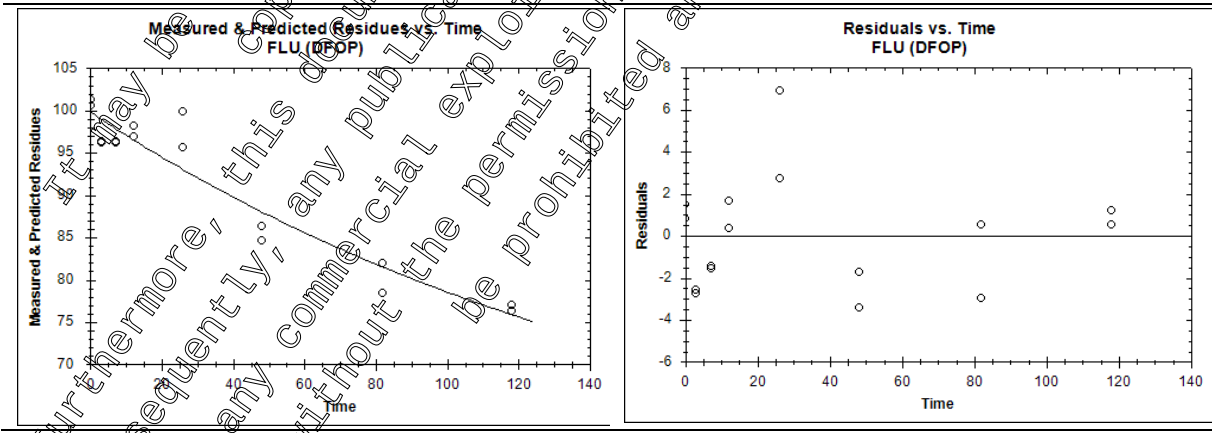
VA = visual assessment, + = good, o = acceptable, - = poor
SWARC = Scaled Weighted Area under Residue Curve
CI = confidence intervall

Trigger Endpoints: SFO fit (parent only) is statistically and visually (χ^2err, t-test) good, DFOP, FOMC and HS fits were alternatively tested. No visual nor statistical improvement could be reached with biphasic models. consequently, **SFO** degradation model is appropriate for trigger endpoints, as it shows lowest χ^2err of all suitable models (SFO, HS).

SFO



DFOP



Degradation of fluopyram-7-hydroxy

Results of the kinetic evaluation for modelling and trigger purpose based on residue data from an aerobic laboratory soil degradation study with fluopyram in EU soils are summarised in the tables below.

Table 7.1.2.1.1-80: FLU-7-OH: kinetic and statistical results of degradation in soil Le Thour for modelling endpoints

Kinetic model, Parent - metabolite	DT_{50} actual	DT_{90} actual	VA	χ^2err	SWARC	k	t-test k	95th CI of k	ff (FLU)
	(d)	(d)		(%)	(-)	(1/d)	(-)	(1/d)	(-)
SFO - SFO	**18.67**	62.01	o	19.68	4.21	0.03713	<0.001	0.01619 to 0.058	**0.4493**
DFOP - SFO	19.03	63.23	o	19.6	4.24	0.036419	0.0231	0.00231 to 0.071	0.4432

VA = visual assessment, + = good, o = acceptable, - = poor
SWARC = Scaled Weighted Area under Residue Curve
CI = confidence intervall

Modelling Endpoints: SFO fit (parent SFO) is statistically good and visually acceptable (χ^2err <25%, t-test < 0.1; formation fraction ff < 1, SWARC <40). Consequently, **SFO** degradation model (**parent SFO**) is appropriate for modelling endpoints.
The metabolite FLU-7-OH is slightly decreasing until the end of study (last 4 time points). Therefore, the free fitted **DT_{50} of 18.67 d is considered as a "reliable DT_{50}"**

SFO/SFO

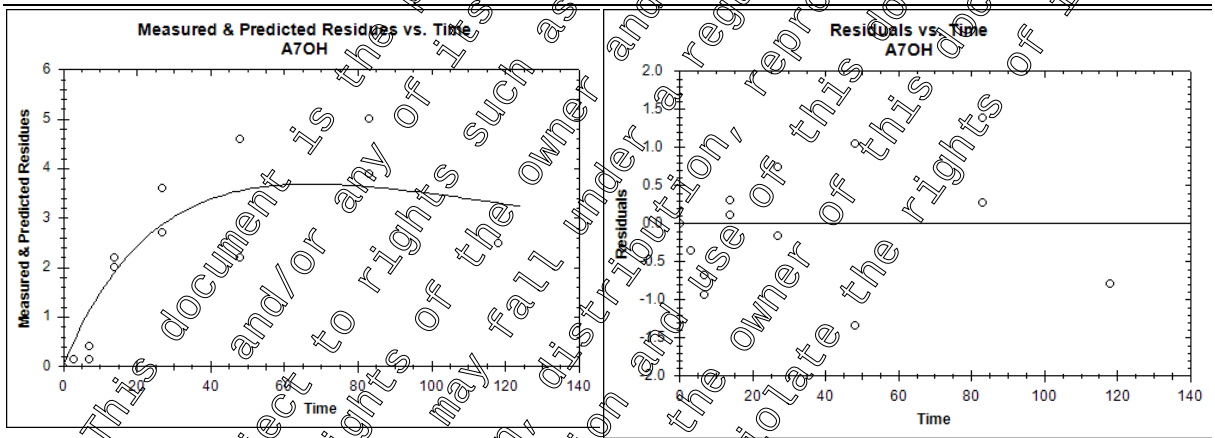


Table 7.1.2.1.1-81: FLU-7-OH: kinetic and statistical results of degradation in soil Le Thour for trigger endpoints, pathway fit

Kinetic model, Parent - metabolite	DT_{50} actual	DT_{90} actual	VA	χ^2err	SWARC	k	t-test k	95th CI of k	ff (FLU)
	(d)	(d)		(%)	(-)	(1/d)	(-)	(1/d)	(-)
SFO - SFO	**18.67**	**62.01**	o	19.68	4.21	0.03713	<0.001	0.01619 to 0.058	**0.4493**

VA = visual assessment, + = good, o = acceptable, - = poor
SWARC = Scaled Weighted Area under Residue Curve
CI = confidence intervall

Trigger Endpoints: SFO fit (parent SFO) is statistically good and visually acceptable (χ^2err < 25%, t-test < 0.1). Consequently, **SFO** degradation model (**parent SFO**) is appropriate for trigger endpoints.

SFO/SFO

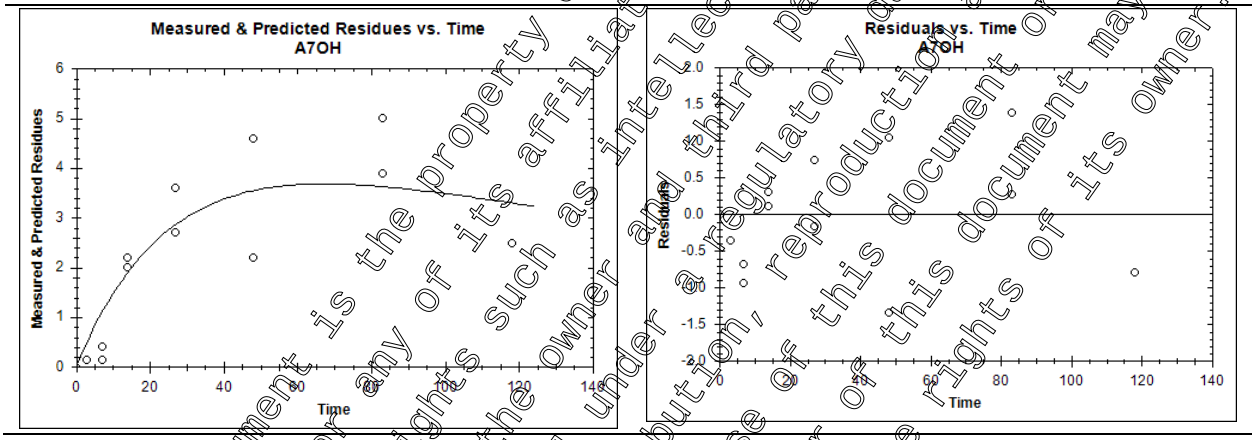


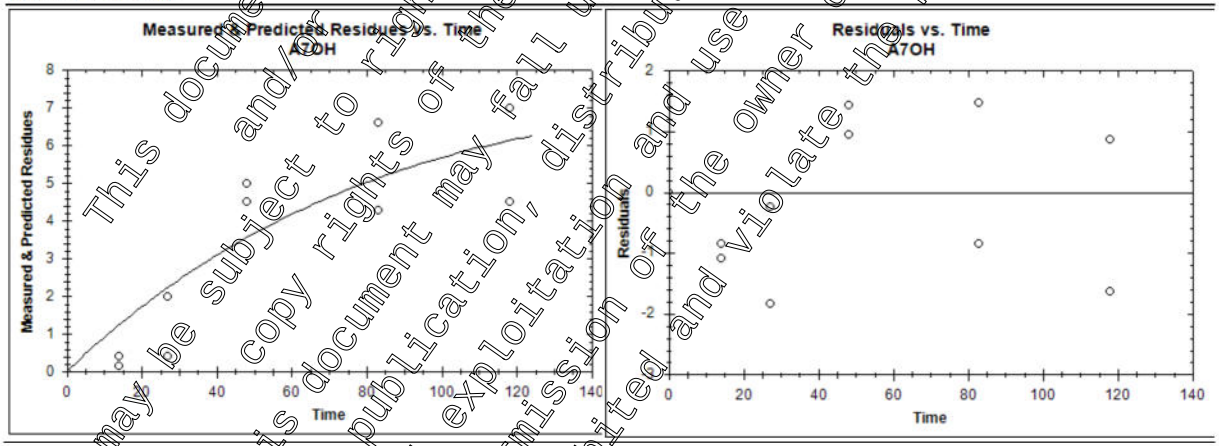
Table 7.1.2.1.1-82: FLU-7-OH: kinetic and statistical results of degradation in soil Brannens for modelling endpoints

Kinetic model, Parent - metabolite	DT_{50} actual	DT_{90} actual	VA	χ^2err	SWARC	k	t-test k	95th CI of k	ff (FLU)
	(d)	(d)		(%)	(-)	(1/d)	(-)	(1/d)	(-)
SFO - SFO, free fit	74.68	248.1	o	19.68	23.22	0.009282	0.108	-0.00505 to 0.024	0.567
DFOP - SFO	88.31	293.4	o	19.60	23.02	0.007849	0.2312	-0.01223 to 0.028	0.5333
SFO - SFO, fixed fit	**93.35** fix	310.1 fix	o	18.00	23.91	0.0074256			**0.5264**

VA = visual assessment, + = good, o = acceptable, - = poor
SWARC = Scaled Weighted Area under Residue Curve
CI = confidence intervall
fixed fit: parent parameters fixed to free fit values, DT_{50} FLU-7-OH fixed to free fit DT_{50} * 1.25

Modelling Endpoints: SFO fit (parent SFO) is statistically and visually acceptable (χ^2err <25%, t-test ~ 0.1, formation fraction ff is <1, SWARC <40). Consequently, SFO degradation model (parent SFO) is appropriate for modelling endpoints.
However, metabolite FLU-7-OH is rising until the end of study (last 4 time points). The pathway fit (free fit) was therefore modified with a fixed DT_{50} value for FLU-7-OH (fixed fit). The DT_{50} of FLU-7-OH was fixed to a conservative value (DT_{50} of free fit * 1.25), formation fractions were fitted and parent parameters were fixed to values derived from the free fit. Finally, this **fixed SFO** degradation model (**parent SFO**) is considered conservatively appropriate for modelling endpoints.
In addition, a more conservative fixed DT_{50} of 1000 d for FLU-7-OH was checked, which shows an over-prediction of the metabolite increase. 1000 d is not consistent with other "reliable" DT_{50}s (weight of evidence) and therefore considered not appropriate.

SFO/SFO free fit



SFO/SFO fixed fit

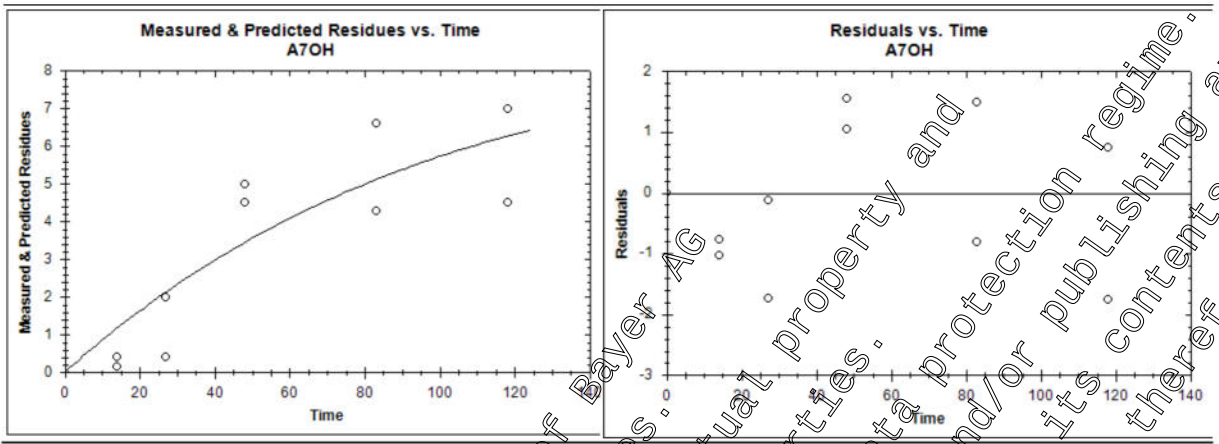


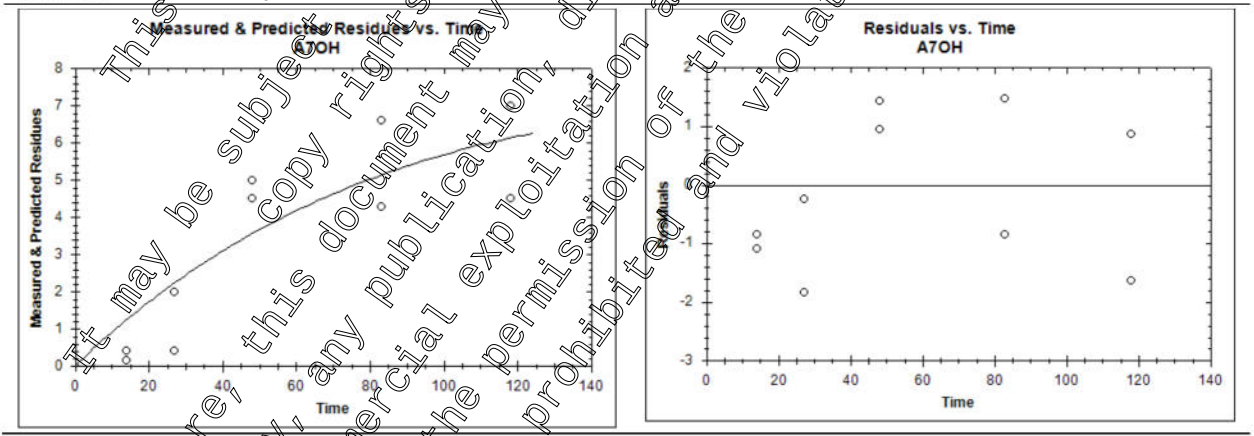
Table 7.1.2.1.1-83: FLU-7-OH: kinetic and statistical results of degradation in soil Brannens for trigger endpoints pathway fit

Kinetic model, Parent - metabolite	DT_{50} actual	DT_{90} actual	VA	χ^2 err	SWARC	k	t-test k	95th CI of k	ff (FLU)
	(d)	(d)		(%)	(-)	(1/d)	(-)	(1/d)	(-)
SFO - SFO	**74.68**	**248.1**	o	9.68	23.22	0.009282	0.108	-0.00505. to 0.024	**0.5671**

VA = visual assessment, + = good, o = acceptable, - = poor
SWARC = Scaled Weighted Area under Residue Curve
CI = confidence intervall

Trigger Endpoints: SFO fit (parent SFO) is statistically and visually acceptable (χ² err <25 %, t-test ~ 0.1, formation fraction < 1). Consequently, **SFO** degradation model (**parent SFO**) is appropriate for trigger endpoints.

SFO/SFO



Moisture and temperature correction factors to normalise DT_{50} values to a moisture of pF2 and 20°C are summarised in the following table.

Table 7.1.2.1.1-84: Moisture and temperature correction factors $f_\theta \cdot f_T$ for DT_{50} normalisation (reference moisture at pF2, 20°C; Q_{10} 2.58), (FOCUS field capacity, θ_{ref}: default of reference soil moisture, pF2, as in FOCUS, 2014b; MWHC: maximum water holding capacity)

Soil	Soil texture (USDA)	Study moist. (% MWHC)	MWHC (g/100 g)	Study moist. θ (g/100 g)	Study temp. T (°C)	measured field capacity θ_{ref} (g/100 g)	f_θ (-)	f_T (-)	$f_\theta \cdot f_T$ (-)
Hoeltinghausen	Sand	54.1 [1]	29.0	15.7 [1]	19.4 [2]	7.5	1.00	0.9447	0.9447
Hornton	Loam	54.8 [1]	54.3	29.8 [1]	19.4 [2]	30.9	0.9739	0.9447	0.9201
Le Thour	Silt loam	55.0 [1]	62.5	34.4 [1]	19.4 [2]	31.2	1.00	0.9447	0.9447
Brannens	Sandy loam	54.2 [1]	39.4	21.4 [1]	19.4 [2]	12.4	1.00	0.9447	0.9447
Balbiano	Sandy loam	54.5 [1]	48.7	26.5 [1]	19.4 [2]	18.7	1.00	0.9447	0.9447
Almayate East	Loam	54.6 [1]	46.6	25.4 [1]	19.4 [2]	27.7	0.9423	0.9447	0.8902

[1] mean measured values used (M-753426-01-1, p. 107); nominal: 55 % MWHC
[2] mean recorded temperature (M-753426-01-1, p. 109)

III. CONCLUSIONS

The laboratory soil $DegT_{50}$ parameters of fluopyram and fluopyram-7-hydroxy for modelling and trigger purpose based on residue data from an aerobic laboratory soil degradation study in EU soils are summarised in the tables below.

Table 7.1.2.1.1-85: Laboratory soil $DegT_{50}$ parameters of fluopyram for modelling purpose (normalised: pF2, 20°C, Q_{10} 2.58)

Fluopyram (FLU)	Dark aerobic conditions						
Soil type (USDA)	pH ($CaCl_2$)	T (°C) / % MWHC	$DegT_{50\ actual}$ / $DT_{90\ actual}$ (d)	$DegT_{50\ mod}$ (d) 20°C pF2 / 10 kPa [1]	St. (χ^2)	Method of calculation
Sand, Hoeltinghausen	4.5	19.4 / 54.1 [2]	1054.2 / >1000	995.9	0.668	SFO
Loam, Hornton	5.9	19.4 / 54.8 [2]	515.2 / >1000	474.0	2.27	SFO
Silt loam, Le Thour	7.4	19.4 / 55.0 [2]	172.8 / 573.9	163.2	1.84	SFO
Sandy loam, Brannens	4.7	19.4 / 54.2 [2]	413.1 / >1000	390.2	1.20	SFO
Sandy loam, Balbiano	7.1	19.4 / 54.5 [2]	366.5 / >1000	346.3	0.999	SFO
Loam, Almayate East	7.7	19.4 / 54.6 [2]	292.9 / 972.9	260.7	2.08	SFO

[1] Normalised to 20°C and pF2, 10 kPa, using Q_{10} of 2.58, Walker equation coefficient 0.7
[2] mean measured values used (M-753426-01-1, p. 107, p. 109)

Table 7.1.2.1.1-86: Laboratory soil $DegT_{50}$ parameters of fluopyram for trigger purpose

Fluopyram (FLU)	Dark aerobic conditions						
Soil type (USDA)		**pH ($CaCl_2$)**	**T (C°) / % MWHC**	**$DegT_{50\ actual}$ / $DT_{90\ actual}$ (d)**	**$DegT_{50\ mod}$ (d) 20°C pF2 / 10 kPa [1]**	**St. (χ^2)**	**Method of calculation**
Sand, Hoeltinghausen		4.5	19.4 / 54.1 [2]	>1000 / >1000	-	0.668	SFO
Loam, Hornton		5.9	19.4 / 54.8 [2]	805.1 / >1000	-	0.742	HS
Silt loam, Le Thour		7.4	19.4 / 55.0 [2]	173.2 / 575.4	-	1.84	SFO
Sandy loam, Brannens		4.7	19.4 / 54.2 [2]	413.3 / >1000	-	1.26	SFO
Sandy loam, Balbiano		7.1	19.4 / 54.5 [2]	366.5 / >1000	-	0.999	SFO
Loam, Almayate East		7.7	19.4 / 54.6 [2]	292.9 / 972.9	-	2.08	SFO

[1] Normalised using a Q_{10} of 2.58 and Walker equation coefficient of 0.7
[2] mean measured values used (M-753426-01-1, p. 107, p. 109)

Table 7.1.2.1.1-87: Laboratory soil $DegT_{50}$ parameters of fluopyram-7-hydroxy for modelling purpose (normalised: pF2, 20°C, Q_{10} 2.58)

fluopyram-7-hydroxy (FLU-7-OH)	Dark aerobic conditions Formation from parent fluopyram in pathway fit; max. occurrence in soil: 5.8 % (Brannens, d 118)						
Soil type (USDA)	**pH ($CaCl_2$)**	**T (C°) / % MWHC**	**$DegT_{50\ actual}$ / $DT_{90\ actual}$ (d)**	**$DegT_{50\ mod}$ (d) 20°C pF2 / 10 kPa [1]**	**ff (FLU-7-OH)**	**St. (χ^2)**	**Method of calculation parent - metabolite**
Silt loam, Le Thour	7.4	19.4 / 55.0 [2]	18.67 / 62.01	17.64	0.4493	19.68	SFO-SFO
Sandy loam, Brannens	4.7	19.4 / 54.2 [2]	93.35 / 310.1	88.19	0.5264	18.00	SFO-SFO (DT_{50} * 1.25 fixed)

[1] Normalised to 20°C and pF2 / 10 kPa, using Q_{10} of 2.58, Walker equation coefficient 0.7
[2] mean measured values used (M-753426-01-1, p. 107, p. 109)

Table 7.1.2.1.1-88: Laboratory soil $DegT_{50}$ parameters of fluopyram-7-hydroxy for trigger purpose (normalised: pF2, 20°C, Q_{10} 2.58)

fluopyram-7-hydroxy (FLU-7-OH)	Dark aerobic conditions Formation from parent fluopyram in pathway fit; max. occurrence in soil: 5.8 % (Brannens, d 118)							
Soil type (USDA)		**pH ($CaCl_2$)**	**T (C°) / % MWHC**	**$DegT_{50\ actual}$ / $DT_{90\ actual}$ (d)**	**$DegT_{50\ mod}$ (d) 20°C pF2 / 10 kPa [1]**	**ff (FLU-7-OH)**	**St. (χ^2)**	**Method of calculation parent - metabolite**
Silt loam, Le Thour		7.4	19.4 / 55.0 [2]	18.67 / 62.01	-	0.4493	19.68	SFO-SFO
Sandy loam, Brannens		4.7	19.4 / 54.2 [2]	74.68 / 248.1	-	0.5671	19.68	SFO-SFO

[1] Normalised to 20°C and pF2 / 10 kPa, using Q_{10} of 2.58; Walker equation coefficient 0.7
[2] mean measured values used (M-753426-01-1, p. 107, p. 109)

3. Assessment and conclusion

Assessment and conclusion by applicant:
The kinetic evaluation followed FOCUS guidances and is considered valid and reliable.

Assessment and conclusion by RMS:
Outcome and conclusion of the study: RMS should indicate if they agree to the results and conclusions of the APPL.

1. Information on the study

Data Point:	KCA 7.1.2.1.1/14
Report Author:	[redacted]
Report Year:	2021
Report Title:	Fluopyram (FLU), FLU-7-OH, TFA: - Kinetic evaluation of aerobic laboratory soil degradation in European soils, including trifluoroacetic acid (Hellpointner and Kasel, 2021; Kirchherr, 2020) according to FOCUS Kinetics using KinGUI 2.1
Report No:	EnSa-20-0873
Document No:	M-762167-01-1
Guideline(s) followed in study:	not applicable
Deviations from current test guideline:	Current Guideline: not applicable (kinetic evaluation)
Previous evaluation:	No, not previously submitted
GLP/Officially recognised testing facilities:	No, not conducted under GLP/Officially recognised testing facilities
Acceptability/Reliability:	Yes

2. Full summary of KCA 7.1.2.1.1/14

Executive Summary

The residue data of fluopyram (FLU) and its degradation product fluopyram-7-hydroxy (FLU-7-OH) determined in two studies (KCA 7.1.1.1/07, M-761739-01-1 and KCA 7.1.2.1.2/06, M-757988-01-1) were evaluated for calculation of trigger and modelling endpoints following the recommendations given by FOCUS Kinetics. Additionally, the formation fractions of the degradation product trifluoroacetate (TFA) were calculated.

The non-normalised DT_{50} values (trigger endpoints) in the tested soils were between 245.0 and 457.1 days for fluopyram and between 5.371 and 85.52 days for fluopyram-7-hydroxy. The normalised (20 °C, pH 2) DT_{50} values (modelling endpoints) were between 204.0 and 416.0 days for fluopyram and between 6.723 and 73.45 for fluopyram-7-hydroxy. The formation fraction values for fluopyram-7-hydroxy (modelling purpose) were between 0.2430 and 0.6689 in the tested soils. For TFA, formation fractions were calculated reflecting TFA formation per CF_3 moiety of fluopyram as 0.1608 to 0.4012 and reflecting TFA formation per fluopyram molecule (i.e. 2 x formation fraction per CF_3 moiety) as 0.3215 and 0.8024 in the tested soils.

I. METHODS

A kinetic modelling analysis of aerobic laboratory soil residue data of fluopyram (FLU), fluopyram-7-hydroxy (FLU-7-OH) and trifluoroacetate (TFA) was conducted in order to derive kinetic parameters suitable for modelling and for trigger purpose, using the software tool KinGUI 2.1. The identification of the appropriate kinetic model followed the recommendations given by FOCUS Kinetics (FOCUS, 2006, 2014a) based on a detailed statistical analysis including visual assessment, χ^2 statistic, significance t-test and correlation analysis, using correspondingly pre-processed residue data. Additionally, the Scaled Weighted Area under Residue Curve (SWARC) was used as a further indicator for the visual assessment and to choose the appropriate model.

The modelling analysis is based on residue data from 2 aerobic laboratory soil degradation studies in 4 European soils. In both studies the same 4 soil batches have been used and investigated, in parallel.

In one study (KCA 7.1.1.1/07, M-761739-01-1) fluopyram was applied (phenyl-UL-^{14}C label), whereas in the other study (KCA 7.1.2.1.2/06, M-757988-01-1) the unlabelled metabolite fluopyram-7-hydroxy was applied. Due to the fact that the same soil batches have been used in both studies, in parallel evaluated DT_{50} values of fluopyram-7-hydroxy should be averaged before further averaging with other soils.

The fluopyram applied study was specially designed to quantify the formation of the metabolite TFA. The determination of TFA residues in this study is based on a non-radioactive analytics, as this was the only way to achieve a sufficiently reliable quantification of the entire TFA residues.

It should be noted, that the kinetic evaluation presented is mainly carried out to obtain a robust description of the overall formation of TFA from the applied fluopyram, which requires a good description of all predecessors in combination. For this reason, bi-phasic parent kinetics was selected for some soils. Without this decision, the TFA formation would not be properly described.

For the fluopyram-7-hydroxy applied study it was assumed the compound directly degraded in the sink. For the fluopyram applied study, the following degradation pathway was considered in the compartment model.

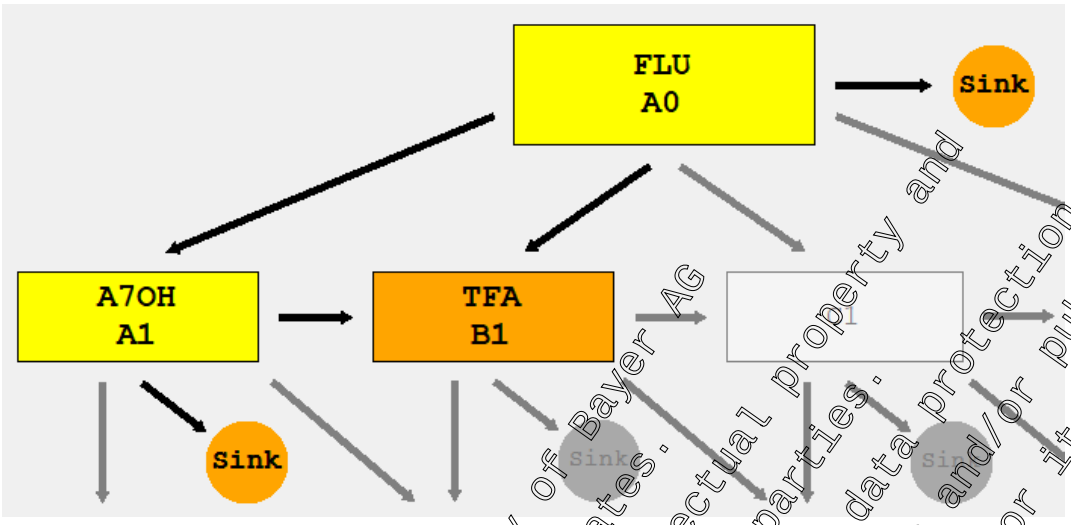


Figure 7.1.2.1.1-9: Compartment model of aerobic soil degradation of fluopyram (FLU = fluopyram, A7OH = FLU-7-OH)

II. RESULTS

Degradation of fluopyram

Results of the kinetic evaluation for modelling and trigger purpose based on residue data from aerobic laboratory soil degradation studies in EU soils are summarised in the tables below.

Table 7.1.2.1.1-89: Fluopyram: kinetic and statistical results of degradation in soil Frankenforst for modelling endpoints, pathway fit

Kinetic model	DT_{50} actual	DT_{90} actual	DT_{50} fast / slow	VA	χ^2err / SWARC	k_1	k_2	g	t-test k_1 / k_2	95th CI of k_1	95th CI of k_2
	(d)	(d)	(d)		(% / -)	(1/d)	(1/d)	(-)	(-)	(1/d)	(1/d)
SFO	**246.4**	818.4	-	+	1.84 / 0.435	0.0028134	-		<0.001	0.00239 to 0.003	-
DFOP	242.2	834.5	<0.001 / 255.1	+	1.54 / 0.147	340100	0.002717	0.0346	<0.001 / <0.001	340100 to 340100	0.00236 to 0.003

VA = visual assessment, + = good, o = acceptable, - = poor
SWARC = Scaled Weighted Area under Residue Curve
CI = confidence intervall

Modelling Endpoints: SFO fit is statistically and visually good (χ^2 err <15%, t-test <0.05). SWARC value is < 40, not indicating a biphasic decline. Consequently, **SFO** degradation model is appropriate for modelling endpoints.

SFO

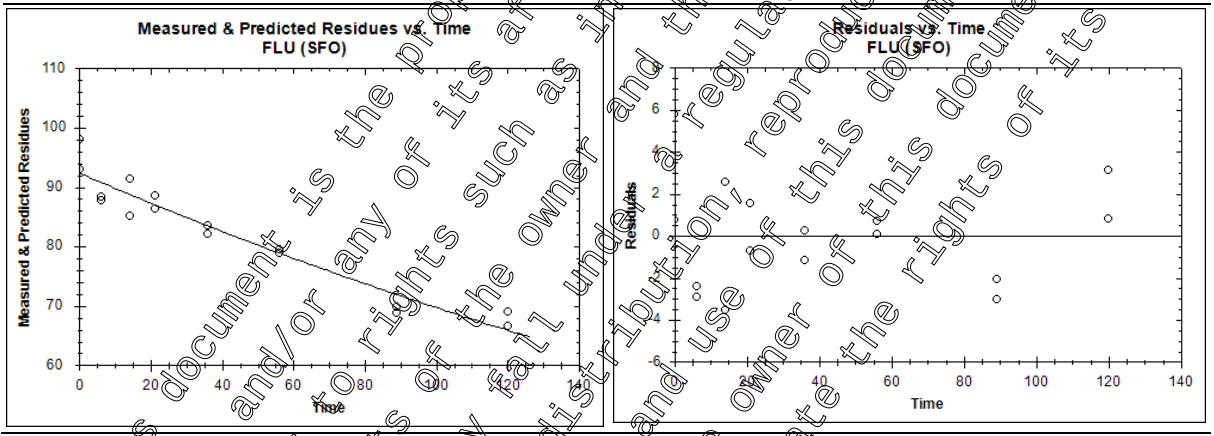


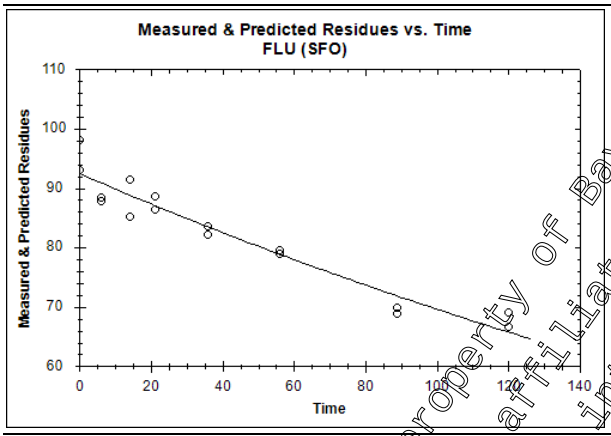
Table 7.1.2.1.1-90: Fluopyram: kinetic and statistical results of degradation in soil Frankenforst for trigger endpoints, parent only

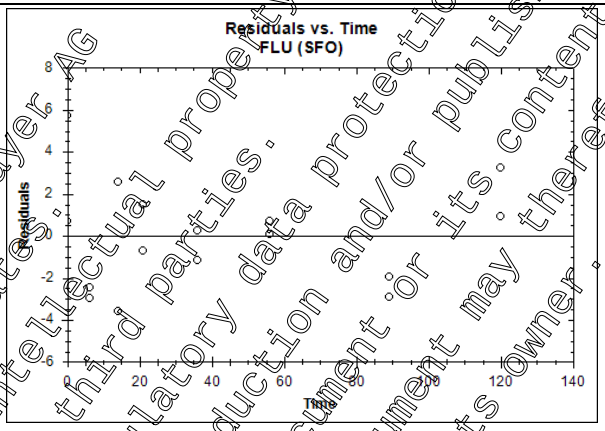
Kinetic model	DT_{50} actual	DT_{90} actual	VA	χ^2err / SWARC	k_1 / α	k_2 / β	g / t_b	t-test k_1 / k_2	95th CI of k_1	95th CI of k_2
	(d)	(d)		(% / -)	(1/d / -)	(1/d / d)	(- / d)	(-)	(1/d)	(1/d)
SFO	244.6	812.4	+	1.84 / 0.448	0.002834	-	-	<0.001	0.00240 to 0.003	-
DFOP	**245.0**	**857.5**	+	1.48 / 2.74	3.157	0.002628	0.0482	<0.001 / <0.001	3.157 to 3.157	0.00221 to 0.003
FOMC	372.7	1000	+	1.79 / 2.54	0.5173	132.232	-	- / -	-	-
HS	245.0	857.5	+	1.48 / 2.74	32	0.002628	0.002	<0.001 / <0.001	32 to 31.999	0.00221 to 0.003

VA = visual assessment, + = good, o = acceptable, - = poor
SWARC = Scaled Weighted Area under Residue Curve
CI = confidence intervall

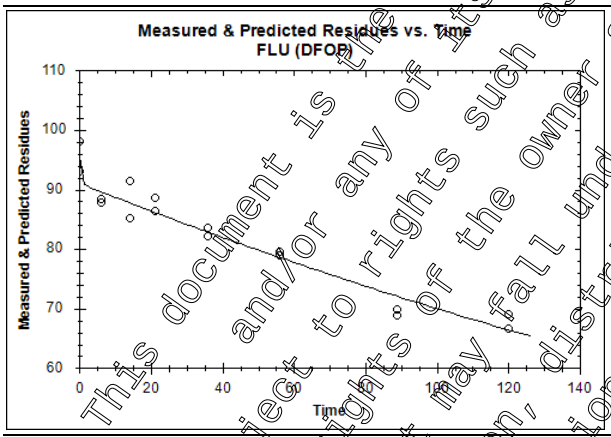
Trigger Endpoints:	SFO fit (parent only) is statistically and visually good (χ^2err, t-test). DFOP, FOMC and HS fits were alternatively tested. For FOMC, DT_{50} and DT_{90} are extrapolated beyond study end. FOMC fit is therefore not suitable, especially for accumulation assessments. DFOP and HS fits are statistically (χ^2err, t-test) and visually good. Consequently, **DFOP** degradation model is appropriate for trigger endpoints, as it shows lowest χ^2err of all suitable models (SFO, DFOP, HS) and is more widespread used as HS.

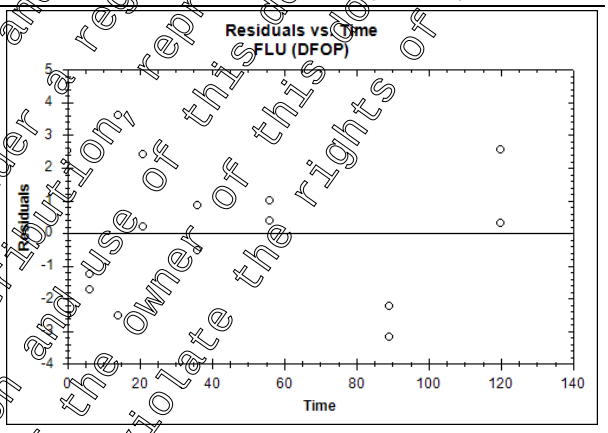
SFO



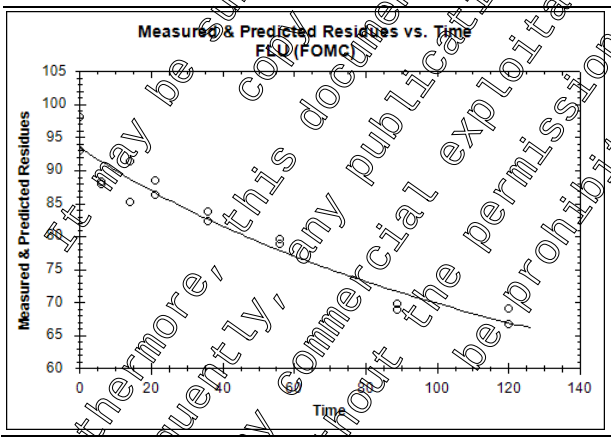


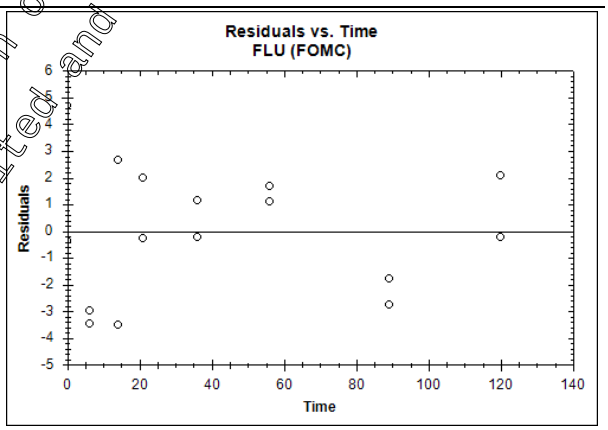
DFOP



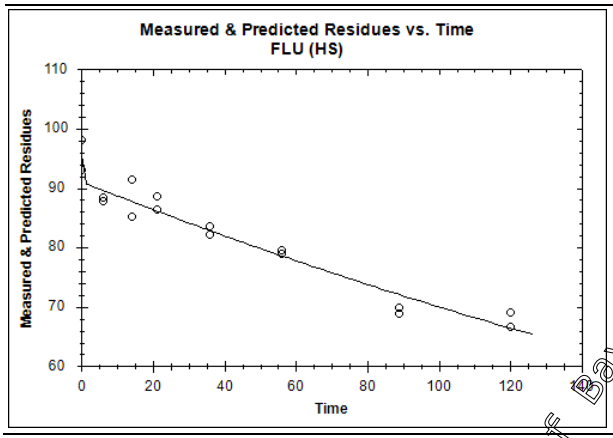


FOMC





HS



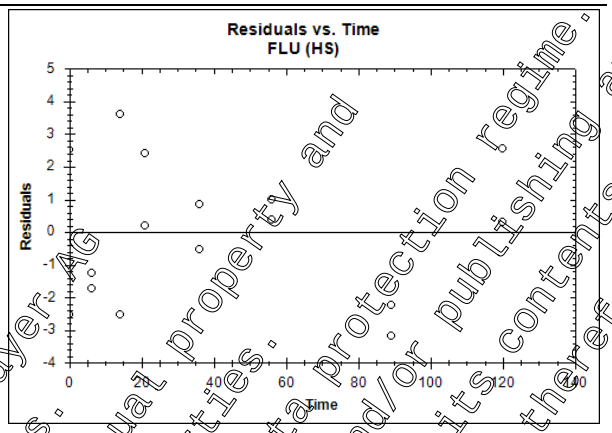


Table 7.1.2.1.1-91: Fluopyram: kinetic and statistical results of degradation in soil Wurmwiese for modelling endpoints, pathway fit

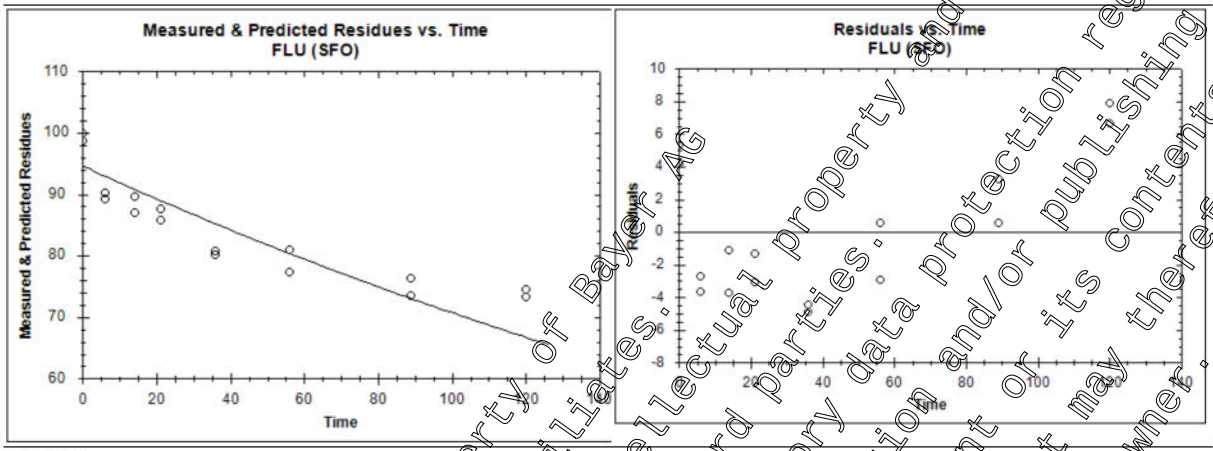
Kinetic model	DT_{50} actual	DT_{90} actual	DT_{50} fast / slow	VA	χ^2err / SWARC	k_1	k_2	g	t-test k_1 / k_2	95th CI of k_1	95th CI of k_2
	(d)	(d)	(d)		(% / -)	(1/d)	(1/d)	(-)	(-)	(1/d)	(1/d)
SFO, free fit	238.4	792.0	-	o	3.72 / 45.1	0.0029074	-	-	<0.001	0.00220 to 0.004	-
SFO, fixed fit 1	238.4	792.0	-	o	3.35 / 45.1	0.0029074	-	-	-	-	-
SFO, fixed fit 2, 95% CI	238.4	792.0	-	o	3.35 / 45.1	0.0029074	-	-	-	-	-
DFOP, free fit	341.0	>1000	**5.108 / 398.8**	+	1.76 / 4.37	0.1357	0.001738	**0.0956**	<0.001 / <0.001	0.06219 to 0.209	0.00127 to 0.002
DFOP, fixed fit 3, 95% CI	341.0	>1000	5.108 / 398.8	+	1.38 / 4.38	0.1357	0.001738	0.0956	-	-	-

VA = visual assessment, + = good, o = acceptable, - = poor
SWARC = Scaled Weighted Area under Residue Curve
CI = confidence intervall
fixed fit 1: SFO parent parameters fixed to free fit values, DT_{50} FLU-7-OH fixed to value derived from metabolite study in the same soil (M-757988-01-1)
fixed fit 2: SFO parent parameters fixed to free fit values, DT_{50} FLU-7-OH fixed to 95th CI rate of free fit.
fixed fit 3: DFOP parent parameters fixed to free fit values, DT_{50} FLU-7-OH fixed to 95th CI rate of free fit.

Modelling Endpoints: SFO fit is statistically good (χerr <15%, t-test <0.05) and visually acceptable. SWARC value is slightly > 40, indicating a biphasic decline.
DFOP was alternatively tested, resulting in a statistically and visually very good fit. Even, metabolite fits of FLU-7-OH and TFA are visually better and statistically reliable, with DFOP parent.
Furtheron, metabolite FLU-7-OH is rising until the end of study. The pathway fit (free fit) was therefore modified with a fixed DT_{50} value for FLU-7-OH (fixed fit). The DT_{50} value of FLU-7-OH was fixed to a conservative value (95% confidence interval k of free fit; or to DT_{50} from metabolite study Kirchheri, 2020, in same soil). Formation fractions were fitted and parent parameters were fixed to values derived from the free fit.
It should be noted, that this kinetic evaluation is carried out mainly to result in a robust description of the formation of TFA, which requires a good description of all predecessors in combination.

Finally, DFOP free fit did show the best visual fit for FLU, FLU-7-OH and TFA in combination with statistically reliable values for all 3 compounds. Consequently, **DFOP free fit** is considered appropriate for modelling endpoints.

SFO free



DFOP free

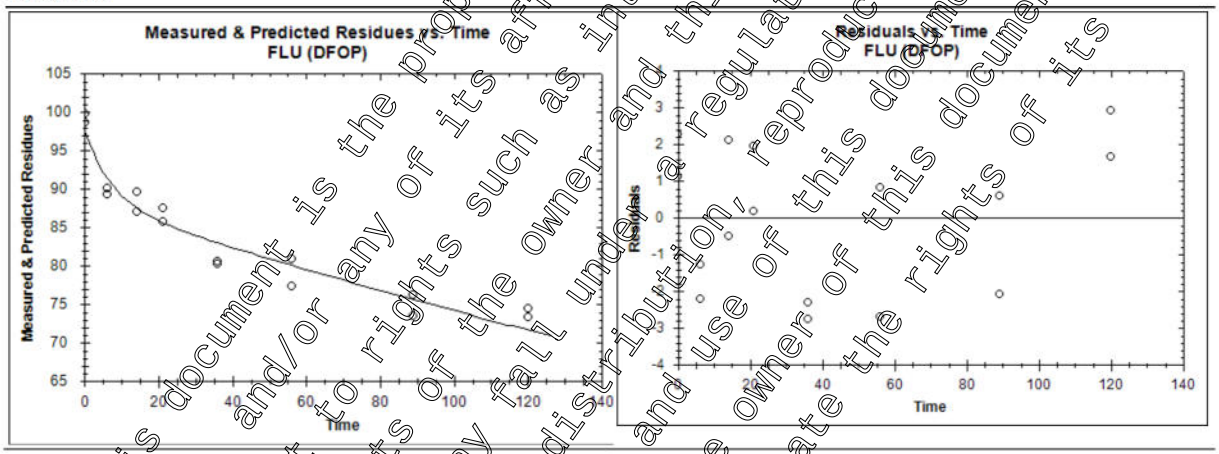


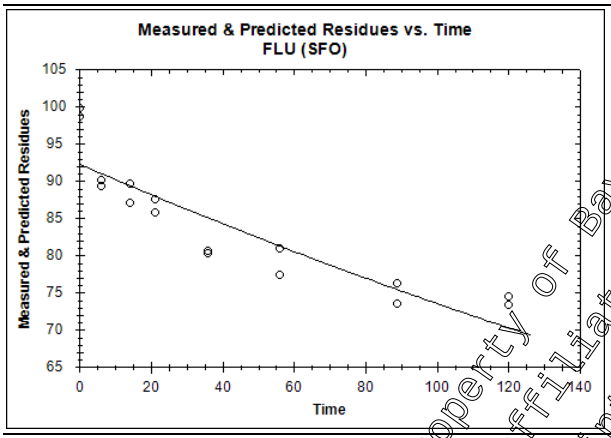
Table 7.1.2.1.1-92: Fluopyram: kinetic and statistical results of degradation in soil Wurmwiese for trigger endpoints, parent only fit

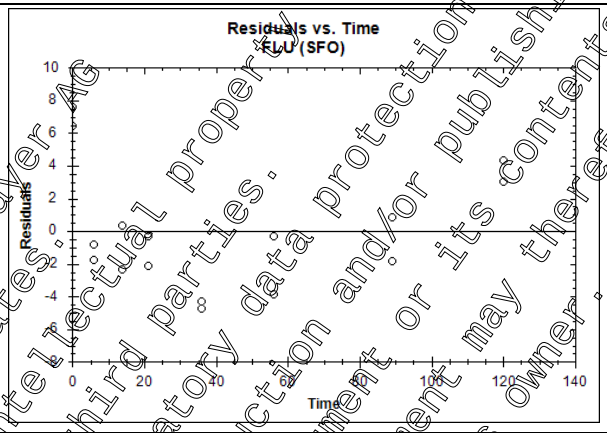
Kinetic model	DT_{50} actual	DT_{90} actual	VA	χ^2 err / SWARC	k_1 / g	k_2 / β	g / t_b	t-test k_1 / k_2	95th CI of k_1	95th CI of k_2
	(d)	(d)		(% / -)	(1/d / -)	(1/d / d)	(- / d)	(-)	(1/d)	(1/d)
SFO	305.5	1015	o	3.23 / 28.4	0.002269	-	-	<0.001 / -	0.00167 to 0.003	-
DFOP	**457.1**	**>1000**	+	1.50 / 0.338	0.08144	0.00118	0.1424	0.013 / 0.004	0.01827 to 0.145	0.00046 to 0.002
FOMC	>1000	>1000	+	1.17 / 0.334	0.0885	4.56508	-	- / -	-	-
HS	320.5	>1000	+	1.83 / 7.06	32.13	0.001833	0.003	<0.001 / <0.001	32.13 to 32.125	0.00144 to 0.002

VA = visual assessment, + = good, o = acceptable, - = poor
SWARC = Scaled Weighted Area under Residue Curve
CI = confidence intervall

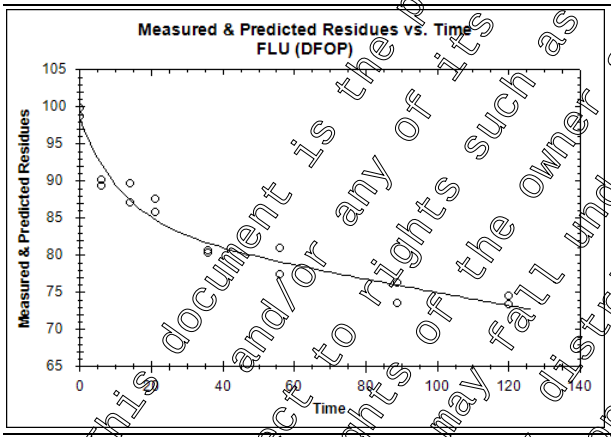
Trigger Endpoints: SFO fit (parent only) is statistically good (χ^2err, t-test) and visually acceptable. DFOP, FOMC and HS fits were alternatively tested. For FOMC, DT_{50} and DT_{90} are extrapolated beyond study end. FOMC fit is therefore not suitable, especially for accumulation assessments. DFOP fit is statistically (χ^2err, t-test) and visually good. Consequently, **DFOP** degradation model is appropriate for trigger endpoints.as it shows lowest χ^2err of all suitable models (SFO, DFOP, HS).

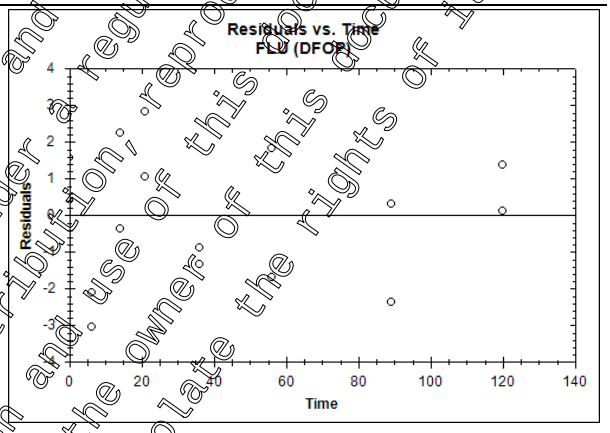
SFO



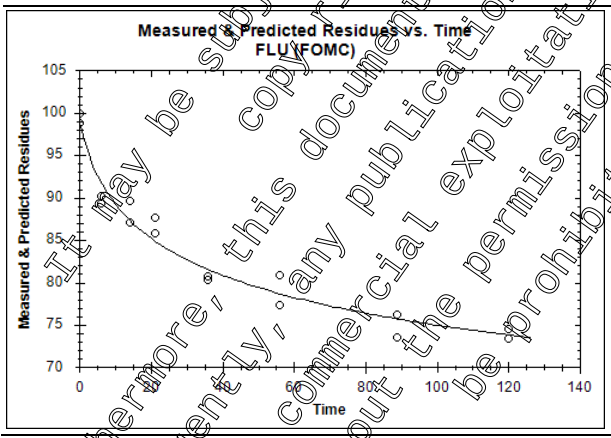


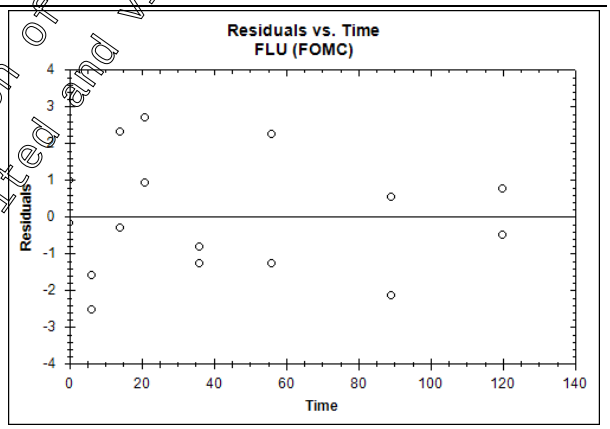
DFOP



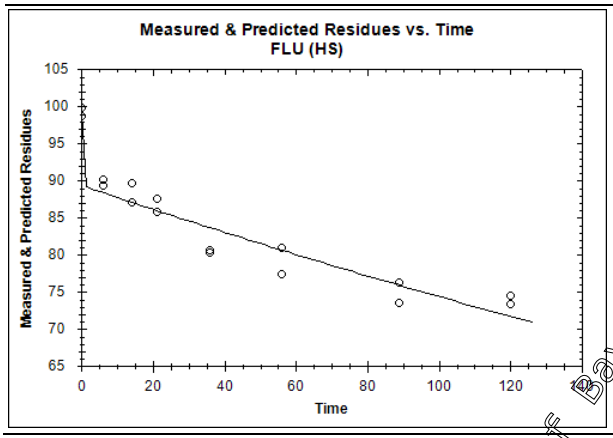


FOMC





HS



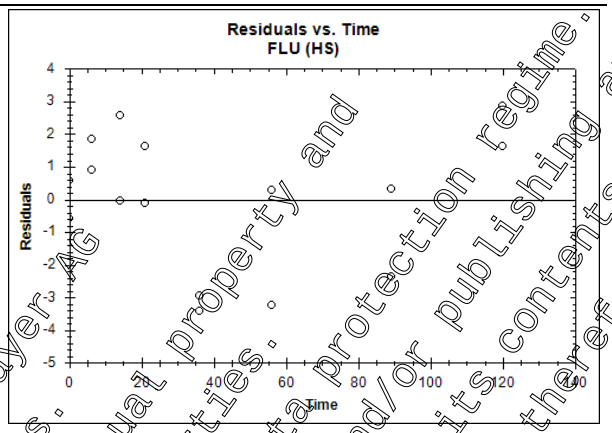


Table 7.1.2.1.1-93: Fluopyram: kinetic and statistical results of degradation in soil Hoefchen am Hohenseh for modelling endpoints, pathway

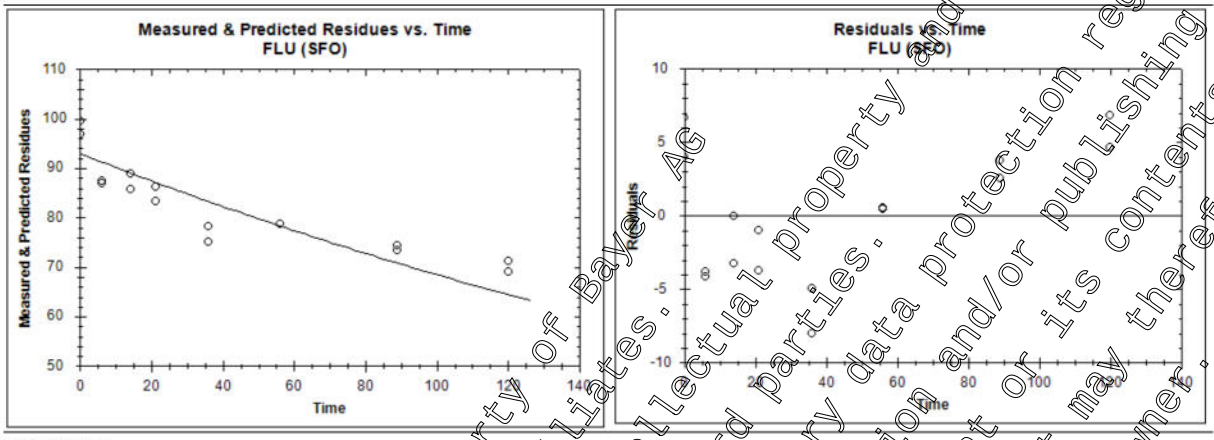
Kinetic model	DT_{50} actual	DT_{90} actual	DT_{50} fast / slow	VA	χ^2err / SWARC	k_1	k_2	g	t-test k_1 / k_2	95th CI of k_1	95th CI of k_2
	(d)	(d)	(d)		(% / -)	(1/d)	(1/d)	(-)	(-)	(1/d)	(1/d)
SFO, free fit	226.8	753.6	-	o	4.02 / 35.1	0.0030556	-	-	<0.001	0.00228 to 0.004	-
SFO, fixed fit 1	226.8	753.6	-	o	3.62 / 35.1	0.0030556	-	-		-	-
SFO, fixed fit 2, 95% CI	226.8	753.6	-	o	3.62 / 35.1	0.0030556	-	-	-	-	-
DFOP, free fit	327.8	>1000	**4.153 / 402.5**	+	2.15 / 2.31	0.1669	0.001722	**0.1208**	<0.001 / <0.001	0.08459 to 0.249	0.00119 to 0.002
DFOP, fixed fit 3. 95% CI	327.8	>1000	4.153 / 402.5	+	1.68 / 2.32	0.1669	0.001722	0.1208	-	-	-

VA = visual assessment, + = good, o = acceptable, - = poor
SWARC = Scaled Weighted Area under Residue Curve
CI = confidence intervall
fixed fit 1: SFO parent parameters fixed to free fit values, DT_{50} FLU-7-OH fixed to value derived from metabolite study in the same soil (M-757988-01-1)
fixed fit 2: SFO parent parameters fixed to free fit values, DT_{50} FLU-7-OH fixed to 95th CI rate of free fit.
fixed fit 3: DFOP parent parameters fixed to free fit values, DT_{50} FLU-7-OH fixed to 95th CI rate of free fit.

Modelling Endpoints: SFO fit is statistically good (χerr <15%, t-test <0.05) and visually acceptable. SWARC value is < 40, not indicating a biphasic decline.
Nevertheless, DFOP was alternatively tested, resulting in a statistically and visually very good fit. Even, metabolite fits of FLU-7-OH and TFA are visually better and statistically reliable, with DFOP parent.
Furtheron, metabolite FLU-7-OH is rising until the end of study. The pathway fit (free fit) was therefore modified with a fixed DT_{50} value for FLU-7-OH (fixed fit). The DT_{50} value of FLU-7-OH was fixed to a conservative value (95% confidence interval k of free fit; or to DT_{50} from metabolite study Kirchheri, 2020, in same soil). Formation fractions were fitted and parent parameters were fixed to values derived from the free fit.
It should be noted, that this kinetic evaluation is carried out mainly to result in a robust description of the formation of TFA, which requires a good description of all predecessors in combination.

Finally, DFOP free fit did show the best visual fit for FLU, FLU-7-OH and TFA in combination with statistically reliable values for all 3 compounds. Consequently, **DFOP free fit** is considered appropriate for modelling endpoints.

SFO free



DFOP free

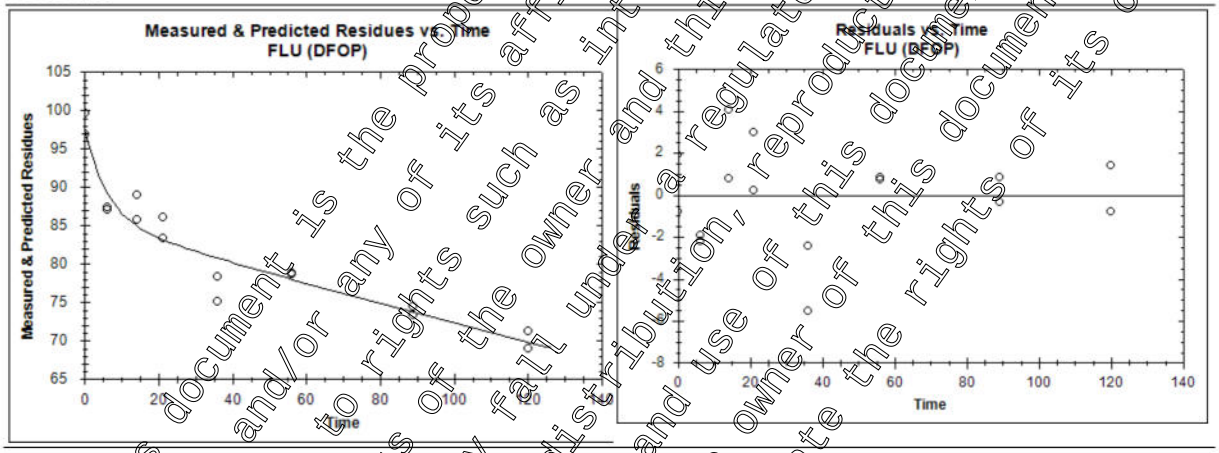


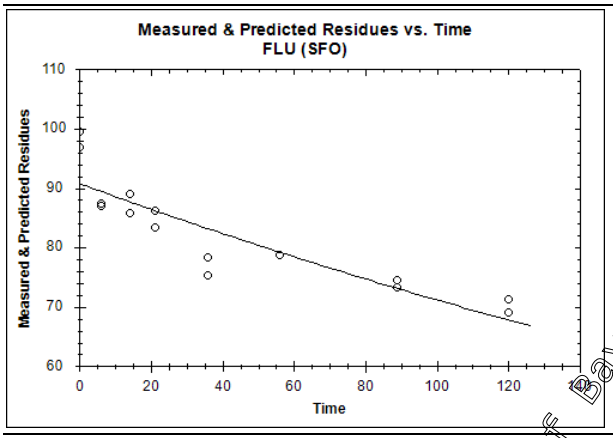
Table 7.1.2.1.1-94: Fluopyram: kinetic and statistical results of degradation in soil Hoefchen am Hohenseh for trigger endpoints, parent only

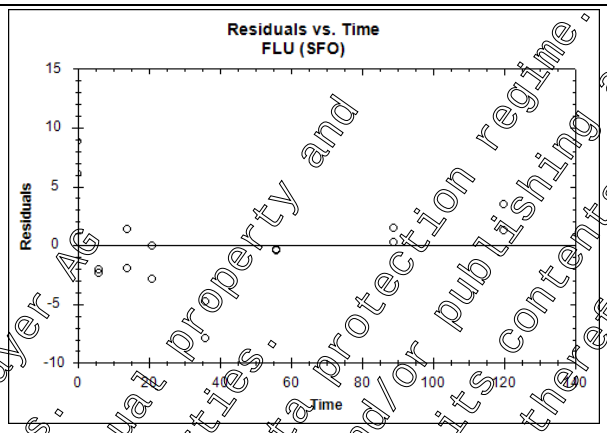
Kinetic model	DT_{50} actual	DT_{90} actual	VA	χ^2err / SWARC	k_1 / α	k_2 / β	g / t_b	t-test k_1 / k_2	95th CI of k_1	95th CI of k_2
	(d)	(d)		(% / -)	(1/d / -)	(1/d / d)	(- / d)	(-)	(1/d)	(1/d)
SFO	285.0	946.9	o	3.60 / 21.0	0.002432	-	-	<0.001	0.00176 to 0.003	-
DFOP	**310.2**	**>1000**	+	2.13 / 2.07	0.2819397	0.0018376	0.1159	0.075 / <0.001	-0.07728 to 0.641	0.00129 to 0.002
FOMC	>1000	>1000	-	2.01 / 1.92	0.09201	4.26038	-	- / -	-	-
HS	296.1	>1000	+	2.17 / 3.41	32.3	0.001955	0.004	<0.001 / <0.001	32.3 to 32.296	0.00149 to 0.002

VA = visual assessment, + = good, o = acceptable, - = poor
SWARC = Scaled Weighted Area under Residue Curve
CI = confidence intervall

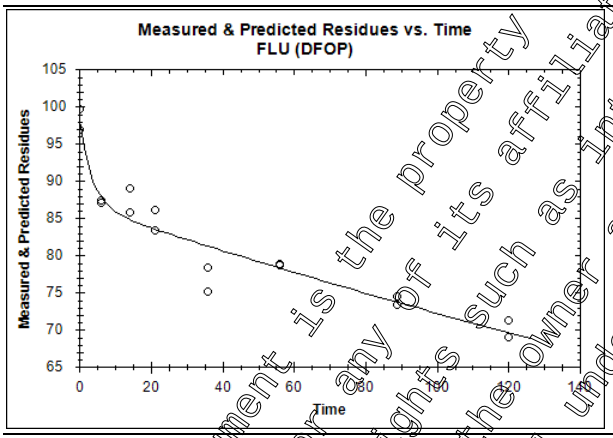
Trigger Endpoints: SFO fit (parent only) is statistically good (χ^2err, t-test) and visually acceptable. DFOP, FOMC and HS fits were alternatively tested. For FOMC, DT_{50} and DT_{90} are extrapolated beyond study end. FOMC fit is therefore not suitable, especially for accumulation assessments. DFOP results in the best visual fit (χ^2err). Consequently, **DFOP** degradation model is appropriate for trigger endpoints.

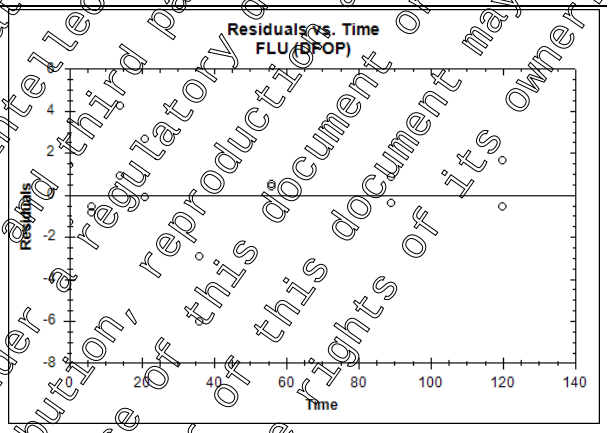
SFO



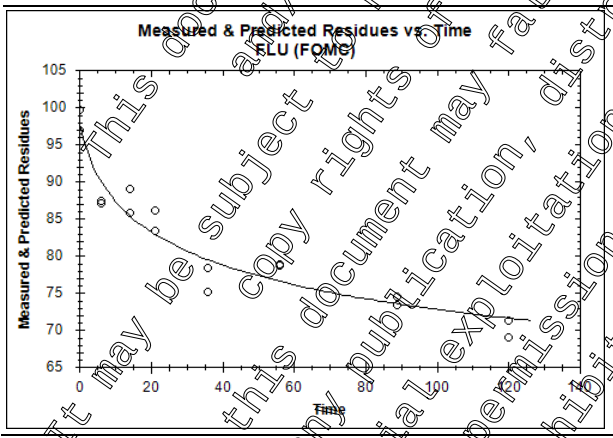


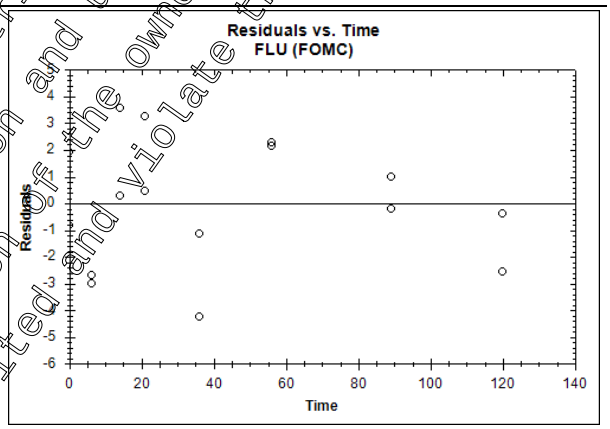
DFOP



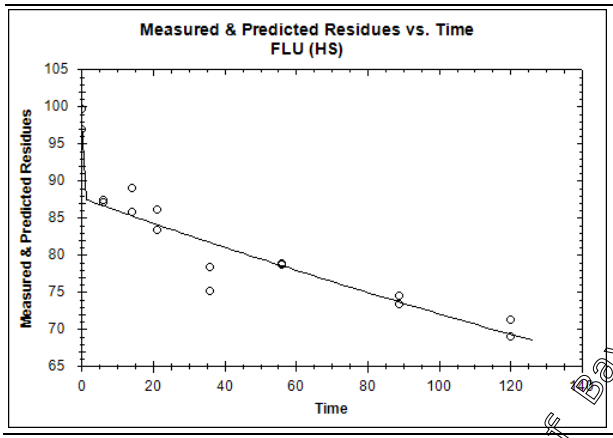


FOMC





HS



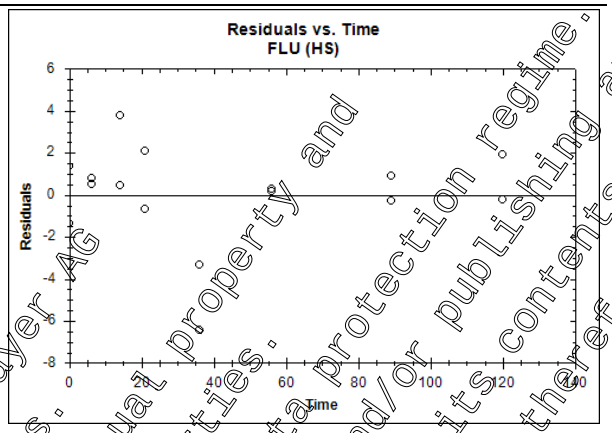


Table 7.1.2.1.1-95: Fluopyram: kinetic and statistical results of degradation in soil Innerdeich for modelling endpoints, pathway fit

Kinetic model	DT_{50} actual	DT_{90} actual	DT_{50} fast / slow	VA	χ^2err / SWARC	k_1	k_2	g	t-test k_1 / k_2	95th CI of k_1	95th CI of k_2
	(d)	(d)	(d)		(% / -)	(1/d)	(1/d)	(-)	(-)	(1/d)	(1/d)
SFO, free fit	212.0	704.1	-	-	4.04 / 64.7	0.00327	-	-	<0.001	0.00243 to 0.004	-
SFO, fixed fit 1, 95% CI	212.0	704.1	-	-	3.64 / 64.7	0.00327	-	-	-	-	-
DFOP, free fit	374.4	>1000	**4.842 / 448.8**	+	0.990 / 0	0.1431593	0.0015446	**0.1085**	<0.001 / <0.001	0.08203 to 0.204	0.00107 to 0.002
DFOP, fixed fit 2, 95% CI	374.4	>1000	4.842 / 448.8	+	0.775 / 0	0.1431593	0.0015446	0.1085	-	-	-

VA = visual assessment, + = good, o = acceptable, - = poor
SWARC = Scaled Weighted Area under Residue Curve
CI = confidence interval
fixed fit 1: SFO parent parameters fixed to free fit values, DT_{50} FLU-7-OH fixed to 95th CI rate of free fit.
fixed fit 2: DFOP parent parameters fixed to free fit values, DT_{50} FLU-7-OH fixed to 95th CI rate of free fit.

Modelling Endpoints: SFO fit is statistically ok (χ^2err <15%, t-test <0.05), but visually not very good. SWARC value is > 40, indicating a biphasic decline.

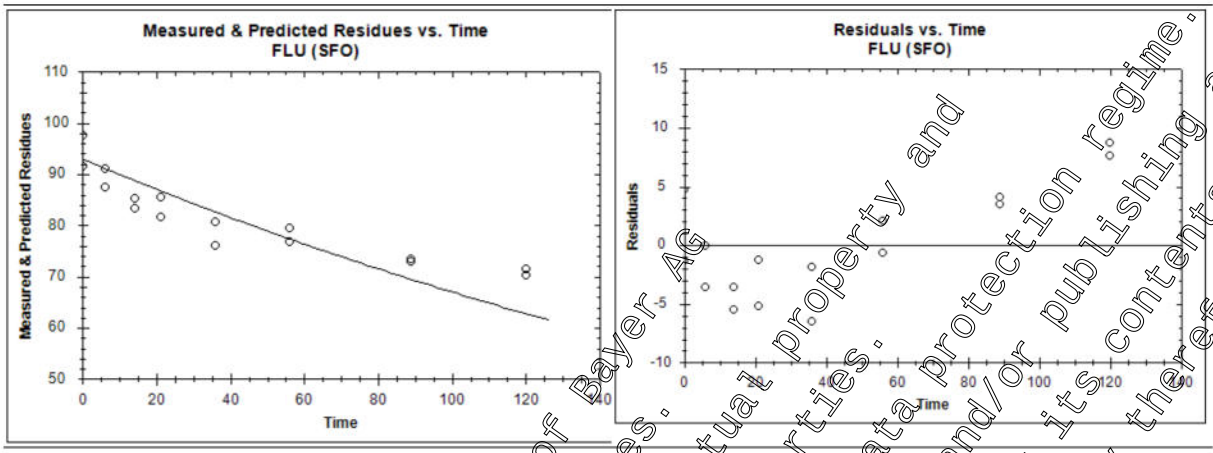
DFOP was alternatively tested, resulting in a statistically and visually very good fit. Even, metabolite fits of FLU-7-OH and TFA are visually better and statistically reliable, with DFOP parent.

Further on, metabolite FLU-7-OH is rising until the end of study. The pathway fit (free fit) was therefore modified with a fixed DT_{50} value for FLU-7-OH (fixed fit). The DT_{50} value of FLU-7-OH was fixed to a conservative value (95% confidence interval k of free fit). Formation fractions were fitted and parent parameters were fixed to values derived from the free fit.

It should be noted, that this kinetic evaluation is carried out mainly to result in a robust description of the formation of TFA, which requires a good description of all predecessors in combination.

Finally, DFOP free fit did show the best visual fit for FLU, FLU-7-OH and TFA in combination with statistically reliable values for all 3 compounds. Consequently, **DFOP free fit** is considered appropriate for modelling endpoints.

SFO free



DFOP free

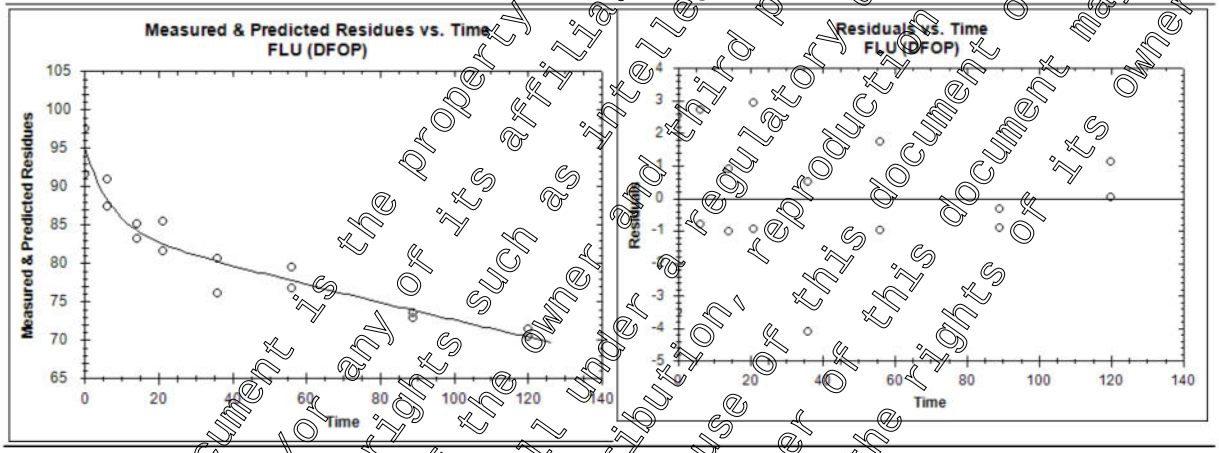


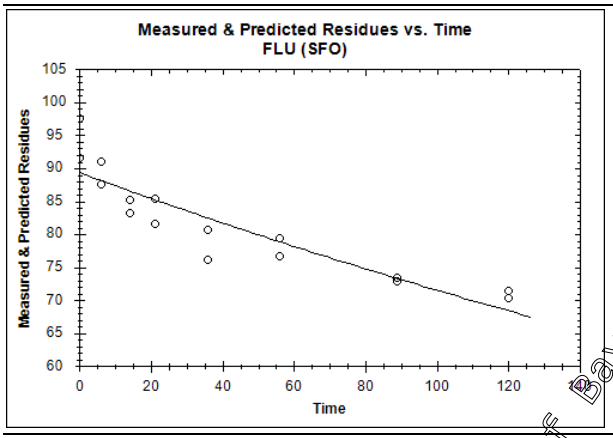
Table 7.1.2.1.1-96: Fluopyram: kinetic and statistical results of degradation in soil Innerdeich for trigger endpoints, parent only fit

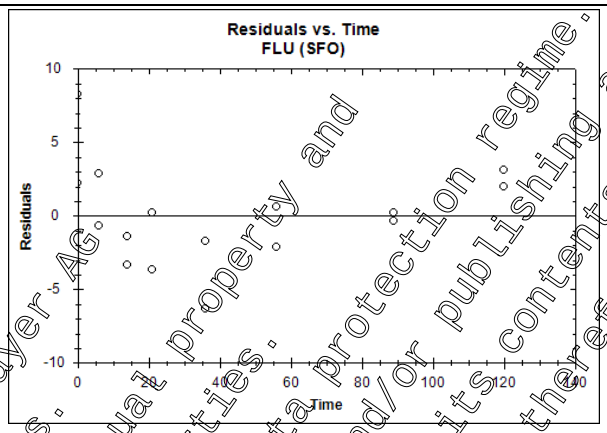
Kinetic model	DT_{50} actual	DT_{90} actual	VA	χ^2err / SWARC	k_1 / α	k_2 / β	g / t_b	t-test k_1 / k_2	95th CI of k_1	95th CI of k_2
	(d)	(d)		(% / -)	(1/d / -)	(1/d / d)	(- / d)	(-)	(1/d)	(1/d)
SFO	312.0	1036	o	3.69 / 1.74	0.002222	-	-	<0.001	0.00166 to 0.003	-
DFOP	**427.3**	**>1000**	+	0.798 / 0	0.08730	0.001314	0.1235	0.037 / 0.003	0.00020 to 0.175	0.00054 to 0.002
FOMC	>1000	>1000	+	0.835 / 0.40	0.19776	7.27392	-	- / -	-	-
HS	323.7	>1000		1.85 / 10.2	31.42	0.001888	0.003	<0.001 / <0.001	31.42 to 31.418	0.00140 to 0.002

VA = visual assessment, + = good, o = acceptable, - = poor
SWARC = Scaled Weighted Area under Residue Curve
CI = confidence intervall

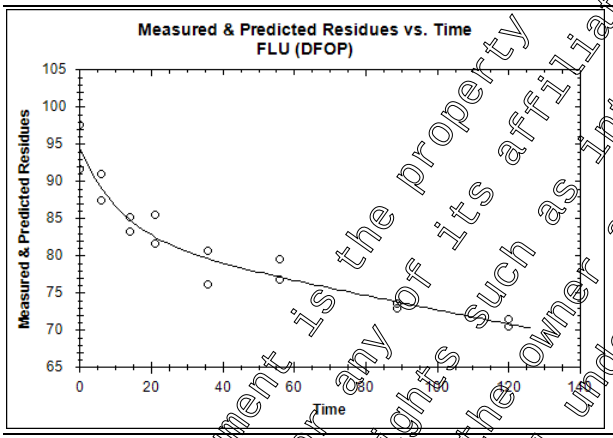
Trigger Endpoints: SFO fit (parent only) is statistically good (χ^2err, t-test) and visually acceptable. DFOP, FOMC and HS fits were alternatively tested. DFOP fit is statistically (χ^2err, t-test) and visually best. Consequently, **DFOP** degradation model is appropriate for trigger endpoints.

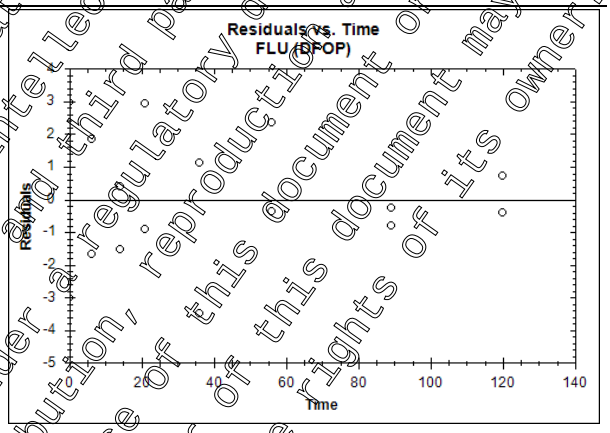
SFO



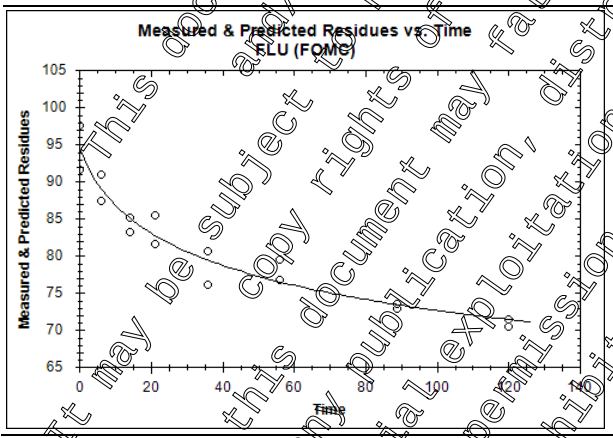


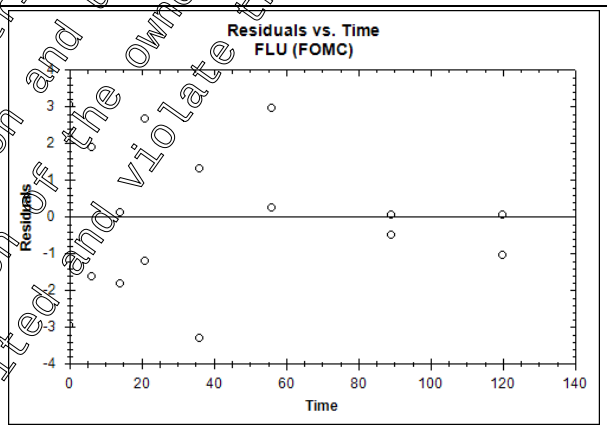
DFOP



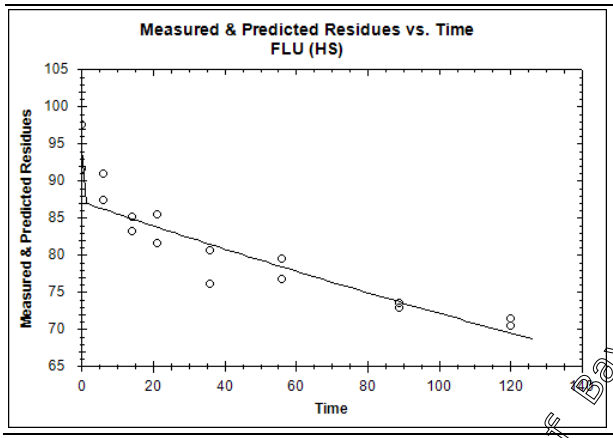


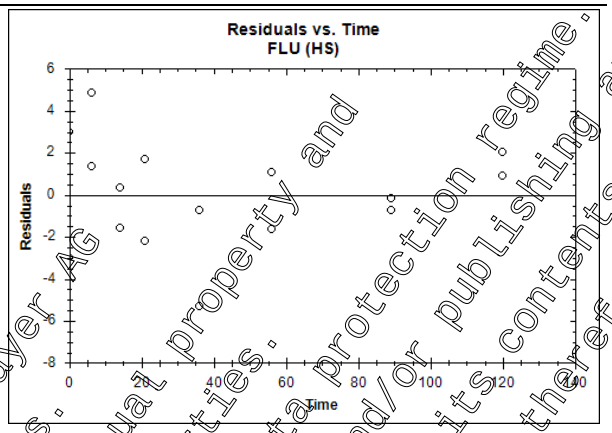
FOMC





HS





Degradation of fluopyram-7-hydroxy

Results of the kinetic evaluation for modelling and trigger purpose based on residue data from aerobic laboratory soil degradation studies in FLU soils are summarised in the tables below.

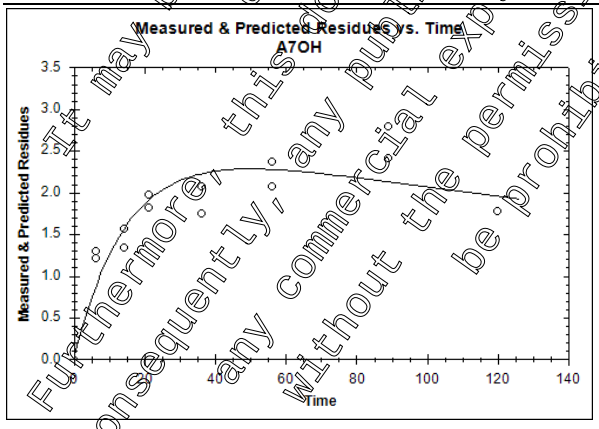
Table 7.1.2.1.1-97: FLU-7-OH (M-761739-01-1): kinetic and statistical results of degradation in soil Frankenforst for modelling endpoints

Kinetic model, Parent - metabolite	DT_{50} actual	DT_{90} actual	VA	χ^2 err	SWARC	k	t-test k	95th CI of k	ff (FLU)
	(d)	(d)		(%)	(-)	(1/d)	(-)	(1/d)	(-)
SFO - SFO	**10.48**	34.80	o	11.7	24.8	0.0661705	<0.001	0.04303 to 0.089	**0.6689**
DFOP - SFO	24.56	81.60	o	9.94	9.48	0.02822	<0.001	0.01552 to 0.041	0.3109

VA = visual assessment, + = good, o = acceptable, - = poor
SWARC = Scaled Weighted Area under Residue Curve
CI = confidence intervall

Modelling Endpoints: SFO fit (parent SFO) is statistically good (χ^2err <25%, t-test < 0.1, formation fraction ff is <1, SWARC <40) and visually acceptable. Consequently, **SFO** degradation model (**parent SFO**) is appropriate for modelling endpoints.

SFO/SFO



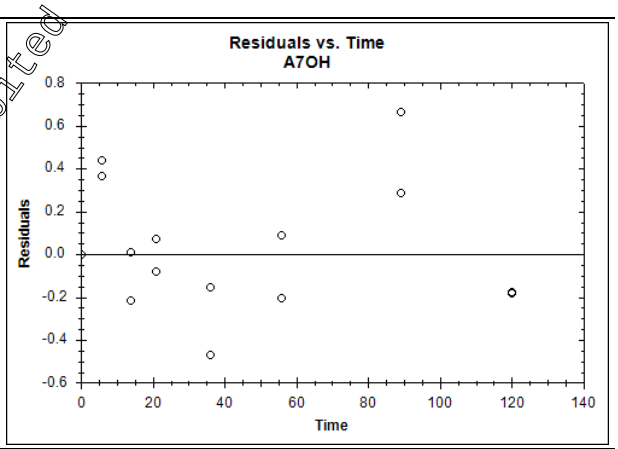


Table 7.1.2.1.1-98: FLU-7-OH (M-761739-01-1): kinetic and statistical results of degradation in soil Frankenforst for trigger endpoints, pathway fit

Kinetic model, Parent - metabolite	DT_{50} actual	DT_{90} actual	VA	χ^2err	SWARC	k	t-test k	95th CI of k	FF (PLU)
	(d)	(d)		(%)	(-)	(1/d)	(-)	(1/d)	(-)
DFOP - SFO	**24.56**	**81.60**	o	9.04	9.48	0.02822	<0.001	0.01552 to 0.041	0.3109

VA = visual assessment, + = good, o = acceptable, - = poor
SWARC = Scaled Weighted Area under Residue Curve
CI = confidence intervall

Trigger Endpoints: SFO fit (parent DFOP) is statistically (χ^2err, t-test) good and visually acceptable. The metabolite is not rising at study end (last 4 data points). Consequently, **SFO** degradation model (**parent DFOP**) is appropriate for trigger endpoints.

DFOP/SFO

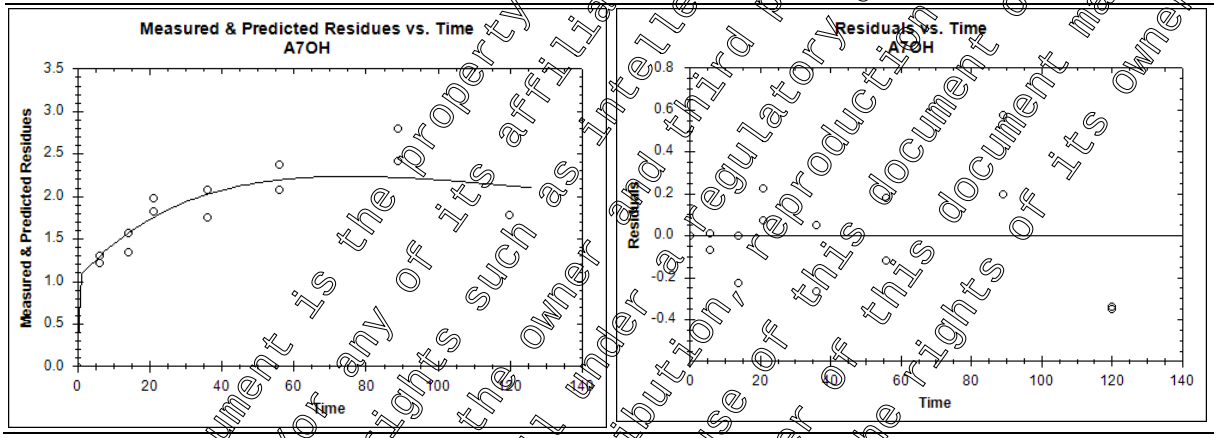


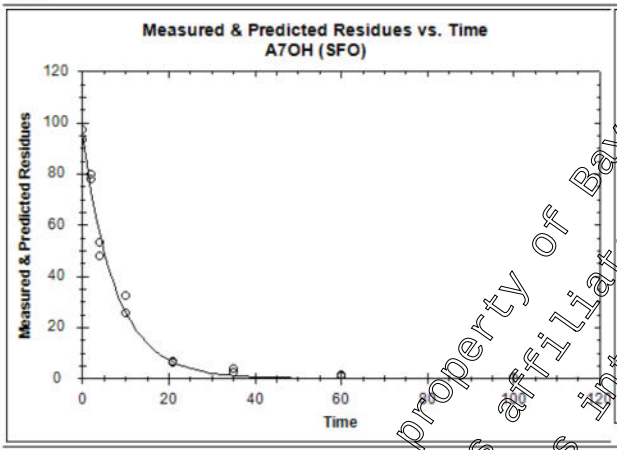
Table 7.1.2.1.1-99: FLU-7-OH (M-757988-01-1): kinetic and statistical results of degradation in soil Frankenforst for modelling and trigger endpoints, metabolite applied

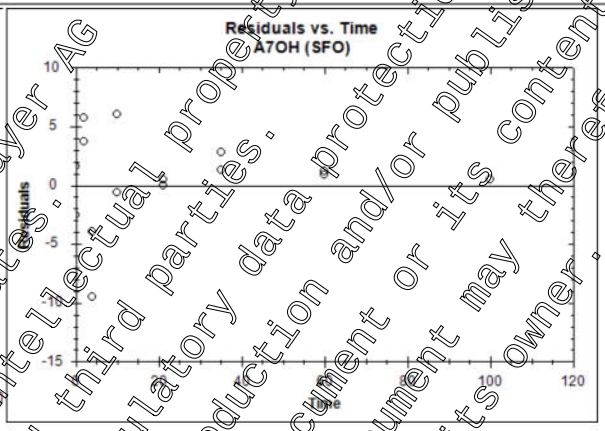
Kinetic model	DT_{50} actual	DT_{90} actual	DT_{50} fast / slow	VA	χ^2err / SWARC	k_1 / α	k_2 / β	g / t_b	t-test k_1 / k_2	95th CI of k_1	95th CI of k_2
	(d)	(d)	(d)		(% / -)	(1/d / -)	(1/d / d)	(- / d)	(-)	(1/d)	(1/d)
SFO	**5.371**	**17.84**	-	+	7.64 / 17.2	0.129064	-	-	<0.001	0.11275 to 0.145	-
DFOP	5.184	18.93	4.791 / 21.45	+	8.36 / 0.771	0.14467	0.03231	0.9260	<0.001 / 0.347	0.07845 to 0.211	-0.12468 to 0.189
DFOP, fixed g	5.137	19.32	3.576 / 7.020	+	7.78 / 4.23	0.19382	0.08979	0.5 fix	<0.001 / <0.001	0.10489 to 0.283	0.05655 to 0.123
FOMC	5.137	19.31	-	+	7.76 / 3.51	6.755	47.539	-	- / -	-	-
HS	5.040	18.90	4.844 / 5.968	+	7.79 / 5.30	0.14308	0.11615	4.00	<0.001 / <0.001	0.09988 to 0.186	0.07974 to 0.153

VA = visual assessment, + good, o acceptable, - poor
SWARC = Scaled Weighted Area under Residue Curve
CI = confidence intervall
fixed g: DFOP run with a fixed g = 0.5. Attempt to link the 2 DFOP rates k to the 2 enatiomers of fluopyram-7-hydroxy. Both enantiomers appear in ratio 50:50 at study start, which may correspond to g = 0.5.

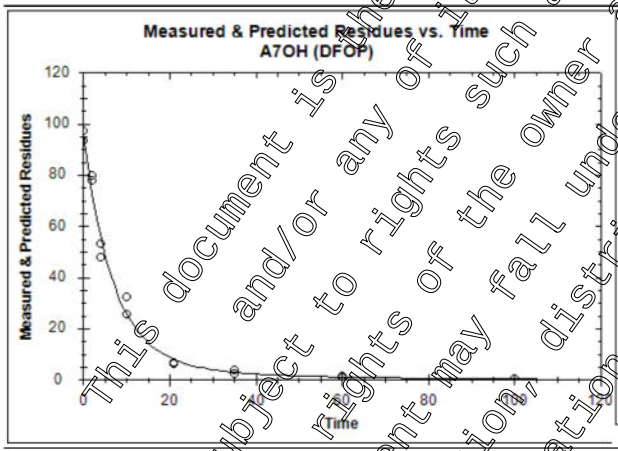
Modelling Endpoints:	SFO fit is statistically and visually good (χ^2err <15%, t-test <0.05). SWARC value is < 40, not indicating a biphasic decline. Consequently, **SFO** degradation model is appropriate for modelling endpoints.
Trigger Endpoints:	SFO fit is statistically and visually good (χ^2err, t-test). DFOP, FOMC and HS fits were alternatively tested. However, SFO fit shows the lowest χ^2err of all kinetic models. Consequently, **SFO** degradation model is appropriate for trigger endpoints.

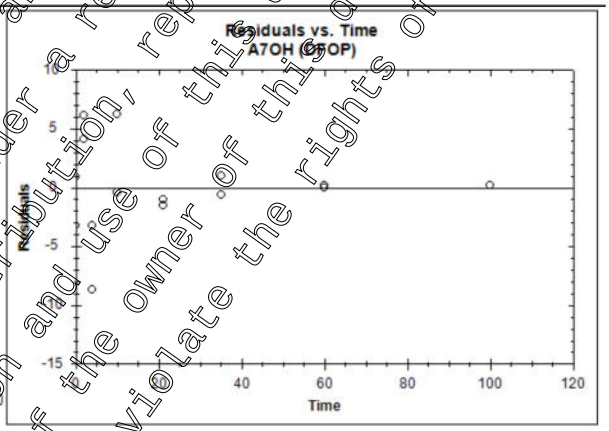
SFO



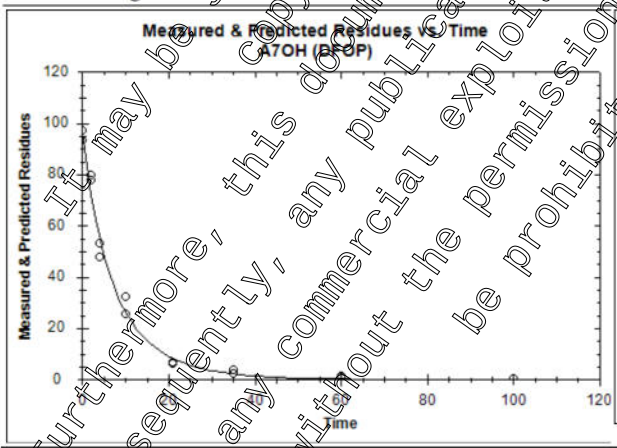


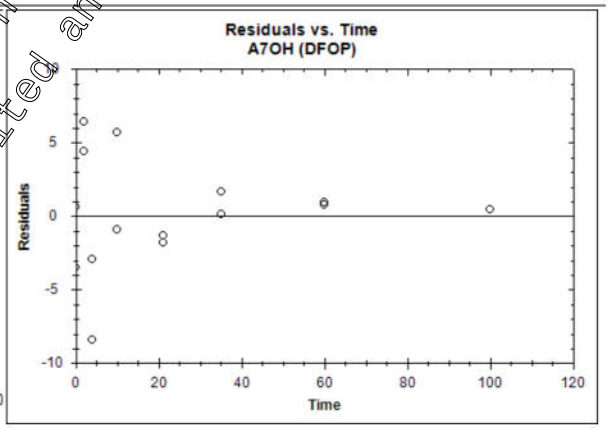
DFOP



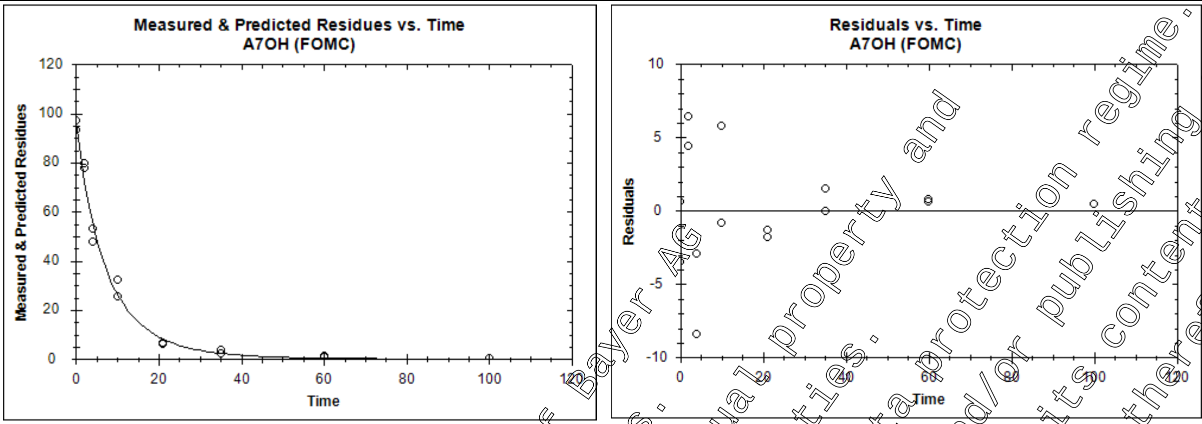


DFOP fixed g





FOMC



HS

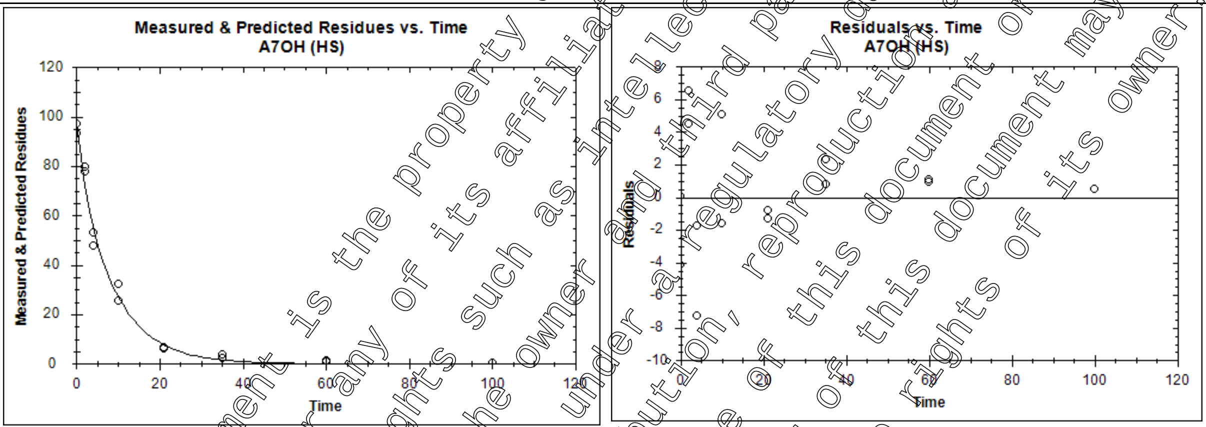


Table 7.1.2.1.1-100: FLU-7-OH (M-761739-01-1): kinetic and statistical results of degradation in soil Wurmwiese for modelling endpoints

Kinetic model, Parent - metabolite	DT_{50} actual	DT_{90} actual	VA	χ^2err	SWARC	k	t-test k	95th CI of k	ff (FLU)
	(d)	(d)		(%)	(-)	(1/d)	(-)	(1/d)	(-)
SFO - SFO, free fit	14.94	49.61	+	11.6	19.7	0.0464106	<0.001	0.03078 to 0.062	0.8068
SFO - SFO, fixed fit 1	27.67 fix	91.92 fix	o	17.9	73.1	0.02504897	-	-	0.5235
SFO - SFO, fixed fit 2, 95% CI	22.52 fix	74.80 fix	o	15.2	26.4	0.0307832	-	-	0.6047
DFOP - SFO, free fit	**66.55**	221.1	+	7.54	10.8	0.01042	0.002	0.00389 to 0.017	**0.3082**
DFOP - SFO, fixed fit 3, 95% CI	178.3 fix	592.4 fix	-	12.7	16.3	0.0038870	-	-	0.2365

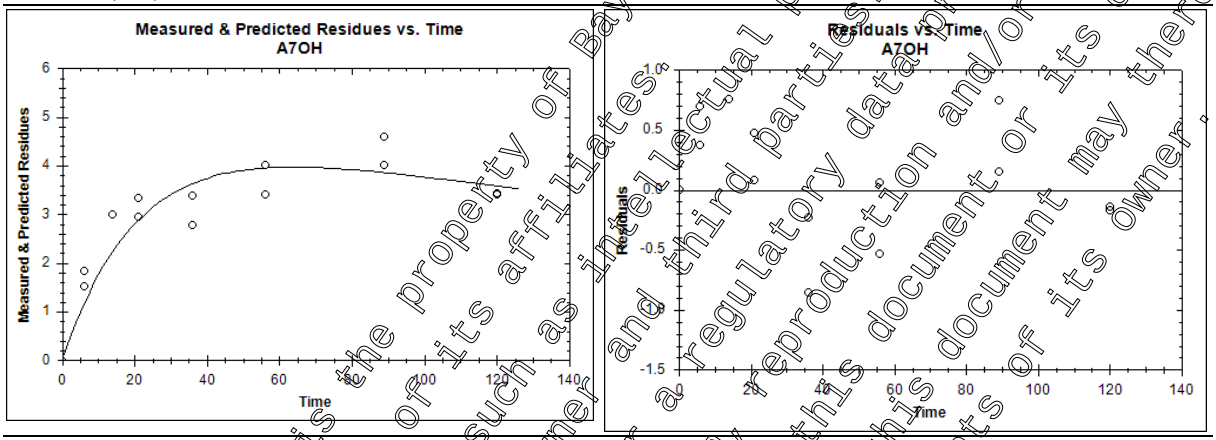
VA = visual assessment, + = good, o = acceptable, - = poor
SWARC = Scaled Weighted Area under Residue Curve
CI = confidence intervall
fixed fit 1: SFO parent parameters fixed to free fit values, DT_{50} FLU-7-OH fixed to value derived from metabolite study in the same soil (M-757988-01-1).
fixed fit 2: SFO parent parameters fixed to free fit values, DT_{50} FLU-7-OH fixed to 95th CI rate of free fit.
fixed fit 3: DFOP parent parameters fixed to free fit values, DT_{50} FLU-7-OH fixed to 95th CI rate of free fit.

Modelling Endpoints: The metabolite FLU-7-OH is rising until the end of study. The pathway fit (parent SFO and DFOP free fit) was therefore modified with a fixed DT_{50} value for FLU-7-OH (fixed fit). The DT_{50} value of FLU-7-OH was fixed to a conservative value (95% confidence interval k of free fit; or to DT_{50} from metabolite study Kirchherr, 2020, in same soil). Formation fractions were fitted and parent parameters were fixed to values derived from the free fit. All fixed fits are visually less good than the free fit.

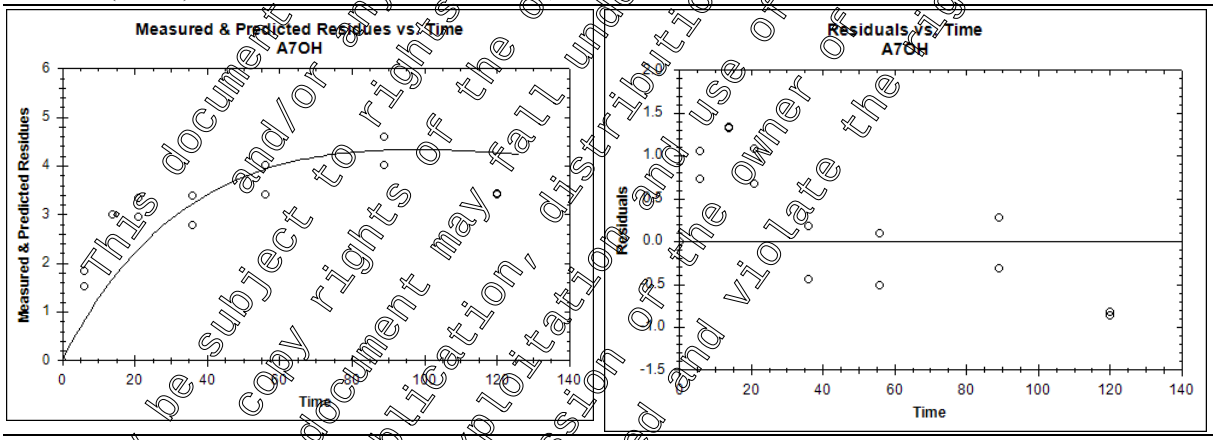
It should be noted, that this kinetic evaluation is carried out mainly to result in a robust description of the formation of TFA, which requires a good description of all predecessors in combination.

Finally, DFOP-SFO free fit did show the best visual fit for FLU, FLU-7-OH and TFA in combination with statistically reliable values for all 3 compounds. Consequently, **DFOP-SFO free fit** is considered appropriate for modelling endpoints.

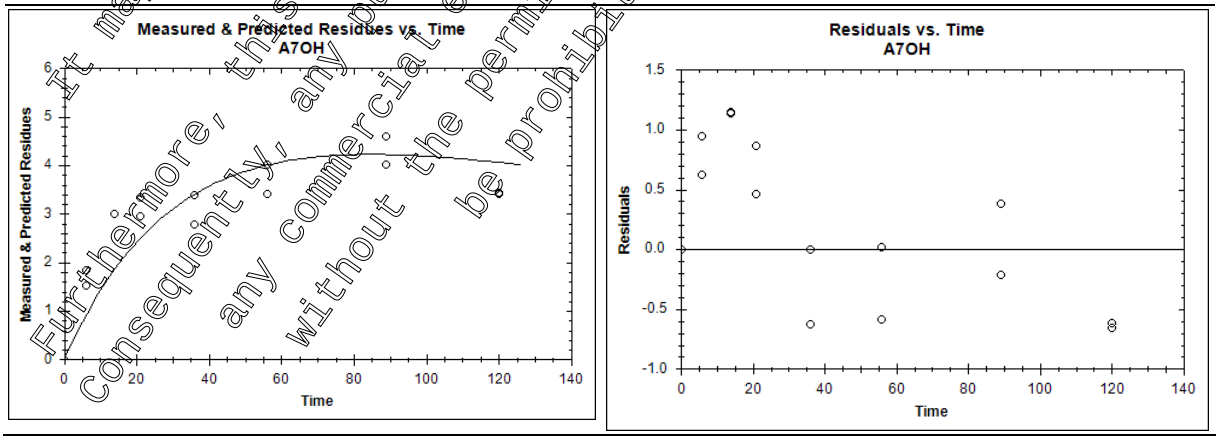
SFO/SFO (free)



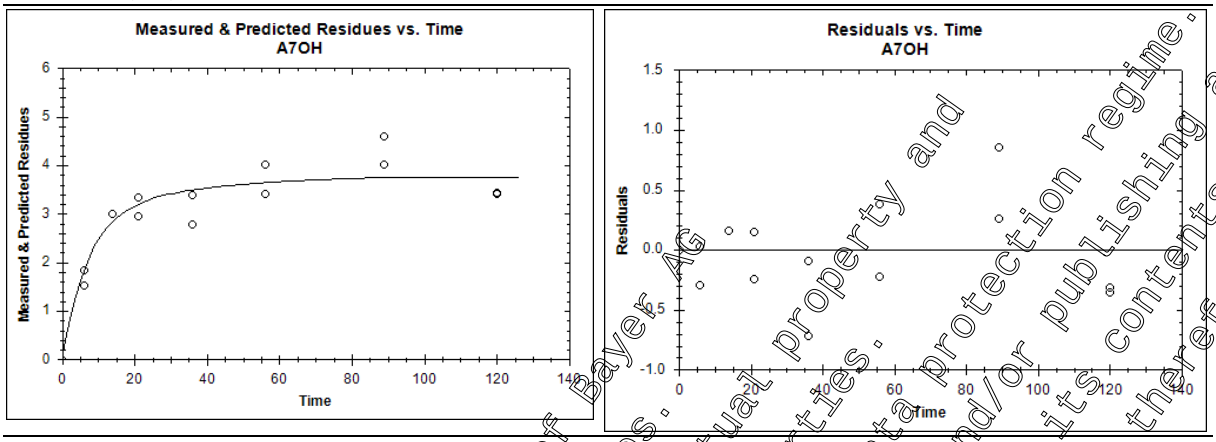
SFO/SFO (fixed 1)



SFO/SFO (fixed 2)



DFOP/SFO (free)



DFOP/SFO (fixed 3)

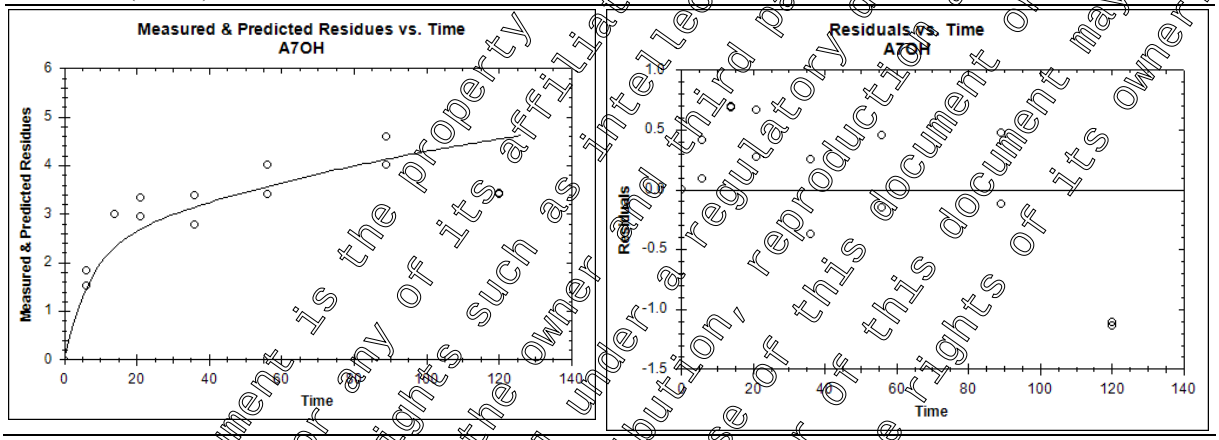


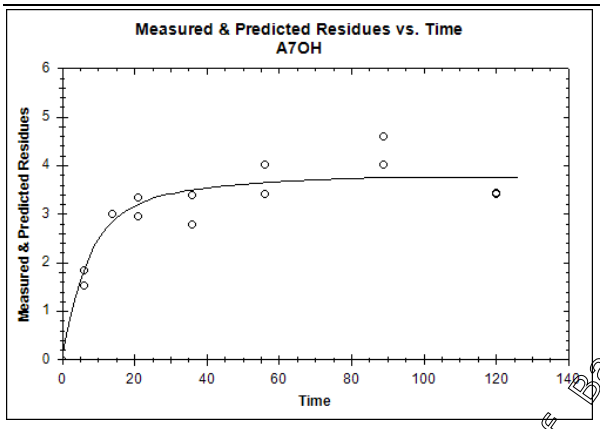
Table 7.1.2.1.1-101: FLU-7-OH (M-761739-01-1): kinetic and statistical results of degradation in soil Wurmwiese for trigger endpoints, pathway fit

Kinetic model, Parent - metabolite	DT_{50} actual	DT_{90} actual	VA	χ^2err	SWARC	k	t-test k	95th CI of k	FF (FLU)
	(d)	(d)		(%)	(-)	(1/d)	(-)	(1/d)	(-)
DFOP - SFO	**66.55**	**221.1**	+	7.54	10.8	0.01042	0.002	0.00389 to 0.017	0.3082

VA = visual assessment, + = good, o = acceptable, - = poor
SWARC = Scaled Weighted Area under Residue Curve
CI = confidence interval

Trigger Endpoints: SFO fit (parent DFOP) is statistically (χ^2err, t-test) good and visually good. Consequently, **SFO** degradation model (**parent DFOP**) is appropriate for trigger endpoints.

DFOP/SFO



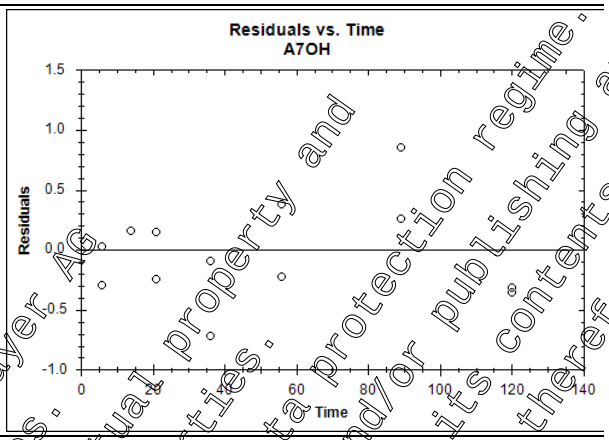


Table 7.1.2.1.1-102: FLU-7-OH (M-757988-01-1): kinetic and statistical results of degradation in soil Wurmwise for modelling and trigger endpoints, metabolite applied

Kinetic model	DT_{50} actual	DT_{90} actual	DT_{50} fast / slow	VA	χ^2err / SWARC	k_1 / α	k_2 / β	g / t_b	t-test k_1 / k_2	95th CI of k_1	95th CI of k_2
	(d)	(d)	(d)		(% / -)	(1/d / -)	(1/d / d)	(- / d)	(-)	(1/d)	(1/d)
SFO	17.24	57.28	-	o	10.8 / 57.2	0.040197	-	-	0.001 / -	0.03164 to 0.049	-
DFOP	14.03	115.0	10.36 / 108.2		6.15 / 4.25	0.066885	0.006407	0.7918	0.001 / 0.219	0.03055 to 0.103	-0.00933 to 0.022
DFOP, fixed g	14.29	87.63	6.757 / 37.72	+	7.37 / 9.11	0.102575	0.018374	0.5 fixed	<0.001 / <0.001	0.05456 to 0.151	0.01334 to 0.023
FOMC	13.92	91.87	**27.26** [1]	+	6.76 / 6.40	1.3798	21.3361	-	- / -	-	-
HS	**14.74**	**113.9**	14.74 / 67.56	+	5.82 / 0.628	0.047036	0.010259	0.7655 / 30.8	<0.001 / 0.015	0.03808 to 0.056	0.00192 to 0.019

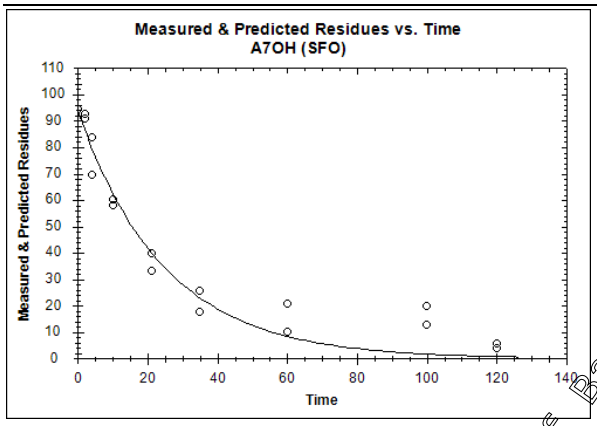
VA = visual assessment: + good, o acceptable, - poor
SWARC = Scaled Weighted Area under Residue Curve
CI = confidence interval
fixed g: DFOP run with a fixed g = 0.5. Attempt to link the 2 DFOP rates k to the 2 enatiomers of fluopyram-7-hydroxy. Both enantiomers appear in ratio 50:50 at study start, which may correspond to g = 0.5.
[1] pseudo DT50 = back-calculated DT90 / 3.32, as modelling endpoint

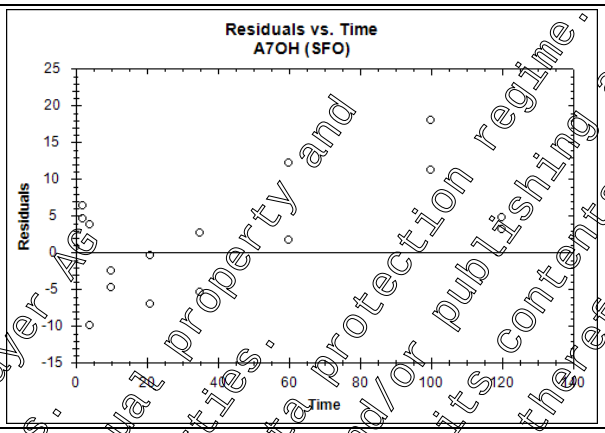
Modelling Endpoints: SFO fit is statistically good (χ^2err <15%, t-test <0.05) and visually almost acceptable. SWARC value is > 40, indicating a biphasic decline. Therefore, DFOP kinetic was tested, but t-test for k_2 failed and fit is therefore not suitable. FOMC fit is statistically and visually good, and appropriate as residues at study end are low (4.7 %). Further on, a biphasic behaviour of metabolites is not straight forward to use in several predictive models, and weight of evidence supports SFO degradation of the metabolite in most other soils, including all parent trials with a pathway evaluation.

Therefore, **FOMC** degradation model is considered appropriate for modelling, with using a back-calculated **DT_{90} / 3.32 as pseudo SFO DT_{50}**.

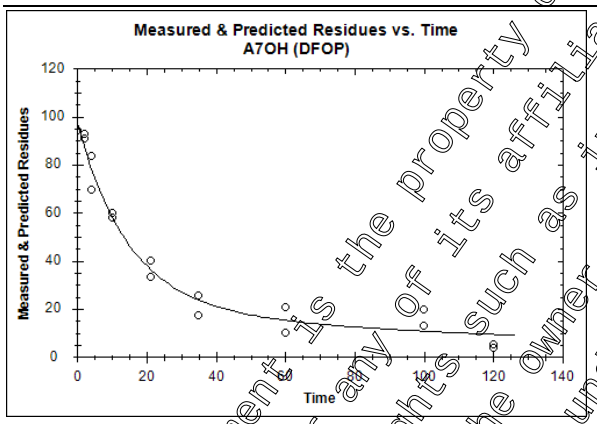
Trigger Endpoints: SFO fit is statistically good (χ^2err, t-test) and visually acceptable. DFOP, FOMC and HS fits were alternatively tested. HS fit shows the lowest χ^2err and visually best fit. Consequently, **HS** degradation model is appropriate for trigger endpoints.

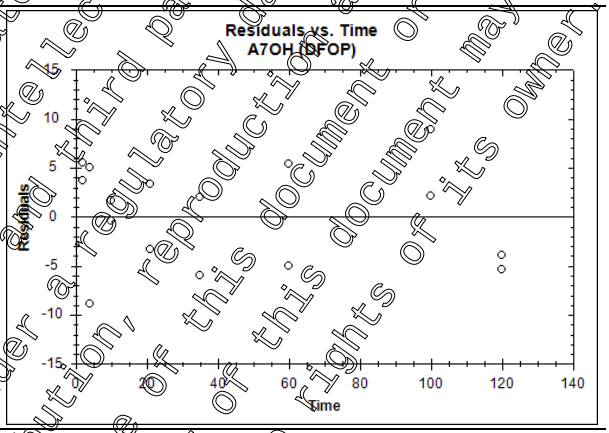
SFO



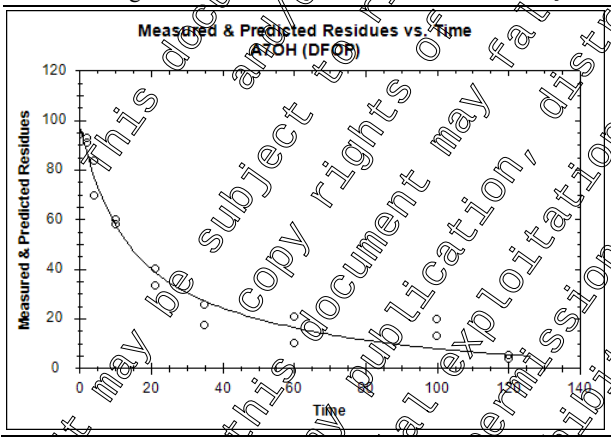


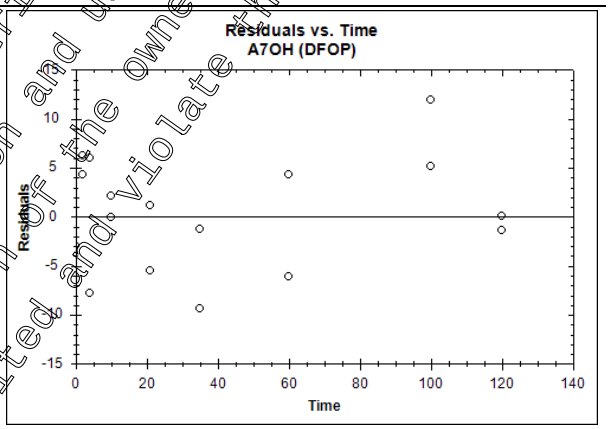
DFOP



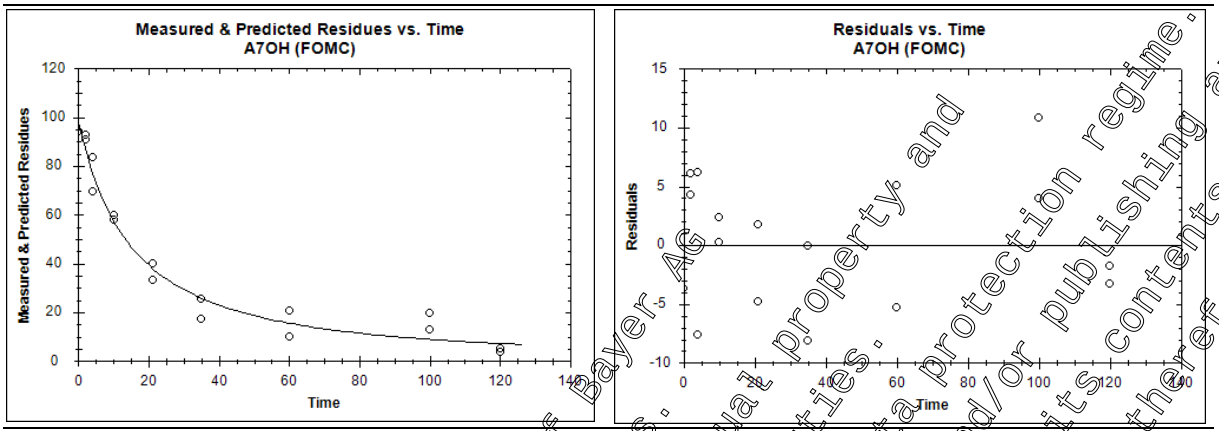


DFOP fixed g





FOMC



HS

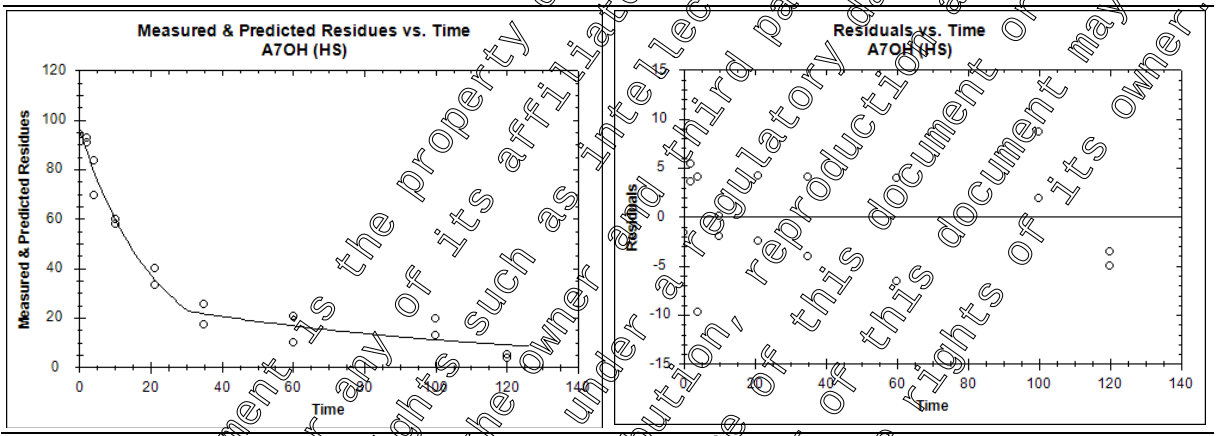


Table 7.1.2.1.1-103: FLU-7-OH (M-761739-01-1): kinetic and statistical results of degradation in soil Hoefchen am Hohensch for modelling endpoints

Kinetic model, Parent - metabolite	DT_{50} actual	DT_{90} actual	VA	χ^2err	SWARC	k	t-test k	95th CI of k	ff (FLU)
	(d)	(d)		(%)	(-)	(1/d)	(-)	(1/d)	(-)
SFO - SFO, free fit	13.07	43.41	+	14.3	18.9	0.053045	<0.001	0.03513 to 0.071	0.8473
SFO - SFO, fixed fit 1, Kirchherr	11.50 fix	38.21 fix	o	10.8	25.8	0.060258	-	-	0.8921
SFO - SFO, fixed fit 2, 95% CI	19.73 fix	65.56 fix	o	15.1	27.0	0.035128	-	-	0.6278
DFOP - SFO, free fit	**85.52**	284.1	+	7.02	10.1	0.008105	0.003	0.00270 to 0.014	**0.2430**
DFOP - SFO, fixed fit 3, 95% CI	256.4 fix	851.9 fix		12.7	69.7	0.002703	-	-	0.1942

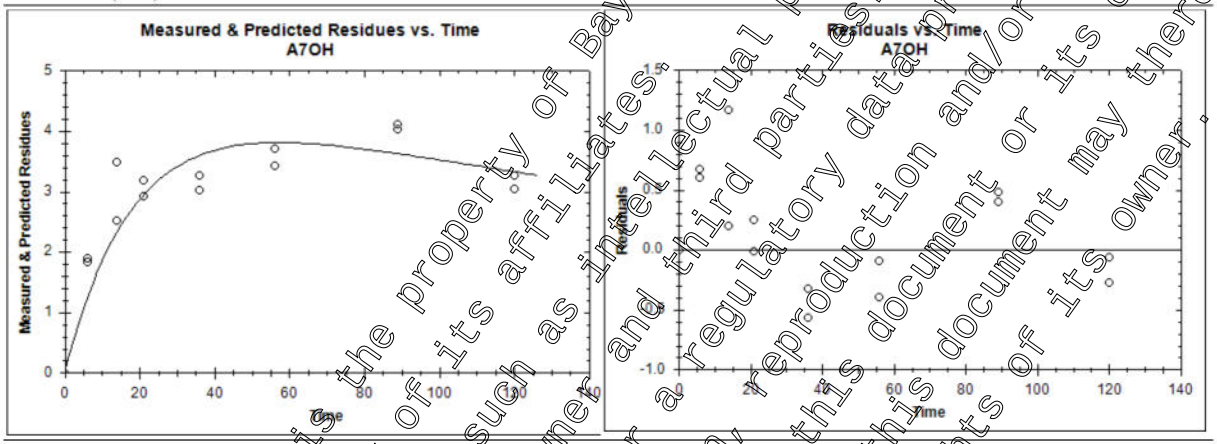
VA = visual assessment, + = good, o = acceptable, - = poor
SWARC = Scaled Weighted Area under Residue Curve
CI = confidence interval
fixed fit 1: SFO parent parameters fixed to free fit values, DT_{50} FLU-7-OH fixed to value derived from metabolite study in the same soil (M-757988-01-1).
fixed fit 2: SFO parent parameters fixed to free fit values, DT_{50} FLU-7-OH fixed to 95th CI rate of free fit.
fixed fit 3: DFOP parent parameters fixed to free fit values, DT_{50} FLU-7-OH fixed to 95th CI rate of free fit.

Modelling Endpoints: The metabolite FLU-7-OH is rising until the end of study. The pathway fit (parent SFO and DFOP free fit) was therefore modified with a fixed DT_{50} value for FLU-7-OH (fixed fit). The DT_{50} value of FLU-7-OH was fixed to a conservative value (95% confidence interval k of free fit; or to DT_{50} from metabolite study Kirchherr, 2020, in same soil). Formation fractions were fitted and parent parameters were fixed to values derived from the free fit. All fixed fits are visually less good than the free fit.

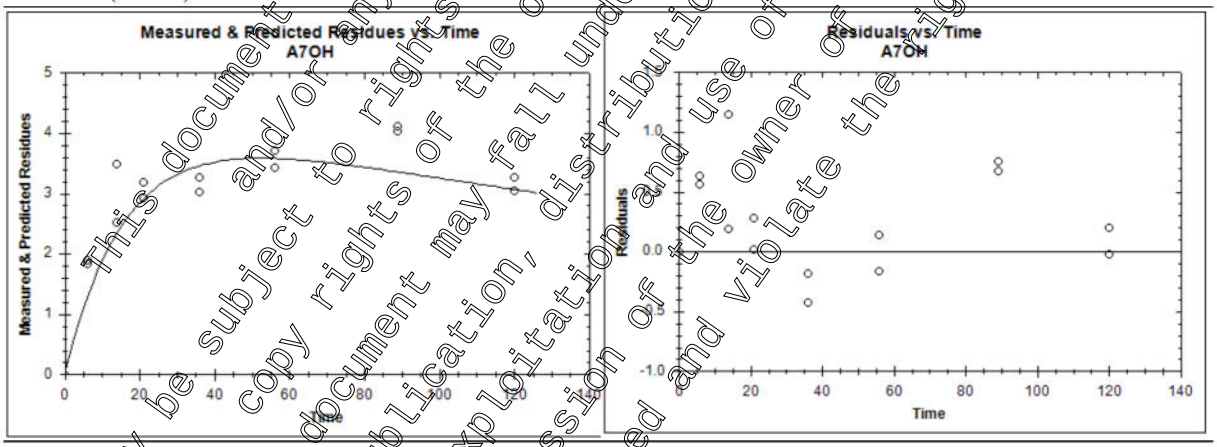
It should be noted, that this kinetic evaluation is carried out mainly to result in a robust description of the formation of TFA, which requires a good description of all predecessors in combination.

Finally, DFOP-SFO free fit did show the best visual fit for FLU, FLU-7-OH and TFA in combination with statistically reliable values for all 3 compounds. Consequently **DFOP-SFO free fit** is considered appropriate for modelling endpoints.

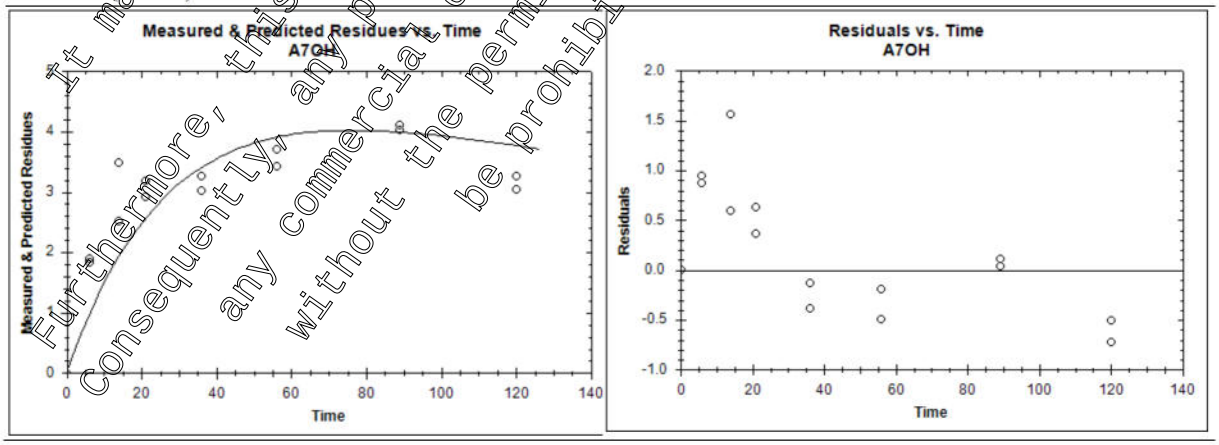
SFO/SFO (free)



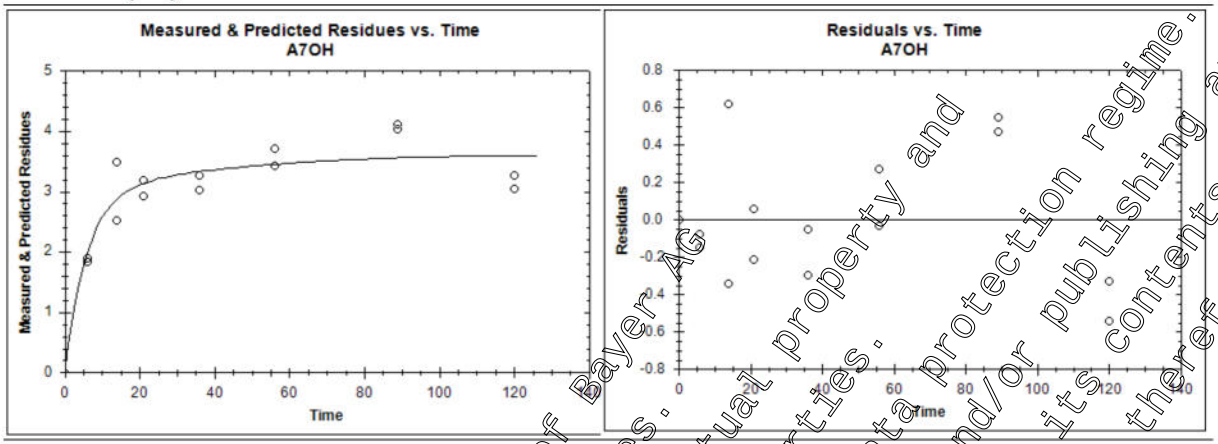
SFO/SFO (fixed 1)



SFO/SFO (fixed 2)



DFOP/SFO (free)



DFOP/SFO (fixed 3)

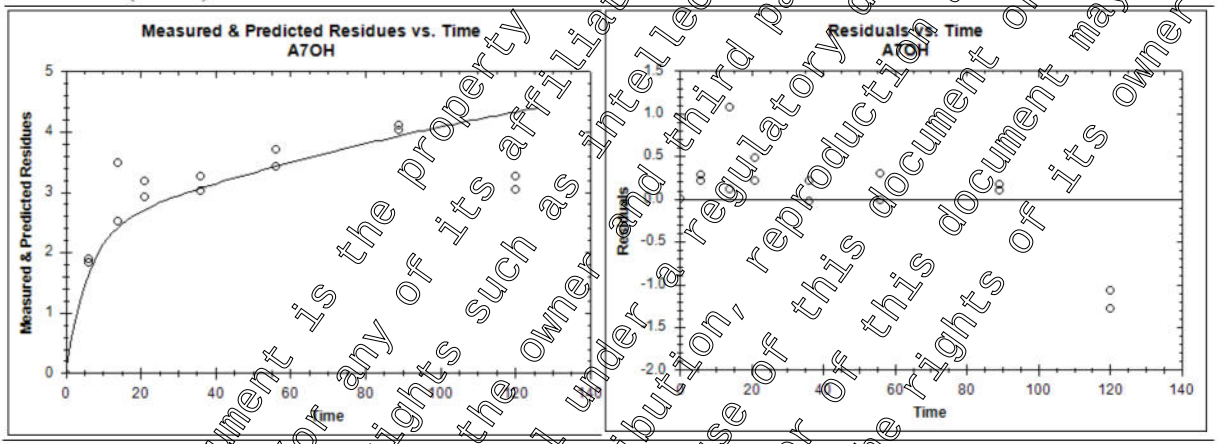


Table 7.1.2.1.1-104: FLU-7-OH (M-761739-01-1): Kinetic and statistical results of degradation in soil Hoefchen am Hohenseh for trigger endpoints, pathway fit

Kinetic model, Parent - metabolite	DT_{50} actual	DT_{90} actual	VA	χ^2err	SWARC	k	t-test k	95th CI of k	FF (FLU)
	(d)	(d)		(%)	(-)	(1/d)	(-)	(1/d)	(-)
DFOP - SFO	**85.52**	**284.1**	+	7.02	10.1	0.008105	0.003	0.00270 to 0.014	0.2430

VA = visual assessment, + = good, o = acceptable, - = poor
SWARC = Scaled Weighted Area under Residue Curve
CI = confidence interval

Trigger Endpoints: SFO fit (parent DFOP) is statistically (χ^2err, t-test) good and visually good. Consequently, **SFO** degradation model (**parent DFOP**) is appropriate for trigger endpoints.

DFOP/SFO

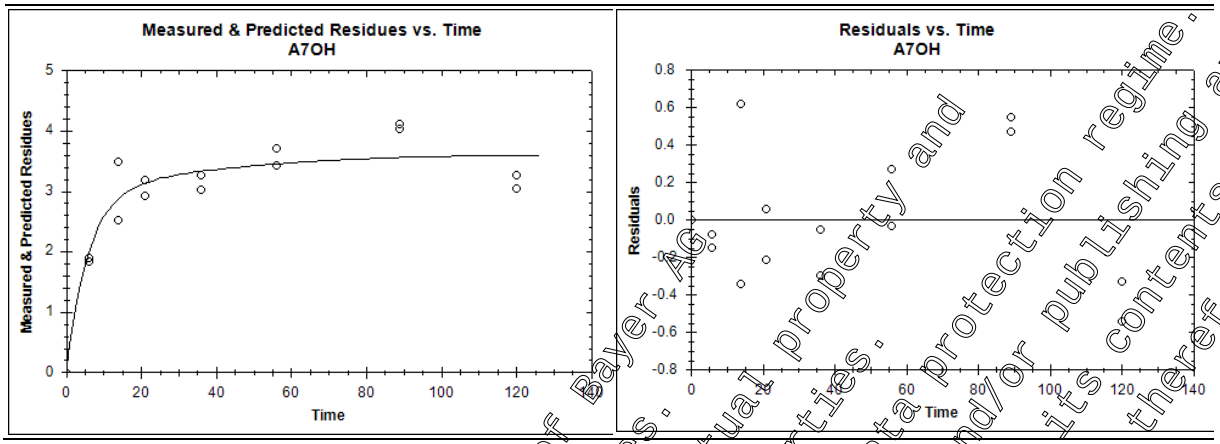


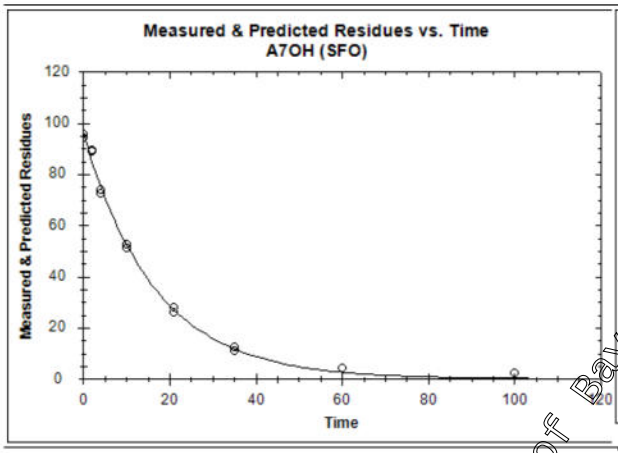
Table 7.1.2.1.1-105: FLU-7-OH (M-757988-01-1): kinetic and statistical results of degradation in soil Hoefchen am Hohensch for modelling and trigger endpoints, metabolite applied

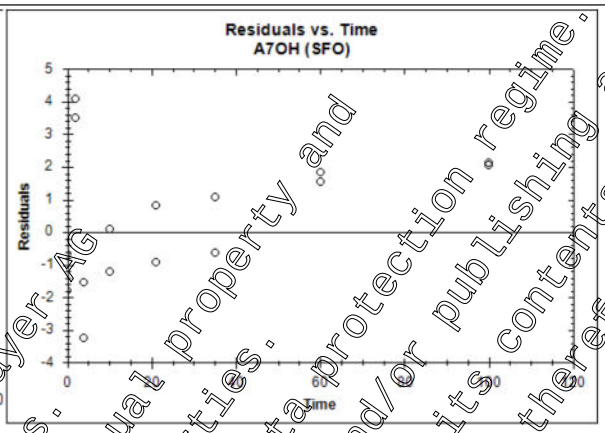
Kinetic model	DT_{50} actual	DT_{90} actual	DT_{50} fast / slow	VA	χ^2err / SWARC	k_1 / α	k_2 / β	g / t_b	t-test k_1 / k_2	95% CI of k_1	95% CI of k_2
	(d)	(d)	(d)		(% / -)	(1/d / -)	(1/d / d)	(- / d)	(-)	(1/d)	(1/d)
SFO	**11.50**	**38.21**	-	+	3.43 / 9.45	0.060258	-	-	<0.001	0.05651 to 0.064	-
DFOP	11.23	39.62	10.87 / >1000	+	3.40 / 0.216	0.06375	<0.00001	0.9783	<0.001 / 0.5	0.05360 to 0.074	-0.05033 to 0.05
DFOP, fixed g	11.17	40.03	8.367 / 15.34	+	3.47 / 2.89	0.082847	0.045199	0.5 fix	<0.001 / <0.001	0.05813 to 0.108	0.03438 to 0.056
FOMC	11.14	40.21	-	+	3.44 / 2.17	9.9	153.547	-	- / -	-	-
HS	11.21	40.48	11.21 / 13.24	+	3.78 / 2.38	0.061823	0.052333	19.4	<0.001 / <0.001	0.05532 to 0.068	0.03748 to 0.067

VA = visual assessment, + good, o acceptable, - poor
SWARC = Scaled Weighted Area under Residue Curve
CI = confidence intervall
fixed g: DFOP run with a fixed g = 0.5. Attempt to link the 2 DFOP rates k to the 2 enatiomers of fluopyram-7-hydroxy. Both enantiomers appear in ratio 50:50 at study start, which may correspond to g = 0.5.

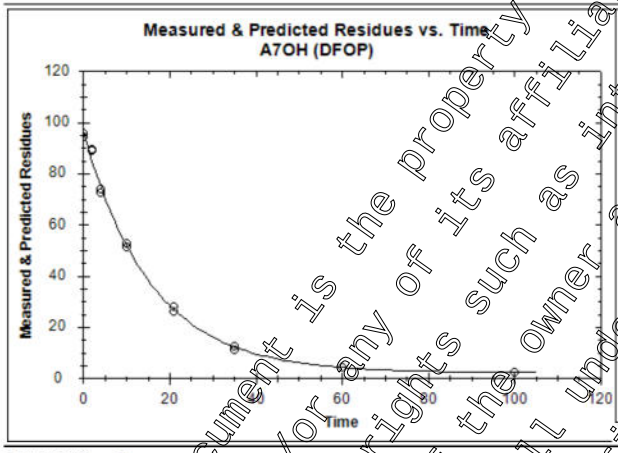
Modelling Endpoints:	SFO fit is statistically and visually good (χ^2err <15%, t-test <0.05). SWARC value is < 40, not indicating a biphasic decline. Consequently, **SFO** degradation model is appropriate for modelling endpoints.
Trigger Endpoints:	SFO fit is statistically and visually good (χ^2err, t-test). DFOP, FOMC and HS fits were alternatively tested. DFOP fit shows the lowest χ^2err of all kinetic models, but t-test for k_2 failed. SFO fit shows the second lowest χ^2err. Consequently, **SFO** degradation model is appropriate for trigger endpoints.

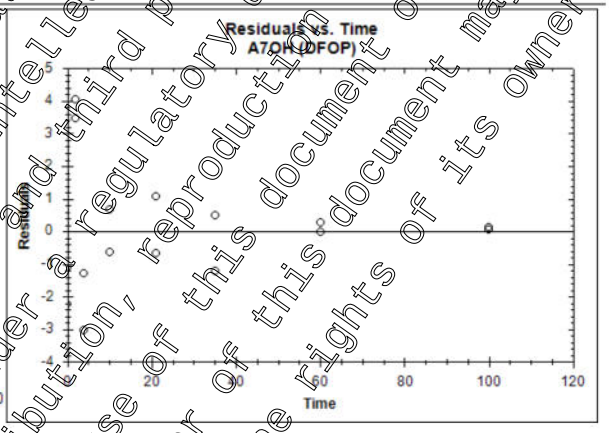
SFO



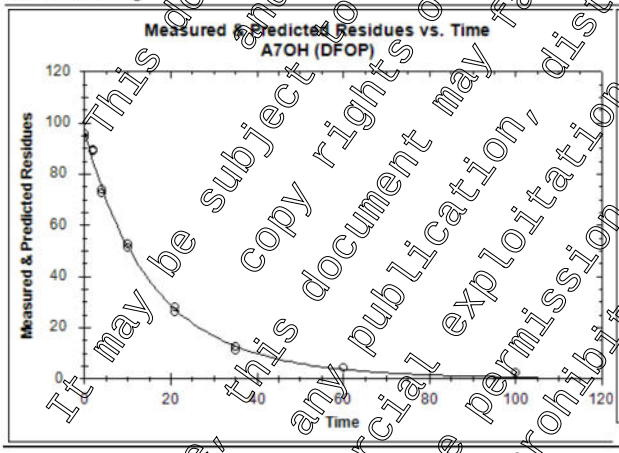


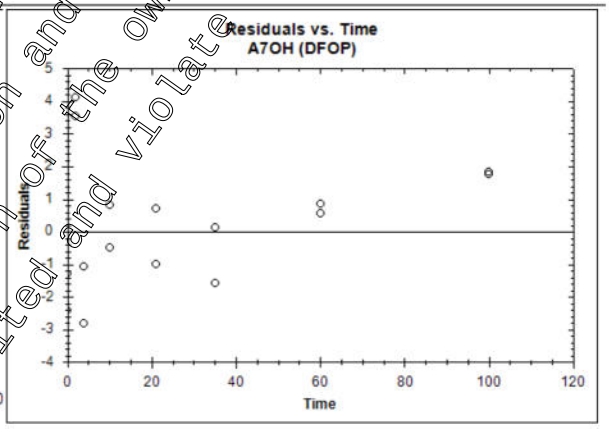
DFOP



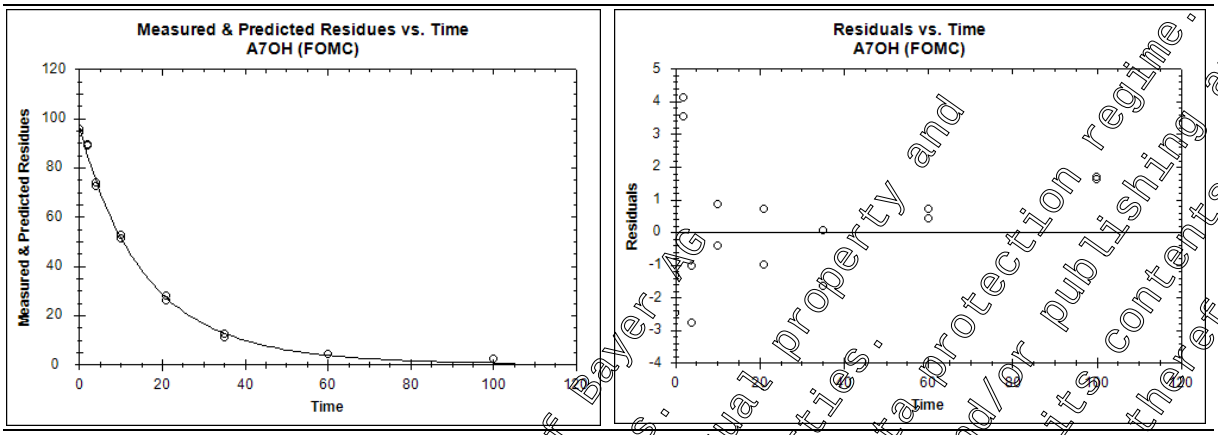


DFOP fixed g





FOMC



HS

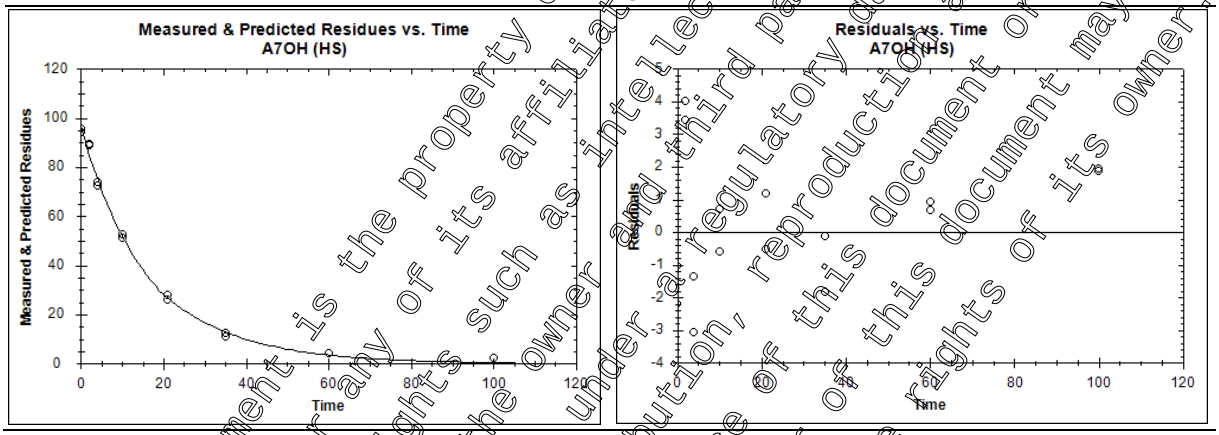


Table 7.1.2.1.1-106: FLU-7-OH (M-761739-01-1): kinetic and statistical results of degradation in soil Innerdeich for modelling endpoints

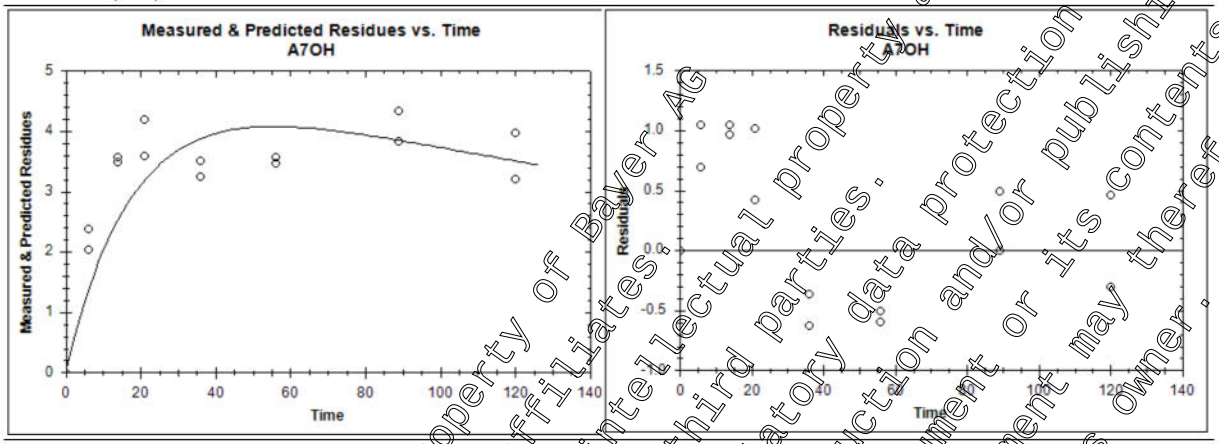
Kinetic model, Parent - metabolite	DT_{50} actual	DT_{90} actual	VA	χ^2err	SWARC	k	t-test k	95th CI of k	ff (FLU)
	(d)	(d)		(%)	(-)	(1/d)	(-)	(1/d)	(-)
SFO - SFO, free fit	12.86	42.71	o	14.8	34.6	0.05391	<0.001	0.03080 to 0.077	0.8668
SFO - SFO, fixed fit 1, 95% CI	22.50 fix	74.76 fix	-	20.9	132	0.0308	-	-	0.5831
DFOP - SFO, free fit	**61.31**	203.7	o	6.14	7.10	0.0113052	<0.001	0.00494 to 0.018	**0.3422**
DFOP - SFO, fixed fit 2, 95% CI	140.2 fix	465.7 fix	-	12.2	74.5	0.0049443	-	-	0.2662

VA = visual assessment, + = good, o = acceptable, - = poor
SWARC = Scaled Weighted Area under Residue Curve
CI = confidence intervall
fixed fit 1: SFO parent parameters fixed to free fit values, DT_{50} FLU-7-OH fixed to 95th CI rate of free fit.
fixed fit 2: DFOP parent parameters fixed to free fit values, DT_{50} FLU-7-OH fixed to 95th CI rate of free fit.

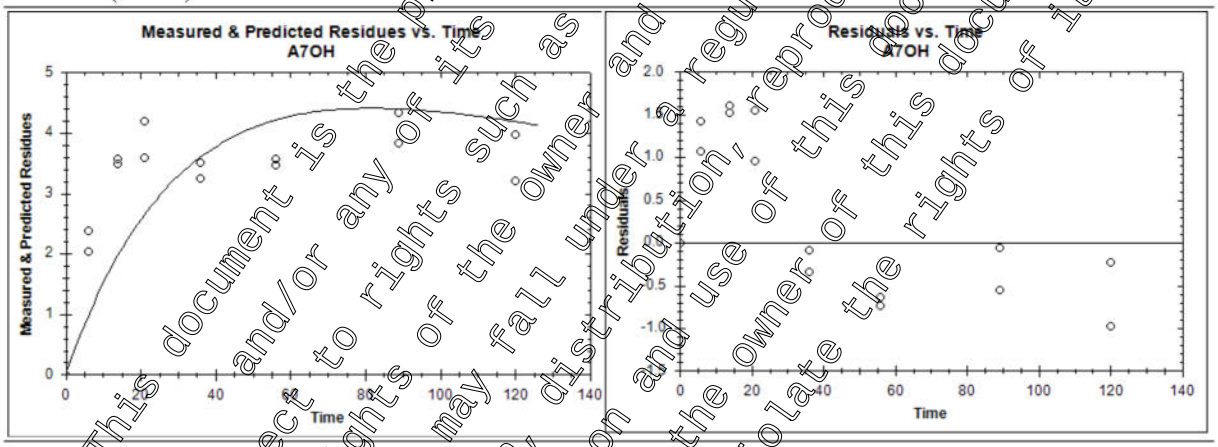
Modelling Endpoints: The metabolite FLU-7-OH is rising until the end of study. The pathway fit (parent SFO and DFOP free fit) was therefore modified with a fixed DT_{50} value for FLU-7-OH (fixed fit). The DT_{50} value of FLU-7-OH was fixed to a conservative value (95% confidence interval k of free fit). Formation fractions were fitted and parent parameters were fixed to values derived from the free fit. All fixed fits are visually less good than the free fit.

It should be noted, that this kinetic evaluation is carried out mainly to result in a robust describtion of the formation of TFA, which requires a good description of all predecessors in combination. Finally, DFOP-SFO free fit did show the best visual fit for FLU, FLU-7-OH and TFA in combination with statistically reliable values for all 3 compounds. Consequently, **DFOP-SFO free fit** is considered appropriate for modelling endpoints

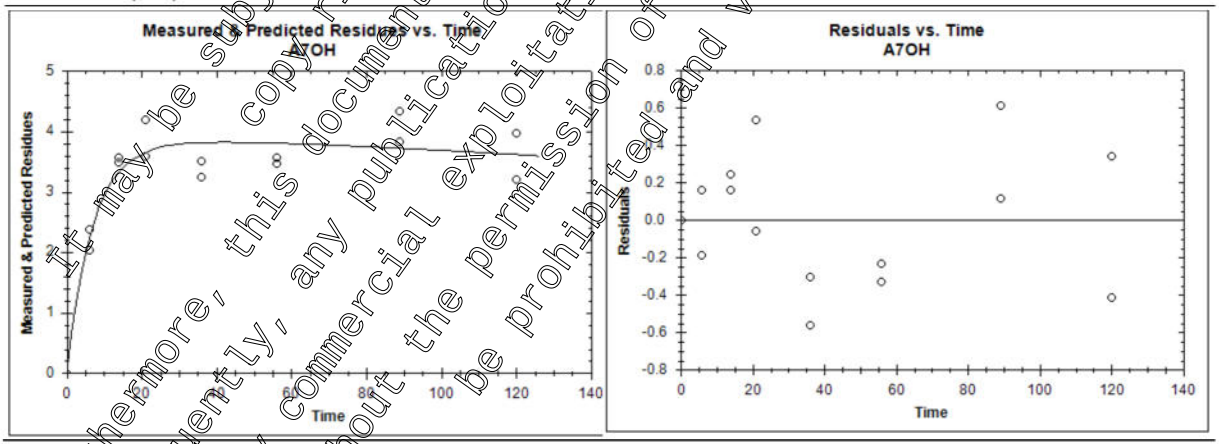
SFO/SFO (free)



SFO/SFO (fixed 1)



DFOP/SFO (free)



DFOP/SFO (fixed 2)

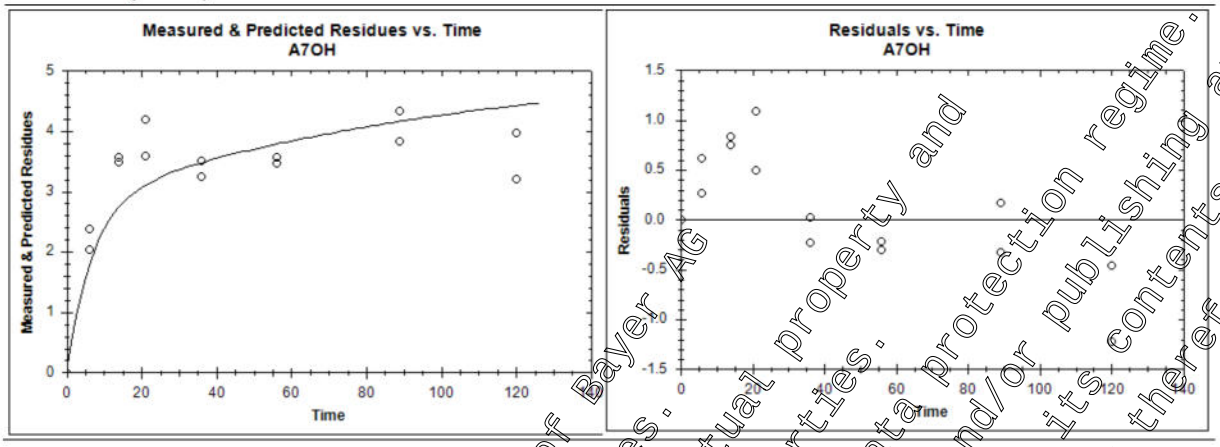


Table 7.1.2.1.1-107: FLU-7-OH (M-761739-01-1): kinetic and statistical results of degradation in soil Innerdeich for trigger endpoints, pathway fit

Kinetic model, Parent - metabolite	DT_{50} actual	DT_{90} actual	VA	χ^2 err	SWARC	k	t-test k	95th CI of k	FF (FLU)
	(d)	(d)		(%)	(-)	(1/d)	(-)	(1/d)	(-)
DFOP - SFO	61.34	203.7	+	9.14	7.10	0.011305	0.001	0.00494 to 0.018	0.3422

VA = visual assessment, + = good, o = acceptable, - = poor
SWARC = Scaled Weighted Area under Residue Curve
CI = confidence interval

Trigger Endpoints: SFO fit (parent DFOP) is statistically (χ^2 err, t-test) good and visually acceptable. Consequently, **SFO** degradation model (**parent DFOP**) is appropriate for trigger endpoints.

DFOP/SFO

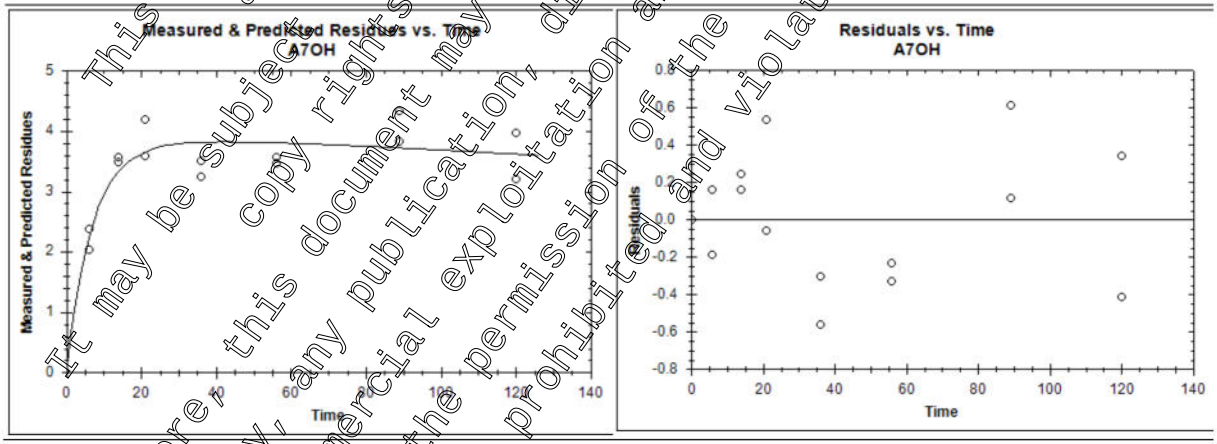


Table 7.1.2.1.1-108: FLU-7-OH (M-757988-01-1): kinetic and statistical results of degradation in soil Innerdeich for modelling and trigger endpoints, metabolite applied

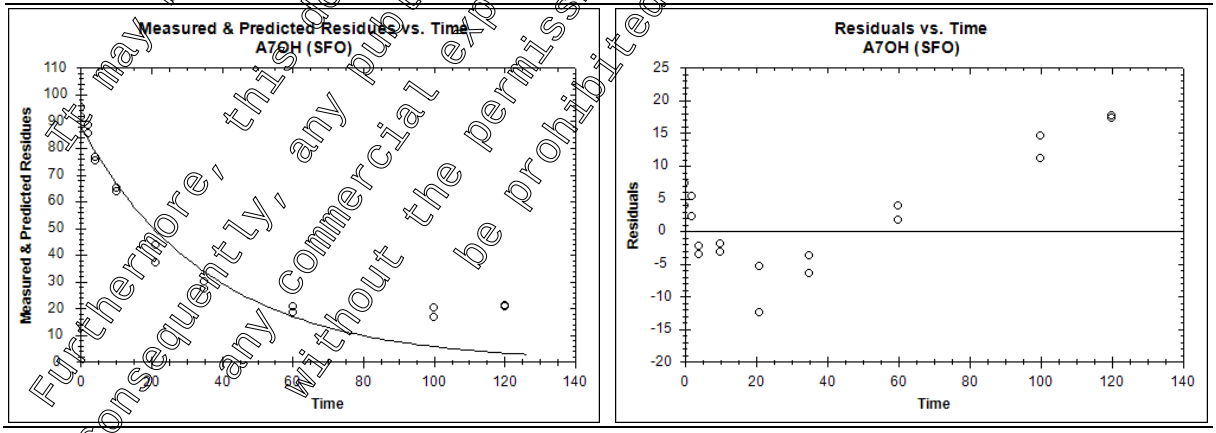
Kinetic model	DT_{50} actual	DT_{90} actual	DT_{50} fast / slow	VA	χ^2err / SWARC	k_1 / α	k_2 / β	g / t_b	t-test k_1 / k_2	95th CI of k_1	95th CI of k_2
	(d)	(d)	(d)		(% / -)	(1/d / -)	(1/d / d)	(- / d)	(-)	(1/d)	(1/d)
SFO	25.20	83.72	-	-	13.6 / 296	0.027503	-	-	<0.001	0.02042 to 0.035	-
DFOP	17.21	>1000	12.17 / >1000	+	3.04 / 7.65	0.05694	<0.00001	0.8005 / 0.5	<0.001 / <0.001	0.04281 to 0.071	-0.00567 to 0.0062
DFOP, fixed g	18.14	153.5	7.174 / 66.09	o	7.05 / 35.1	0.096616	0.010488	0.5 fix	<0.001 / <0.001	0.05924 to 0.134	0.00812 to 0.013
FOMC	17.03	216.1	-	o	6.05 / 22.3	0.7794	11.8842	-	-	-	-
HS	**17.63**	**284.2**	17.63 / 167.8, **85.60** [1]	+	4.05 / 3.68	0.039316	0.004131	0.7167 / 32.1	<0.001 / 0.009	0.03440 to 0.044	0.00411 to 0.007

VA = visual assessment, + good, o acceptable, - poor
SWARC = Scaled Weighted Area under Residue Curve
CI = confidence intervall
fixed g: DFOP run with a fixed g = 0.5. Attempt to link the 2 DFOP rates k to the 2 enantiomers of fluopyram-7-hydroxy. Both enantiomers appear in ratio 50:50 at study start, which may correspond to g = 0.5.
[1] pseudo DT50 = back-calculated DT90 / 3.32 as modelling endpoint

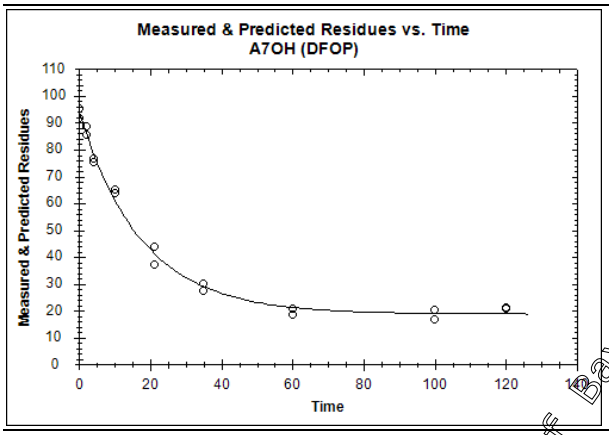
Modelling Endpoints: SFO fit is statistically good (χ^2err <15%, t-test <0.05), but visually poor. SWARC value is > 40, indicating a biphasic decline.
Therefore, DFOP kinetic was tested, but t-test for k_2 failed and fit is therefore not suitable. HS fit is statistically and visually good. However, the slow phase, starting after 32 d, describes only ¼ of the metabolite degradation, which reached residues of already 20.8 % at study end.
Further on, a biphasic behaviour of metabolites is not straight forward to use in several predictive models, and weight of evidence supports SFO degradation of the metabolite in most other soils, including all parent trials with a pathway evaluation.
Therefore, **HS** degradation model is considered appropriate for modelling, but using a back-calculated **DT_{90} / 3.32 as pseudo SFO DT_{50}**. This would be similar to the standard approach for FOMC, especially to take into account the full observed degradation curve.

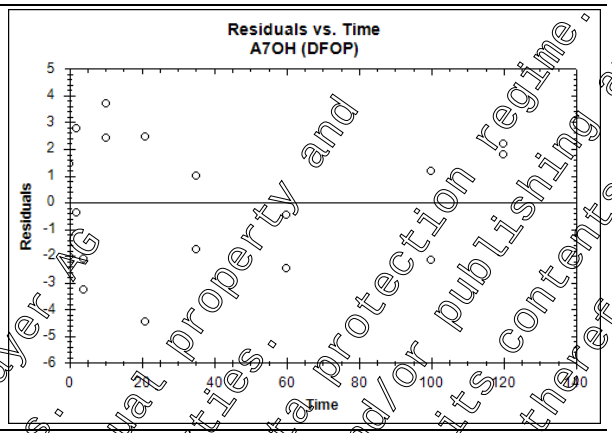
Trigger Endpoints: SFO fit is statistically good (χ^2err, t-test), but visually poor. DFOP, FOMC and HS fits were alternatively tested. HS fit shows a low χ^2err and visually best fit. Consequently, **HS** degradation model is appropriate for trigger endpoints.

SFO

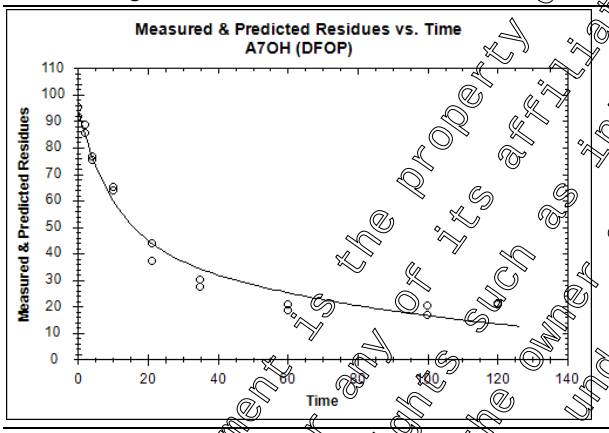


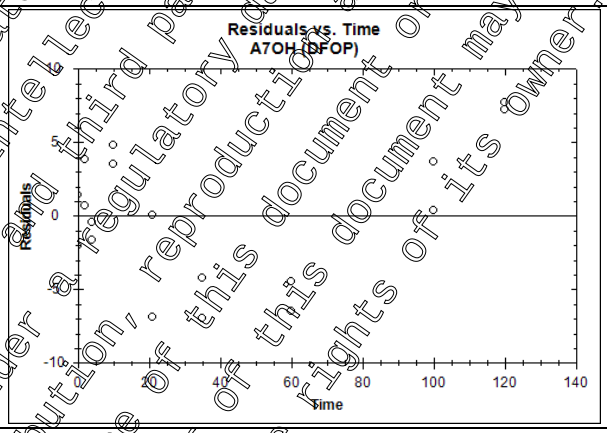
DFOP



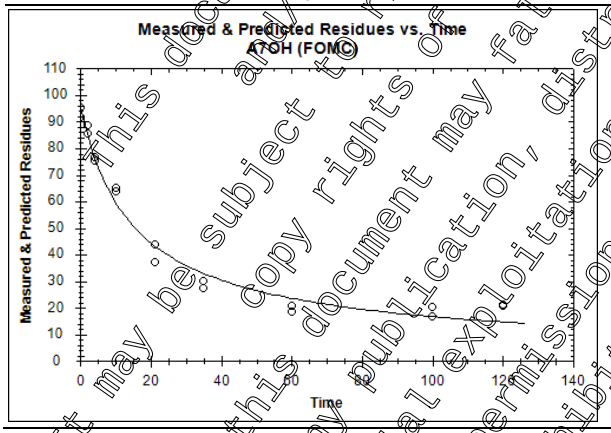


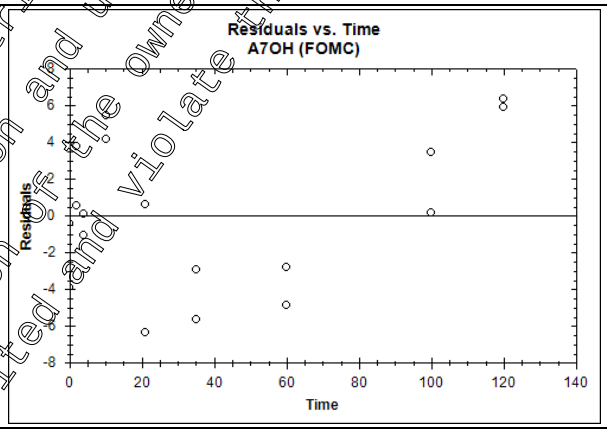
DFOP fixed g



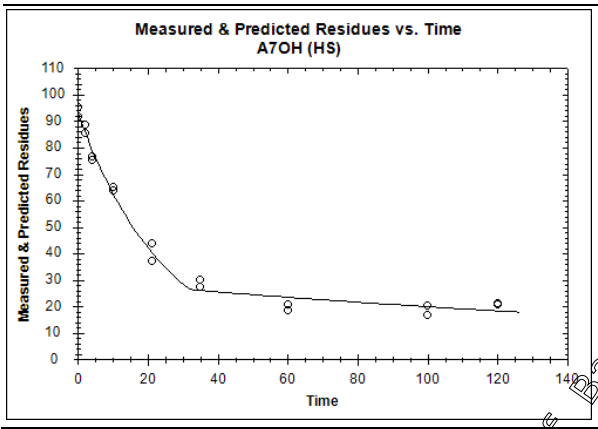


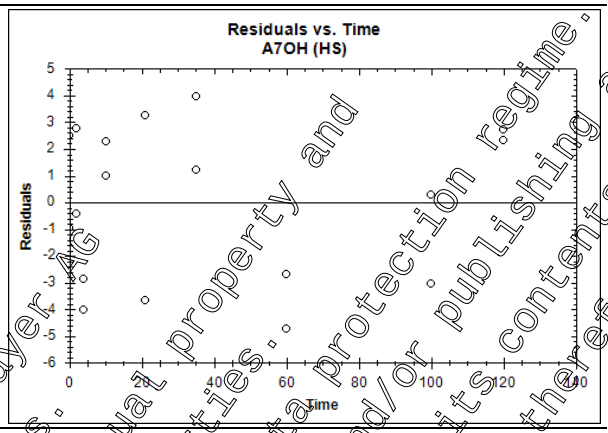
FOMC





HS





Degradation of trifluoroacetic acid

In the experimental study (KCA 7.1.1.1.07, M-761739-01-1) the observed, reported TFA residues (non-radioactive analytics) where expressed assuming a theoretical maximum overall occurrence of 100 % (equivalent to formation fraction 1). This could alternatively be understood as if the TFA formation from one CF_3 moiety has been followed only, assuming that the other CF_3 moiety degrades exactly in parallel.

The reported residues where used directly in this KinGUI evaluation, as the model is limited to a formation fraction of 1 anyway. The original KinGUI formation fractions than reflect the TFA formation per CF_3 moiety, or as related to a maximum formation fraction of 1.

For a correct description of the molecular split (2 moles out of 1 parent mole), all formation fractions leading to TFA (i.e. FLU - TFA, 7-OH - TFA, overall FLU - TFA) from KinGUI need to be multiplied by a factor of 2.

Results of the kinetic evaluation for modelling purpose based on residue data from aerobic laboratory soil degradation study in EU soils are summarised in the tables below.

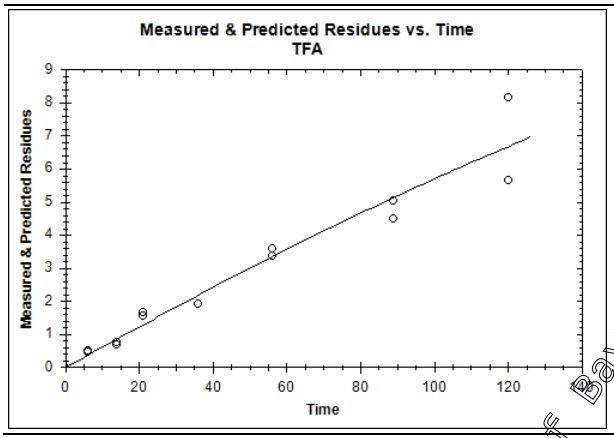
Table 7.1.2.1.1-109: TFA (M-761739-01-1): kinetic and statistical results of degradation in soil Frankenforst for modelling endpoints

Kinetic model, ***Parent***	DT_{50} actual	DT_{90} actual	VA	χ^2err	SWARC	k	t-test k	95th CI of k	ff (FLU)	ff (7-OH)
	(d)	(d)		(%)	(-)	(1/d)	(-)	(1/d)	(-)	(-)
SFO	no deg.	no deg.	+	6.95	0	no deg.	-	-	**0.2267**	**0.0430**
DFOP	no deg.	no deg.	+	6.59	0.530	no deg.	-	-	0.0912	0.6100

VA = visual assessment, + = good, o = acceptable, - = poor
SWARC = Scaled Weighted Area under Residue Curve
CI = confidence interval
no deg. = no degradation assumed

Modelling Endpoints: SFO fit (parent SFO) is statistically and visually good (χ^2err <25%, formation fraction ff is <1, SWARC <40). Consequently, **SFO** degradation model (**parent SFO**) is appropriate for modelling endpoints.

SFO/SFO



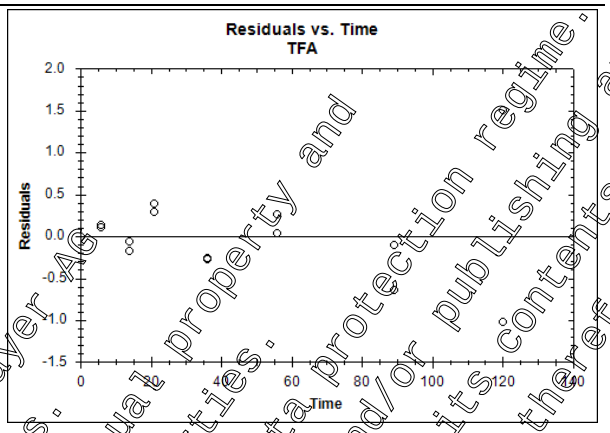


Table 7.1.2.1.1-110: TFA (M-761739-01-1): kinetic and statistical results of degradation in soil Wurmwiese for modelling endpoints

Kinetic model, ***Parent***	DT_{50} actual	DT_{90} actual	VA	χ^2err	SWARC	k	t-test k	95th CI of k	ff (FLU)	ff (7-OH)
	(d)	(d)		(%)	(-)	(1/d)	(-)	(1/d)	(-)	(-)
SFO, free fit	no deg.	no deg.	o	14.2	48.4	no deg.	-	-	0.1932	0.0767
SFO, fixed fit 1	no deg.	no deg.	-	13.7	31.5	no deg.			0.2364	0.0171
SFO, fixed fit 2, 95% CI	no deg.	no deg.	o	13.7	29.1	no deg.	-		0.2412	0.0018
DFOP, free fit	no deg.	no deg.	+	12.5	0.972	no deg.	-	-	**0.0930**	**1.0000**
DFOP, fixed fit 3, 95% CI	no deg.	no deg.		19.5	104	no deg.	-	-	0.1690	1.0000

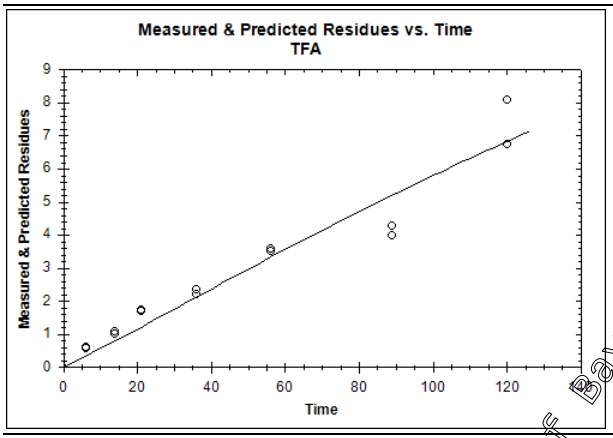
VA = visual assessment, + = good, o = acceptable, - = poor
SWARC = Scaled Weighted Area under Residue Curve
CI = confidence intervall
no deg. = no degradation assumed
fixed fit 1: SFO parent parameters fixed to free fit values, DT_{50} FLU-7-OH fixed to value derived from metabolite study in the same soil (M-757988-01-1).
fixed fit 2: SFO parent parameters fixed to free fit values, DT_{50} FLU-7-OH fixed to 95th CI rate of free fit.
fixed fit 3: DFOP parent parameters fixed to free fit values, DT_{50} FLU-7-OH fixed to 95th CI rate of free fit.

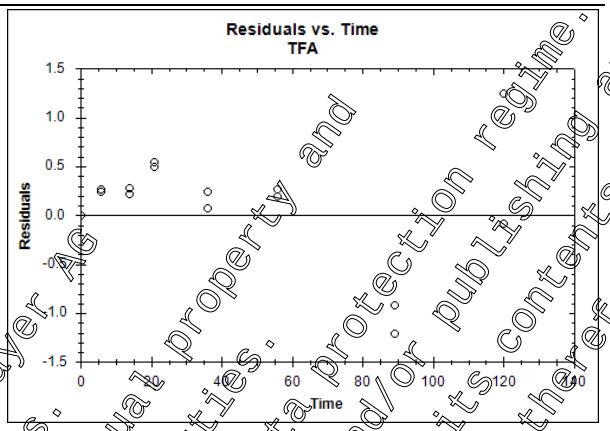
Modelling Endpoints: The metabolite FLU-7-OH is rising until the end of study. The pathway fit (parent SFO and DFOP free fit) was therefore modified with a fixed DT_{50} value for FLU-7-OH (fixed fit). The DT_{50} value of FLU-7-OH was fixed to a conservative value (95% confidence interval k of free fit; or to DT_{50} from metabolite study Kirchherr, 2020, in same soil). Formation fractions were fitted and parent parameters were fixed to values derived from the free fit. All fixed fits are visually less good than the free fit.

It should be noted, that this kinetic evaluation is carried out mainly to result in a robust describtion of the formation of TFA, which requires a good description of all predecessors in combination.

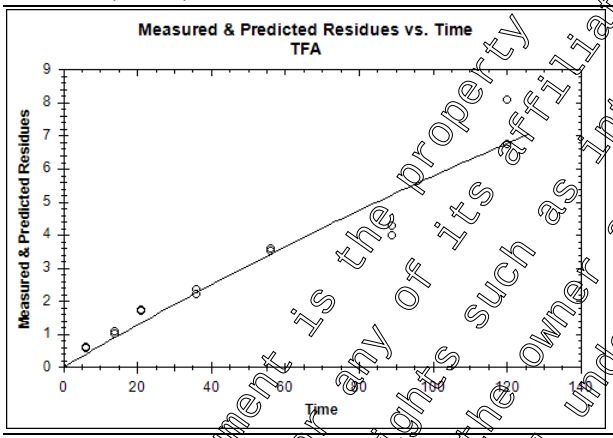
Finally, parent DFOP free fit did show the best visual fit for FLU, FLU-7-OH and TFA in combination with statistically reliable values for all 3 compounds. The good fit for TFA can be seen at the lowest SWARC value. Consequently, **parent DFOP free fit** is considered appropriate for modelling endpoints.

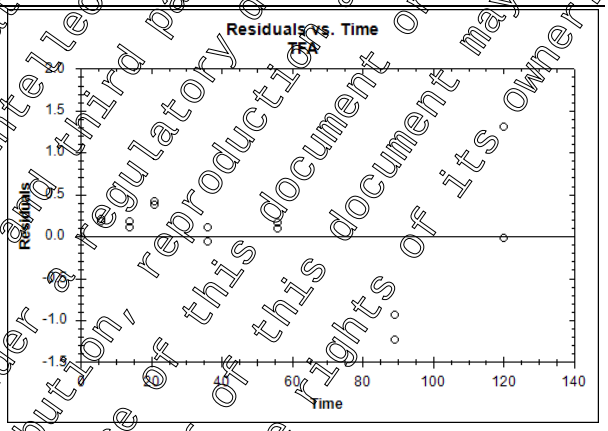
SFO/SFO (free)



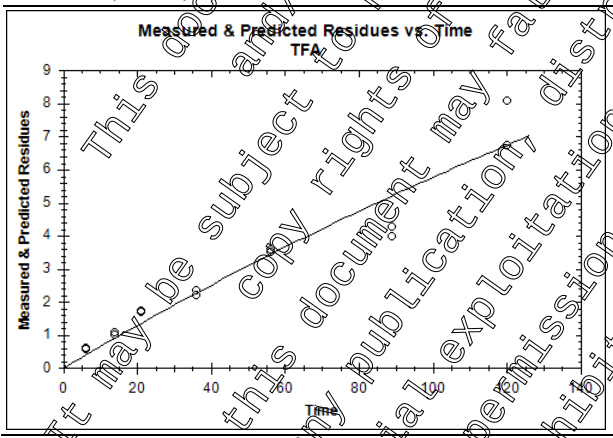


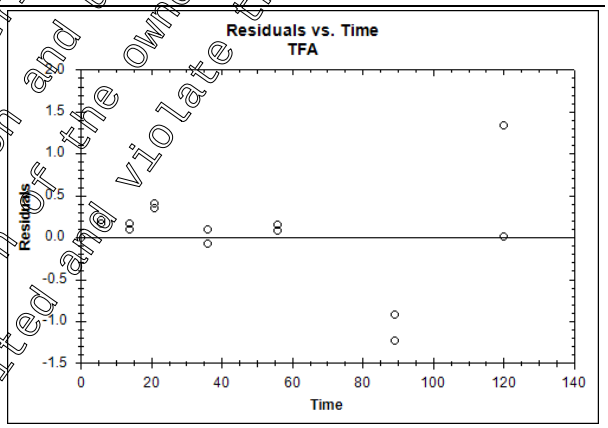
SFO/SFO (fixed 1)



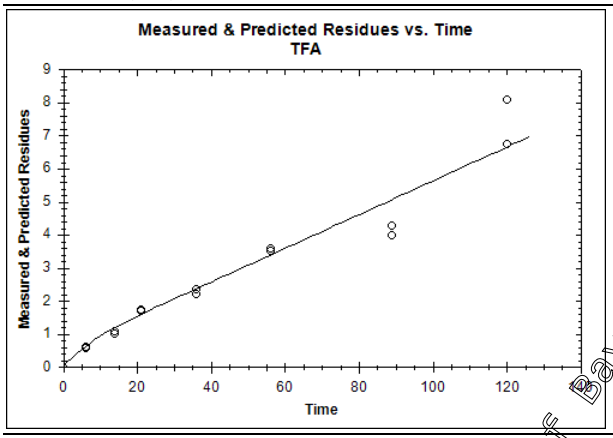


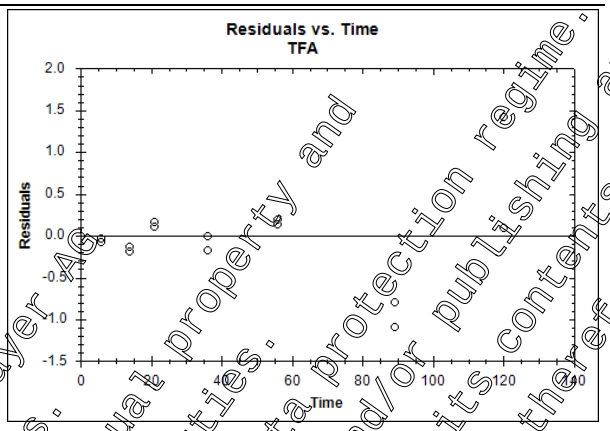
SFO/SFO (fixed 2)



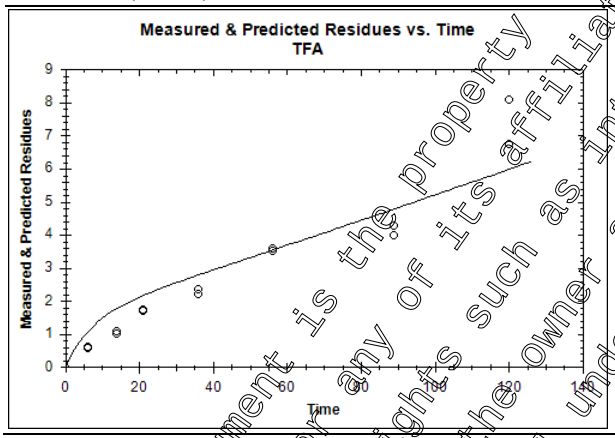


DFOP/SFO (free)





DFOP/SFO (fixed 3)



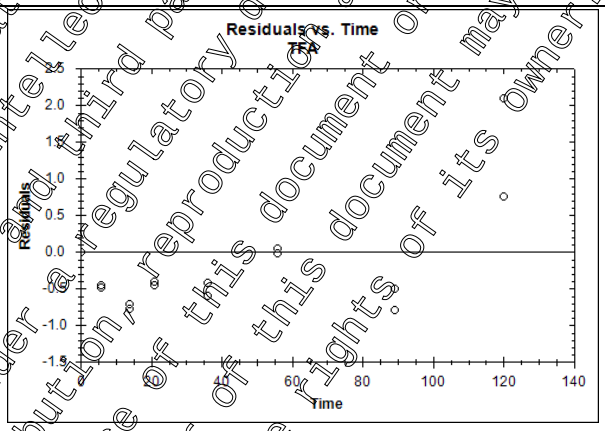


Table 7.1.2.1.1-111: TFA (M-761739-01-1): kinetic and statistical results of degradation in soil Hoefchen am Hohensch for modelling endpoints

Kinetic model, ***Parent***	DT_{50} actual (d)	DT_{90} actual (d)	VA	χ^2err (%)	SWARC (-)	k (1/d)	t-test k (-)	95th CI of k (1/d)	ff (FLU) (-)	ff (7-OH) (-)
SFO, free fit	no deg.	no deg.	o	12.8	31.3	no deg.	-	-	0.1527	0
SFO, fixed fit 1	no deg.	no deg.	o	14.9	47.5	no deg.	-	-	0.1079	0.0587
SFO, fixed fit 2, 95% CI	no deg.	no deg.	o	12.8	31.8	no deg.	-	-	0.1526	0
DFOP, free fit	no deg.	no deg.	+	8.98	0	no deg.	-	-	**0.0563**	**0.8508**
DFOP, fixed fit 3, 95% CI	no deg.	no deg.		15.5	87.6	no deg.	-	-	0.0973	1.0000

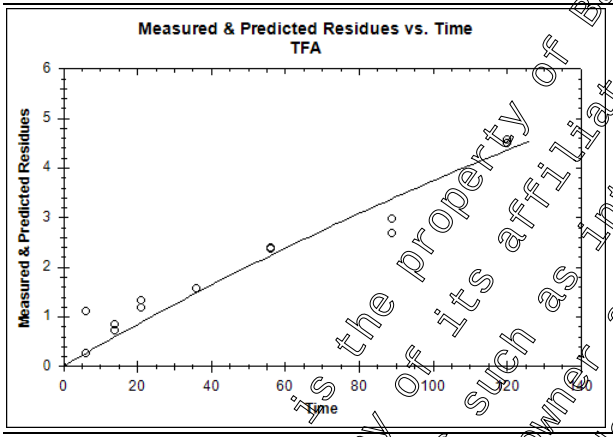
VA = visual assessment, + = good, o = acceptable, - = poor
SWARC = Scaled Weighted Area under Residue Curve
CI = confidence interval
no deg. = no degradation assumed
fixed fit 1: SFO parent parameters fixed to free fit values, DT_{50} FLU-7-OH fixed to value derived from metabolite study in the same soil (M-757988-01-1).
fixed fit 2: SFO parent parameters fixed to free fit values, DT_{50} FLU-7-OH fixed to 95th CI rate of free fit.
fixed fit 3: DFOP parent parameters fixed to free fit values, DT_{50} FLU-7-OH fixed to 95th CI rate of free fit.

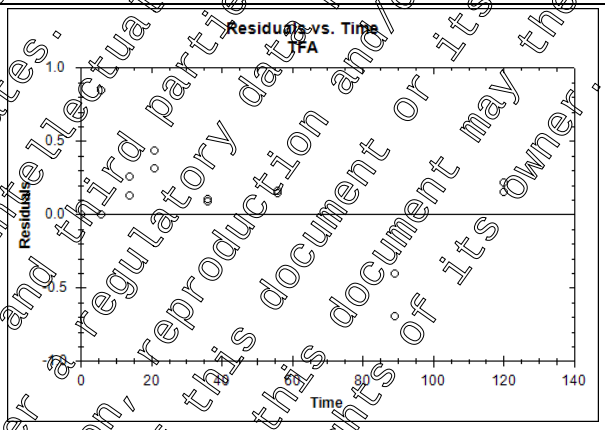
Modelling Endpoints: The metabolite FLU-7-OH is rising until the end of study. The pathway fit (parent SFO and DFOP free fit) was therefore modified with a fixed DT_{50} value for FLU-7-OH (fixed fit). The DT_{50} value of FLU-7-OH was fixed to a conservative value (95% confidence interval k of free fit; or to DT_{50} from metabolite study Kirchherr, 2020, in same soil). Formation fractions were fitted and parent parameters were fixed to values derived from the free fit. All fixed fits are visually less good than the free fit.

It should be noted, that this kinetic evaluation is carried out mainly to result in a robust description of the formation of TFA, which requires a good description of all predecessors in combination.

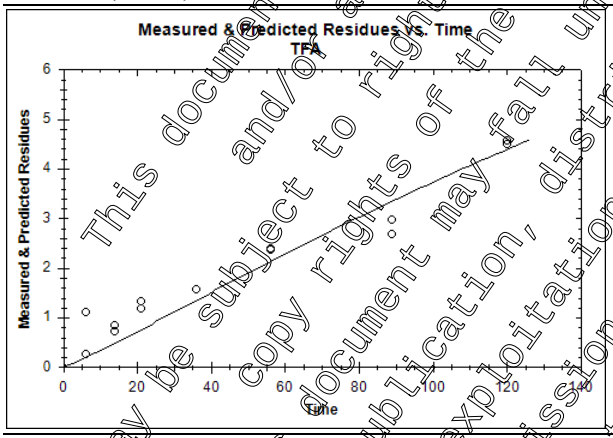
Finally, parent DFOP free fit did show the best visual fit for FLU, FLU-7-OH and TFA in combination with statistically reliable values for all 3 compounds. The good fit for TFA can be seen at the lowest SWARC value. Consequently, **parent DFOP free fit** is considered appropriate for modelling endpoints.

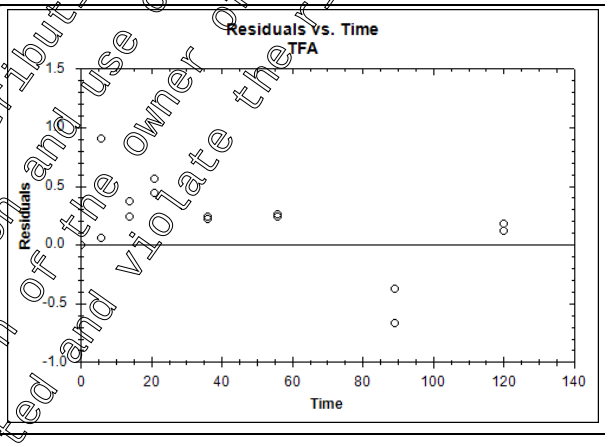
SFO/SFO (free)



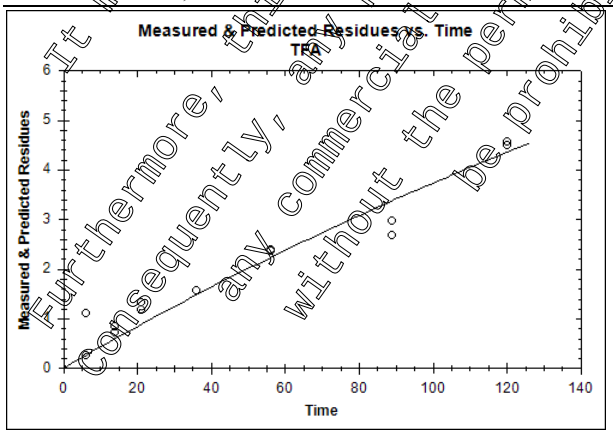


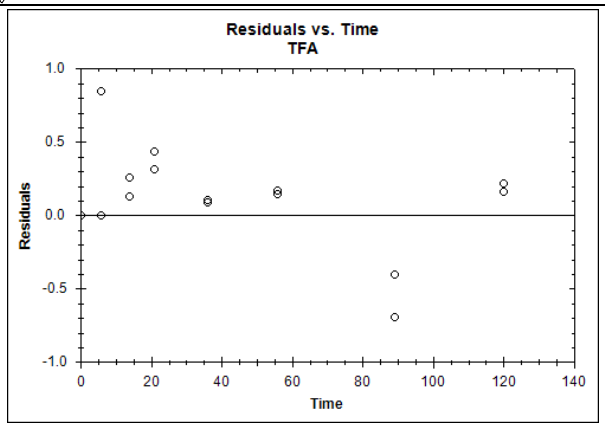
SFO/SFO (fixed 1)



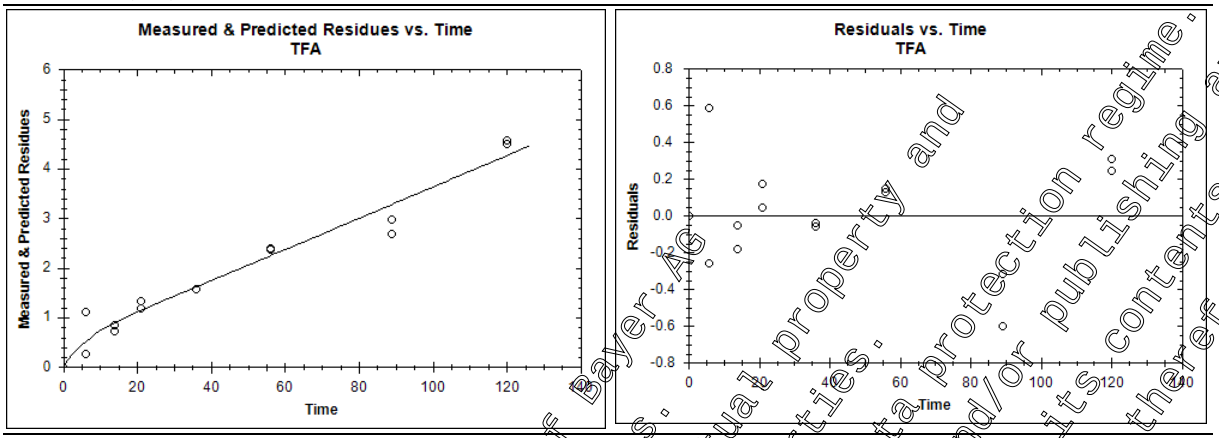


SFO/SFO (fixed 2)





DFOP/SFO (free)



DFOP/SFO (fixed 3)

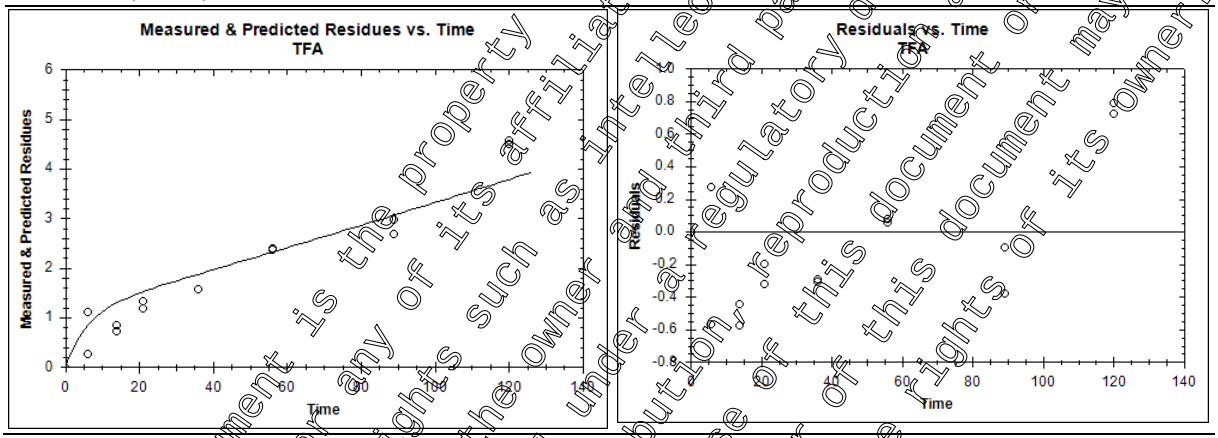


Table 7.1.2.1.1-112: TFA (M-761739-01-1): kinetic and statistical results of degradation in soil Innerdeich for modelling endpoints

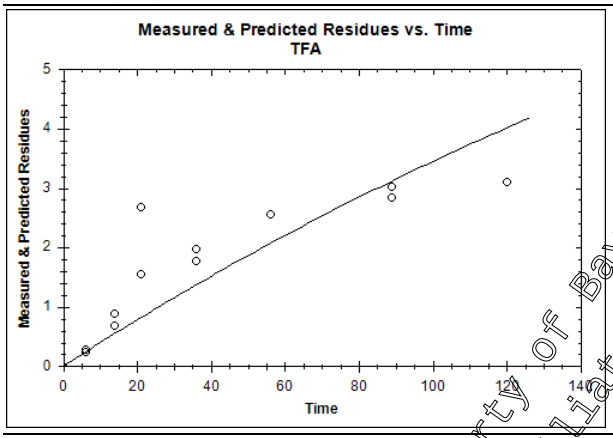
Kinetic model, ***Parent***	DT_{50} actual	DT_{90} actual	VA	χ^2err	SWARC	k	t-test k	95th CI of k	ff (FLU)	ff (7-OH)
	(d)	(d)		(%)	(-)	(1/d)	(-)	(1/d)	(-)	(-)
SFO, free fit	no deg.	no deg.	-	27.2	146	no deg.	-	-	0.1332	0
SFO, fixed fit 1, 95% CI	no deg.	no deg.		27.5	144	no deg.	-	-	0.1356	0
DFOP, free fit	no deg.	no deg.	o	16.2	45.5	no deg.	-	-	**0.1143**	**0.1358**
DFOP, fixed fit 3, 95% CI	no deg.	no deg.	o	16.3	10.8	no deg.	-	-	0.1185	0.2482

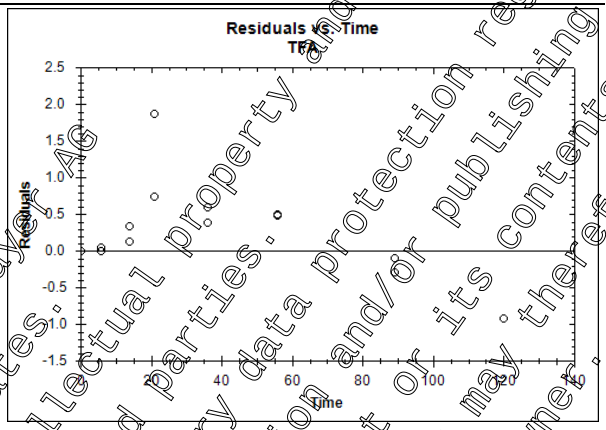
VA = visual assessment, + = good, o = acceptable, - = poor
SWARC = Scaled Weighted Area under Residue Curve
CI = confidence interval
no deg. = no degradation assumed
fixed fit 1: SFO parent parameters fixed to free fit values, DT_{50} FLU-7-OH fixed to 95th CI rate of free fit.
fixed fit 2: DFOP parent parameters fixed to free fit values, DT_{50} FLU-7-OH fixed to 95th CI rate of free fit.

Modelling Endpoints: The metabolite FLU-7-OH is rising until the end of study. The pathway fit (parent SFO and DFOP free fit) was therefore modified with a fixed DT_{50} value for FLU-7-OH (fixed fit). The DT_{50} value of FLU-7-OH was fixed to a conservative value (95% confidence interval k of free fit). Formation fractions were fitted and parent parameters were fixed to values derived from the free fit. All fixed fits are visually less good than the free fit.
It should be noted, that this kinetic evaluation is carried out mainly to result in a robust describtion of the formation of TFA, which requires a good description of all predecessors in combination.

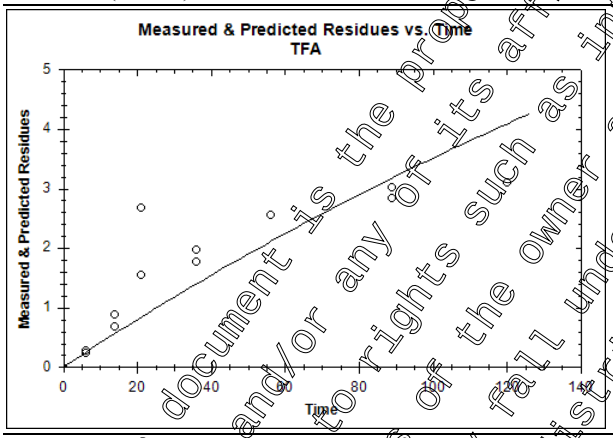
Finally, parent DFOP free fit did show the best visual fit for FLU, FLU-7-OH and TFA in combination with statistically reliable values for all 3 compounds. Consequently, **parent DFOP free fit** is considered appropriate for modelling endpoints.

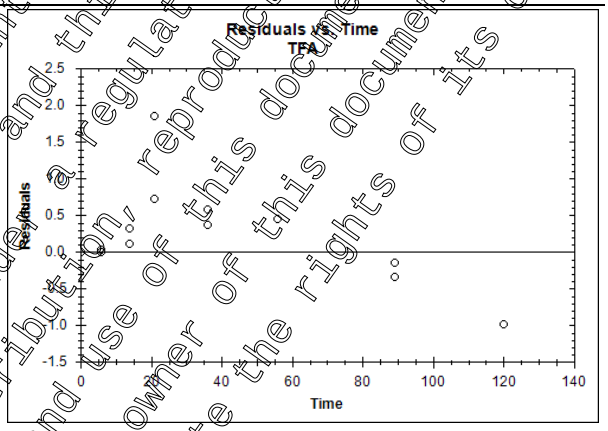
SFO/SFO (free)



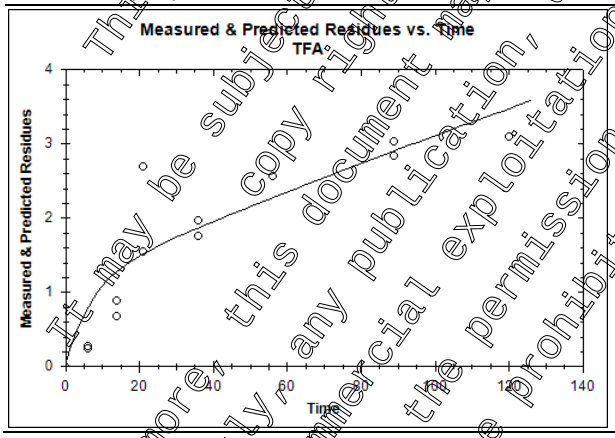


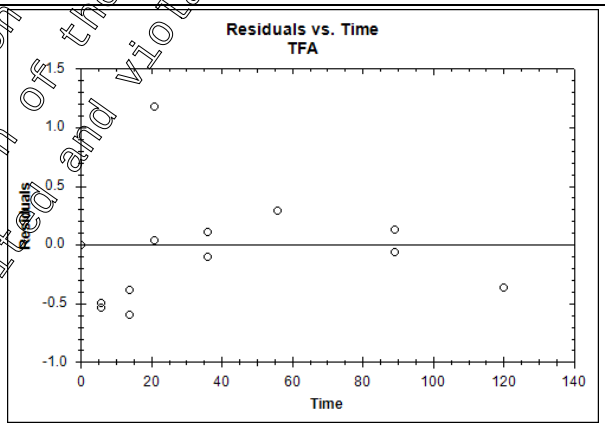
SFO/SFO (fixed 1)



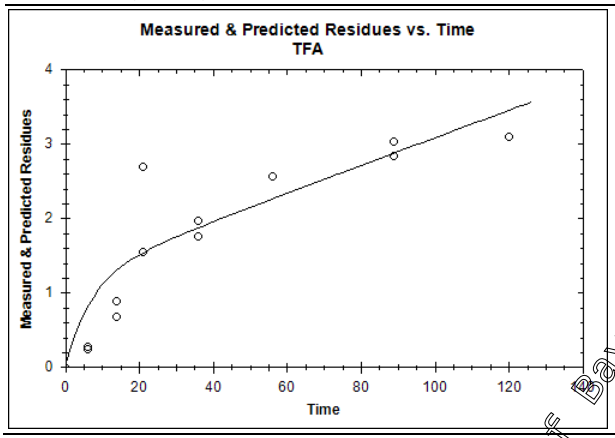


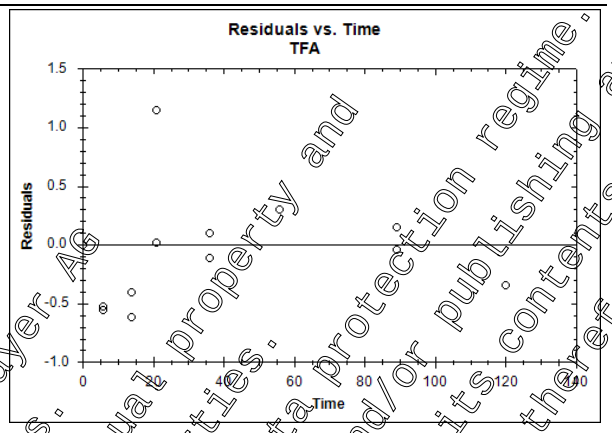
DFOP/SFO (free)





DFOP/SFO (fixed 2)





Normalisation

Moisture and temperature correction factors to normalise DT_{50} values to a moisture of pF2 and 20°C are summarised in the following.

Table 7.1.2.1.1-113: Moisture and temperature correction factors $f_\theta \cdot f_T$ for DT_{50} normalisation (reference moisture at pF2, 20°C; Q_{10} 2.58), (measured field capacity, θ_{ref}: measured moisture at pF2; MWHC: maximum water holding capacity)

Soil	Soil texture (USDA)	Study moist. (% MWHC) [3]	MWHC (g/100 g)	Study moist. θ (g/100 g)	Study temp. T (°C) [3]	measured field capacity θ_{ref} (g/100 g)	f_θ (-)	f_T (-)	$f_\theta \cdot f_T$ (-)
Frankenforst [1]	Silt loam	54.2	54.5	29.5	19.4	34.7	0.8934	0.9270	0.8282
Wurmwiese [1]	Loam	54.4	55.1	30.0	19.2	20.9	1.00	0.9270	0.9270
Hoefchen am Hohenseh [1]	Silt loam	54.4	58.3	31.7	19.2	28.8	1.00	0.9270	0.9270
Innerdeich [1]	Sandy loam	54.5	39.4	21.5	19.2	13.4	1.00	0.9270	0.9270
Frankenforst [2]	Silt loam	52.6	54.5	28.7	21.09	34.7	0.8749	1.1088	0.9701
Wurmwiese [2]	Loam	52.9	55.1	29.1	21.09	20.9	1.00	1.1088	1.1088
Hoefchen am Hohenseh [2]	Silt loam	52.8	58.3	30.8	21.09	28.8	1.00	1.1088	1.1088
Innerdeich [2]	Sandy loam	51.6	39.4	20.3	21.09	13.4	1.00	1.1088	1.1088

[1] M-761739-01-1, KCA 7.1.1.1/07
[2] M-757988-01-1, KCA 7.1.2.1.2/06
[3] mean measured values used

Calculation of overall formation fraction of TFA

It should be noted, that the kinetic evaluation presented is mainly carried out to obtain a robust description of the overall formation of TFA from the applied fluopyram, which requires a good description of all predecessors in combination. This has been taken into account in the decision of the most appropriate pathway fits.

One parent molecule fluopyram can theoretically degrade to 2 TFA molecules (molecule split), as the molecule has 2 CF_3 moieties at different functional groups. This would mean a total molar yield or

formation fraction of 2, or an occurrence of 200% of the originally available parent molecules, as worst case.

The degradation behaviour of both CF_3 groups could not be identified separately because the evaluated TFA residues are based a the non-radioactive analytics in the experimental study (M-761739-01-1). A radioactive analytics was carried out in addition, using the UL-phenyl label. However, most phenyl related TFA findings have been below the LOD, so that no separation or differentiation between both moieties could be done. Thus, finally the summed degradation of both CF_3 moieties in total is evaluated.

In the experimental study, the observed, reported TFA residues (non-radioactive analytics) where expressed assuming a theoretical maximum overall occurrence of 100 % (equivalent to formation fraction 1). This could alternatively be understood as if the TFA formation from one CF_3 moiety has been followed only, assuming that the other CF_3 moiety degrades exactly in parallel.

The reported residues where used directly in this KinGUI evaluation, as the model is limited to a formation fraction of 1 anyway. The original KinGUI formation fractions than reflect the TFA formation per CF_3 moiety, or as related to a maximum formation fraction of 1.
For a correct description of the molecular split (2 moles out of 1 parent mole), all formation fractions leading to TFA (i.e. FLU - TFA, 7-OH - TFA, overall FLU - TFA) from KinGUI have to be multiplied by a factor of 2.

For a correct description of the molecular split or molar yield (2 moles out of 1 parent mole) for defining a maximum occurrence of TFA, the experimentally reported % values (Hellpointner and Hennig, 2021) have to be multiplied by a factor of 2, to reflect the molar yield per FLU molecule, and not only per CF_3 moiety.

In addition, the evaluation of an overall formation fraction of TFA from FLU is recommended to allow for a simplified pathway for exposure assessments, and finally robust description of TFA formation.
The ratio between all 5 paths of the fitted pathway (FLU – 7-OH, 7-OH – TFA, FLU – TFA, FLU – sink, 7-OH - sink) is correctly determined in 4 soils, here. In case the formation fractions from FLU to 7-OH from other soils would be averaged with the ones from these soils, no corresponding information for the remaining paths would be available. In case of significantly different formation fractions from FLU to 7-OH in these and other soils, this would lead to an unrealistic shift of the overall formation behaviour of TFA.
To overcome this, it is recommended to evaluate an overall formation fraction of TFA from FLU, via all metabolites and parallel pathways from these 4 soils. Then the pathway for predictive modelling can be simplified, including only 3 separate parallel paths from FLU, namely to 7-OH, to TFA and to a sink, without any further interconnection between the metabolites. This will avoid an unrealistic influencing of one path when new data for another path will be available.
The overall formation fraction of TFA, per soil, is calculated as

$$\text{ff overall TFA} = \text{ff Flu} \rightarrow \text{7\_OH} * \text{ff 7\_OH} \rightarrow \text{TFA} + \text{ff Flu} \rightarrow \text{TFA} \quad (1)$$

This overall formation fraction of TFA and consequently simplified pathway is strongly recommended for predictive modelling.

Table 7.1.2.1.1-114: Recalculation of overall formation fractions ff from fluopyram to TFA in soil, for modelling purpose (M-761739-01-1)

Soil	ff (FLU - 7-OH) fitted pathway [1]	ff (FLU - TFA) fitted pathway, related to max. ff 1, per CF_3 moiety [2]	ff (7-OH - TFA) fitted pathway, related to max. ff 1, per CF_3 moiety [3]	ff overall (FLU - TFA) simplified pathway, related to max. ff 1, per CF_3 moiety [4]	ff overall (FLU - TFA) simplified pathway, related to max. ff 2, per FLU molecule [4]
Silt loam, Frankenforst	0.6689	0.2267 CF3	0.0430 CF3	0.2555 CF3	0.5109 FLU
Loam, Wurmwiese	0.3082	0.0930 CF3	1.0000 CF3	0.4012 CF3	0.8024 FLU
Silt loam, Hoefchen am Hohensee	0.2430	0.0563 CF3	0.8508 CF3	0.2630 CF3	0.5261 FLU
Sandy loam, Innerdeich	0.3422	0.1143 CF3	0.1358 CF3	0.1608 CF3	0.3215 FLU
Arithmetic mean				**0.2701 CF3**	**0.5402 FLU**

[1] formation fraction for single path FLU to 7-OH in pathway fit
[2] formation fraction for single path FLU to TFA in pathway fit
[3] formation fraction for single path 7-OH to TFA in pathway fit
[4] overall formation fraction, for parent to TFA via all metabolites and parallel pathways
= ff FLU - 7-OH * ff 7-OH - TFA + ff FLU - TFA
CF3 formation fraction, reflecting TFA formation per CF_3 moiety of FLU
FLU formation fraction, reflecting TFA formation per FLU molecule, i.e. 2 x formation fraction per CF_3 moiety, as FLU has 2 CF_3 moieties.

Unfortunately, some models or calculations cannot deal with formation fractions > 1 (e.g. KinGUI, PELMO, etc.).
For a correct predictive modelling of the molecule split several options exist:

1. Use overall formation fraction reflecting TFA formation per FLU molecule (related to max. ff 2), in combination with the correct molar mass of TFA (e.g. in PEARL),
2. Use formation fraction reflecting TFA formation per CF_3 moiety (related to max. ff 1), in combination with the molar mass of 2 TFA molecules (e.g. in PELMO).
3. Separate runs can be carried out, each describing a separate part of the pathway (e.g. in PELMO).

III. CONCLUSIONS

The laboratory soil $DegT_{50}$ parameters of fluopyram and fluopyram-7-hydroxy for modelling and trigger purpose and the formation fraction of TFA for modelling porpose based on residue data from aerobic laboratory soil degradation studies in EU soils are summarised in the tables below.

Table 7.1.2.1.1-115: Laboratory soil $DegT_{50}$ parameters of fluopyram for modelling purpose (normalised: pF2, 20°C, Q10 2.58; M-761739-01-1)

Fluopyram (FLU)	Dark aerobic conditions						
Soil type (USDA)		**pH ($CaCl_2$)**	**T (C°) / % MWHC**	**$DegT_{50\ actual}$ / $DT_{90\ actual}$ (d)**	**$DegT_{50\ mod}$ (d) 20°C pF2 / 10 kPa [1]**	**St. (χ^2)**	**Method of calculation**
Silt loam, Frankenforst		7.3	19.2 / 54.2 [2]	246.4 / 818.4	204.0	1.84	SFO
Loam, Wurmwiese		5.1	19.2 / 54.4 [2]	341.0 / >1000	$DT_{50\ fast}$ 4.735 d, **$DT_{50\ slow}$ 369.7 d,** g 0.0936	1.76	DFOP
Silt loam, Hoefchen am Hohensee		5.7	19.2 / 54.4 [2]	327.8 / >1000	$DT_{50\ fast}$ 3.850 d, **$DT_{50\ slow}$ 373.1 d,** g 0.1208	2.15	DFOP
Sandy loam, Innerdeich		6.2	19.2 / 54.5 [2]	374.4 / 1000	$DT_{50\ fast}$ 4.488 d, **$DT_{50\ slow}$ 416.0 d,** g 0.1085	0.990	DFOP

[1] Normalised using a Q_{10} of 2.58 and Walker equation coefficient of 0.7
[2] mean measured values used

Table 7.1.2.1.1-116: Laboratory soil $DegT_{50}$ parameters of fluopyram for trigger purpose M-761739-01-1)

Fluopyram (FLU)	Dark aerobic conditions					
Soil type (USDA)	**pH ($CaCl_2$)**	**T (C°) / % MWHC**	**$DegT_{50\ actual}$ / $DT_{90\ actual}$ (d)**	**$DegT_{50\ mod}$ (d) 20°C pF2 / 10 kPa [1]**	**St. (χ^2)**	**Method of calculation**
Silt loam, Frankenforst	7.3	19.2 / 54.2 [2]	245.0 / 857.5		1.48	DFOP
Loam, Wurmwiese	6.1	19.2 / 54.4 [2]	467.1 / >1000		1.50	DFOP
Silt loam, Hoefchen am Hohensee	5.7	19.2 / 54.4 [2]	310.2 / >1000		2.13	DFOP
Sandy loam, Innerdeich	6.2	19.2 / 54.5 [2]	427.3 / >1000		0.798	DFOP

[1] Normalised using a Q_{10} of 2.58 and Walker equation coefficient of 0.7
[2] mean measured values used

Table 7.1.2.1.1-117: Laboratory soil $DegT_{50}$ parameters of fluopyram-7-hydroxy for modelling purpose (normalised: pF2, 20°C, Q10 2.58)

Fluopyram-7-hydroxy (FLU-7-OH)	**Dark aerobic conditions** **- formation from parent fluopyram in pathway fit,** **- metabolite applied study**						
Soil type (USDA)	**pH ($CaCl_2$)**	**T (C°) / % MWHC**	**$DegT_{50\ actual}$ / $DT_{90\ actual}$ (d)**	**$DegT_{50\ mod}$ (d) 20°C pF2 / 10 kPa [1]**	**ff (FLU - 7-OH)**	**St. (χ^2)**	**Method of calculation parent - metabolite**
Silt loam, Frankenforst [5]	7.3	19.2 / 54.2 [4]	10.48 / 34.80	8.675	0.6689	11.7	SFO-SFO
Silt loam, Frankenforst [6]	7.3	21.09 / 52.6 [4]	5.371 / 17.84	5.210		7.64	SFO [2]
Silt loam, Frankenforst [5], [6]	7.3			**6.723**			geomean of above 2
Loam, Wurmwiese [5]	5.1	19.2 / 54.4 [4]	66.55 / 221.1	61.69	0.3082	7.54	DFOP-SFO
Loam, Wurmwiese [6]	5.1	21.09 / 52.9 [4]	13.92 / 91.87	30.68 [3]	-	6.75	FOMC [2]
Loam, Wurmwiese [5], [6]	5.1			**43.51**			geomean of above 2
Silt loam, Hoefchen am Hohenseh [5]	5.7	19.2 / 54.4 [4]	85.62 / 284.4	79.28	0.2430	7.02	DFOP-SFO
Silt loam, Hoefchen am Hohenseh [6]	5.7	21.09 / 52.8 [4]	11.50 / 38.21	12.75	-	3.43	SFO [2]
Silt loam, Hoefchen am Hohenseh [5], [6]	5.7			**31.80**			geomean of above 2
Sandy loam, Innerdeich [5]	6.2	19.2 / 54.5 [4]	61.31 / 203.7	56.83	0.3422	6.14	DFOP-SFO
Sandy loam, Innerdeich [6]	6.2	21.09 / 51.6 [4]	17.63 / 284.2	94.92 [3]	-	4.05	HS [2]
Sandy loam, Innerdeich [5], [6]	6.2			**73.45**			geomean of above 2

[1] Normalised using a Q_{10} of 2.58 and Walker equation coefficient of 0.7
[2] metabolite applied study
[3] pseudo DT_{50} = DT_{90} / 3.32 used as DT_{50} for modelling endpoints
[4] mean measured values used
[5] M-761739-01-1
[6] M-757988-01-1, metabolite applied study

Table 7.1.2.1.1-118: Laboratory soil $DegT_{50}$ parameters of fluopyram-7-hydroxy for trigger purpose

Fluopyram-7-hydroxy (FLU-7-OH)	**Dark aerobic conditions** **- formation from parent fluopyram in pathway fit,** **- metabolite applied study**						
Soil type (USDA)	**pH ($CaCl_2$)**	**T (C°) / % MWHC**	**$DegT_{50\ actual}$ / $DT_{90\ actual}$ (d)**	**$DegT_{50\ mod}$ (d) 20°C pF2 - 10 kPa [1]**	**ff (FLU - 7-OH)**	**St. (χ^2)**	**Method of calculation parent - metabolite**
Silt loam, Frankenforst [4]	7.3	19.2 / 54.2 [3]	24.56 / 81.60		0.3109	9.04	DFOP-SFO
Silt loam, Frankenforst [5]	7.3	21.09 / 52.6 [3]	5.371 / 17.84			7.64	SFO [2]
Loam, Wurmwiese [4]	5.1	19.2 / 54.4 [3]	66.55 / 221.1		0.3082	7.54	DFOP-SFO
Loam, Wurmwiese [5]	5.1	21.09 / 52.9 [3]	14.74 / 113.9		-	5.82	HS [2]
Silt loam, Hoefchen am Hohenseh [4]	5.7	19.2 / 54.4 [3]	**85.52 / 284.1**		0.3430	7.02	DFOP-SFO
Silt loam, Hoefchen am Hohenseh [5]	5.7	21.09 / 52.8 [3]	11.50 / 38.21		-	3.43	SFO [2]
Sandy loam, Innerdeich [4]	6.2	19.2 / 54.5 [3]	62.31 / 209.7		0.3422	6.14	DFOP-SFO
Sandy loam, Innerdeich [5]	6.2	21.09 / 51.6 [3]	17.63 / 284.2 $DT_{50\ fast}$ 17.63 d $DT_{50\ slow}$ 167.8 d tb 32.1 d = g 0.7167 $DT_{50\ pseudo}$ 85.6 d		-	4.05	HS [2]

[1] Normalised using a C_{ref} of 2.58 and Walker equation coefficient of 0.7
[2] metabolite applied study
[3] mean measured values used
[4] M-761739-01-1
[5] M-757988-01-1, metabolite applied study

Table 7.1.2.1.1-119: Laboratory soil formation fractions of trifluoroacetic acid for modelling purpose (M-761739-01-1.1)

Trifluoroacetic acid (TFA)	Dark aerobic conditions overall formation, from parent to TFA via all metabolites and parallel pathways; max. occurrence in soil: 14.8 % per FLU molecule 7.4 % per CF_3 moiety							
Soil type (USDA)	**pH ($CaCl_2$)**	**T (C°) / % MWHC**	**DT_{50} / DT_{90} (d)**	**$DT_{50\ mod}$ (d) 20°C pF2 / 10 kPa**	**ff overall (FLU - TFA) per CF_3 $_{CF3}$**	**ff overall (FLU - TFA) per FLU $_{FLU}$**	**χ^2**	**Method of calculation *parent***
Silt loam, Frankenforst	7.3	19.2 / 54.2 [2]	- [1]	- [1]	0.2555 $_{CF3}$	0.5109 $_{FLU}$	6.95	SFO
Loam, Wurmwiese	5.1	19.2 / 54.4 [2]	- [1]	- [1]	0.4012 $_{CF3}$	0.8024 $_{FLU}$	12.5	DFOP
Silt loam, Hoefchen an Hohensee	5.7	19.2 / 54.4 [2]	- [1]	- [1]	0.2630 $_{CF3}$	0.5261 $_{FLU}$	8.98	DFOP
Sandy loam, Innerdeich	6.2	19.2 / 54.3 [2]	- [1]	- [1]	0.1608 $_{CF3}$	0.3215 $_{FLU}$	16.2	DFOP
Geometric mean								
Arithmetic mean					0.2701 $_{CF3}$	**0.5402** $_{FLU}$		
pH dependence								

[1] no degradation assumed
[2] mean measured values used
CF3 formation fraction, reflecting TFA formation per CF_3 moiety of FLU
FLU total molar yield, formation fraction, reflecting TFA formation per FLU molecule, i.e. 2 x formation fraction per CF_3 moiety, as FLU has 2 CF_3 moieties

3. Assessment and conclusion

Assessment and conclusion by applicant:
The kinetic evaluation followed FOCUS guidances and is considered valid and reliable.

Assessment and conclusion by RMS:
Outcome and conclusion of the study. RMS should indicate if they agree to the results and conclusions of the APPL.

1. Information on the published literature article

Data Point:	KCA 7.1.2.1.1/15
Report Author:	Zhang, Y.; Xu, J.; Dong, F.; Liu, X.; Wu, X.; Zheng, Y.
Report Year:	2014
Report Title:	Response of microbial community to a new fungicide fluopyram in the silty-loam agricultural soil
Report No:	M-754119-01-1
Document No:	M-754119-01-1
Guideline(s) followed in study:	--
Deviations from current test guideline:	Current Guideline: OECD 307 (2002) information provided in the article not sufficient to assess the guideline deviations
Previous evaluation:	No, not previously submitted
GLP/Officially recognised testing facilities:	not applicable
Acceptability/Reliability:	Yes

2. Full summary of KCA 7.1.2.1.1/15

Executive Summary

The degradation of non-labelled fluopyram in soil was studied in a laboratory experiment at three application rates: at the recommended field rate (T1, 0.5 mg/kg soil), three-fold recommended field rate (T3, 1.5 mg/kg soil) and ten-fold recommended field rate (T10, 5 mg/kg soil). T1, T3 and T10 correspond to the maximum recommended field dosage (75 g a.s./ha), three-fold recommended field dosage and ten-fold recommended field dosage, respectively. The degradation was investigated in a Chinese oil under aerobic conditions in the dark at 25 °C and 50% air humidity for 90 days. Soil moisture content was adjusted and maintained to 60 % of MWHC.

The test was performed using 500 mL brown glass pots covered with sterile cotton plugs. Triplicate pots were processed and analysed at 7, 15, 30, 45, 60 or 90 days.

Fluopyram was extracted from the soil using water and acetonitrile and detected by ultraperformance liquid chromatography–tandem mass spectrometry (UPLC–MS/MS).

Satisfactory linearities in the range of 0.01–5.0 mg/L of fluopyram were obtained when the correlation coefficients (R^2) were higher than 0.99. The mean recoveries of fluopyram at three levels (0.01 mg/kg, 0.5 mg/kg and 5 mg/kg) ranged from 80.2 to 84.0% with relative standard deviations (RSD) from 2.5 to 7.8%. These data indicated that the extraction method was satisfactory for analysis of fluopyram residues.

There was a steady decrease in fluopyram content for all treatments (0.5, 1.5 and 5 mg/kg) during the experiment. By the end of the experimental period, the fluopyram concentrations remaining in the soil samples after 90 days were 0.186 mg/kg, 0.620 mg/kg and 2.481 mg/kg, respectively.

The first order half-lives of the fluopyram at levels of 0.5, 1.5 and 5 mg/kg in soil were calculated to be 64.2, 81.5 and 93.6 days, respectively.

I. MATERIALS AND METHODS

A. MATERIALS

1. Test Item

Fluopyram	
Batch No	Not given (supplier: Fluka Co)
Chemical purity	99.4%

2. Test soil

The soil was collected from a field of Shangzhuang Farm in Beijing, China. The soil had not been subjected to conventional-tillage and not treated with pesticide in the previous 2 years. Soil (top 0–15 cm) was collected with a stainless steel soil tube drill with a diameter of 3 cm. The soil samples were taken to the laboratory in coolers, then mixed, sieved with 2 mm mesh to remove the plant tissue, and subjected to physicochemical characterization. The soil was adjusted to a soil moisture of 40 % maximum water holding capacity (MWHC) and then pre-incubated for 10 days with distilled water in the dark at 25°C and 50 % air humidity.

Soil was characterized for pH (7.8 in water, 1:2.5), organic carbon (17.5 g/kg), soil texture (3.1% clay, 61.3% silt, 35.6% sand), $NH4^+$ (N: 9.1 mg/kg), NO_3 (N: 7.9 mg/kg), rapid available potassium (239.0 mg/kg), available phosphorus (11.3 mg/kg).

B. STUDY DESIGN

1. Experimental Conditions

Incubation experiments were conducted in 500 mL brown-glass pots covered with sterile cotton plugs. To avoid the potential effects of solvents upon the microbiological activity of the soils, a portion of the soil (20 g) was first spiked with 0.1mL of stock solution in acetone and stirred for 5 min. The spiked soils were allowed to air-dry for 10 min, and then the remaining soil (100 g) was added and mixed thoroughly for another 5 min, yielding the final concentrations of 0.5, 1.5 and 5 mg fluopyram/kg soil (based on dry weight) (T1, T3 and T10, respectively). T1, T3 and T10 correspond to the maximum recommended field dosage (75 g a.s./ha), three-fold recommended field dosage and ten-fold recommended field dosage, respectively. An equal volume of acetone (0.1 mL) was added to fluopyram-free controls (CK). The soil moisture content was 24.8%, adjusted to 60% MWHC.

The pots were incubated in the dark at 25°C and 50% humidity for 90 days. Throughout the incubation period, distilled water was added to the soil to compensate for any water loss that exceeded 5 percent of the initial amount added.

2. Sampling

Triplicate pots were removed from the environmental chamber at random after different incubation time intervals (7, 15, 30, 45, 60 or 90 days).

3. Analytical Procedures

A 10.0 g sample of soil was extracted for 2 h in 5 mL of water and 20 mL of acetonitrile. After centrifugation, 1.5 mL of the upper layer was transferred into a 2.0 mL dispersive-SPE tube containing 50 mg of PSA and 150 mg of $MgSO_4$. Then, the tubes were vortexed for 1 min and centrifuged for 5 min. The resulting supernatants were filtered through 0.22 μm nylon syringe filters for UPLC–MS/MS analysis.

The amount of fluopyram in soil extracts were determined by ultraperformance liquid chromatography–tandem mass spectrometry (UPLC–MS/MS).

The degradation rate of fluopyram in soil was fitted to a first-order kinetic model. The rate constant (k) (d^{-1}) was determined using the algorithm $Ct/C_0 = e^{-kt}$. Linear regression ($\ln(C_t/C_0)$ of the chemical data and time) was used to calculate the time in which the fluopyram concentration in the soil was reduced by 50% (DT_{50}).

Microbial biomass carbon (an indicator of the overall size of the soil microbial community) was determined by the chloroform fumigation-extraction

II. RESULTS AND DISCUSSION

Analysis of microbial biomass showed that the microbial carbon was >100 mg/kg soil throughout the study for all concentrations.

Satisfactory linearities in the range of 0.01–5.0 mg/L of fluopyram were obtained when the correlation coefficients (R^2) were higher than 0.99. The mean recoveries of fluopyram at three levels (0.01 mg/kg, 0.5 mg/kg and 5 mg/kg) ranged from 80.2 to 84.0% with relative standard deviations (RSD) from 2.5 to 7.8%. These data indicated that the extraction method was satisfactory for analysis of fluopyram residues.

There was a steady decrease in fluopyram content for all treatments during the experiment. By the end of the experimental period, the fluopyram concentrations remaining in the soil samples after 90 days were 0.186 mg/kg, 0.620 mg/kg and 2.481 mg/kg, respectively. The results are summarised in the table below.

Table 7.1.2.1.1-120: Degradation of fluopyram in soil at three different initial concentrations

Incubation time (day)	T1 (0.5 mg/kg)		T3 (1.5 mg/kg)		T10 (5 mg/kg)	
	Fluopyram residue (mg/kg)	Degradation rate (%)	Fluopyram residue (mg/kg)	Degradation rate (%)	Fluopyram residue (mg/kg)	Degradation rate (%)
0	0.5		1.5		5	–
7	0.478	16.5	1.059	29.4	4.100	18.0
15	0.367	26.6	0.990	34.0	3.808	23.8
30	0.246	50.8	0.899	40.1	3.462	30.8
45	0.235	53.0	0.747	50.2	2.977	40.5
60	0.219	56.3	0.704	53.1	2.686	46.3
90	0.186	62.8	0.620	58.6	2.481	50.4
Regression	$y = 0.4274 \times e^{-0.0108x}$		$y = 1.2102 \times e^{-0.0085x}$		$y = 4.4249 \times e^{-0.0074x}$	
equation	$r^2 = 0.8665$		$r^2 = 0.8508$		$r^2 = 0.9124$	
Half-life (days)	64.2		81.5		93.6	

CK: without fluopyram addition; T1: 0.5 mg fluopyram/kg soil dry weight; T3: 1.5 mg fluopyram/kg soil dry weight; T10: 5 mg fluopyram/kg soil dry weight.

Degradation of fluopyram in the soil was subjected to the first-order model. The half-life of fluopyram in levels of 0.5, 1.5 and 5 mg/kg treatment was 64.2, 81.5 and 93.6 days, respectively.

III. CONCLUSIONS

The half-lives of the fluopyram at levels of 0.5, 1.5 and 5 mg/kg in soil were calculated to be 64.2, 81.5 and 93.6 days, respectively.

3. Assessment and conclusion

Assessment and conclusion by applicant:
The degradation study was conducted in laboratory in one soil at three different application rates. Satisfactory linearities in the tested range were obtained when the correlation coefficients (R^2) were higher than 0.99. The mean recoveries of fluopyram at three levels ranged from 80.2% to 84.0% with relative standard deviations (RSD) from 2.5 percent to 7.8 percent. These data indicated that the extraction method was satisfactory for analysis of fluopyram residues. The limit of detection of the analytical method is not provided.
Half-lives were calculated for all three concentrations using first order kinetics.
The information of this publication is regarded as supportive information.

Assessment and conclusion by RMS:
Outcome and conclusion of the study: RMS should indicate if they agree to the results and conclusions of the APPL.

1. Information on the published literature article

Data Point:	KCA 7.1.2.1.1/16
Report Author:	Sun, T.; Li, M.; Saleem, M.; Zhang, X.; Zhang, Q.
Report Year:	2020
Report Title:	The fungicide fluopyram promotes pepper growth by increasing the abundance of p-solubilizing and n-fixing bacteria
Report No:	M-759539-01-1
Document No:	M-759539-01-1
Guideline(s) followed in study:	--
Deviations from current test guideline:	Current Guideline: not applicable, general deficiencies: No analytical results given for control soil (background concentration). Storage length of frozen samples prior to analysis is not given. Preparation of soil (air-dried, sieved) not reported. Application method to soil is not reported (soil overspray, etc.?) Soil moisture during the study is not given at the start and during the study, nor are the irrigation details given. It is unclear if T1 is one day after dosing of FLU and/or after transplanting the crops Sampling procedure of the 10-g soil aliquots out of 1000 g total mass is not reported.
Previous evaluation:	No, not previously submitted
GLP/Officially recognised testing facilities:	not applicable
Acceptability/Reliability:	Yes

2. Full summary of KCA 7.1.2.1.1/16

Executive Summary
The dissipation of fluopyram in one soil was studied in a growth room under controlled conditions: 22 ± 1 °C; 70 ± 2% humidity; 6000 lux light intensity with a 12/12 h light-dark cycle. The degradation was investigated in a soil.

Fluopyram was applied as suspension concentrate at three application rates: T1, 0.5 mg/kg soil, T3, 1.5 mg/kg soil and T10, 5 mg/kg soil.

The test was performed using plastic pots containing about 1000 g soil with the different concentrations of fluopyram into which one-month pre-grown pepper seedling were transplanted. The pots were randomly placed in the growth chamber while the seedlings were uniformly irrigated with distilled water as needed. During the experimental period, no leaching or drainage under the pots was observed.

Triplicate pots were processed and analysed after 1, 3, 7, 14, 21, 30 and 45 days.

Fluopyram was extracted from the soil using acidified acetonitrile (1% acetic acid) and detected by liquid chromatography–tandem mass spectrometry (LC–MS/MS). The recoveries of fluopyram at 0.1, 1.0, and 5.0 mg/kg addition levels were 87.2 to 93.5% with relative standard deviations of 2.76–6.93%. The limit of quantification of the analytical method was 0.005 mg/kg.

Fluopyram dissipated from the soil during the experimental period. At the last sampling time (45 days) it was not detected for the lowest concentration (0.5 and 1.5 mg/kg), while 0.26 mg/kg of fluopyram were detected in soil extracts for the highest concentration (5.0 mg/kg).

The dissipation of fluopyram in the soil fitted well to the first-order model with half-lives of 4.5, 7.4, and 11.2 days for fluopyram concentrations of 0.5, 1.5, and 5 mg/kg, respectively.

I. MATERIALS AND METHODS

A. MATERIALS

1. Test Item

Fluopyram (Lufuda 41.7% a.s. suspension concentrate (SC))
Batch No: Not given (supplier: Bayer Crop Science)
Chemical purity: 41.7%

2. Test soil

One soil was used and characterized for pH (6.8, medium not reported), organic matter (25.3 g/kg) and soil texture (0.4% clay, 68.4% silt, 31.2% sand).

B. STUDY DESIGN

1. Experimental Conditions

Incubation experiments were conducted in plastic pots (13 × 13 × 11 cm) containing about 1000 g soil with different concentrations of the fluopyram into which one-month pre-grown pepper seedling were transplanted. The concentrations of fluopyram were set as: 0.5 mg/kg (T1), 1.5 mg/kg (T3), 5.0 mg/kg (T10) dry weight soil. Additionally, control soil was prepared not spiked with fluopyram.

The pots were incubated in a growth room under controlled conditions (22 ± 1 °C; 70 ± 2% humidity; 6000 lux light intensity with a 12/12 h light-dark cycle) for 45 days. The pots were randomly placed in the growth chamber while the seedlings were uniformly irrigated with the distilled water as needed. During the experimental period, no leaching or drainage under the pots was observed.

2. Sampling

Triplicate pots were sampled after 1, 3, 7, 17, 21, 30 and 45 days. At each sampling pepper plants and bulk soil were randomly taken and immediately stored at -20 °C.

3. Analytical Procedures

10.0 g of soil was placed into a 50 mL polypropylene centrifuge tube containing 10 mL acidified acetonitrile (with 1% acetic acid), 4.0 g anhydrous magnesium sulphate, and 1.0 g anhydrous sodium acetate. The tube was vortexed for 10 min and centrifuged afterwards. An aliquot of 3 mL of the soil extract was then transferred into a 15 mL polypropylene centrifuge tube containing 150 mg primary secondary amine (PSA), 50 mg bondesil C_{18} and 750 mg magnesium sulphate. The mixture was vortexed for 1 min followed by centrifugation. The resulting supernatant was filtered through a 0.22 µm syringe filter for liquid chromatography–tandem mass spectrometry (LC–MS/MS) analysis.

The amount of fluopyram in soil extracts were determined by LC–MS/MS. The recoveries of fluopyram at 0.1, 1.0, and 5.0 mg/kg addition levels were 87.2–93.5% with relative standard deviations of 2.76–6.93%. The limit of quantification of the analytical method was 0.005 mg/kg.

The dissipation of fluopyram from soil was fitted to a first order exponential decay equation.

II. RESULTS AND DISCUSSION

Fluopyram dissipated from the soil during the experimental period. At the last sampling time (45 days) it was not detected for the lowest concentration (0.5 and 1.5 mg/kg), while 0.26 mg/kg of fluopyram were detected in soil extracts for the highest concentration (5.0 mg/kg).

Table 7.1.2.1.1-121: Dissipation of fluopyram in one soil cropped with pepper plants at three different initial concentrations

Incubation time (day)	T1 (0.5 mg/kg)	T3 (1.5 mg/kg)	T10 (5.0 mg/kg)
	Fluopyram residue (mg/kg)	Fluopyram residue (mg/kg)	Fluopyram residue (mg/kg)
1	0.42 ± 0.04	1.34 ± 0.03	4.85 ± 0.28
3	0.33 ± 0.02	1.15 ± 0.05	4.36 ± 0.13
7	0.15 ± 0.02	0.87 ± 0.03	3.34 ± 0.15
14	0.06 ± 0.01	0.46 ± 0.04	2.78 ± 0.06
21	ND	0.25 ± 0.02	2.06 ± 0.07
30	ND	0.08 ± 0.01	1.08 ± 0.05
45	ND	ND	0.26 ± 0.05
Regression equation	$y = 0.4925 \times e^{-0.154x}$	$y = 1.5745 \times e^{-0.094x}$	$y = 5.6086 \times e^{-0.062x}$
r^2	0.9939	0.9909	0.9613
Half-life (days)	4.5	7.4	11.2

ND: no detected, below the determination level

III. CONCLUSIONS

The dissipation half-lives of 0.5, 1.5, and 5 mg/kg of fluopyram in soil cropped with pepper plants were 4.5, 7.4, and 11.2 days, respectively.

Overall, the results suggest that fluopyram is a readily degradable pesticide and it does not pose risk to soil microbial communities and plant growth under experimental conditions

3. Assessment and conclusion

Assessment and conclusion by applicant:
In this study dissipation from soil was investigated in soil pots cropped with pepper plants. Thus, two processes degradation and uptake to plants were involved in the dissipation of fluopyram. The calculated half-lives accounts for both processes and are thus dissipation half-lives.
The study was conducted under controlled condition in one soil at three different application rates.
The analytical method was suited for the detection of fluopyram. The recoveries of fluopyram at 0.1, 1.0, and 5.0 mg/kg addition levels were 87.2–93.5% with relative standard deviations of 2.76–6.93%.
The limit of quantification of the method determined was 0.005 mg/kg.
Half-lives were calculated for all three concentrations using first order kinetics.
The information of this publication is regarded as supportive information.

Assessment and conclusion by RMS:
Outcome and conclusion of the study**:** RMS should indicate if they agree to the results and conclusions of the APPL.

CA 7.1.2.1.2 Aerobic degradation of metabolites, breakdown and reaction products

Data Point:	KCA 7.1.2.1.2/01
Report Author:	[redacted]
Report Year:	2011
Report Title:	[Pyridyl-2,6-14C]AE C656948: Aerobic metabolism/degradation and time-dependent sorption in soils
Report No:	MEF-07/424
Document No:	M-398413-01-1
Guideline(s) followed in study:	OECD Guideline 307, Aerobic and Anaerobic Transformation in Soil (2002); Commission Directive 95/36/EC amending Council Directive91/414/EEC (Annexes I and II, Fate and Behavior in the Environment) (1995); SETAC Procedures for Assessing the Environmental Fate and Ecotoxicity of Pesticides (1995); US EPA Subdivision N, Section 162-1, Aerobic soil metabolism (1982); OECD: Guideline 106, Adsorption/Desorption (2001) (only where applicable); Equivalent to US EPA OPPTS Guideline No. 835.4100
Deviations from current test guideline:	Current Guideline: OECD 307 (2002); OECD 106 (2000) (Only in parts) None
Previous evaluation:	yes, evaluated and accepted DAR (2011)
GLP/Officially recognised testing facilities:	Yes conducted under GLP/Officially recognised testing facilities
Acceptability/Reliability:	Yes

The experimental study is summarised and discussed under point KCA 7.1.1.1/01 of this document. The kinetic evaluation is summarised under KCA 7.1.2.1.1/09.

Data Point:	KCA 7.1.2.1.2/02
Report Author:	[redacted]
Report Year:	2008
Report Title:	[Phenyl-UL-14C]AE C656948: Aerobic soil metabolism/degradation and time-dependent sorption in four soils
Report No:	MEF-06/295
Document No:	M-298296-01-1
Guideline(s) followed in study:	OECD: Guideline 307, Aerobic and Anaerobic Transformation in Soil (2002); Commission Directive 95/36/EC amending Council Directive 91/414/EEC (Annexes I and II, Fate and Behavior in the Environment (1995); SETAC Procedures for Assessing the Environmental Fate and Ecotoxicity of Pesticides (1995); US EPA Subdivision N, Section 162-1, Aerobic soil metabolism (1982); OECD: Guideline 106, Adsorption/Desorption (2000) (Only where applicable); Equivalent to US EPA OPPTS Guideline No. 835.4200
Deviations from current test guideline:	Current Guideline: OECD 307 (2002), OECD 106 (2000) (Only in parts) None
Previous evaluation:	yes, evaluated and accepted DAR (2011)
GLP/Officially recognised testing facilities:	Yes, conducted under GLP/Officially recognised testing facilities
Acceptability/Reliability:	Yes

The experimental study is summarised and discussed under point KCA 7.1.1.1/02 of this document. The kinetic evaluation is summarised under KCA 7.1.2.1.1/09.

Data Point:	KCA 7.1.2.1.2/03
Report Author:	[redacted]
Report Year:	2020
Report Title:	Amendment no. 01: Rate of degradation of [phenyl-ul-14C]-fluopyram in brazilian soils
Report No:	1962-BS120-135-08
Document No:	M-349503-02-1
Guideline(s) followed in study:	OECD - Guideline for the Testing of Chemicals. Method 307 "Aerobic and anaerobic transformation in soil" (Adopted: 24th April 2002)
Deviations from current test guideline:	Current Guideline: OECD 307 (2002) The cation exchange capacity is not reported. In the experimental set-up up to six flasks were connected to the same trapping system.
Previous evaluation:	No, not previously submitted
GLP/Officially recognised testing facilities:	Yes, conducted under GLP/Officially recognised testing facilities
Acceptability/Reliability:	Yes

The experimental study is summarised and discussed under point KCA 7.1.1.1/04 of this document. The kinetic evaluation was done in a separate study and is summarised under KCA 7.1.2.1.1/11. The representativeness of the tested Brasilian soils for European agricultural areas was assessed in a separate study and is summarised under KCA 7.1.2.1.1/05.

Data Point:	KCA 7.1.2.1.2/04
Report Author:	[redacted]
Report Year:	2020
Report Title:	Fluopyram: Aerobic Metabolism / degradation and time - Dependent sorption in 6 soils
Report No:	M12505406-3
Document No:	M-753426-01-1
Guideline(s) followed in study:	OECD Test Guideline No. 307 (2002) OECD Test Guideline No. 106 (2000, only in parts) Guidance on how aged sorption studies for pesticides should be conducted, analysed and used in the regulatory process (2012, revised draft 2016) Current revision dates Sep 2016 [this draft guidance was updated based on the PPR statement on aged sorption, EFSA Journal 2015;13(7):4175]
Deviations from current test guideline:	Current Guideline: OECD 307 (2002), OECD 106 (2000) (Only in parts) None
Previous evaluation:	No, not previously submitted
GLP/Officially recognised testing facilities:	Yes, conducted under GLP/Officially recognised testing facilities
Acceptability/Reliability:	Yes

The experimental study is summarised and discussed under point KCA 7.1.1.1/06 of this document. The kinetic evaluation is summarised under KCA 7.1.2.1.1/13.

Data Point:	KCA 7.1.2.1.2/05
Report Author:	[redacted]
Report Year:	2021
Report Title:	Fluopyram: Aerobic degradation and determination of BCS-AA10065 and trifluoroacetic acid (TFA) in 4 soils
Report No:	EnSa-20-0811
Document No:	M-761739-01-1
Guideline(s) followed in study:	OECD Test Guideline No. 307 (2002); Commission Regulation (EU) No 283/2013 in accordance with Regulation (EC) No 1107/2009; US EPA OCSPP Test Guideline No. 835.4100 / 835.4200 (2008); SANCO/3029/99 rev. 4: EU guidance document for generating and reporting methods of analysis in support of pre-registration data requirements (2000)
Deviations from current test guideline:	Current Guideline: OECD 307 (2002) None
Previous evaluation:	No, not previously submitted
GLP/Officially recognised testing facilities:	Yes, conducted under GLP/Officially recognised testing facilities
Acceptability/Reliability:	Yes

The experimental study is summarised and discussed under point KCA 7.1.1.1/07 of this document. The kinetic evaluation is summarised under KCA 7.1.2.1.1/14.

1. Information on the study

Data Point:	KCA 7.1.2.1.2/06
Report Author:	[redacted]
Report Year:	2020
Report Title:	Fluopyram-7-hydroxy (BCS-AA10065) - Aerobic degradation in four soils at 20 °C in the dark
Report No:	S20-02196
Document No:	M-757988-01-1
Guideline(s) followed in study:	OECD Guideline No. 307, 2002 SANCO/3029/99 rev.4
Deviations from current test guideline:	Current Guideline: OECD 307 (2002) None
Previous evaluation:	No, not previously submitted
GLP/Officially recognised testing facilities:	Yes, conducted under GLP/Officially recognised testing facilities
Acceptability/Reliability:	Yes

2. Full summary of KCA 7.1.2.1.2/06

Executive Summary

The rate of degradation of fluopyram-7-hydroxy (BCS-AA10065), a soil degradation product of the active substance fluopyram, was investigated in four soils. The test was performed under aerobic conditions in the dark in the laboratory at 21.1 °C and 52 to 56% of the maximum water holding capacity (mean during study duration) for 100 days for soils FF and HH and 120 days for soils WW and IN.

Soil	Soil ID	Source	Texture (USDA)	pH [1]	OC [%]
Frankenforst	FF	Königswinter, Germany	Silt loam	7.3	2.3
Wurmwiese	WW	Monheim, Germany	Loam	5.1	2.1
Höfchen am Hohenseh	HH	Burscheid, Germany	Silt loam	5.7	2.3
Innerdeich	IN	Monheim, Germany	Sandy loam	6.2	1.8

[1] pH value was derived from aqueous 0.01 M $CaCl_2$ suspension

The test was performed in static test systems, consisting of flasks filled with soil and closed with a foam plug allowing free oxygen exchange.

The application rate was 6.94 µg per vessel and 100 g soil (dry weight), which was equivalent to 0.0694 mg fluopyram-7-hydroxy/kg soil (dry weight).

Duplicate test systems were processed and analysed 0, 2, 4, 10, 21, 35, 60 and 100 days after treatment (DAT) for all soils and additionally at DAT-120 for soils WW and IN.

At each sampling interval, the soil (treated flasks and concurrent recoveries) was extracted three times at ambient temperature using acetonitrile/water (4/1, *v/v*). Additionally, the soil was extracted with acetonitrile/water (4/1, *v/v*) using a microwave at 55 °C. Extracts and soil were separated by centrifugation and decantation. Afterwards, the ambient and microwave extracts were combined and about 1 mL of the extracts was centrifuged using a mini-star microcentrifuge for 5 minutes, transferred into a glass vial and diluted with water for HPLC-MS/MS analysis.

The amount of fluopyram-7-hydroxy in soil extracts was determined by HPLC-MS/MS.

Method development and validation was performed successfully within this study. Recoveries of both individual enantiomers and the racemate were between 87.2 and 109.5% for the LOQ level and between 90.5 and 100.6% for the 22-fold LOQ level.

In addition, the extraction efficiency during the study was demonstrated by concurrent recovery samples. The concurrent recoveries of fortified samples were between 88.8 and 104.0%.

For fluopyram-7-hydroxy the amount determined directly after application was 95.4% of the applied amount (% AA) in soil FF, 94.4% AA in soil WW, 95.0% AA in soil HH and 93.7% AA in soil IN.

Fluopyram-7-hydroxy dissipated to values <LOD and < LOQ (2.3%) in soils FF and HH within 100 days and to values < LOQ (4.8%) and 20.8% of the applied amount in soils WW and IN within 120 days, respectively.

I. MATERIALS AND METHODS

A. MATERIALS

1. Test Item

Fluopyram-7-hydroxy

Sample ID:	RDL 224-31-2
Chemical Purity:	99.7% (w/w)

2. Soil

Soils were sampled freshly from the fields (upper horizon of 0 to 20 cm) and sieved to a particle size of ≤ 2 mm. The soils were chosen to represent an agricultural soil of European origin. No pesticides were used for the previous 5 years. Soil were stored at ambient temperature for seven days prior use. Characteristics of the test soil are presented in the table below.

Table 7.1.2.1.2- 1: Characteristics of test soils

Soil Designation	Frankenforst (FF)	Wurmwiese (WW)	Höfchen am Hohenseh (HH)	Innerdeich (IN)
Geographic Location				
City	Vinxel	Monheim am Rhein	Burscheid	Monheim am Rhein
State	North Rhine Westphalia	North Rhine Westphalia	North Rhine Westphalia	North Rhine Westphalia
Country	Germany	Germany	Germany	Germany
Soil Taxonomic Classification (USDA)	No information available			
Soil Series	No information available			
Textural Class (USDA)	Silt loam	Loam	Silt loam	Sandy loam
Sand (%) [50 µm – 2 mm]	25	49	21	75
Silt (%) [2 µm – 50 µm]	54	30	62	14
Clay (%) [< 2 µm]	21	21	17	11
pH (soil/0.01 M $CaCl_2$ 1/2)	7.3	5.1	5.7	6.2
pH (soil/water 1/1)	7.6	5.5	6.1	6.5
pH (saturated paste)	7.5	5.5	6.1	6.5
pH (soil/1 N KCl 1/1)	7.0	4.9	5.5	6.1
Organic Carbon (combustion) (%)	2.3	2.1	2.3	1.8
Organic Matter (%) [1]	4.0	3.6	4.0	3.1
Cation Exchange Capacity (meq/100 g)	17.7	11.5	11.3	9.6
Water Holding Capacity maximum (g H_2O *ad* 100 g soil DW)	54.5	55.1	58.3	39.4
at 1/10 bar (pF 2.0) (%)	34.7	20.9	28.8	13.4
at 1/3 bar (pF 2.0) (%)	20.6	16.1	19.8	10.0
Bulk Density (disturbed) (g/cm^3)	1.10	1.15	1.03	1.33
Microbial Biomass (mg microbial carbon / 100 g soil DW)				
after arrival	73.4	60.5	74.6	56.3
start untreated/treated [2]	84.1 / 84.9	56.0 / 55.2	65.0 / 70.3	50.0 / 54.7
35 d untreated/treated [2]	71.7 / 75.1	39.0 / 43.3	46.8 / 47.0	36.9 / 37.1
100 d untreated/treated [2]	55.6 / 59.4	24.0 / 27.1	35.3 / 34.4	20.5 / 22.3
120 d untreated/treated [2]	48.6 / 59.4	23.8 / 24.1	31.4 / 28.9	20.9 / 18.9

USDA: United States Department of Agriculture, DAT: days after treatment, DW: dry weight
[1] calculated as: OM (%) = OC (%) · 1.724
[2] treated biomass samples were supplemented with the same amount of solvent as the treated flasks

B. STUDY DESIGN

1. Experimental conditions

Static test systems were used, consisting of Erlenmeyer flasks filled with soil and closed with a foam plug allowing free oxygen exchange.

100 g of sieved soil (dry weight equivalents) were weighed into each test vessel and soil moisture was adjusted to 55 ± 5% of the maximum water holding capacity and the test systems were acclimated for at least 5 days at test conditions.

The test item was applied with an actual concentration of racemic fluopyram-7-hydroxy of 6.94 µg/100 g dry soil based on an intended maximum single field application rate of parent fluopyram of 250 g/ha and a metabolite formation of 10%. For each of the fluopyram-7-hydroxy enantiomers this corresponds to 3.47 µg per vessel and 0.00347 mg/kg soil. An application solution of racemic

fluopyram-7-hydroxy with a concentration of 17.35 µg/mL was prepared in water from a stock solution prepared in acetonitrile. Aliquots of 400 µL of the application solution were applied to each test system and after application the test vessels (except DAT-0), were closed with foam plugs.

Test systems were incubated under aerobic conditions in the dark for up to 120 days at 20 ± 2°C and 55 ± 5% of the maximum water holding capacity.

2. Sampling
Duplicate test systems were processed and analysed 0, 2, 4, 10, 21, 35, 60 and 100 days after treatment (DAT) for all soils and additionally at DAT-120 for soils WW and IN.

Microbial soil biomass was determined in untreated biomass test systems after arrival and at start, after 35 days, after 100 days and after 120 days as well as in biomass test systems treated only with the application solvent at start, after 35 days, after 100 days and after 120 days.

3. Analytical procedures
At each sampling interval, the soil (treated flasks and concurrent recoveries) was extracted three times at ambient temperature using acetonitrile/water (4/1, *v/v*). Additionally, the soil was extracted with acetonitrile/water (4/1, *v/v*) using a microwave at 55 °C. Extracts and soil were separated by centrifugation and decantation. Afterwards, the ambient and microwave extracts were combined and about 1 mL of the extracts was centrifuged using a mini-star microcentrifuge for 5 minutes, transferred into a glass vial and diluted with water for HPLC-MS/MS analysis.

At each sampling interval, samples for concurrent recoveries were applied at concentration of 7.634 µg racemic fluopyram-7-hydroxy in water (22 fold LOQ) and with 0.347 µg in water (LOQ level) for all soils. The concurrent recoveries at LOQ (7.634 mg/kg) and 22-fold LOQ level (0.347 mg/kg) were each applied in duplicate. Concurrent recovery samples were processed as described for degradation samples.

The amount of each enantiomer of fluopyram-7-hydroxy in soil extracts was determined by HPLC-MS/MS using a chiral method. The chromatographic conditions resulted in retention times of about 21.2-21.9 min and 21.9-22.4 min for the two test item enantiomers. Each of the enantiomers was quantified using the transition of m/z 413 to m/z 145. In addition, the two enantiomers were qualified by the transition m/z 413 to m/z 173. The amount of racemic fluopyram-7-hydroxy was calculated by addition of the peak areas of both enantiomers.

The method was validated according to SANTE/2020/12830, Rev.1. Within the sequence, the detector linearity was confirmed over the calibration range of interest by constructing a calibration function of peak area versus concentration ranging from 0.043 ng/mL to 7.5 ng/mL (7-point-calibration) for each enantiomer. This corresponds to a calibration range of 0.086 ng/mL to 15 ng/mL for racemic fluopyram-7-hydroxy. Quantitative evaluation was done by comparison of the peak areas of both enantiomers from soil extracts with this calibration curve. Accuracy and repeatability were assessed on the basis of a set of recovery samples. For this purpose, 100 g untreated soil (calculated as dry weight) were adjusted with water to approx. 55 % MWHC and fortified at LOQ level and at 22-fold LOQ level with test item solution.

Full details and acceptable validation data to support the analytical method are presented within document M-CA 4, which comply with the EU regulatory requirements outlined within SANTE/2020/12830, Rev.1.

II. RESULTS AND DISCUSSION

A. DATA

Degradation of racemic fluopyram-7-hyxdroxy and its individual enantiomers in soil extracts is summarized in Table 7.1.2.1.2- 2 to Table 7.1.2.1.2- 5.

Table 7.1.2.1.2- 2: Degradation of racemic fluopyram-7-hyxdroxy and its individual enantiomers in soil Frankenforst under aerobic conditions (expressed as% AA)

Compound	Replicate	DAT							
		0	2	4	10	21	35	60	100
Racemic fluopyram-7-hyxdroxy	1	93.2	79.7	47.7	25.8	6.9	<LOQ (3.8)	<LOQ (1.2)	<LOD
	2	97.4	77.7	53.2	32.4	6.4	<LOQ (2.3)	<LOQ (1.0)	<LOD
	Mean	**95.4**	**78.7**	**50.4**	**29.1**	**6.6**	**<LOQ (3.1)**	**<LOQ (1.1)**	**<LOD**
Enantiomer 1	1	93.1	98.3	70.0	44.7	11.5	6.5	<LOQ (1.8)	<LOD
	2	96.8	97.4	78.1	56.5	10.5	<LOQ (3.6)	<LOQ (1.6)	<LOD
	Mean	**95.1**	**98.0**	**74.1**	**50.7**	**11.0**	**5.0**	**<LOQ (1.7)**	**<LOD**
Enantiomer 2	1	93.7	60.2	24.6	6.9	LOQ (2.2)	LOQ (1.2)	<LOD	<LOD
	2	97.7	57.1	27.0	8.1	LOQ (2.2)	LOQ (1.0)	<LOD	<LOD
	Mean	**95.7**	**58.8**	**25.8**	**7.5**	**<LOQ (2.2)**	**<LOQ (1.1)**	**<LOD**	**<LOD**

Table 7.1.2.1.2- 3: Degradation of racemic fluopyram-7-hyxdroxy and its individual enantiomers in soil Wurmwiese under aerobic conditions (expressed as% AA)

Compound	Replicate	DAT								
		0	2	4	10	21	35	60	100	120
Racemic fluopyram-7-hyxdroxy	1	94.4	90.9	69.7	60.0	33.3	17.6	20.6	19.7	<LOQ (4.0)
	2	94.4	92.8	83.6	57.9	39.9	25.6	10.2	12.9	5.5
	Mean	**94.4**	**91.9**	**76.7**	**58.9**	**36.6**	**21.6**	**15.4**	**16.3**	**<LOQ (4.8)**
Enantiomer 1	1	95.1	91.9	70.3	59.8	30.3	15.4	18.8	19.4	<LOQ (3.9)
	2	94.2	93.9	85.6	56.5	37.2	23.7	9.4	11.9	5.2
	Mean	**94.8**	**93.1**	**78.1**	**58.2**	**33.7**	**19.6**	**14.1**	**15.7**	**<LOQ (4.6)**
Enantiomer 2	1	93.7	89.9	69.5	60.3	36.0	19.7	22.6	20.1	<LOQ (4.1)
	2	95.5	91.6	81.6	59.3	42.9	27.6	11.0	14.0	5.8
	Mean	**94.2**	**90.8**	**75.5**	**59.9**	**39.5**	**23.7**	**16.8**	**17.0**	**< LOQ (5.0)**

Table 7.1.2.1.2- 4: Degradation of racemic fluopyram-7-hyxdroxy and its individual enantiomers in soil Höfchen am Hohenseh under aerobic conditions (expressed as% AA)

Compound	Replicate	DAT							
		0	2	4	10	21	35	60	100
Racemic fluopyram-7-hyxdroxy	1	94.4	89.3	72.3	51.5	26.2	12.8	<LOQ (4.4)	<LOQ (2.4)
	2	95.5	88.8	74.1	52.7	28.0	11.0	<LOQ (4.1)	<LOQ (2.3)
	Mean	**95.0**	**89.0**	**73.2**	**52.2**	**27.1**	**11.9**	**<LOQ (4.3)**	**<LOQ (2.3)**
Enantiomer 1	1	93.9	97.7	84.7	69.3	38.6	19.1	6.0	<LOQ (3.2)
	2	94.5	97.1	86.2	70.7	41.5	16.3	5.6	<LOQ (3.1)
	Mean	**94.2**	**97.4**	**85.6**	**70.0**	**40.1**	**17.7**	**5.9**	**<LOQ (3.1)**
Enantiomer 2	1	95.1	80.7	59.4	33.7	13.7	6.4	<LOQ (2.8)	<LOQ (1.6)
	2	96.3	80.1	61.7	34.5	14.4	5.7	<LOQ (2.6)	<LOQ (1.5)
	Mean	**95.7**	**80.4**	**60.5**	**34.0**	**14.1**	**6.1**	**< LOQ (2.7)**	**< LOQ (1.5)**

Table 7.1.2.1.2- 5: Degradation of racemic fluopyram-7-hyxdroxy and its individual enantiomers in soil Innerdeich under aerobic conditions (expressed as% AA)

Compound	Replicate	DAT								
		0	2	4	10	21	35	60	100	120
Racemic fluopyram-7-hyxdroxy	1	95.4	88.6	76.5	65.0	43.9	30.0	18.7	20.2	21.0
	2	91.9	85.4	75.4	63.6	37.0	27.2	20.7	16.9	20.6
	Mean	**93.7**	**87.0**	**75.9**	**64.4**	**40.5**	**28.6**	**19.7**	**18.5**	**20.8**
Enantiomer 1	1	94.5	100.0	92.2	90.1	68.0	47.3	30.0	34.9	37.2
	2	91.1	97.4	91.1	89.2	54.8	41.8	34.0	28.5	35.7
	Mean	**92.8**	**98.8**	**91.6**	**89.6**	**61.4**	**44.5**	**32.0**	**31.7**	**36.5**
Enantiomer 2	1	96.3	76.7	60.2	39.9	19.8	12.5	7.3	<LOQ (4.9)	<LOQ (4.1)
	2	92.8	73.2	59.1	38.0	19.1	12.8	7.4	<LOQ (4.6)	<LOQ (4.6)
	Mean	**94.5**	**74.9**	**59.7**	**38.9**	**19.5**	**12.6**	**7.3**	**<LOQ (4.8)**	**<LOQ (4.4)**

B. METHOD VALIDATION

The calibration curves were linear in a range of 0.043 ng/mL (0.000347 mg/kg, limit of detection (LOD)) to 7.5 ng/mL for each enantiomer ($r \geq 0.995$). The limit of quantification (LOQ) was set to 0.217 ng/mL (0.00174 mg/kg) for each enantiomer.

Method development and validation was performed successfully within this study. During the method validation, recoveries in soil FF were between 87.6 to 94.1%, with mean values of 91.5% at LOQ level and 92.5% at 22-fold LOQ level for racemic fluopyram-7-hydroxy, between 88.1 to 96.0%, with mean values of 92.5% at LOQ level and 92.4% at 22-fold LOQ level for Enantiomer 1 and between 87.2 – 93.6%, with mean values of 90.5% at LOQ level and 92.8% at 22-fold LOQ level for Enantiomer 2. Recoveries in soil WW were between 92.0 to 108.4%, with mean values of 103.3% at LOQ level and 95.6% at 22-fold LOQ level for racemic fluopyram-7-hydroxy, between 92.0 to 107.2%, with mean values of 104.0% at LOQ level and 95.7% at 22-fold LOQ level for Enantiomer 1 and between 92.2 to 109.5%, with mean values of 102.7% at LOQ level and 95.6% at 22-fold LOQ level for Enantiomer 2. Recoveries in soil HH were between 94.5 to 104.3%, with mean values of 98.6% at LOQ level and 98.0 at 22-fold LOQ level for racemic fluopyram-7-hydroxy, between 94.5 to 104.3%, with mean values of 98.6% at LOQ level and 98.2% at 22-fold LOQ level for Enantiomer 1 and between 94.5 to 104.3%, with mean values of 98.7% at LOQ level and 97.8% at 22-fold LOQ level for Enantiomer 2. Recoveries in soil IN were between 88.5 to 96.5%, with mean values of 94.1% at LOQ level and 92.8% at 22-fold LOQ level for racemic fluopyram-7-hydroxy, between 88.8 to 98.0%, with mean values of 93.6% at LOQ level and 92.1% at 22-fold LOQ level of the Enantiomer 1 and between 88.2 – 98.6%, with mean values of 94.7% at LOQ level and 93.5% at 22-fold LOQ level for the second enantiomer

The accuracy and precision were considered acceptable with regard to SANTE/2020/12830, Rev.1 since mean recoveries were in the range of 70 and 110 % with relative standard deviations below 20%. The determined values of the blank samples used for recovery experiments were less than 20 % of the assigned LOQ of the test item. The LOD was set to 1/5 of the LOQ.

In addition, the extraction efficiency during the study was demonstrated by concurrent recovery samples. Untreated IN soil samples were fortified at each sampling interval with Fluopyram-7-hydroxy, two at the LOQ level (corresponding to 5% of the application rate) and two at 22-fold LOQ level (corresponding to 100% of the application rate). For Fluopyram-7-hydroxy recoveries of all concurrent recovery samples were between 89.3 and 97.6% of the applied amount at the LOQ level and between 90.3 and 103.6 % at the 22-fold LOQ level. For enantiomer 1 the recoveries of all concurrent recovery samples were between 89.9 and 99.2% of the applied amount at the LOQ level and between 90.1 and

103.0 % at the 22-fold LOQ level. For enantiomer 2 the recoveries of all concurrent recovery samples were between 88.8 and 100.3 % of the applied amount at the LOQ level and between 90.4 and 104.0 % at the 22-fold LOQ level.

The soil samples were worked up and extracts were stored until analysis below -18 °C. The extracts were analysed up to 2 days later. Thereafter, the extracts were stored in a freezer below -18 °C. At every sampling interval concurrent recoveries were worked up an analysed simultaneously. All concurrent recoveries were between 89.9% and 103.0% for Enantiomer 1 and between 88.8% and 104.0% for Enantiomer 2, so no storage stability check was necessary.

C. TRANSFORMATION OF THE TEST ITEM

The amount of racemic fluopyram-7-hydroxy determined directly after application was 95.4% of applied amount (% AA) in soil FF, 94.4% in soil WW, 95.0% in soil HH and 93.7% in soil IN. Residues of test item declined to < LOD and < LOQ (2.3%) in soil FF and soil HH after 100 days of incubation to < LOQ (4.8%) and 20.8% in soil WW and soil IN after 120 days of incubation, respectively.

The amount of enantiomer 1 determined directly after application was 95.1% in soil FF, 94.8% in soil WW, 94.2% in soil HH and 92.8% in soil IN. Residues of enantiomer 1 declined to < LOD and < LOQ (3.1 %) in soil FF and soil HH after 100 days of incubation and to < LOQ (4.6%) and 36.5% in soil WW and soil IN after 120 days of incubation, respectively.

The amount of enantiomer 2 determined directly after application was 95.7% in soil FF, 94.2% in soil WW, 95.7% in soil HH and 94.5% in soil IN. Residues of enantiomer 2 declined to < LOD and < LOQ (1.5%) in soil FF and soil HH after 100 days of incubation to < LOQ (5.0%) and < LOQ (4.4%) in soil WW and soil IN after 120 days of incubation, respectively.

D. KINETICS

Kinetic evaluation according to current guidance can be found under KCA 7.1.2.1.1/14 (M-762167-01-1).

III. CONCLUSIONS

Racemic fluopyram-7-hydroxy as well as its individual enantiomers were rapidly to fast degraded in soil under aerobic conditions in the dark in the laboratory.

3. Assessment and conclusion

Assessment and conclusion by applicant:
The study and its data are considered valid and reliable for use in risk assessment.

Assessment and conclusion by RMS:
Outcome and conclusion of the study: RMS should indicate if they agree to the results and conclusions of the APPL.

1. Information on the study

Data Point:	KCA 7.1.2.1.2/07
Report Author:	[redacted]
Report Year:	2012
Report Title:	[1-14C]trifluoroacetate : Aerobic degradation in four European soils
Report No:	EnSa-12-0393
Document No:	M-439283-01-1
Guideline(s) followed in study:	Commission Directive 95/36/EC amending Council Directive 91/414 (Annexes II and III, Fate and Behavior in the Environment), 1995 Regulation (EC) No.1107/2009 of the European Parliament and of the council of 21 October 2009 OECD Test Guideline No. 307, 2002 US EPA OCSPP Test Guidelines OPPTS 835.4100, 2008
Deviations from current test guideline:	Current Guideline: OECD 307 (2002) None
Previous evaluation:	yes, evaluated and accepted RAR flurtamone (2016)
GLP/Officially recognised testing facilities:	Yes, conducted under GLP/Officially recognised testing facilities
Acceptability/Reliability:	Yes

2. Full summary of KCA 7.1.2.1.2/07

Executive Summary

The degradation of [1-^{14}C]trifluoroacetate (TFA) was studied in four aerobic European soils in the dark at an average temperature of 20.0 °C (19.8 – 20.4 °C) and at max. 55% of MWHC for a maximum period of 120 days.

Soil ID	Source	Texture (USDA)	pH [1]	OC [%]
AX	Monheim, Germany	Sandy loam	6.2	1.6
DD	Blankenheim	Clay Loam	7.3	5.5
WW	Monheim am Rhein	Sandy loam	5.1	1.9
HH	Burscheid	Silt loam	6.4	2.4

[1] pH values were derived from aqueous 0.01 M $CaCl_2$ suspensions

The test system consisted of Erlenmeyer flasks equipped with traps for the collection of CO_2 and volatile organic compounds. Samples were treated at 20 µg test item/100 g dry weight of soil and analysed after 0, 3, 7, 14, 28, 43, 59, 92 and 120 days of incubation. At each sampling date the soil samples were extracted three times at ambient temperature and once with respect to the formation of non-extractable residues by hot (microwave) extraction. The amounts of radioactivity in the extracts as well as the amounts of trapped volatiles were determined by liquid scintillation counting (LSC). Aliquots of the combined organic extracts were concentrated and analysed and quantified by TLC. The identification of the test item in the application solution was achieved by HPLC-MS and HPLC-MS/MS. The test conditions outlined in the study protocol were maintained throughout the study.

Mean material balances accounted for 100.4, 100.5, 100.0, and 101.2% of the applied radioactivity (AR) for the four soils used.

The test item TFA was not degraded under laboratory conditions during an incubation time of 120 days. Significant amounts of volatiles and non-extractable residues were not formed during the study. The half-life of TFA calculated by the best fit kinetics according to FOCUS (single first order, SFO, for trigger evaluation) results in >1000 days under aerobic conditions in all four tested soils.

I. MATERIALS AND METHODS

A. MATERIALS

1. Test Item

[1-^{14}C]trifluoroacetate, (BCS-AZ56567, sodium salt of trifluoroacetic acid, TFA)

Batch No	KML 9072
Specific activity	3.48 MBq/mg
Radiochemical purity	> 98%

2. Test Soils

The metabolism of [1-^{14}C]trifluoroacetate in soil under aerobic conditions was investigated in four agricultural soils at 20°C. The soil characteristics are listed below.

Table 7.1.2.1.2- 6: Properties of soils

Parameter	Result Value			
Soil abbreviation/ soil ID	AX	DD	WW	HH
Geographic Location [1]	Monheim am Rhein	Blankenheim	Monheim am Rhein	Burscheid
Soil Taxonomic Classification (USDA)	Sandy, mixed, mesic Typic Cambudoll	Fine-loamy, mixed, active, frigid Typic Entrudept	Loamy, mixed, mesic Typic Argudall	Loamy, mixed, mesic Typic Argudalf
Textural Class (USDA)	Sandy loam	Clay Loam	Sandy Loam	Silt loam
Sand (%)	77	29	57	25
Silt (%)	14	40	26	60
Clay (%)	9	31	17	15
pH in $CaCl_2$ (1:2)	6.2	7.3	5.1	6.4
pH in water (1:1)	6.5	7.6	5.4	6.7
pH in water (saturated paste)	6.3	7.4	5.2	6.5
pH in KCl (1N)	6.0	7.1	4.7	6.1
Organic Matter (%)	2.8	9.5	3.3	4.1
Organic Carbon (%)	1.6	5.5	1.9	2.4
Cation Exchange Capacity (meq/100g)	8.7	21.2	10.0	13.6
Water Holding Capacity at pF 2.5 (g H_2O *ad* 100 g DW)	12.2	34.9	18.2	26.3
Maximum Water Holding Capacity (g H_2O *ad* 100 g DW)	46.9	84.9	57.6	62.0
Bulk Density (disturbed, g/cm³)	1.26	0.97	1.13	1.08
Soil Biomass at:				
0 days	536	2930	423	833
59 days	589	3344	459	844
120 days	248	1412	424	387

[1] in North Rhine-Westphalia, Germany

B. STUDY DESIGN

1. Experimental Conditions

The soils were collected from agricultural areas of Germany and were taken fresh from the field. A few days before starting the study, the soil was sieved to a particle size of ≤ 2 mm. Subsequently the soil moisture was determined by drying aliquots of the soils at 105°C. Ultrapure water was added to adjust each soil aliquot to 55% of the maximum water holding capacity. The weights of all test vessels were recorded, and the samples were pre-equilibrated at about 20°C in the dark over a weekend.

The incubation systems were static systems and consisted of Erlenmeyer flasks (300 mL) with 100 g soil (dry weight) for each sampling interval. The flasks were closed with trap attachments, which were easily permeable for oxygen. The traps contained soda lime for absorption of CO_2 and a polyurethane foam plug for adsorption of volatile organic compounds.

An application solution, with a concentration of approximately 20 µg/mL in water, was prepared. 1 mL of this was applied dropwise, by use of a micropipette, to each pre-equilibrated soil sample, giving a treatment rate of 20 µg/vessel equivalent to a field rate of 75 g/ha (calculated based on information in the report). Dose checks were taken during the application procedure.

Water loss due to evaporation from the soil was determined by weighing the sampled flasks without the traps on each processing day. If necessary, the evaporated portions were replaced. Determination of the soil microbial viability (microbial biomass) was performed at the start, in the middle (DAT-59) and at the end (DAT-120) of the study.

2. Sampling

Samples (in duplicate) were taken at 0, 3, 7, 14, 28, 43, 59, 92 and 120 days after treatment. The corresponding trap attachments were collected to determine the amount of $^{14}CO_2$ and organic volatiles. At the respective sampling dates, the soil samples from each flask were extracted completely. The extracts were analysed by liquid scintillation counting (LSC) and TLC within one day. TLC analysis was normally performed within a day but always within a maximum of three days. HPLC analysis was performed on 120 day samples within two days of extraction. After analysis, the extracts were stored cold. The trap attachments containing soda lime and PU foam were processed within about two weeks. Bound residues were analysed by combustion and LSC within three weeks after sampling.

3. Analytical Procedures

For soil extraction the entire soil amount of each test vessel was transferred into a centrifuge beaker and extracted using a mechanical shaker. The extraction procedure comprised an extraction with 100 mL acetonitrile/water 50/50 (v/v) followed by two extractions with 80 mL acetonitrile/water 50/50 (v/v) at ambient temperature. These extracts were combined, and the radioactivity was determined by LSC. The final extraction used 80 mL acetonitrile/water 50/50 (v/v) with microwave heating to 70°C. After separation from soil, the radioactivity in the microwave extract was determined by LSC.

The residual radioactivity (bound residues) in freeze-dried, homogenised soil was determined by combustion of three aliquots (approx. 1 g) of each sample followed by LSC.

Volatile organic compounds possibly contained in the foam plugs were extracted by shaking with ethyl acetate. Aliquots of the extracts were submitted to LSC measurement. Chromatographic analyses of the PU foam extracts were not performed, because they contained ≤ 0.1% of the AR in all test systems.

For determination of $^{14}CO_2$, the soda lime contained in the trap attachments was dissolved in hydrochloric acid. The liberated CO_2 was absorbed by a special absorption/ scintillation cocktail and radioactivity was measured by liquid scintillation counting.

Prior to chromatographic analysis, the cold and microwave organic extracts were combined. Aliquots were concentrated and radio-assayed to allow the determination of recovery. Aliquots of the concentrates were analysed by TLC and the concentrated extracts sampled at DAT-120 were additionally analysed by HPLC.

For TLC analysis aliquots of the concentrates of the extracts were spotted on silica gel plates (Si60, F_{254}, 20 cm x 20 cm Merck) using an automatic applicator. The plates were developed with ethyl acetate/2-propanol/ultrapure water/ glacial acetic acid (65/24/11/1, v/v/v/v) in a plate chamber without solvent saturation. The distribution of radioactive zones on the plates was measured using a Bio-Imaging Analyzer (BAS 2000, Fuji Co.). Radioactive regions on the tracks were quantified using the software package AIDA (Raytest). The quantification of the test item and the degradation products in the extracts was calculated based on the distribution of the TLC-zones and the amount of radioactivity in the extracts.

The HPLC method used a system that comprised a Purospher Star RP18-e (Merck), 250 x 4.6 mm, 5 µm column connected to a radioactivity detector fitted with a solid cell and to a UV detector set at 254 nm. The mobile phase was a gradient of 1% formic acid in water containing 5 mM ammonium formate against 1% formic acid in acetonitrile containing 5mM ammonium formate used for the purity check of the stock solution and without addition of ammonium formate for the confirmation of the TLC analysis on DAT-120.

The electro-spray ionization MS spectra (ESI) were obtained with a LTQ Orbitrap XL mass spectrometer (Thermo, San Jose, CA; U.S.A.). The HPLC instrument used for chromatography was an Agilent HP1100 with a Nucleodur C18 Gravity, 3 µm, 250 x 2 mm (MN) column. The mobile phase was a gradient of 0.1% formic acid in water against 0.1% formic acid in acetonitrile. The flow from the HPLC column was split between a UV-detector followed by a radioactivity detector (Ramona Star) and the MS spectrometer.

II. RESULTS AND DISCUSSION

A. EXTRACTION AND QUANTITATION OF RADIOACTIVITY IN SOIL SAMPLES

The mean material balance was 100.4, 100.5, 100.0, and 101.2% of applied radioactivity (AR). The test item was stable under the conditions of extraction and accounted for 97.7, 98.4, 98.7, and 99.2% of AR in the combined organic soil extracts at DAT-0. These results demonstrate that the extraction method was well suitable to extract the compound from the soil matrix. The recoveries of radioactivity after the concentration step were determined for DAT-0 and DAT-120 samples and were 101% to 105% for all samples examined.

A good selectivity and reproducibility demonstrated the suitability for separation and quantification of the TLC method. The TLC limit of quantification (LOQ) was determined to be 2.1% of AR (LOD = 0.7% AR).
The material balance and its mean and distribution of applied radioactivity are shown in the following tables.

Table 7.1.2.1.2- 7: Recovery and distribution of applied radioactivity in soil AX

Fraction		% applied radioactivity at days after treatment:								
	Syst No.	0	3	7	14	28	43	59	92	120
TFA [1]	A	97.8	99.8	100.9	99.9	97.7	100.2	101.3	101.7	98.0
	B	97.5	99.6	100.1	100.5	97.3	99.6	101.3	101.0	99.2
	mean	**97.7**	**99.7**	**100.5**	**100.2**	**97.5**	**99.9**	**101.3**	**101.4**	**98.6**
Carbon Dioxide	A	n.a.	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1
	B	n.a.	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1
	mean	**n.c.**	**< 0.1**	**< 0.1**	**< 0.1**	**< 0.1**	**< 0.1**	**< 0.1**	**< 0.1**	**< 0.1**
Organic Volatiles	A	n.a.	< 0.1	< 0.1	0.2	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1
	B	n.a.	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1
	mean	**n.c.**	**< 0.1**	**< 0.1**	**< 0.1**	**< 0.1**	**< 0.1**	**< 0.1**	**< 0.1**	**< 0.1**
Ambient Extract	A	96.2	98.0	99.2	98.1	95.8	98.3	99.0	99.7	95.9
	B	95.9	97.9	98.4	98.5	95.4	97.8	99.3	99.0	97.0
	mean	96.1	98.0	98.8	98.3	95.6	98.0	99.1	99.4	96.5
Microwave Extract	A	1.6	1.8	1.6	1.8	1.9	1.9	2.1	2.0	2.1
	B	1.6	1.7	1.7	2.0	1.9	1.9	2.0	2.0	2.1
	mean	1.6	1.7	1.7	1.9	1.9	1.9	2.1	2.0	2.1
Total Extractable Residues[1]	A	97.8	99.8	100.9	99.9	97.7	100.2	101.3	101.7	98.0
	B	97.5	99.6	100.1	100.5	97.3	99.6	101.3	101.0	99.2
	mean	**97.7**	**99.7**	**100.5**	**100.2**	**97.5**	**99.9**	**101.3**	**101.4**	**98.6**
Non-Extractable Residues	A	0.6	0.6	0.8	0.7	0.7	0.9	0.7	0.7	0.8
	B	0.6	0.6	0.8	0.6	0.7	0.9	0.9	0.6	0.8
	mean	**0.6**	**0.6**	**0.8**	**0.6**	**0.7**	**0.9**	**0.8**	**0.7**	**0.8**
Total Recovery	A	98.4	100.3	101.7	100.8	98.4	101.1	101.9	102.4	98.8
	B	98.1	100.3	100.9	101.1	98.1	100.6	102.2	101.7	100.0
	mean	**98.2**	**100.4**	**101.3**	**101.0**	**98.2**	**100.9**	**102.1**	**102.1**	**99.4**

n.a not analysed, n.c. not calculated

[1] no degradation observed, thus %AR total extractable = %AR of the test item

Table 7.1.2.1.2- 8: Recovery and distribution of applied radioactivity soil DD

Fraction		% applied radioactivity at days after treatment:								
	Syst No.	0	3	7	14	28	43	59	92	120
TFA [1]	A	98.5	98.6	100.5	99.4	96.0	99.1	100.5	100.3	96.1
	B	98.3	101.0	99.9	99.5	96.7	99.6	99.5	100.2	96.8
	mean	**98.4**	**99.8**	**100.2**	**99.4**	**96.4**	**99.4**	**100.0**	**100.2**	**96.4**
Carbon Dioxide	A	n.a.	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1
	B	n.a.	< 0.1	< 0.1	0.1	< 0.1	< 0.1	< 0.1	0.1	< 0.1
	mean	**n.c.**	**< 0.1**	**< 0.1**	**< 0.1**	**< 0.1**	**< 0.1**	**< 0.1**	**< 0.1**	**< 0.1**
Organic Volatiles	A	n.a.	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1
	B	n.a.	0.1	0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1
	mean	**n.c.**	**< 0.1**	**0.1**	**< 0.1**	**< 0.1**	**< 0.1**	**< 0.1**	**< 0.1**	**< 0.1**
Ambient Extract	A	95.9	96.1	98.2	96.9	93.5	96.5	97.8	97.3	93.4
	B	95.8	98.5	97.5	97.0	94.2	97.4	96.6	97.2	94.1
	mean	**95.9**	**97.3**	**97.8**	**96.9**	**93.9**	**96.9**	**97.2**	**97.2**	**93.8**
Microwave Extract	A	2.5	2.5	2.4	2.5	2.5	2.6	2.8	2.9	2.7
	B	2.5	2.5	2.3	2.5	2.5	2.3	2.8	3.0	2.7
	mean	**2.5**	**2.5**	**2.4**	**2.5**	**2.5**	**2.4**	**2.8**	**3.0**	**2.7**
Total Extractable Residues[1]	A	98.5	98.6	100.5	99.4	96.0	99.1	100.5	100.3	96.1
	B	98.3	101.0	99.9	99.5	96.7	99.6	99.5	100.2	96.8
	mean	**98.4**	**99.8**	**100.2**	**99.4**	**96.4**	**99.4**	**100.0**	**100.2**	**96.4**
Non-Extractable Residues	A	1.3	1.2	1.2	1.3	1.4	1.6	1.7	1.6	2.0
	B	1.4	1.2	1.4	1.3	1.3	1.8	1.9	1.8	2.1
	mean	**1.3**	**1.2**	**1.3**	**1.3**	**1.4**	**1.7**	**1.8**	**1.7**	**2.0**
Total Recovery	A	99.8	99.8	101.8	100.8	97.4	100.7	102.2	101.9	98.1
	B	99.7	102.3	101.4	100.8	98.2	101.4	101.3	102.0	98.8
	mean	**99.7**	**101.0**	**101.6**	**100.8**	**97.8**	**101.1**	**101.8**	**101.9**	**98.5**

n.a not analysed, n.c. not calculated

[1] no degradation observed, thus % AR total extractable = % AR of the test item

Table 7.1.2.1.2- 9: Recovery and distribution of applied radioactivity in soil WW

Fraction		% applied radioactivity at days after treatment:								
	Syst No.	0	3	7	14	28	43	59	92	120
TFA [1]	A	98.4	99.9	99.6	99.6	96.3	99.9	100.6	100.0	97.0
	B	98.9	99.5	99.8	98.8	95.5	99.4	98.9	99.3	98.2
	mean	**98.7**	**99.7**	**99.7**	**99.2**	**95.9**	**99.6**	**99.7**	**99.7**	**97.6**
Carbon Dioxide	A	n.a.	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1
	B	n.a.	< 0.1	< 0.1	0.1	< 0.1	< 0.1	< 0.1	0.1	< 0.1
	mean	**n.c.**	**< 0.1**	**< 0.1**	**< 0.1**	**< 0.1**	**< 0.1**	**< 0.1**	**< 0.1**	**< 0.1**
Organic Volatiles	A	n.a.	0.1	< 0.1	0.1	0.1	< 0.1	< 0.1	< 0.1	0.1
	B	n.a.	< 0.1	0.1	< 0.1	< 0.1	< 0.1	n.d.	< 0.1	< 0.1
	mean	**n.c.**	**< 0.1**	**< 0.1**	**< 0.1**	**< 0.1**	**< 0.1**	**< 0.1**	**< 0.1**	**< 0.1**
Ambient Extract	A	96.7	98.0	97.6	97.3	94.2	97.8	97.8	97.3	94.7
	B	97.0	97.6	97.8	96.8	93.4	97.2	96.4	96.6	95.9
	mean	**96.8**	**97.8**	**97.7**	**97.0**	**93.8**	**97.5**	**97.1**	**96.9**	**95.3**
Microwave Extract	A	1.8	1.9	2.0	2.3	2.1	2.1	2.8	2.7	2.3
	B	1.9	1.9	2.0	2.0	2.1	2.3	2.4	2.8	2.4
	mean	**1.8**	**1.9**	**2.0**	**2.1**	**2.1**	**2.2**	**2.6**	**2.7**	**2.3**
Total Extractable Residues[1]	A	98.4	99.9	99.6	99.6	96.3	99.9	100.6	100.0	97.0
	B	98.9	99.5	99.8	98.8	95.5	99.4	98.9	99.3	98.2
	mean	**98.7**	**99.7**	**99.7**	**99.2**	**95.9**	**99.6**	**99.7**	**99.7**	**97.6**
Non-Extractable Residues	A	1.1	1.0	1.0	0.9	1.1	1.3	1.1	1.1	1.3
	B	0.9	1.2	1.1	1.2	1.1	1.2	1.3	1.2	1.3
	mean	**1.0**	**1.1**	**1.0**	**1.0**	**1.1**	**1.2**	**1.2**	**1.1**	**1.3**
Total Recovery	A	99.5	101.1	100.6	100.5	97.4	101.2	101.7	101.1	98.3
	B	99.9	100.7	100.9	100.0	96.6	100.6	100.2	100.5	99.6
	mean	**99.7**	**100.9**	**100.8**	**100.3**	**97.0**	**100.9**	**100.9**	**100.8**	**99.0**

n.a not analysed, n.c. not calculated

[1] no degradation observed, thus % AR total extractable = % AR of the test item

Table 7.1.2.1.2- 10: Recovery and distribution of applied radioactivity in soil HH

Fraction		% applied radioactivity at days after treatment:								
	Syst No.	0	3	7	14	28	43	59	92	120
TFA [1]	A	99.1	101.3	101.1	100.0	97.1	100.3	102.5	102.5	97.9
	B	99.3	100.0	100.4	100.0	96.9	100.6	101.0	101.7	98.7
	mean	**99.2**	**100.7**	**100.7**	**100.0**	**97.0**	**100.5**	**101.7**	**102.1**	**98.3**
Carbon Dioxide	A	n.a.	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1
	B	n.a.	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1
	mean	**n.c.**	**< 0.1**	**< 0.1**	**< 0.1**	**< 0.1**	**< 0.1**	**< 0.1**	**< 0.1**	**< 0.1**
Organic Volatiles	A	n.a.	0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1
	B	n.a.	< 0.1	0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1
	mean	**n.c.**	**< 0.1**	**< 0.1**	**< 0.1**	**< 0.1**	**< 0.1**	**< 0.1**	**< 0.1**	**< 0.1**
Ambient Extract	A	96.8	98.8	98.9	97.4	94.7	97.7	99.8	99.6	95.1
	B	96.9	97.6	97.8	97.4	94.4	98.4	98.4	98.8	95.9
	mean	96.9	98.2	98.4	97.4	94.5	98.1	99.1	99.2	95.5
Microwave Extract	A	2.3	2.5	2.3	2.6	2.4	2.7	2.7	2.9	2.8
	B	2.4	2.4	2.5	2.6	2.6	2.2	2.6	2.9	2.8
	mean	**2.4**	**2.4**	**2.4**	**2.6**	**2.5**	**2.4**	**2.6**	**2.9**	**2.8**
Total Extractable Residues[1]	A	99.1	101.3	101.1	100.0	97.1	100.3	102.5	102.5	97.9
	B	99.3	100.0	100.4	100.0	96.9	100.6	101.0	101.7	98.7
	mean	**99.2**	**100.7**	**100.7**	**100.0**	**97.0**	**100.5**	**101.7**	**102.1**	**98.3**
Non-Extractable Residues	A	0.9	1.0	1.0	1.0	1.2	1.1	1.3	1.2	1.1
	B	0.9	1.1	1.0	0.9	1.1	1.6	1.3	1.3	1.2
	mean	**0.9**	**1.0**	**1.0**	**0.9**	**1.1**	**1.3**	**1.3**	**1.3**	**1.2**
Total Recovery	A	100.0	102.4	102.2	101.0	98.3	101.4	103.8	103.7	99.0
	B	100.2	101.1	101.5	101.0	98.0	102.2	102.3	103.0	100.0
	mean	**100.1**	**101.8**	**101.8**	**101.0**	**98.2**	**101.8**	**103.1**	**103.4**	**99.5**

n.a not analysed, n.c. not calculated

[1] no degradation observed, thus %AR total extractable = %AR of the test item

B. MATERIAL BALANCE

Material balance of applied radioactivity from samples were between 97.0% and 103.4% for all soils at all time-points. No time-dependent tendency was observed for the total recovery over the study period, demonstrating that no significant radioactivity dissipated from the flasks or was lost during processing.

C. EXTRACTABLE AND NON-EXTRACTABLE RESIDUES

At the end of the incubation period the recovered radioactivity in the extracts was effectively unchanged at 96.4 to 98.6% of AR. Non-extractable ^{14}C-residues increased only marginally from 0.6, 1.3, 1.0 and 0.9% of AR at DAT-0 to 0.8, 2.0, 1.3 and 1.2% of AR at the end of the study (DAT-120).

D. VOLATILISATION

No $^{14}CO_2$ was formed during the study period. No significant amounts of volatile organic compounds were detected in the polyurethane foam of the trap attachments (values being ≤ 0.1% of AR at all sampling intervals).

E. DEGRADATION OF TEST ITEM

In this laboratory study TFA was not degraded in dark aerobic soils during an incubation of 120 days at 20 °C and a soil moisture of approx. 55% of MWHC. Therefore, the total extractable percentages in the tables above are corresponding to the concentrations of TFA at each time-point in each soil. The calculated half-life of the test item was >1000 days (SFO kinetics).

III. CONCLUSIONS

The test item TFA was not degraded under the prevailing laboratory conditions during an incubation duration of 120 days. Significant amounts of volatiles and non-extractable residues were not observed.

The half-life of TFA was calculated by the best fit kinetics according to FOCUS (single first order, SFO, for trigger evaluation) resulted in >1000 days under aerobic conditions in all four tested soils.

3. Assessment and conclusion

Assessment and conclusion by applicant:
The study and its data are considered as valid and reliable for use in risk assessment.

Assessment and conclusion by RMS:
Outcome and conclusion of the study: RMS should indicate if they agree to the results and conclusions of the APPL.

1. Information on the study

Data Point:	KCA 7.1.2/1.2/08
Report Author:	[redacted]
Report Year:	2012
Report Title:	[1-14C]Trifluoroacetate: Concentration dependent mineralization under aerobic conditions
Report No:	EnSa-12-0445
Document No:	M-441501-01-1
Guideline(s) followed in study:	Commission Directive 95/36/EC amending Council Directive 91/414 (Annexes II and III, Fate and Behavior in the Environment), 1995 Regulation (EC) No.1107/2009 of the European Parliament and of the council of 21 October 2009 OECD Test Guideline No. 307, 2002 US EPA OCSPP Test Guidelines OPPTS 835.4100, 2008
Deviations from current test guideline:	Current Guideline: OECD 307 (2002) Only the formation of CO2 (mineralisation) was determined in the study. Analysis of soil samples and determination of the material balance was not addressed in the scope of the study.
Previous evaluation:	yes, evaluated and accepted RAR Flurtamone (2016)
GLP/Officially recognised testing facilities:	Yes, conducted under GLP/Officially recognised testing facilities
Acceptability/Reliability:	Yes

2. Full summary of KCA 7.1.2.1.2/08

Executive Summary
The potential influence of the concentration of [1-^{14}C]trifluoroacetate on the mineralisation was investigated in four different soils.

Soil ID	Source	Texture (USDA)	pH [1]	OC [%]
AX	Monheim, Germany	Sandy loam	6.2	1.6
DD	Blankenheim	Clay Loam	7.3	5.5
WW	Monheim am Rhein	Sandy loam	5.1	1.9
HH	Burscheid	Silt loam	6.4	2.4

[1] pH values were derived from aqueous 0.01 M $CaCl_2$ suspensions

Samples were incubated under aerobic conditions in the dark at 20.0°C (mean during study duration) and approx. 55 % MWHC (maximum water holding capacity) for 120 days. Trifluoroacetate was applied to soil samples at actual concentrations of 20.9 µg/100 g soil dry weight, 1.05 µg/100 g soil dry weight, and 0.1 µg/100 g soil dry weight equivalent to field rates of 75 g/ha, 40 g/ha and 0.4 g/ha, respectively. The test systems were equipped with traps for the collection of $^{14}CO_2$. Samples (traps) were analysed after 30, 59 and 120 days of incubation. At each sampling date, the amounts of trapped CO_2 were determined by liquid scintillation counting (LSC). The identification of the test item in the application solution was achieved by HPLC-MS and HPLC-MS/MS. According to the design as supplementary study no sampling and analysis of the soil was performed, no material balance established.

The results clearly indicate that the level of mineralisation was very low, not surpassing 0.3% AR over an incubation period of 120 d. Obviously, the concentration of TFA has a negligible effect on its mineralisation.

I. MATERIALS AND METHODS

A. MATERIALS

1. Test Item

[1-^{14}C]trifluoroacetate (sodium salt of trifluoroacetic acid, TFA)
Sample ID: KML 9072
Specific activity: 3.48 MBq/mg
Radiochemical purity: > 98%

2. Test Soils

The mineralisation of [1-^{14}C]trifluoroacetate in soil under aerobic conditions was investigated in four agricultural soils at 20°C. The soil characteristics are listed below.

Table 7.1.2.1.2- 11: Properties of soils

Parameter	Result/Value			
Soil abbreviation/ soil ID	AX	DD	WW	HH
Geographic Location [1]	Monheim am Rhein	Blankenheim	Monheim am Rhein	Burscheid
Soil Taxonomic Classification (USDA)	Sandy, mixed, mesic Typic Cambudoll	Fine-loamy, mixed, active, frigid Typic Eutrudept	Loamy, mixed, mesic Typic Argudalf	Loamy, mixed, mesic Typic Argudalf
Textural Class (USDA)	Sandy loam	Clay Loam	Sandy Loam	Silt loam
Sand (%)	77	29	57	25
Silt (%)	14	40	26	60
Clay (%)	9	31	17	15
pH in $CaCl_2$ (1:2)	6.2	7.3	5.1	6.4
pH in water (1:1)	6.5	7.5	5.4	6.7
pH in water (saturated paste)	6.3	7.4	5.2	6.5
pH in KCl (1N)	6.0	7.1	4.7	6.1
Organic Matter (%)	2.8	9.5	3.3	4.1
Organic Carbon (%)	1.6	5.5	1.9	2.4
Cation Exchange Capacity (meq/100g)	8.7	21.2	10.0	13.6
Water Holding Capacity at pF 2.5 (%)	12.2	34.9	18.2	26.3
Maximum Water Holding Capacity (%)	46.9	84.9	50.6	62.0
Bulk Density (disturbed, g/cm^3)	1.26	0.97	1.13	1.08
Soil Biomass at:				
0 days	642	3145	598	1016
59days	484	2798	316	696
120 days	323	1931	173	499

[1] in North Rhine-Westphalia, Germany

B. STUDY DESIGN

1. Experimental Conditions

The soils were collected from agricultural areas of Germany and were sampled fresh from the field. A few days before starting the study, the soil was sieved to a particle size of ≤ 2 mm. Subsequently, the soil moisture was determined by drying aliquots of the soils at 105°C.

Soil aliquots were adjusted to a soil moisture of 55% of the maximum water holding capacity by adding ultrapure water. The weights of all test vessels were recorded, and the samples were pre-equilibrated at about 20°C in the dark over a weekend. The incubation systems were static systems. Soil samples (100 g dry weight) were weighted into Erlenmeyer flasks (300 mL) for each sampling interval. Flasks were closed with trap attachments, which were easily permeable for oxygen. The traps contained soda lime for adsorption of CO_2 and a polyurethane foam plug for adsorption of volatile organic compounds.

Three TFA application solutions with concentrations of approximately 20 µg/mL, 1 µg/mL and 0.1 µg/mL in water were prepared. 1 mL of the respective application solution was applied dropwise, by use of a micropipette, to each pre-equilibrated soil sample. The actual applied amounts of trifluoroacetate were 20.9 µg/100 g soil dry weight (equivalent to a field rate of 75 g/ha), 1.05 µg/100 g soil dry weight (equivalent to a field rate of 40 g/ha), and 0.1 µg/100 g soil dry weight (equivalent to a field rate of 0.4 g/ha).
Dose checks were taken during the application procedure.

Water loss due to evaporation from the soil was determined by weighing the sampled flasks without the traps on each processing day. If necessary, the evaporated portions were replaced.

Determination of the soil microbial viability (microbial biomass) was performed at the start, in the middle (DAT-59) and at the end (DAT-120) of the study.

Samples were incubated under aerobic conditions in the dark at 20.0°C (mean during study duration) and approx. 55% MWHC (maximum water holding capacity) for 120 days.

2. Sampling

The trap attachments from samples (in duplicate from each concentration treatment) were taken at 30, 59 and 120 days after treatment. These trap attachments containing soda lime and PU foam were processed within eight days. Prior to opening the incubation vessels, the entire vessel and trap were placed in a desiccator. Volatile (radioactive) compounds, possibly still present in the vessel, were transferred into the trap attachment by evaporating the entire system for 15 min.

3. Analytical Procedures

For determination of $^{14}CO_2$, the soda lime contained in the trap attachments was dissolved in 60 mL 18% hydrochloric acid. The liberated CO_2 was absorbed by a special absorption / scintillation cocktail and radioactivity was measured by liquid scintillation counting. The identification of the test item in the application solution was achieved by HPLC-MS and HPLC-MS/MS.

II. RESULTS AND DISCUSSION

The test conditions were maintained throughout the study. No significant amounts of radioactivity could be detected in the processed soda lime traps.

The levels of radioactivity trapped in the soda lime from the applied concentrations of 1.1 µg and 0.1 µg/ 100g soil dry weight (dw) are below the limit of detection (LoD) of 0.6 Bq for almost all samples.

Table 7.1.2.1.2- 12: Mineralisation of TFA in soil AX under aerobic conditions

Sampling	Replicate	RA_{total} (Bq)	CO_2 % AR	RA_{total} (Bq)	CO_2 % AR	RA_{total} (Bq)	CO_2 % AR
		20.9 µg/ 100g soil (dw)		1.1 µg/ 100 g soil (dw)		0.1 µg/ 100g soil (dw)	
DAT-30	1	4.46	0.0061	0.34	0.0093	0.00	0.000
	2	4.48	0.0062	0.22	0.0060	0.09	0.025
	mean	*4.47*	*0.0062*	*0.28*	*0.0077*	*0.05*	*0.013*
DAT-59	1	5.31	0.0073	0.31	0.0085	0.64	0.179
	2	5.34	0.0074	0.54	0.0147	0.79	0.221
	mean	*5.33*	*0.0074*	*0.43*	*0.0116*	*0.71*	*0.200*
DAT-120	1	5.35	0.0074	0.40	0.0109	0.44	0.123
	2	5.22	0.0072	0.57	0.0155	0.39	0.109
	mean	*5.29*	*0.0073*	*0.49*	*0.0132*	*0.42*	*0.116*

LOD: 0.6 Bq, LOQ: 0.9 Bq, values calculated in the summary are given in *italics*
RA_{total} corresponds to the radioactivity in Bq absorbed by the soda lime

Table 7.1.2.1.2- 13: Mineralisation of TFA in soil DD under aerobic conditions

Sampling	Replicate	RA_{total} (Bq)	CO_2 % AR	RA_{total} (Bq)	CO_2 % AR	RA_{total} (Bq)	CO_2 % AR
		20.9 µg/ 100g (dw)		1.1 µg/ 100 g (dw)		0.1 µg/ 100g (dw)	
DAT-30	1	4.88	0.0067	0.51	0.0139	0.15	0.042
	2	4.96	0.0068	0.72	0.0196	0.02	0.006
	mean	*4.92*	*0.0068*	*0.62*	*0.0168*	*0.09*	*0.024*
DAT-59	1	5.44	0.0075	0.37	0.0101	0.81	0.227
	2	5.73	0.0079	0.56	0.0153	0.17	0.048
	mean	*5.59*	*0.0077*	*0.47*	*0.0127*	*0.49*	*0.138*
DAT-120	1	5.26	0.0072	1.56	0.0425	0.82	0.230
	2	5.55	0.0076	0.58	0.0158	0.46	0.129
	mean	*5.41*	*0.0074*	*1.07*	*0.0292*	*0.64*	*0.180*

LOD: 0.6 Bq, LOQ: 0.9 Bq, values calculated in the summary are given in *italics*
RA_{total} corresponds to the radioactivity in Bq absorbed by the soda lime

Table 7.1.2.1.2- 14: Mineralisation of TFA in soil WW under aerobic conditions

Sampling	Replicate	RA_{total} (Bq)	CO_2 % AR	RA_{total} (Bq)	CO_2 % AR	RA_{total} (Bq)	CO_2 % AR
		20.9 µg/ 100g (dw)		1.1 µg/ 100 g (dw)		0.1 µg/ 100g (dw)	
DAT-30	1	4.68	0.0064	0.28	0.0076	0.14	0.039
	2	4.99	0.0069	0.24	0.0065	0.00	0.000
	mean	*4.84*	*0.0067*	*0.26*	*0.0071*	*0.07*	*0.020*
DAT-59	1	5.24	0.0072	0.49	0.0134	0.06	0.017
	2	5.49	0.0076	0.45	0.0123	0.16	0.045
	mean	*5.37*	*0.0074*	*0.47*	*0.0129*	*0.11*	*0.031*
DAT-120	1	6.04	0.0083	0.37	0.0055	1.24	0.348
	2	5.81	0.0080	0.71	0.0194	0.34	0.095
	mean	*5.93*	*0.0082*	*0.64*	*0.0175*	*0.79*	*0.222*

LOD: 0.6 Bq, LOQ: 0.9 Bq, values calculated in the summary are given in *italics*
RA_{total} corresponds to the radioactivity in Bq absorbed by the soda lime

Table 7.1.2.1.2- 15: Mineralisation of TFA in soil HH under aerobic conditions

Sampling	Replicate	RA_{total} (Bq)	CO_2 % AR	RA_{total} (Bq)	CO_2 % AR	RA_{total} (Bq)	CO_2 % AR
		20.9 µg/ 100g (dw)		1.1 µg/ 100 g (dw)		0.1 µg/ 100g (dw)	
DAT-30	1	4.96	0.0068	2.82	0.0769	0.41	0.115
	2	4.77	0.0066	0.41	0.0112	0.25	0.070
	mean	*4.87*	*0.0067*	*1.62*	*0.0441*	*0.33*	*0.093*
DAT-59	1	5.39	0.0074	0.42	0.0115	0.31	0.087
	2	5.44	0.0075	0.26	0.0071	0.58	0.163
	mean	*5.42*	*0.0075*	*0.34*	*0.0093*	*0.45*	*0.125*
DAT-120	1	5.06	0.0070	0.74	0.0202	0.55	0.154
	2	5.24	0.0072	0.86	0.0234	0.39	0.109
	mean	*5.15*	*0.0071*	*0.80*	*0.0218*	*0.47*	*0.132*

LOD: 0.6 Bq, LOQ: 0.9 Bq, values calculated in the summary are given in *italics*
RA_{total} corresponds to the radioactivity in Bq absorbed by the soda lime

III. CONCLUSIONS

The results clearly indicate that the level of mineralisation was very low, not surpassing 0.3% AR over an incubation period of 120 d. Obviously, the concentration of TFA has a negligible effect on its mineralisation.

3. Assessment and conclusion

Assessment and conclusion by applicant:
The study and its data are considered as supportive information with no use in risk assessment.

Assessment and conclusion by RMS:
Outcome and conclusion of the study: RMS should indicate if they agree to the results and conclusions of the APPL.

Data Point:	KCA 7.1.2.1.2/09
Report Author:	[redacted]
Report Year:	2021
Report Title:	Fluopyram (FLU): Kinetic evaluation of aerobic laboratory soil degradation in European soils (Babczinski, 2008, Menke and Telscher, 2008) according to FOCUS kinetics using KinGUI 2.1
Report No:	EnSa-20-0335
Document No:	M-761966-01-1
Guideline(s) followed in study:	not applicable
Deviations from current test guideline:	Current Guideline: not applicable (kinetic evaluation)
Previous evaluation:	No, not previously submitted
GLP/Officially recognised testing facilities:	No, not conducted under GLP/Officially recognised testing facilities
Acceptability/Reliability:	Yes

The kinetic evaluation is summarised under KCA 7.1.2.1.1/09 (M-761966-01-1).

Data Point:	KCA 7.1.2.1.2/10
Report Author:	[redacted]
Report Year:	2021
Report Title:	Fluopyram (FLU): Kinetic evaluation of aerobic laboratory soil degradation in Brazilian soil according to FOCUS kinetics using KinGUI 2.1
Report No:	EnSa-20-0606
Document No:	M-761965-01-1
Guideline(s) followed in study:	not applicable
Deviations from current test guideline:	Current Guideline: not applicable (kinetic evaluation)
Previous evaluation:	No, not previously submitted
GLP/Officially recognised testing facilities:	No, not conducted under GLP/Officially recognised testing facilities
Acceptability/Reliability:	Yes

The kinetic evaluation is summarised under KCA 7.1.2.1.1/11 (M-761968-01-1).

Data Point:	KCA 7.1.2.1.2/11
Report Author:	[redacted]
Report Year:	2021
Report Title:	Fluopyram (FLU): Kinetic evaluation of aerobic laboratory soil degradation in European soils ([redacted], 2020) according to FOCUS kinetics using KinGUI 2.1
Report No:	EnSa-20-0773
Document No:	M-761969-01-1
Guideline(s) followed in study:	not applicable
Deviations from current test guideline:	Current Guideline: not applicable (kinetic evaluation)
Previous evaluation:	No, not previously submitted
GLP/Officially recognised testing facilities:	No, not conducted under GLP/Officially recognised testing facilities
Acceptability/Reliability:	Yes

The kinetic evaluation is summarised under KCA 7.1.2.1.1/13 (M-761969-01-1).

Data Point:	KCA 7.1.2.1.2/12
Report Author:	[redacted]
Report Year:	2021
Report Title:	Fluopyram (FLU), FLU-7-OH, TFA: - Kinetic evaluation of aerobic laboratory soil degradation in European soils, including trifluoroacetic acid ([redacted] 2020) according to FOCUS Kinetics using KinGUI 2.1
Report No:	EnSa-20-0873
Document No:	M-762167-01-1
Guideline(s) followed in study:	not applicable
Deviations from current test guideline:	Current Guideline: not applicable (kinetic evaluation)
Previous evaluation:	No, not previously submitted
GLP/Officially recognised testing facilities:	No, not conducted under GLP/officially recognised testing facilities
Acceptability/Reliability:	Yes

The kinetic evaluation is summarised under KCA 7.1.2.1.1/14 (M-762167-01-1).

CA 7.1.2.1.3 Anaerobic degradation of the active substance

Data Point:	KCA 7.1.2.1.3/01
Report Author:	[redacted]
Report Year:	2008
Report Title:	[Phenyl-UL-^{14}C] and [pyridinyl-2,6-^{14}C]AE C656948: Anaerobic soil metabolism
Report No:	MEGMP080-1
Document No:	M-292028-02-1
Guideline(s) followed in study:	US EPA Subdivision N, Section 162-2 US EPA OPPTS Guideline No. 835.4300 OECD Guidelines for Testing of Chemicals, Guideline 307 Canada PMRA DACO No. 8.2.3.4.4
Deviations from current test guideline:	Current Guideline: OECD 307 (2002) Biomass was only determined at study start (no determination at end of aerobic degradation and no determination of anaerobic microorganisms was performed).
Previous evaluation:	yes, evaluated and accepted (DAR, 2011)
GLP/Officially recognised testing facilities:	Yes, conducted under GLP/Officially recognised testing facilities
Acceptability/Reliability:	Yes

The experimental study is summarised and discussed under point KCA 7.1.1.2/01. Fluopyram is considered stable under anaerobic conditions and consequently no degradation rate could be calculated.

CA 7.1.2.1.4 Anaerobic degradation of metabolites, breakdown and reaction products

Fluopyram is considered stable under anaerobic conditions and no degradation products were observed.

CA 7.1.2.2 Field studies

The studies on route and rate degradation performed with the active substance fluopyram under laboratory conditions revealed soil DT_{50} values greater than 60 days. In consequence, field studies at European and US sites were conducted to investigate the behaviour of fluopyram under field conditions. The experimental data from existing and new field dissipation studies were evaluated by kinetic modelling to determine field degradation half-lives of fluopyram as modelling input for environmental risk assessments and for comparison with trigger values.

For the field dissipation data obtained on US field sites, an ecoregion crosswalk using the ENASGIPS approach was conducted additionally to verify if the field sites are representative for European conditions. For trigger purposes three out of five US locations were regarded as representative for European conditions. Half-lives for trigger purposes were in the range of 20.9 to >1000 days (geometric mean: 254 days), respective DT_{90} values were calculated to be in the range of 498 to >1000 days.

Additionally, the Ctb checklist was considered for further evaluation of study results. Considering both the ecoregion crosswalk and the Ctb checklist, it could be shown that just two US field sites are representative for European conditions for modelling purposes. In consequence, they were included in further evaluations herein. Endpoints of fluopyram for modelling purposes derived from field studies were normalised to a temperature of 20°C and a soil moisture of pF 2 and were evaluated according to FOCUS degradation kinetics. The geometric mean $DegT_{50}$ of fluopyram was calculated to be 298 days.

Table 7.1.2.2- 1: Degradation times of fluopyram under field conditions (data sets used for DT_{50} modelling purpose, only)

Parent	**Aerobic field conditions**								
Soil type (USDA)	**Location (country or USA state)**	**Reference**	**pH[1]**	**Depth (cm)**	**$DegT_{50}$ actual (d)**	**DT_{90} actual (d)**	**St. (χ^2)**	**$DegT_{50\ matrix}$ (d) norm[2]**	**Method of calculation**
Loamy sand	North Rose, New York, USA	M-306809-01-2	5.9	15	281.7	936	12.5	281.7	SFO
Sandy loam	Ephrata, Washington, USA	M-306817-01-2	7.5	15	144.8	742	3.03	$DT_{50\ slow}$: 257.4	DFOP
Sandy clay loam	Little Oliver, Malton, UK	M-758583-01-1	5.3	20	153.8	510.8	8.31	153.8	SFO
Loam	Auchy-les-Mines, France	M-758583-01-1	7.3	20	871.6	>1000	4.59	871.6	SFO
Silt loam	Urbanowice, Poland	M-758583-01-1	5.2	20	605.3	>1000	7.60	605.3	SFO
Clay loam	Charles River Farm, Lleida, Spain	M-758583-01-1	7.8	20	306.2	>1000	15.2	306.2	SFO
Loam	Sindos, Greece	M-758583-01-1	6.6	20	>1000	>1000	4.99	1000 (default)	SFO

Parent	Aerobic field conditions								
Soil type (USDA)	**Location (country or USA state)**	**Reference**	**pH[1]**	**Depth (cm)**	**DegT$_{50}$ actual (d)**	**DT$_{90}$ actual (d)**	**St. (χ^2)**	**DegT$_{50}$ $_{matrix}$ (d) norm[2]**	**Method of calculation**
Loamy fine sand	Hoeltinghausen, Emstek, Germany	M-758589-01-1	5.6	20	244.3	>1000	6.82	DT$_{50\ fast}$ 8.548 d, **DT$_{50\ slow}$ 453.9 d,** tb 4.02 d = g 0.2784	HS
Silt loam	Hornton, Banbury, UK	M-758589-01-1	6.1	20	263.7	875.9	4.63	263.7	SFO
Silt loam	Le Thour, France	M-758589-01-1	7.5	20	83.91	278.7	6.16	83.91	SFO
Sandy loam	Brannens, France	M-758589-01-1	4.4	50	180.5	599.6	8.61	180.5	SFO
Loam	Balbiano, Italy	M-758589-01-1	7.2	40	203.0	674.2	6.47	203.0	SFO
Silt loam	Almayate East, Spain	M-758589-01-1	7.7	20	221.3	735.3	10.2	221.3	SFO
Geometric mean (if not pH dependent)								298.08	
pH dependence					No				

[1] Measured in $CaCl_2$, topsoil
[2] Normalised using a 1/10 or 2.58 and Walker equation coefficient of 0.7, values are DegT$_{50matrix}$

Table 7.1.2.2- 2: Dissipation times of fluopyram under field conditions (trigger purpose)

Parent	Aerobic conditions								
Soil type (USDA)	**Location**	**Reference**	**pH[1]**	**Depth (cm)**	**DisT$_{50}$ actual (d)**	**DisT$_{90}$ actual (d)**	**St. (χ^2)**	**DT$_{50}$ (d) Norm[2]**	**Method of calculation**
Silt loam (grass)	Hoefchen, Burscheid, Germany	M-293999-01-1	6.2	20	137.5	1030	7.43	-	DFOP
Sandy loam (grass)	Little Shelford, UK	M-293999-01-1	7.3	20	172.2	>1000	6.87	-	DFOP
Loam (grass)	Staffanstorp, Sweden	M-293999-01-1	7.3	20	178.7	1075	5.96	-	DFOP
Silt loam (grass)	Vatteville, France	M-293999-01-1	6.6	20	376.9	>1000	11.1	-	SFO
Loam (grass)	Vilobi d'Onyar, Spain	M-293999-01-1	6.1	20	99.32	498.4	20.2	-	HS
Silt loam (grass)	Albaro, Italy	M-293999-01-1	7.4	20	20.89	511.3	7.06	-	DFOP

Parent	Aerobic conditions								
Soil type (USDA)	**Location**	**Reference**	**pH[1]**	**Depth (cm)**	**DisT$_{50}$ actual (d)**	**DisT$_{90}$ actual (d)**	**St. (χ^2)**	**DT$_{50}$ (d) Norm[2]**	**Method of calculation**
Sandy loam (bare soil)	Huron/ Kerman, California, USA	M-306820-01-2	7.3	15	161.2	>1000	12.1	-	HS
Loamy sand (bare soil)	North Rose, New York, USA	M-306809-01-2	5.9	15	350.5	>1000	10.6	-	DFOP
Sandy loam (bare soil)	Ephrata, Washington, USA	M-306817-01-2	7.5	15	194.4	>1000	3.35	-	DFOP
Sandy clay loam	Little Oliver, Malton, UK	M-758583-01-1	5.3	20	307.6	1022	8.96	-	SFO
Loam	Auchy-les-Mines, France	M-758583-01-1	7.3	20	>1000	>1000	4.74	-	SFO
Silt loam	Urbanowice, Poland	M-758583-01-1	5.2	20	765.7	>1000	6.97	-	SFO
Clay loam	Charles River Farm, Lleida, Spain	M-758583-01-1	7.8	20	301.6	1002	15.2	-	SFO
Loam	Sindos, Greece	M-758583-01-1	6.6	20	>1000	>1000	4.89	-	SFO
Loamy fine sand	Hoeltinghausen, Emstek, Germany	M-758589-01-1	5.6	20	608.9	>1000	7.89	-	HS
Silt loam	Horton, Banbury, UK	M-758589-01-1	6.1	20	520.6	>1000	3.79	-	HS
Silt loam	Le Thour, France	M-758589-01-1	7.8	20	150.1	498.6	9.19	-	SFO
Sandy loam	Brannens, France	M-758589-01-1	4.4	50	2200	>1000	4.87	-	HS
Loam	Balbiano, Italy	M-758589-01-1	7.2	40	205.5	682.7	8.52	-	SFO
Silt loam	Almayate East, Spain	M-758589-01-1	7.7	20	225.0	>1000	2.00	-	DFOP
Maximum (n=20)					1000				

[1] Measured in $CaCl_2$

[2] Normalised using a Q10 of 2.58 and Walker equation coefficient of 0.7, values are $DegT_{50matrix}$

The half-lives of fluopyram derived from field data of 20 field sites were calculated to be at least partly longer than 1 year. Residues of fluopyram could be present in soil one year after application. Consequently, this was addressed by an accumulation study at two field locations (Monheim, Germany and Tarascon, France) following annual applications for up to approximately 8 years. The total residues of fluopyram in soil following annual treatment degraded to 13.5% at the Monheim site (Germany), and to 13.4% at the Tarascon site (France) compared to the nominal applied amount. A plateau concentration was reached for fluopyram residues in soil at both sites after eight (site Monheim, Germany) or six annual applications (site Tarascon, France).

Assessment of pH dependency of degradation of fluopyram in soil on the basis of normalised DegT$_{50}$ values of the laboratory and the field

The pH dependency of the normalised DT$_{50}$ of fluopyram in soil was assessed using the Input Decision Tool v3.3 of Federal Environment Agency (UBA), Germany. If pH values measured in H_2O were not available, they were converted from available pH values measured in other media. The results of laboratory and field studies were evaluated separately.

The assessment shows no significant correlation between the pH values and the normalised DT$_{50}$ for fluopyram derived from aerobic laboratory soil and field degradation studies. All levels of significance were >0.05.

Table 7.1.2.2- 3: Correlation parameters for DegT$_{50}$ values and pH values for fluopyram derived from laboratory and field studies

Compound	Degradation study type (aerobic)	Kendall tau (stringency of the correlation)	p (level of significance)
Fluopyram	laboratory studies	-0.235	0.091
Fluopyram	field studies	-0.103	0.669

Figure 7.1.2.2- 1: Correlation between pH and DT$_{50}$ values of fluopyram derived from laboratory and field studies

Assessment of pH dependency of degradation of fluopyram-7-hydroxy in soil on the basis of normalised DegT$_{50}$ values of the laboratory

The pH dependency of the normalised DT$_{50}$ values of fluopyram-7-hydroxy in soil was assessed using the German Input Decision Tool v3.3 of Federal Environment Agency (UBA), Germany. If pH values measured in H_2O were not available, they were converted from pH values measured in other media.

Some DT$_{50}$ values were derived from degradation studies which were conducted in parallel on identical soils batches. The kinetic evaluation was done separately but the geometric mean of the normalised modelling DT$_{50}$ values for these soils was used for assessment of pH dependency.

The assessment did not show a significant correlation between the pH values and the normalised DT$_{50}$ for fluopyram-7-hydroxy for data derived from laboratory studies. The level of significance was >0.05.

Table 7.1.2.2- 4: Correlation parameters for DegT$_{50}$ values and pH values for fluopyram-7-hydroxy derived from laboratory studies

Compound	Degradation study type (aerobic)	Kendall tau (stringency of the correlation)	p (level of significance)
fluopyram-7-hydroxy	laboratory studies	-0.317	0.112

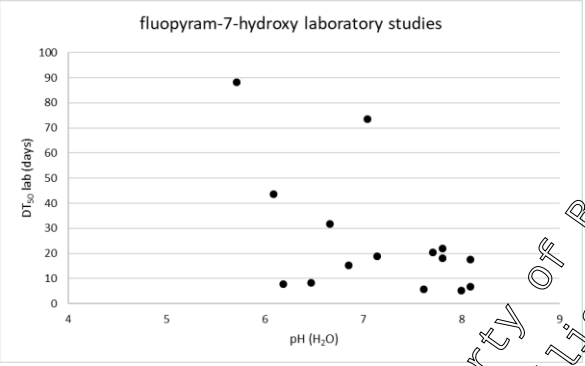


Figure 7.1.2.2- 2: Correlation between pH and DT_{50} values of fluopyram-7-hydroxy derived from laboratory studies

Assessment of pH dependency of normalised DT_{50} of trifluoroacetic acid (TFA) in soil

The pH dependency of the normalised DT_{50} values of TFA in soil was not assessed. DT_{50} trigger endpoints of TFA were calculated to be >1000 days in all soils. Separate modelling endpoints for TFA were not derived.

1. Information on the study

Data Point:	KCA 7.1.2.2/01
Report Author:	[redacted]
Report Year:	2020
Report Title:	Determination of the dislodgeable foliar residues (DFR) of fluopyram, prothioconazole and prothioconazole-desthio in/on spring wheat after spray application of BIX+FLU+DTZ EC 65+65+130A G under protected conditions in Germany, Denmark and Northern France - Final report
Report No.:	IF20-05267956
Document No:	M-758592-01-1
Guideline(s) followed in study:	US EPA OPPTS 875.2100 Foliar Dislodgeable Residue Dissipation
Deviations from current test guideline:	Current Guideline: US EPA OPPTS 875.2100 (1996) none
Previous evaluation:	No, not previously submitted
GLP/Officially recognised testing facilities:	Yes, conducted under GLP/Officially recognised testing facilities
Acceptability/Reliability:	Yes

2. Full summary of KCA 7.1.2.2/01

Executive Summary

The purpose of this specific dislodgeable foliar residue study (DFR) was to generate dislodging solution samples to determine the amount of dislodgable residues of fluopyram (AE C656948), prothioconazole (JAU 6476) and prothioconazole-desthio on spring wheat leaves after a foliar spray application to the treated plot with BIX+FLU+PTZ EC 65+65+130A G, an emulsifiable concentrate containing 65 g/L fluopyram (AE C656948) and 130 g/L prothioconazole (JAU 6476). From these data, a foliar dissipation half-life of the washable substance amount on leaf surfaces can be derived for fluopyram. Results for prothioconazole (JAU 6476) and prothioconazole-desthio are not presented in this summary.

The study included 3 supervised field residue trials with spring wheat covered by foliar tunnels, which prevented washoff by rain and irrigation (drip), and guaranteed a light transmission of at least 80%. The tunnels were left open at both ends. The trials were conducted in northern Europe (Germany, Denmark and Northern France) during the 2020 season. The application rate of fluopyram was 0.078 kg/ha in all trials.

The average recoveries were within the acceptable range of 70 – 110%; RSD values are below 20%.

The level of residues of fluopyram found in the treated samples are summarised in the table below. No residues above the LOQ were found in the control samples. Results in summary tables were neither corrected for concurrent recoveries nor field spikes recoveries.

Table 7.1.2.2- 5: Residue summary of fluopyram in/on wheat leaves washings

No. of trials	Sample timing	Matrix	n	Residue fluopyram [µg/L] min - max
3	0 DAT	wheat leaves / washings	9	< LOD – 137
	5 hours after application	wheat leaves / washings	9	< LOD – 109
	1 DAT	wheat leaves / washings	9	39.2 – 72.2
	2 DAT	wheat leaves / washings	9	< LOD – 52.5
	3 DAT	wheat leaves / washings	9	14.1 – 52.9
	5 DAT	wheat leaves / washings	9	< 10 – 21.4
	7 DAT	wheat leaves / washings	9	< LOD – 25.0
	9-10 DAT	wheat leaves / washings	9	< LOD – 11.4
	11-12 DAT	wheat leaves / washings	9	< LOD – < 10
	14 DAT	wheat leaves / washings	9	< LOD – < 10

DAT = Days after treatment, 0 DAT = directly after treatment when the spray had dried

The analytical results show that residues of fluopyram declines in washings from wheat leaves. The residues of fluopyram derived from the German trial 20-00032-01 were below the LOQ within 12 days after last application. The residues of fluopyram derived from the Danish trial 20-00032-02 were below the LOQ within 7 days after last application. The residues of fluopyram derived from the French trial 20-00032-03 were also below the LOQ within 7 days after last application.

I. MATERIALS AND METHODS

A. MATERIALS

1. Test Item:

BIX+FLU+PTZ EC 65+65+130A G	EC emulsifiable concentrate
Active ingredients	bixafen (65 g/L), fluopyram[1] (65 g/L), prothioconazole[1] (130 g/L)
Batch number	2020-001412-01
Certificate number	TOX21579-00
Content active substance fluopyram	Nominal: 65 g/L, actual: 64.57 g/L

[1] residue samples were analysed for fluopyram, prothioconazole and prothioconazole-desthio; only results related to fluopyram are presented here.

B. STUDY DESIGN

1. Field phase:

This study comprised 3 supervised residue trials with spring wheat in Germany, Denmark and Northern France. At each trial site there was one treated plot consisted of 3 subplots. The trials were placed under polytunnels which guaranteed a light transmission of at least 80%. The tunnels were left open at both ends and were open to wind. Field trials were intended to be carried out as close as possible to normal open field conditions, but with an exclusion of any water to the foliar surface, to exclude wash-off of the active ingredients form the leaf surfaces. If necessary, irrigation could be provided by drip irrigation. Information about the trials is given in the table below.

Table 7.1.2.2- 6: Description of the trial locations and cropping information on treated plots

Trial number	20-00032-01	20-00032-02	20-00032-03
Trial location	49685 Emstek	6200 Røllum	51110 Auménancourt
Country	Germany	Denmark	France
Area of trial	Foliar tunnel	Foliar tunnel	Foliar tunnel
Size of tunnel [length x width x height]	13.5 m x 4.0 m x 2.0 m	10 m x 6 m x 3 m	50 m x 5 m x 4 m
Plot number	T (sub1, sub2, sub3)	T (sub1, sub2, sub3)	T (sub1, sub2, sub3)
Plot size [m^2]	36 (12 per subplot)	30 (10 per subplot)	30 (10 per subplot)
Type of soil	silt loam	loamy sand	loam
pH-value of soil	6.1 (water)	4.4 ($CaCl_2$)	8.1 (water)
Content of organic C [%]	2.0	0.8	1.2
Test system	Spring wheat	Spring wheat	Spring wheat
Variety	Licamero	Licamero	Feeling
Crop density	350 seeds/m^2	350 seeds/m^2	350 seeds/m^2
Date of sowing	2020-03-18	2020-04-08	2020-04-10
Start of flowering	2020-06-12	-	2020-06-13
End of flowering	2020-06-17		2020-06-17
Row Spacing [cm]	12	12.5	15

The soil characterization was not conducted according to GLP.

Sprayers were calibrated before each application. Climatic and irrigation data were recorded (without GLP) during the conduct of the study. The application rate of fluopyram was 0.078 kg/ha in all trials.

2. Collecting of Leaf Samples

Samples were collected in a manner designed to obtain representative samples. For trials 20-00032-01 and 20-00032-03 leaf samples were collected by sampling 40 leaves manually and cutting them into rectangles of 2.5 cm length and 1 cm width resulting in a total leaf surface area of 200 cm^2 which were put into a jar. For trial 20-00032-02 samples were taken by sampling 80 leaf discs using a leaf punch sampler with a diameter of 1.25 cm. The leaf rectangles/discs represented a total double-sided leaf surface area of 200 cm^2. After each sample was collected, the sampling jar was capped and transported to the Test Site under chilled conditions.

Nominal sampling times were -0 days after treatment (control sample before treatment), 0 DAT (directly after treatment when the spray had dried), 5 hours after application, 1 DAT, 2 DAT, 3 DAT, 5 DAT, 7 DAT, 10±1 DAT, 12±1 DAT and 14±1 DAT.

Field fortification samples were used to demonstrate the stability of the samples during storage period of the study and the ability of the analytical laboratory to recover an analyte fortified into a sample at the field test site.

The determination of the leaf area over time was done by scanning whole leaves using a portable leaf area meter, which uses an optical scanner to take the measurements. Therefore, each leaf was placed on

the board of the scanner and covered with a clear sheet. The scanner head was rolled over the leaf to determine the exact leaf area. The leaf area was determined to be in the range of 1773 – 2101 mm^2 and 3122 – 3514 mm^2 for the leaves sampled at the field site in Germany and Denmark, respectively.

3. Dislodging of Leaf Samples

The dislodging of the leaf samples was performed as soon as possible, but not later than 3 hours after collection. The samples were dislodged by adding 100 mL of a 0.01% Aerosol OT solution (i.e. docusate sodium salt) which corresponds to a surfactant. The Aerosol OT solution was freshly prepared with tap water on the day of use. Each jar containing the leaf material and the 100 mL 0.01% Aerosol OT solution was capped securely and placed on a shaker operating at approximately 200 cycles per minute for a period of approximately 10 min. The solution was decanted from the leaf material into an appropriate labelled container. The dislodging procedure was repeated for each sample with a fresh 100 mL aliquot of the Aerosol solution. The second rinse was again decanted and added to the first one. Immediately after dislodging the leaves, the jar was capped and placed in a deep freezer. The dislodged leaves were discarded after dislodging.

4. Analytical procedures

Shortly before analysis, the specimens were thawed completely and shaken to ensure a homogenous specimen. The storage period of deep-frozen samples intended for the analysis ranged between 15 and 64 days.

The analytical method used for the determination of fluopyram residues was based on method 01158/M001 (M-502699-01-1). Residues were determined from specimen material after dilution with acetonitrile and addition of the internal standard. An aliquot of the extract was injected into a high-performance liquid chromatograph and subjected to reversed phase chromatography coupled with tandem mass spectrometry (MS/MS) equipped with a TurboIonSpray (ESI) interface operated in positive ion mode and multiple reaction monitoring (MRM).

The dislodgeable foliar residues of fluopyram were determined according to method 01158/M001.

The validity of the results was confirmed by fortification experiments, considering three different concentrations, which were carried out together with the analysis of the specimen.

The quantification was done by internal standardization using internal stable labelled standards. The limit of quantitation (LOQ) is 10 µg/L, corresponding to 200 cm^2 leave surface. The limit of detection (LOD) was set to 3 µg/L. Storage stability of extracts was proven for 14 days. The maximum storage time between extraction and sample analysis was 13 days with exception for sample 20-00032-01-010 were storage time was 15 days. Stability was proven through procedural recoveries. During each set of analysis, a calibration curve was established with at least seven concentration levels and used for quantitation. For each calibration curve, the correlation coefficient R was above 0.999.

Full details and acceptable validation data to support the analytical method are presented within document M-CA 4, which comply with the EU regulatory requirements outlined within SANTE/2020/12830, Rev.1.

II. RESULTS AND DISCUSSION

A. RESULTS

The analytical results of treated samples are summarised in the following tables. They were not corrected for concurrent recoveries nor field spikes recoveries. Values below the LOQ and above the LOD are displayed in brackets in µg/L, i.e. < 10 (x.xx) for fluopyram.

Table 7.1.2.2- 7: Residue summary on wheat leaf washings from Germany for fluopyram

Trial No. / Country	Sample No. 20-00032-01	Plot	Sampling Timing	Sampling timing [hours after application]	Growth stage [BBCH]	Fluopyram [µg/L]
20-00032-01 Germany	-012	T	0 DAT	01:02	41	<LOD*
	-014	T	5 hours after application	05:02	41	<LOD*
	-016	T	1 DAT	27:32	47	39.3
	-018	T	2 DAT	48:02	55	22.6
	-020	T	3 DAT	71:52	57	41.2
	-022	T	5 DAT	-	59	18.9
	-024	T	7 DAT	-	59	21.9
	-026	T	9 DAT	-	61	< 10 (9.89)
	-028	T	12 DAT	-	65	< 10 (6.16)
	-030	T	14 DAT	-	65	< 10 (5.77)
	-042	T	0 DAT	01:12	41	<LOD*
	-044	T	5 hours after application	05:12	41	<LOD*
	-046	T	1 DAT	27:42	47	55.6
	-048	T	2 DAT	48:12	55	31.4
	-050	T	3 DAT	72:02	57	32.6
	-052	T	5 DAT	-	59	19.3
	-054	T	7 DAT	-	59	20.5
	-056	T	9 DAT	-	61	11.4
	-058	T	12 DAT	-	65	< 10 (6.61)
	-060	T	14 DAT	-	65	< 10 (4.77)
	-072	T	0 DAT	01:22	41	<LOD*
	-074	T	5 hours after application	05:22	41	<LOD*
	-076	T	1 DAT	27:52	47	58.6
	-078	T	2 DAT	48:22	55	33.9
	-080	T	3 DAT	72:12	57	26.4
	-082	T	5 DAT	-	59	21.4
	-084	T	7 DAT	-	59	25.0
	-086	T	9 DAT	-	61	< 10 (6.42)
	-088	T	12 DAT	-	65	< 10 (4.47)
	-090	T	14 DAT	-	65	< 10 (5.75)

* Results are implausible. Unfortunately, no explanation for this could be found either in the field part or in the analytical part.
DAT = Days after treatment, 0 DAT = directly after treatment when the spray had dried

Table 7.1.2.2- 8: Residue summary on wheat leaf washings from Denmark for fluopyram

Trial No. / Country	Sample No. 20-00032-02	Plot	Sampling Timing	Sampling timing [hours after application]	Growth stage [BBCH]	Fluopyram [µg/L]
20-00032-02 Denmark	-012	T	0 DAT	00:47	45	94.7
	-014	T	5 hours after application	05:02	45	103
	-016	T	1 DAT	28:36	49	58.7
	-018	T	2 DAT	53:24	51	45.2
	-020	T	3 DAT	74:44	55	52.9
	-022	T	5 DAT	-	59	10 (3.50)
	-024	T	7 DAT	-	65	< 10 (8.69)
	-026	T	10 DAT	-	65	< 10 (3.81)
	-028	T	11 DAT	-	65	10 (9.23)
	-030	T	14 DAT	-	69	<LOD
	-042	T	0 DAT	00:47	45	107
	-044	T	5 hours after application	05:02	45	109
	-046	T	1 DAT	28:36	49	65.7
	-048	T	2 DAT	53:24	51	47.1
	-050	T	3 DAT	74:44	55	27.8
	-052	T	5 DAT	-	59	< 10 (9.69)
	-054	T	7 DAT	-	65	< 10 (9.17)
	-056	T	10 DAT	-	65	< 10 (6.49)
	-058	T	14 DAT	-	65	< 10 (5.46)
	-060	T	14 DAT	-	69	< 10 (4.30)
	-072	T	0 DAT	00:47	45	137
	-074	T	5 hours after application	05:02	45	76.9
	-076	T	1 DAT	28:36	49	72.2
	-078	T	2 DAT	53:24	51	52.5
	-080	T	3 DAT	74:44	55	29.8
	-082	T	5 DAT	-	59	10.9
	-084	T	7 DAT	-	65	<LOD
	-086	T	10 DAT	-	65	<LOD
	-088	T	11 DAT	-	65	<LOD
	-090	T	14 DAT	-	69	<LOD

DAT = Days after treatment, 0 DAT = directly after treatment when the spray had dried

Table 7.1.2.2- 9: Residue summary on wheat leaf washings from Northern France for fluopyram

Trial No. / Country	Sample No. 20-00032-03	Plot	Sampling Timing	Sampling timing [hours after application]	Growth stage [BBCH]	Fluopyram [µg/L]
20-00032-03 Northern France	-012	T	0 DAT	00:51	43	57.2
	-014	T	5 hours after application	05:05	43	69.5
	-016	T	1 DAT	25:02	43	45.9
	-018	T	2 DAT	49:43	45	19.6
	-020	T	3 DAT	72:21	51	17.0
	-022	T	5 DAT	-	52	10 (8.18)
	-024	T	7 DAT	-	52	< 10 (6.80)
	-026	T	9 DAT	-	58	< 10 (7.32)
	-028	T	12 DAT	-	65	<LOD
	-030	T	14 DAT	-	69	<LOD
	-042	T	0 DAT	01:05	43	84.2
	-044	T	5 hours after application	05:15	43	57.2
	-046	T	1 DAT	25:13	43	47.6
	-048	T	2 DAT	49:52	45	<LOD
	-050	T	3 DAT	72:27	51	14.1
	-052	T	5 DAT	-	52	10.0
	-054	T	7 DAT	-	52	< 10 (5.66)
	-056	T	9 DAT	-	58	< 10 (5.73)
	-058	T	12 DAT	-	65	<LOD
	-060	T	14 DAT	-	69	< 10 (3.39)
	-072	T	0 DAT	01:10	43	54.9
	-074	T	5 hours after application	05:26	43	48.0
	-076	T	1 DAT	25:24	43	48.2
	-078	T	2 DAT	50:00	45	21.0
	-080	T	3 DAT	72:32	51	16.2
	-082	T	5 DAT	-	52	< 10 (6.26)
	-084	T	7 DAT	-	52	< 10 (6.10)
	-086	T	9 DAT	-	58	< 10 (4.12)
	-088	T	12 DAT	-	65	<LOD
	-090	T	14 DAT	-	69	<LOD

DAT = Days after treatment, 0 DAT = directly after treatment when the spray had dried

The analytical results of treated samples, corrected for field spikes recoveries, are summarised below. Only results that have been corrected are shown. The results were corrected with the corresponding field spike recoveries when the mean of the three recoveries per level and trial was < 70%. Residues between >LOQ - ≤ 50 µg/L were corrected with the mean of the 10 µg/L fortification level, residues between >50 µg/L - ≤500 µg/L were corrected with the mean of the 100 µg/L fortification level and residues >500 µg/L would be corrected with the mean of the 1000 µg/L fortification level.

Table 7.1.2.2- 10: Residue summary on wheat leaf washings corrected for field spikes recoveries from Northern France for fluopyram

Trial No. / Country	Sample No. 20-00032-03	Plot	Sampling Timing	Growth stage [BBCH]	Fluopyram [µg/L]
20-00032-03 Northern France	-012	T	0 DAT	43	99.2
	-014	T	5 hours after application	43	121
	-042	T	0 DAT	43	122
	-044	T	5 hours after application	43	82.9
	-072	T	0 DAT	43	79.3
	-074	T	5 hours after application	43	64.4
	-076	T	3 DAT	43	64.7
	-078	T	2 DAT	45	28.1
	-080	T	3 DAT	51	21.7

DAT = Days after treatment, 0 DAT = directly after treatment when the spray had dried

B. DISCUSSION

No deviations occurred during the conduct of this study which had any negative impact on the quality of this study.

No residues above the LOQ were found in the control samples. The means of the concurrent recoveries were within the acceptable range of 70 – 110%. RSD values were below 20%.

The analytical results show that residues of fluopyram decline in washings from wheat leaves. The residues of fluopyram derived from the German trial 20-00032-01 were below the LOQ within 12 days after last application. The residues of fluopyram derived from the Danish trial 20-00032-02 and of the French trial 20-00032-03 were below the LOQ µg/L within 7 days after last application.

III. CONCLUSIONS

Altogether, the study results demonstrate that fluopyram residues in washings from wheat leaves decline within the test duration. From these data, a degradation half-life on leaf surfaces can be derived for fluopyram. The kinetic evaluation following current FOCUS guidance was conducted separately and is summarised under KCA 7.1.2.2/02 (M-761989-01-1).

3. Assessment and conclusion

Assessment and conclusion by applicant:
The study and its data are considered as valid and reliable for use in risk assessment.

Assessment and conclusion by RMS:
Outcome and conclusion of the study: RMS should indicate if they agree to the results and conclusions of the APPL.

1. Information on the study

Data Point:	KCA 7.1.2.2/02
Report Author:	[redacted]
Report Year:	2021
Report Title:	Fluopyram (FLU): - Kinetic evaluation of dislodgeable foliar residues in wheat after application of BIX+FLU+PTZ EC 65+65+130 excluding rain impact according to FOCUS kinetics using KinGUI 2.1
Report No:	EnSa-20-0876
Document No:	M-761989-01-1
Guideline(s) followed in study:	not applicable
Deviations from current test guideline:	Current Guideline: not applicable (kinetic evaluation)
Previous evaluation:	No, not previously submitted
GLP/Officially recognised testing facilities:	No, not conducted under GLP/Officially recognised testing facilities
Acceptability/Reliability:	Yes

The experimental study is summarised and discussed under KCA 7.1.2.2/01 (M-758592-01-1). The kinetic evaluation following current FOCUS guidance was conducted separately and is summarised below.

2. Full summary of KCA 7.1.2.2/02

Executive Summary

The dislodgeable foliar residue data of fluopyram (FLU), obtained on spring wheat under protected conditions, was evaluated to derive kinetic parameters suitable for an environmental risk assessment, following the recommendations given by FOCUS Kinetics.

The dislodgeable foliar dissipation $DisT_{50}$ values for fluopyram were between 1.403 and 3.892 days in the tested trials.

I. METHODS

A kinetic modelling analysis of European dislodgeable foliar residues (DFR) study data under protected conditions of fluopyram (FLU) was conducted in order to derive kinetic parameters suitable for an environmental risk assessment, using the software tool KinGUI 2.1. The identification of the appropriate kinetic model followed the recommendations given by FOCUS Kinetics (FOCUS, 2006, 2014a) based on a detailed statistical analysis including visual assessment, χ^2 statistic, significance t-test and correlation analysis. In an environmental context, dislodgeable foliar residues studies on leaf surfaces, which are not impacted by precipitation events, are used to describe the dissipation or decline behaviour of the washable substance amount on leaf surfaces. Such washable amounts may be available for washoff during rain events in the field. Here evaluated foliar DT_{50} values of washable amounts can be used to describe the washoff effects correctly, for modelling purpose.

The modelling analysis is based on European dislodgeable foliar residues on spring wheat under protected conditions in a polytunnel at field and after spray application of BIX+FLU+PTZ EC 65+65+130A G (KCA 7.1.2.2/01, M-758592-01-1). The polytunnels prevented washoff by rain and irrigation (drip), they guaranteed a light transmission of at least 80 %. The tunnels were left open at both ends to allow wind and climate exchange, to keep conditions very close to field conditions.

Three trials took place applying in June 2020 at BBCH growth stages of 41 - 45. The leaf area was analysed during study duration and stayed almost constant, without any significant dependency on BBCH stages. Washable residues were reported in µg/L dislodging solution.

Concentrations of the metabolites of fluopyram were not analysed. It was assumed the parent directly degraded into sink.

II. RESULTS

Degradation of fluopyram

Results of the kinetic evaluation for modelling endpoints based on foliar residue data from dislodgeable foliar residues (DFR) under protected conditions (tunnel) at European fields are summarised in the tables below.

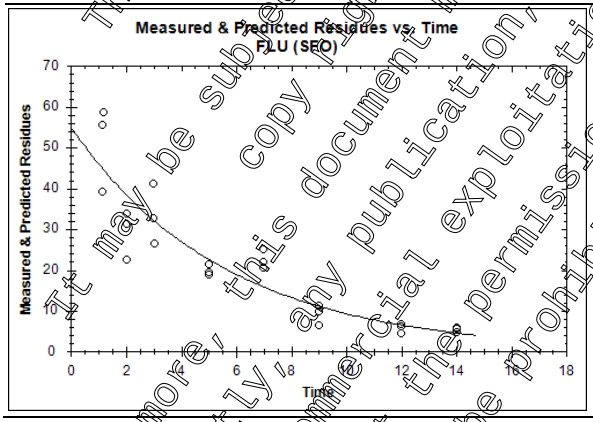
Table 7.1.2.2- 11: Fluopyram: kinetic and statistical results of dissipation of dislodgeable foliar residues on spring wheat at site Germany for modelling endpoints

Kinetic model	DT_{50} actual	DT_{90} actual	DT_{50} fast / slow	VA	χ^2err / SWARC	k_1	k_2	g	t-test k_1 / k_2	95th CI of k_1	95th CI of k_2
	(d)	(d)	(d)		(% / -)	(1/d)	(1/d)	(-)	(-)	(1/d)	(1/d)
SFO	**3.892**	12.93	-	+	21.8 / 6.20	0.1781	-	-	<0.001	0.12944 to 0.227	-
DFOP	0.1387	0.4714	0.1369 / 4.871	+	19.6 / 19.1	5.064	0.1423	0.9904	<0.001 / <0.001	4.4140 to 5.715	0.09321 to 0.191

VA = visual assessment, + = good, o = acceptable, - = poor
SWARC = Scaled Weighted Area under Residue Curve
CI = confidence interval

Modelling Endpoints: SFO fit is statistically and visually good (χ^2err, t-test <0.05), SWARC value is < 40, not indicating a biphasic decline. χ^2err is > 15 %, but < 25%, mainly reflecting the scattering data, deviating on both sides of the dissipation curve (Implausible residues < LOQ before day 1 were ignored for the fit). Consequently, **SFO** degradation model is appropriate for modelling endpoints.

SFO



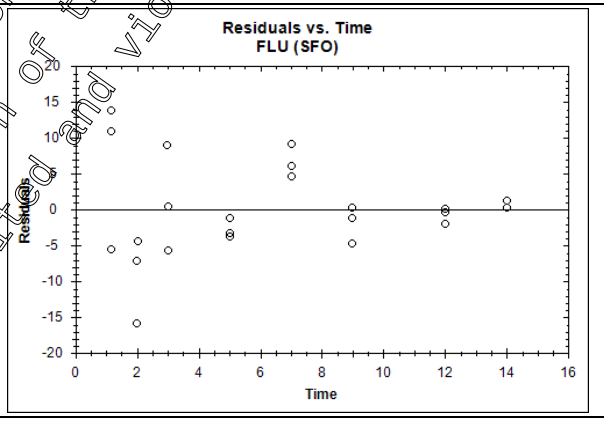


Table 7.1.2.2- 12: Fluopyram: kinetic and statistical results of dislodgeable foliar residues on spring wheat at site Denmark for modelling endpoints

Kinetic model	DT_{50} actual	DT_{90} actual	DT_{50} fast / slow	VA	χ^2err / SWARC	k_1	k_2	g	t-test k_1 / k_2	95th CI of k_1	95th CI of k_2
	(d)	(d)	(d)		(% / -)	(1/d)	(1/d)	(-)	(-)	(1/d)	(1/d)
SFO	**1.751**	5.815	-	+	8.22 / 9.73	0.39596	-	-	<0.001	0.32765 to 0.464	-
DFOP	0.4961	4.793	0.0115 / 1.850	+	7.78 / 9.15	60.37	0.3746	0.3979	0.5 / <0.001	-66720 to 66730	0.2553 to 0.494

VA = visual assessment, + = good, o = acceptable, - = poor
SWARC = Scaled Weighted Area under Residue Curve
CI = confidence intervall

Modelling Endpoints: SFO fit is statistically and visually good (χ^2err <15%, t-test <0.05). SWARC value is < 40, not indicating a biphasic decline. Consequently, **SFO** degradation model is appropriate for modelling endpoints.

SFO

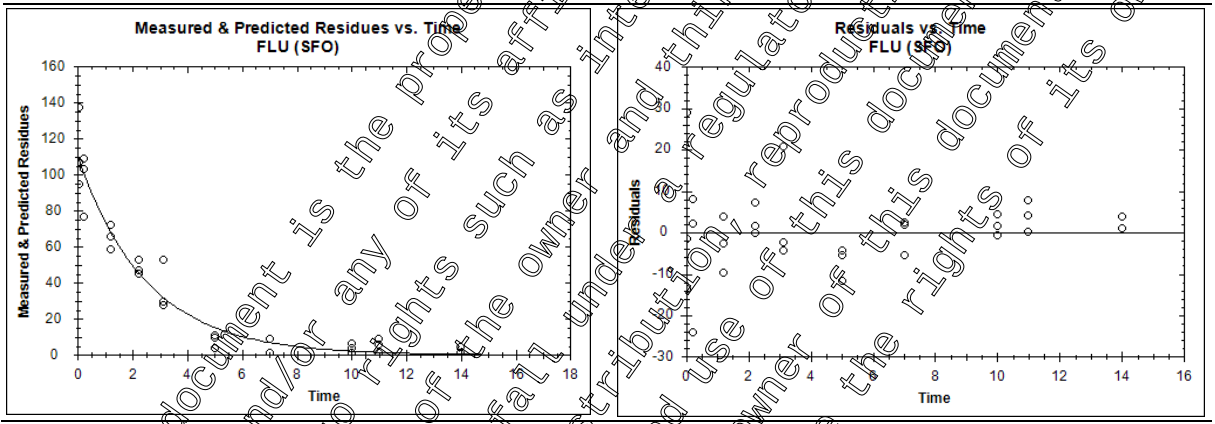


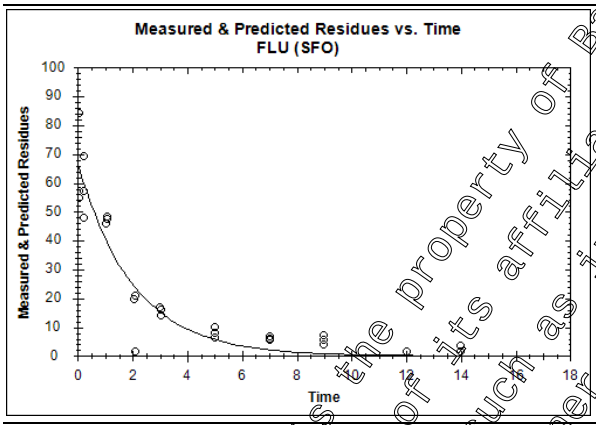
Table 7.1.2.2- 13: Fluopyram: kinetic and statistical results of dislodgeable foliar residues on spring wheat at site Northern France for modelling endpoints

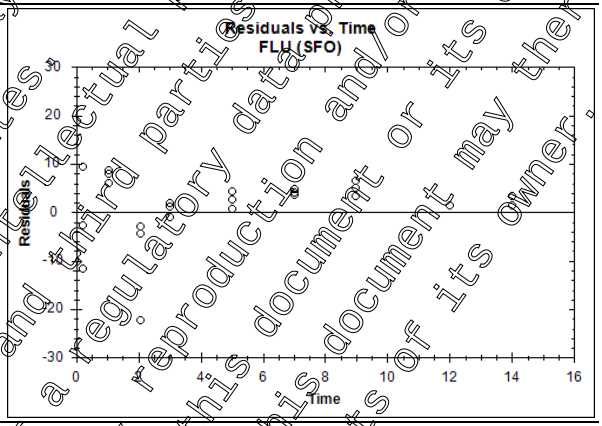
Kinetic model	DT_{50} actual	DT_{90} actual	DT_{50} fast / slow	VA	χ^2err / SWARC	k_1	k_2	g / tb	t-test k_1 / k_2	95th CI of k_1	95th CI of k_2
	(d)	(d)	(d)		(% / -)	(1/d)	(1/d)	(-)	(-)	(1/d)	(1/d)
SFO	**1.403**	4.661	-	o	20.1 / 63.3	0.49396	-	-	<0.001	0.37553 to 0.612	-
DFOP	1.289	5.381	1.146 / 4.85	+	21.1 / 8.95	0.60513	0.05848	0.9111	0.005 / 0.408	0.17568 to 1.035	- 0.42737 to 0.544
HS	1.253	6.700	1.253; 3.223; 2018 P)	+	20.9 / 0.764	0.55334	0.21507	2.547	<0.001 / 0.031	0.38533 to 0.721	- 0.00055 to 0.431

VA = visual assessment, + = good, o = acceptable, - = poor
SWARC = Scaled Weighted Area under Residue Curve
CI = confidence intervall
P) = pseudo SFO DT50 = DT90 / 3.32

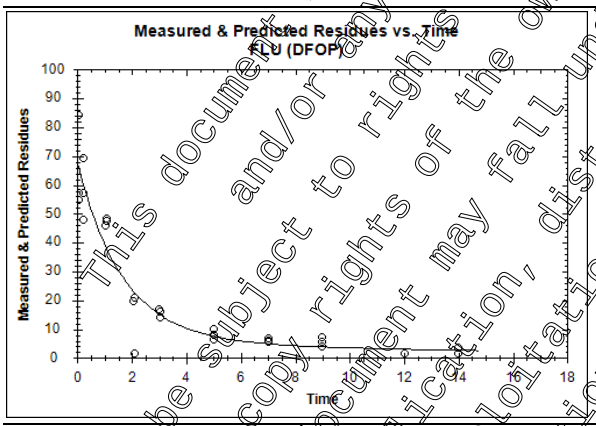
Modelling Endpoints: SFO fit is statistically and visually still acceptable (χ^2err <25%, t-test <0.05). SWARC value is > 40, indicating a biphasic decline. Therefore, biphasic fits were tested. For DFOP fit, t-test of k_2 fails and ratio of DFOP DT_{90}/DT_{50} (5.38 d / 1.29 d) is 4.2 (< 5), showing that the behaviour is not sufficiently biphasic. Thus, DFOP is not suitable. HS is statistically and visually good. But χ^2err could not be improved with biphasic fits.
Moreover, residues are < 10 % of M0 (SFO M0: 66.8 µg/L) already before day 7 and are low at study end (3.2 % of M0). Overall, 90 % of the residues are described sufficiently well with SFO, the dissipation is not very significantly biphasic, the weight of evidence supports SFO dissipation in other trials, and a biphasic behaviour for foliar DT_{50} is not straight forward to use in several predictive models. Consequently, **SFO** degradation model is considered appropriate for modelling endpoints.

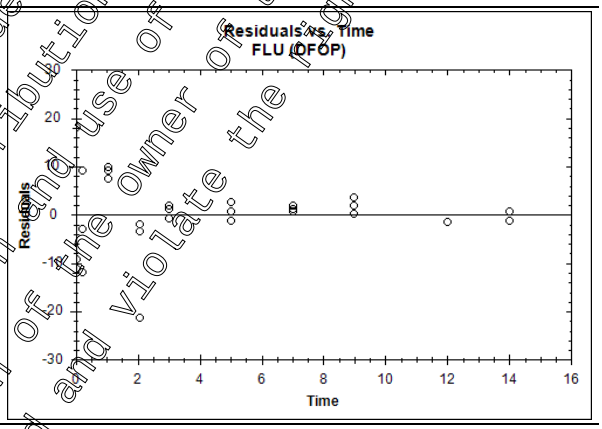
SFO



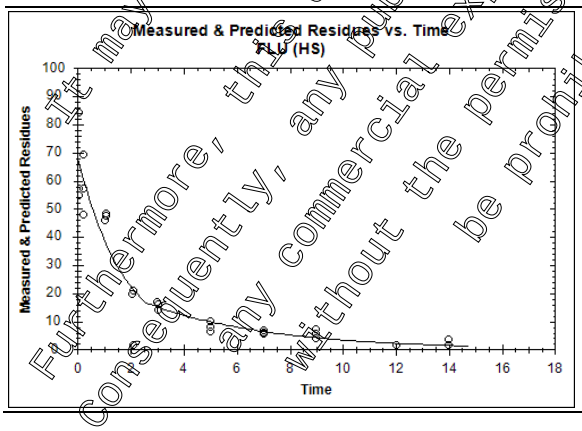


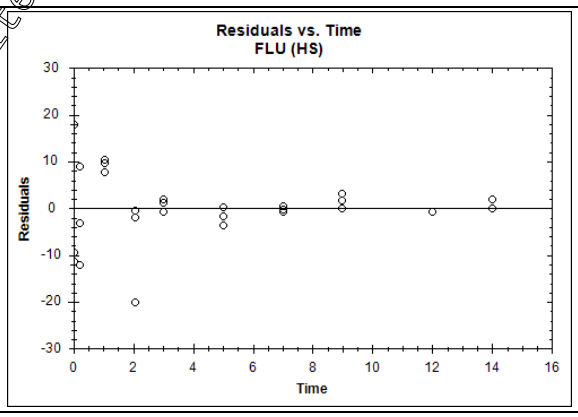
DFOP





HS





III. CONCLUSIONS

The dislodgeable foliar $DisT_{50}$ parameters of fluopyram for modelling purpose based on foliar residue data from dislodgeable foliar residues (DFR) under protected conditions (tunnel) at European fields are summarised in the tables below.

Table 7.1.2.2- 14: Dislodgeable foliar $DisT_{50}$ parameters of fluopyram on spring wheat (product BIX+FLU+PTZ EC 65+65+130A G), modelling purpose

Fluopyram (FLU)	Dislodgeable foliar dissipation, excluding rain impact on spring wheat, product BIX+FLU+PTZ EC 65+65+130A G								
Trial [1]	EU zone	Kinetic model	Kinetic parameters	χ^2 err (%)	Prob > t	$DT_{50\ actual}$ (d)	$DT_{90\ actual}$ (d)	$DT_{50\ fast}$ (d)	$DT_{50\ slow}$ (d)
Germany, Emstek	N	SFO	k: 0.1781 1/d	21.8	k: <0.001	3.892	12.93	-	-
Denmark, Rødlum	N	SFO	k: 0.39596 1/d	8.22	k: <0.001	1.751	5.815	-	-
Northern France, Auménancourt	N	SFO	k: 0.49396 1/d	20.1	k: <0.001	1.403	4.661	-	-
Geometric mean (n=3)						**2.122**			

[1] M-758592-01-1

3. Assessment and conclusion

Assessment and conclusion by applicant:
The kinetic evaluation followed FOCUS guidances and is considered valid and reliable.

Assessment and conclusion by RMS:
Outcome and conclusion of the study: RMS should indicate if they agree to the results and conclusions of the APPL.

CA 7.1.2.2.1 Soil dissipation studies

1. Information on the study

Data Point:	KCA 7.1.2.2.1/01
Report Author:	[redacted]
Report Year:	2007
Report Title:	Determination of the residues of AE C656948 in/on soil after spraying of AE C656948 (250 SC) in the field in Germany, United Kingdom, Sweden, France, Spain and Italy
Report No:	RA-2052/05
Document No:	M-293999-01-1
Guideline(s) followed in study:	Commission Directive 95/36/EC amending Council Directive 91/414/EEC (Annexes I and II, Fate and Behaviour in the Environment), July 14, 1995; SETAC Procedures for Assessing the Environmental Fate and Ecotoxicity of Pesticides (1995); BBA guideline, part IV, 4-1, Fate and Behavior of Plant Protection Compounds in Soil (1986); ECPA Guidance Document on Field Soil Dissipation Studies (1997)
Deviations from current test guideline:	Current Guideline: Guidance Document for Conducting Pesticide Terrestrial Field Dissipation Studies (2015) None
Previous evaluation:	yes, evaluated and accepted DAR (2011)
GLP/Officially recognised testing facilities:	Yes, conducted under GLP/Officially recognised testing facilities
Acceptability/Reliability:	Yes

2. Full summary of KCA 7.1.2.2.1/01

Executive Summary

Soil dissipation of fluopyram under European field conditions was investigated after application of fluopyram 250 SC at six sites carried out on bare soil plots in Burscheid (Germany), Little Shelford (United Kingdom), Staffanstorp (Sweden), Vatteville (Northern France), Vilobi d'Onyar (Spain) and on grass in Albaro (Italy). The sites are located in the ecoregions Northern and Southern Europe.

Fluopyram 250 SC was sprayed once pre-emergence onto the soil at 1.0 L/ha, corresponding to 250 g a.i./ha. Soil samples were taken 0 to 740 days post-application to a maximum depth of 50 cm and analysed for fluopyram.
Soil samples of 20 g were extracted in a microwave extractor with 40 mL of a mixture of water/acetonitrile (1/4, v/v). After extraction, subsamples of the extracts were centrifuged to remove fine particles of the soil. Identification and quantitation of the analyte was done by high performance liquid chromatography using MS/MS detection in the Multiple Reaction Monitoring mode. Possible matrix effects were eliminated by using an internal standard solution of isotopically labelled reference item. This solution was added to the sample solutions after extraction. The LOQ of the method was 5 µg/kg. The LOD of the method was 1.5 µg/kg for fluopyram.

The amount of fluopyram decreased from DAT-0 to study end (DAT-726) from 230 to 40.1 g/ha at Burscheid (Germany), from DAT-0 to DAT-740 from 266 to 62.4 g/ha at Little Shelford (UK), from DAT-0 to DAT-730 from 277 to 65.4 g/ha at Staffanstorp (Sweden), from DAT-0 to DAT-734 from 213 to 66.1 g/ha at Vatteville (France), from DAT-0 to DAT-729 from 230 to 7.99 g/ha at Vilobi d'Onyar (Spain) and from DAT-0 to DAT-731 from 209 to 16.2 g/ha at Albaro (Italy).

Quantifiable residues of fluopyram were detected to a maximum depth of 20 cm. Only in the trial R 2005 0333/4 (Italy) slight amounts of fluopyram (between LOD and LOQ) were detected at a single

sampling event in the 20-30 cm soil layer. At study completion fluopyram residues in soil corresponded to 3.2% to 26.5% of the applied amount.

I. MATERIALS AND METHODS

A. MATERIALS

1. Test Item

Chemical Name	Fluopyram
Type of Formulation	250 SC (Suspension concentrate)
Batch Number	OP250119
Content of active substance	250 g/L

2. Test Sites

The sites selected were typical for uses of fluopyram. The sites were neither subjected to erosion, flooding nor run-off. The test plots were nearly flat and not very stony. The identification, its locations and site details are presented in the table below

Table 7.1.2.2.1- 1: Geographic location, site description and climatic data at the study sites

Trial No.	R 2005 0326/1		R 2005 0328/8	
Designation	Burscheid, Germany, VG08, Plot 4011, (Hoefchen)		Little Shelford, United Kingdom, ENG2, Block 3/1	
Country	Germany		United Kingdom	
Ecoregion	Northern EU		Northern EU	
Plot Size (qm²)	225		370	
Site History	2002 Grass 2003 Grass 2004 Grass no pesticide use		unknown	
Distance from weather station used for climatic measurements	0 km		0.5 km (sunshine hours 30 km)	
Meteorological conditions compared to long-term average within normal levels (Yes/No)	Yes In 2006 wet May and dry and hot July; dry and hot April in 2007 compared to the long-term average		Yes In 2006 hot summer/autumn. In 2005 dry summer/autumn, in 2007 wet spring except for dry April compared to the long-term average. Strong variations in rainfalls compared to the long-term average.	
Other details, if any	-			
Depth compartment (cm) [1]	0 – 30	30 – 50	0 – 30	30 – 50
Surface soil texture (USDA)	Silt loam	Loam	Sandy loam	Sandy loam
Sand (%)	14.8	33.2	64.2	60.0
Silt (%)	65.3	46.5	20.8	25.1
Clay (%)	19.9	20.3	15.0	14.9
pH (water)	6.9	7.1	8.1	8.6
pH ($CaCl_2$)	6.2	6.2	7.3	7.6
CEC (meq/100g)	11.3	11.8	16.4	14.0
Chalk (% carbon)	<0.1	<0.1	11.0	18.5
Organic carbon (%)	1.07	0.31	1.08	0.49
Bulk density (g/cm³) [2]	1.29	1.31	1.26	1.29
WHC max (g/100 g)	43.3	37.1	43.4	38.2
WHC pF 2 (vol%)	42.8	36.6	24.8	24.2
Initial soil moisture (g/100g)	17.8	n.a.	11.9	n.a.

[1] Analysis of soil segments 50-75 cm and 75-100 not applicable; n.a. = not analysed

[2] Values taken from DAR, 2011

Trial No.	R 2005 0329/6		R 2005 0331/8	
Designation	Staffanstorp, Sweden, SWD2, Plot T		Vatteville, France, FR28, Plot Les Fossettes	
Country	Sweden		France	
Ecoregion	Northern EU		Northern EU	
Plot Size (qm²)	520		360	
Site History	2002 Cabbage 2003 Spring barley 2004 Winter wheat 14 pesticides reported		2000 Winter Wheat 2001 Winter rape 2002 Winter Wheat 2003 Maize 2004 Winter Wheat 42 pesticides reported	
Distance from weather station used for climatic measurements	3 km		0.3 km (sunshine and temperature 15 km)	
Meteorological conditions compared to long-term average within normal levels (Yes/No)	No In 2006 dry and hot July and warm winter 2006/2007; compared to the long-term average. Partly strong variations in rainfalls compared to the long-term average. Especially April/September 2005 and July 2006 dry and August/October 2006 wet compared to the long-term average.		Yes In autumn 2005 rainfalls showed strong variations compared to the long-term average. In 2006 hot July in 2007 hot and dry April compared to the long-term average.	
Other details, if any	-		-	
Depth compartment (cm) [1]	0 – 30	30 – 50	0 – 30	30 – 50
Surface soil texture (USDA)	Loam	Loam	Silt loam	Silt loam
Sand (%)	51.1	43.0	18.5	15.1
Silt (%)	29.5	36.2	69.6	65.0
Clay (%)	19.4	20.8	11.9	19.9
pH (water)	8.1	8.6	7.3	7.4
pH ($CaCl_2$)	7.3	7.4	6.6	6.6
CEC (meq/100g)	18.0	18.6	6.9	9.9
Chalk (% carbon)	1.3	1.4	< 0.1	<0.1
Organic carbon (%)	1.38	0.77	0.79	0.37
Bulk density (g/cm³) [2]	1.27	1.26	1.28	1.30
WHC max (g/100 g)	41.6	38.7	41.7	36.3
WHC pF 2 (vol%)	30.0	31.0	38.4	37.3
Initial soil moisture (g/100 g)	13.2	n.a.	14.8	n.a.

[1] Analysis about soil segments 50-75 cm and 75-100 not applicable, n.a. = not analysed

[2] Values taken from DAR 2011

Trial No.	R 2005 0332/6		R 2005 0333/4	
Designation	Vilobi d'Onyar, Spain, SPA1, Plot Poligono 8 Parcela 54		Albaro, Italy, IT09, Plot Marcomcini	
Country	Spain		Italy	
Ecoregion	Southern EU		Southern EU	
Plot Size (qm²)	360		816	
Site History	2000 Corn, ryegrass 2002 Sorghum, wheat 2003 fallow 2004 Ryegrass 2005 Ryegrass 3 pesticides reported		2002 Soil 2003 Soil 2004 Soil 1 pesticide reported	
Distance from weather station used for climatic measurements	1 km (global radiation 11 km)		0.15 km (global radiation 10 km)	
Meteorological conditions compared to long-term average within normal levels (Yes/No)	No In general rainfalls showed strong variations compared to the long-term average.		No In general rainfalls showed strong variations compared to the long-term average.	
Other details, if any			-	
Depth compartment (cm) [1]	0 – 30	30 – 50	0 – 30	30 – 50
Surface soil texture (USDA)	Loam	Loam	Silt loam	Silt loam
Sand (%)	47.4	41.1	22.0	18.1
Silt (%)	37.8	33.6	53.5	54.8
Clay (%)	14.8	25.3	24.5	27.1
pH (water)	6.7	7.3	8.2	8.3
pH ($CaCl_2$)	6.1	6.5	7.4	7.5
CEC (meg/100g)	7.4	10.6	19.1	20.9
Chalk (% carbon)	< 0.1	< 0.1	13.0	13.4
Organic carbon (%)	0.68	0.26	1.21	1.11
Bulk density (g/cm³) [2]	1.28	1.27	1.65	1.16
WHC max (g/100 g)	36.2	35.8	49.7	50.8
WHC pF 2 (vol%)	26.3	27.8	40.1	44.1
Initial soil moisture (g/100g)	10.2	n.a.	14.9	n.a.

[1] Analysis about soil segments 50-75 cm and 75-100 not applicable, n.a. = not analysed
[2] Values taken from DAR, 2011

The soil cultivation and the agronomic and maintenance activities on the trial plots were conducted according to the usual local agricultural practice and had no influence on the conduct or results of these trials. Before application, the soil was prepared to have a fine crumb structure.

B. STUDY DESIGN

1. Experimental Conditions

Fluopyram 250 SC was sprayed once with a nominal application rate of 1.0 L product/ha and a nominal water rate of 300 L/ha, corresponding to 250 g fluopyram per hectare. The control plots were located 5 m to 14 m distance from the treated plots. The product was applied on bare soil after sowing of grass except for trial R 2005 0333/4 (Albaro) where grass was sown 10 days after application. Details of the application equipment are given in the Table below.

Table 7.1.2.2.1- 2: Data on the application equipment

Trial No.	Device	Nozzle Type	Working Width (m)	No. of Nozzles	Pressure (bar)
Burscheid, Germany R 2005 0326/1	Knapsack-sprayer / spraying boom	Lumark 03	1.5	3	2.0
Little Shelford, United Kingdom R 2005 0328/8	Knapsack sprayer / spraying boom	Lumark Flat Fan	2.5	5	2.1
Staffanstorp, Sweden R 2005 0329/6	Knapsack-sprayer / spraying boom	Teejet Flat	3.2	8	3.0
Vatteville, France R 2005 0331/8	Knapsack-sprayer / spraying boom	Teejet XR8001VS	2	8	2.0
Vilobi d'Onyar, Spain R 2005 0332/6	Knapsack sprayer / spraying boom	Teejet 11002	2	4	2.4
Albaro, Italy R 2005 0333/4	Knapsack-sprayer / spraying boom	Teejet 03-XR	4	8	2.0

2. Sampling and sample processing

A treated and an untreated plot were used for each test site. First samples immediately after application were taken to a depth of 10 cm with a soil piercer (Ø 50 mm). All subsequent samplings were performed with a "Wacker Hammer" (Ø 48-49.5 mm) and taken to a maximum depth of 50 cm. All treated samples at day 0 consisted of 20 control samples of 10 or 20 soil cores and were taken randomly over the area to obtain representative samples. The samples were taken on the following occasions: 0 (post-application; each 0-10 cm), 12-15, 25-28, 55-58, 100-107, 146-168, 201-223, 266-273, 363-377, 479-485, 592-613 and 651-740 days (each 0-50 cm) after treatment. From the control plot, samples were taken on the following occasions: 0 days before application (in case of trial R 2005 0328/8 after application) 363-371 and 651-740 days after application.

The samples were deep-frozen within 24 hours and stored at - 18 °C or below until preparation (time period of 18 – 409 days between deep freezing and last extraction). The deep-frozen samples were cut into 10 cm segments, the cores for each depth segment were combined and milled in a hammer mill and carefully homogenized. At the time when writing the study report a storage stability study was in progress to determine the effect of frozen storage on residues of fluopyram. The test item was confirmed to be stable through 10 months of frozen storage (see KCA 7.1.2.2.1/12, M-348402-01-1). No fluopyram could be detected in the control samples (< LOD).

In addition, for soil characterisation samples were taken on day -19, -3, 6, 13, 15 and 146 after application from the treated plots to a depth of 50 cm.

The sampling spots were distributed randomly over the plots to obtain representative samples. Prior to packaging, each sample was labelled to allow clear identification.

3. Irrigation and weather data

Air temperature, precipitation including irrigation, and sunshine data were recorded from weather stations located at each of the test sites. Air temperature, precipitation including irrigation, and sunshine data were recorded during the field tests. The recordings demonstrate that the temperatures represent typical conditions for the trial sites in Spain (R 2005 0332/6) and Italy (R 2005 0333/4) for the years 2005 to 2007 compared to the long-term average. For the test sites in Northern Europe (Germany, United Kingdom, Sweden and France) July 2006 was very hot with regard to the long-term average. In trial R 2005 0328/8 (United Kingdom) also June 2006 was very hot compared to the long-term average. In trial R 2005 0329/6 (Sweden) the January 2007 was milder than the long-term average. The overall

precipitation was normal in trial R 2005 0326/1 (Germany, Burscheid) except for April 2007 which was dry. At the test site in the United Kingdom (R 2005 0328/8) precipitation was below the average in 2006 and 2007. At the test site in Sweden and at the test sites in Southern Europe (Spain, R 2005 0332/6 and Italy, R 2005 0333/4) rainfalls showed strong variations compared to the long-term average. Seasonal deviations from the average precipitation values were observed in either direction, wet or dry. The rainfall at the test site in France (R 2005 0331/8) was normal compared to the long-term average.

4. Description of analytical procedure

The analytical method for fluopyram is BCS Method No. 00973 (see M-265498-01-1). The method was validated with a silt loam soil (Hoefchen) and a sandy loam soil (Laacher Hof). The mass spectrometric detector showed linear correlation between concentration and peak area ratio in the range of about 1.0 to 120 µg/L with a correlation coefficient of 0.99985 (1/x weighted). The overall mean recovery of the method was 101% for fluopyram with a relative standard deviation (RSD) of 2.2%. The LOQ of the method was 5 µg/kg. The LOD of the method was 1.5 µg/kg for fluopyram. The blank values in all control samples were below the LOD.

Soil samples of 20 g were extracted in a microwave extractor with 40 mL of a mixture of water/acetonitrile (1/4, v/v). After extraction, subsamples of the extracts were centrifuged to remove fine particles of the soil. Identification and quantitation of the analyte was done by high performance liquid chromatography using MS/MS detection in the Multiple Reaction Monitoring mode. Possible matrix effects were eliminated by using an internal standard solution of isotopically labelled reference item. This solution was added to the sample solutions after extraction.

Full details and acceptable validation data to support the analytical method are presented within document M-CA 4, which comply with the EU regulatory requirements outlined within SANTE/2020/12830, Rev.1.

II. RESULTS AND DISCUSSION

A. DATA

The measured initial mean concentrations (n = 4) of fluopyram for the test sites were 230 g/ha (Burscheid, Germany), 266 g/ha (Little Shelford, United Kingdom), 277 g/ha (Staffanstorp, Sweden), 213 g/ha (Vatteville, France), 230 g/ha (Vilobi d'Onyar, Spain), and 209 g/ha (Albaro, Italy) representing 83.7% to 111% of the intended dose rate. These deviations appear to be acceptable since soil concentrations can vary considerably due to several uncertainties related to the first samplings after application

Table 7.1.2.2.1- 3: Residues of fluopyram (g/ha) in field soil samples

Burscheid (Germany) R 2005 0326/1			Little Shelford (UK) R 2005 0328/8			Staffanstorp (Sweden) R 2005 0329/6		
DAT [Days]	(g/ha)	(%)	DAT [Days]	(g/ha)	(%)	DAT [Days]	(g/ha)	(%)
0	230	91.9	0	266	106.0	0	277	111.0
12	181	72.3	13	251	101.0	15	184	73.7
25	187	75.0	27	196	78.4	28	191	76.2
56	172	69.0	55	160	63.9	56	184	73.5
104	128	51.0	102	164	65.7	100	158	63.3
151	102	40.9	146	125	50.1	153	125	49.8
201	86.9	34.8	211	146	58.2	210	126	50.3
266	74.9	30.0	270	117	46.8	272	114	45.5
363	75.7	30.3	365	95.4	38.2	365	104	41.7
481	53.0	21.2	481	98.9	39.6	485	68.6	27.5
592	35.4	14.2	613	69.1	27.6	601	72.0	28.8
726	40.1	16.0	740	62.4	25.0	730	65.4	26.1

DAT: days after treatment

Table 7.1.2.2.1- 4: Residues of fluopyram (g/ha) in field soil samples (continued)

Vatteville (France) R 2005 0331/8			Vilobi d'Onyar (Spain) R 2005 0332/6			Albaro (Italy) R 2005 0333/4		
DAT [Days]	(g/ha)	(%)	DAT [Days]	(g/ha)	(%)	DAT [Days]	(g/ha)	(%)
0	213	85.0	0	230	92.1	0	209	83.7
14	216	86.3	13	144	57.8	15	116	46.2
28	162	64.8	27	153	61.1	28	95.8	38.3
56	166	66.5	55	171	68.5	55	99.3	39.7
107	131	52.3	100	124	49.7	101	69.6	27.8
153	164	65.5	168	33.6	13.5	151	55.8	22.3
210	133	53.1	223	90.5	36.2	210	50.5	20.2
267	95.9	38.4	273	66.1	26.4	270	44.5	17.8
364	121	48.6	377	47.6	19.0	367	33.9	13.6
484	79.0	31.6	484	16.4	6.55	479	20.2	8.10
607	65.4	26.2	603	8.89	3.55	598	23.6	9.43
734	66.1	26.5	729	7.99	3.20	731	16.2	6.49

Table 7.1.2.2.1- 5: Residues of fluopyram (ng/kg) in field soil samples in Burscheid, Germany

		DAT [days]												
Depths, cm	**Rep**	**0 (T1)**	**0 (T2)**	**12**	**25**	**56**	**104**	**151**	**201**	**266**	**363**	**481**	**592**	**726**
0-10	1	190	186	138	130	112	79.6	62.0	52.6	45.2	50.6	34.8	21.6	27.6
	2	189	184	139	134	112	76.0	58.5	52.7	45.8	50.8	33.8	22.4	28.0
	Mean	***190***	***185***	***139***	***132***	***112***	***77.8***	***60.25***	***52.7***	***45.5***	***50.7***	***34.3***	***22.0***	***27.8***
10-20	1	N.A.	N.A.	LOD	LOD	LOD	LOD	LOD	LOD	LOD	3.03[1]	LOD	LOD	1.76[1]
	2	N.A.	N.A.	LOD	LOD	LOD	LOD	LOD	LOD	LOD	2.86[1]	LOD	LOD	LOD
	Mean	***N.C.***	***N.C.***	***LOD***	***LOD***	***LOD***	***LOD***	***LOD***	***LOD***	***LOD***	***2.95[1]***	***LOD***	***LOD***	***1.76[1]***
20-30	1	N.A.	N.A.	LOD	LOD	LOD	LOD	LOD	LOD	LOD	LOD	LOD	LOD	LOD
	2	N.A.	N.A.	LOD	LOD	LOD	LOD	LOD	LOD	LOD	LOD	LOD	LOD	LOD
	Mean	***N.C.***	***N.C.***	***LOD***	***LOD***	***LOD***	***LOD***	***LOD***	***LOD***	***LOD***	***LOD***	***LOD***	***LOD***	***LOD***
30-40	1	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	LOD	LOD	LOD	LOD	LOD	LOD	LOD
	2	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	LOD	LOD	LOD	LOD	LOD	LOD	LOD
	Mean	***N.C.***	***N.C.***	***N.C.***	***N.C.***	***N.C.***	***N.C.***	***LOD***	***LOD***	***LOD***	***LOD***	***LOD***	***LOD***	***LOD***
40-50	1	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	LOD	LOD	LOD	LOD	LOD	LOD	LOD
	2	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	LOD	LOD	LOD	LOD	LOD	LOD	LOD
	Mean	***N.C.***	***N.C.***	***N.C.***	***N.C.***	***N.C.***	***N.C.***	***LOD***	***LOD***	***LOD***	***LOD***	***LOD***	***LOD***	***LOD***
Total		***190***	***185***	***139***	***132***	***112***	***77.8***	***60.25***	***52.7***	***45.5***	***53.7***	***34.3***	***22.0***	***29.6***

N.D. = not detected, below method detection limit, N.A. = not analysed, DAT: Days after treatment
Values calculated in the summary are given in *italics*
[1] Value below LOQ, but higher than LOD

Table 7.1.2.2.1- 6: Residues of fluopyram (µg/kg) in field soil samples in Little Shelford, UK

		DAT [days]												
Depths, cm	**Rep**	**0 (T1)**	**0 (T2)**	**13**	**27**	**55**	**102**	**146**	**211**	**270**	**365**	**481**	**613**	**740**
0-10	1	207	208	153	116	124	107	86.6	93.1	77.5	69.3	63.3	42.2	40.7
	2	209	206	168	112	117	108	86.4	93.3	76.7	66.2	63.2	40.5	42.0
	Mean	***208***	***207***	***161***	***114***	***121***	***108***	***86.5***	***93.2***	***77.1***	***67.8***	***63.3***	***41.4***	***41.4***
10-20	1	N.A.	N.A.	8.01	4.64[1]	LOD	LOD	LOD	LOD	LOD	1.85[1]	2.50[1]	3.32[1]	LOD
	2	N.A.	N.A.	7.98	4.74[1]	LOD	LOD	LOD	LOD	LOD	1.78[1]	2.34[1]	3.28[1]	LOD
	Mean	***N.C.***	***N.C.***	***8.0***	***4.69[1]***	***LOD***	***LOD***	***LOD***	***LOD***	***LOD***	***1.82[1]***	***2.42[1]***	***3.30[1]***	***LOD***
20-30	1	N.A.	N.A.	LOD	LOD	LOD	LOD	LOD	LOD	LOD	LOD	LOD	LOD	LOD
	2	N.A.	N.A.	LOD	LOD	LOD	LOD	LOD	LOD	LOD	LOD	LOD	LOD	LOD
	Mean	***N.C.***	***N.C.***	***LOD***	***LOD***	***LOD***	***LOD***	***LOD***	***LOD***	***LOD***	***LOD***	***LOD***	***LOD***	***LOD***
30-40	1	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	LOD	LOD	LOD	LOD	LOD	LOD	LOD
	2	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	LOD	LOD	LOD	LOD	LOD	LOD	LOD
	Mean	***N.C.***	***N.C.***	***N.C.***	***N.C.***	***N.C.***	***N.C.***	***LOD***	***LOD***	***LOD***	***LOD***	***LOD***	***LOD***	***LOD***
40-50	1	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	LOD	LOD	LOD	LOD	LOD	LOD	LOD
	2	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	LOD	LOD	LOD	LOD	LOD	LOD	LOD
	Mean	***N.C.***	***N.C.***	***N.C.***	***N.C.***	***N.C.***	***N.C.***	***LOD***	***LOD***	***LOD***	***LOD***	***LOD***	***LOD***	***LOD***
Total		***208***	***207***	***169***	***118.7***	***121***	***108***	***86.5***	***93.2***	***77.1***	***69.0***	***65.7***	***44.7***	***41.4***

N.D. = not detected, below method detection limit, N.A. = not analysed, DAT: Days after treatment
Values calculated in the summary are given in *italics*
[1] Value below LOQ, but higher than LOD

Table 7.1.2.2.1- 7: Residues of fluopyram (µg/kg) in field soil samples in Staffanstrop, Sweden

		DAT [days]												
Depths, cm	**Rep**	**0 (T1)**	**0 (T2)**	**15**	**28**	**56**	**100**	**153**	**210**	**272**	**365**	**485**	**601**	**730**
0-10	1	204	202	130	116	106	105	83.2	76.1	89.3	67.5	41.3	41.0	34.7
	2	207	205	125	116	106	101	86.9	78.8	89.2	69.9	41.5	39.3	34.4
	Mean	***205.5***	***204***	***118***	***116***	***106***	***103***	***85.1***	***77.5***	***89.3***	***68.7***	***41.40***	***40.2***	***34.6***
10-20	1	N.A.	N.A.	1.96[1]	LOD	LOD	LOD	LOD	2.07[1]	10.6	3.72[1]	5.42	9.85	12.4
	2	N.A.	N.A.	LOD	1.89[1]	LOD	LOD	LOD	2.15[1]	11.0	3.51[1]	5.34	9.32	12.9
	Mean	***N.C.***	***N.C.***	***1.96[1]***	***1.89[1]***	***LOD***	***LOD***	***LOD***	***2.11[1]***	***10.8***	***3.62[1]***	***5.38***	***9.59***	***12.7***
20-30	1	N.A.	N.A.	LOD	LOD	LOD	LOD	LOD	LOD	LOD	LOD	LOD	LOD	LOD
	2	N.A.	N.A.	LOD	LOD	LOD	LOD	LOD	LOD	LOD	LOD	LOD	LOD	LOD
	Mean	***N.C.***	***N.C.***	***LOD***	***LOD***	***LOD***	***LOD***	***LOD***	***LOD***	***LOD***	***LOD***	***LOD***	***LOD***	***LOD***
30-40	1	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	LOD	LOD	LOD	LOD	LOD	LOD	LOD
	2	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	LOD	LOD	LOD	LOD	LOD	LOD	LOD
	Mean	***N.C.***	***N.C.***	***N.C.***	***N.C.***	***N.C.***	***N.C.***	***LOD***	***LOD***	***LOD***	***LOD***	***LOD***	***LOD***	***LOD***
40-50	1	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	LOD	LOD	LOD	LOD	LOD	LOD	LOD
	2	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	LOD	LOD	LOD	LOD	LOD	LOD	LOD
	Mean	***N.C.***	***N.C.***	***N.C.***	***N.C.***	***N.C.***	***N.C.***	***LOD***	***LOD***	***LOD***	***LOD***	***LOD***	***LOD***	***LOD***
Total		***205.5***	***204***	***314***	***117.9***	***106***	***103***	***85.1***	***79.6***	***100.1***	***72.3***	***46.8***	***49.8***	***47.3***

N.D.: not detected, below method detection limit, N.A.: not analysed, DAT: Days after treatment
Values calculated in the summary are given in *italics*
[1] Value below LOQ, but higher than LOD

Table 7.1.2.2.1- 8: Residues of fluopyram (µg/kg) in field soil samples in Vatteville, France

		DAT [days]												
Depths, cm	**Rep**	**0 (T1)**	**0 (T2)**	**14**	**28**	**56**	**107**	**153**	**210**	**267**	**364**	**484**	**607**	**734**
0-10	1	151	153	131	111	83.8	106	106	82.7	71.3	75.2	50.5	40.2	37.3
	2	158	153	117	102	82.4	100	104	85.6	68.2	74.9	49.8	40.2	36.6
	Mean	***155***	***153***	***124***	***107***	***83.1***	***103***	***105***	***84.2***	***69.8***	***74.1***	***50.15***	***40.20***	***36.90***
10-20	1	N.A.	N.A.	2.77[1]	LOD	LOD	LOD	LOD	LOD	3.42[1]	5.75	4.20[1]	4.71[1]	7.02
	2	N.A.	N.A.	2.76[1]	LOD	LOD	LOD	LOD	LOD	3.64[1]	5.89	4.19[1]	4.44[1]	7.05
	Mean	***N.C.***	***N.C.***	***2.77[1]***	***LOD***	***LOD***	***LOD***	***LOD***	***LOD***	***3.53[1]***	***5.82***	***4.20[1]***	***4.58[1]***	***7.04***
20-30	1	N.A.	N.A.	LOD	LOD	LOD	LOD	LOD	LOD	LOD	LOD	LOD	LOD	LOD
	2	N.A.	N.A.	LOD	LOD	LOD	LOD	LOD	LOD	LOD	LOD	LOD	LOD	LOD
	Mean	***N.C.***	***N.C.***	***LOD***	***LOD***	***LOD***	***LOD***	***LOD***	***LOD***	***LOD***	***LOD***	***LOD***	***LOD***	***LOD***
30-40	1	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	LOD	LOD	LOD	LOD	LOD	LOD	LOD
	2	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	LOD	LOD	LOD	LOD	LOD	LOD	LOD
	Mean	***N.C.***	***N.C.***	***N.C.***	***N.C.***	***N.C.***	***N.C.***	***LOD***	***LOD***	***LOD***	***LOD***	***LOD***	***LOD***	***LOD***
40-50	1	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	LOD	LOD	LOD	LOD	LOD	LOD	LOD
	2	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	LOD	LOD	LOD	LOD	LOD	LOD	LOD
	Mean	***N.C.***	***N.C.***	***N.C.***	***N.C.***	***N.C.***	***N.C.***	***LOD***	***LOD***	***LOD***	***LOD***	***LOD***	***LOD***	***LOD***
Total		***155***	***153***	***126.8***	***107***	***83.1***	***103***	***105***	***84.2***	***73.3***	***79.9***	***54.4***	***44.8***	***43.9***

N.D. = not detected, below method detection limit, N.A. = not analysed, DAT = Days after treatment
Values calculated in the summary are given in *italics*
[1] Value below LOQ, but higher than LOD

Table 7.1.2.2.1- 9: Residues of fluopyram (µg/kg) in field soil samples in Vilobí d'Onyar, Spain

		DAT [days]												
Depths, cm	**Rep**	**0 (T1)**	**0 (T2)**	**13**	**27**	**58**	**100**	**168**	**223**	**273**	**377**	**484**	**603**	**729**
0-10	1	166	161	85.4	91.7	94.3	74.4	33.8	45.2	33.2	22.7	8.61	5.13	[4.31]
	2	160	159	83.5	88.3	95.2	71.2	32.8	45.2	33.9	22.5	8.72	5.18	[4.28]
	Mean	***163***	***160***	***84.5***	***90.0***	***94.8***	***72.8***	***33.3***	***45.2***	***33.6***	***22.6***	***8.67***	***5.16***	***4.30***
10-20	1	N.A.	N.A.	LOD	LOD	LOD	1.84[1]	LOD	3.66[1]	4.86[1]	4.49[1]	1.71[1]	LOD	LOD
	2	N.A.	N.A.	LOD	LOD	LOD	1.95[1]	LOD	4.04[1]	4.38[1]	4.50[1]	1.76[1]	LOD	LOD
	Mean	***N.C.***	***N.C.***	***LOD***	***LOD***	***LOD***	***1.90[1]***	***LOD***	***3.85[1]***	***4.62[1]***	***4.50[1]***	***1.74[1]***	***LOD***	***LOD***
20-30	1	N.A.	N.A.	LOD	LOD	LOD	LOD	LOD	LOD	LOD	LOD	LOD	LOD	LOD
	2	N.A.	N.A.	LOD	LOD	LOD	LOD	LOD	LOD	LOD	LOD	LOD	LOD	LOD
	Mean	***N.C.***	***N.C.***	***LOD***	***LOD***	***LOD***	***LOD***	***LOD***	***LOD***	***LOD***	***LOD***	***LOD***	***LOD***	***LOD***
30-40	1	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	LOD	LOD	LOD	LOD	LOD	LOD	LOD
	2	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	LOD	LOD	LOD	LOD	LOD	LOD	LOD
	Mean	***N.C.***	***N.C.***	***N.C.***	***N.C.***	***N.C.***	***N.C.***	***LOD***	***LOD***	***LOD***	***LOD***	***LOD***	***LOD***	***LOD***
40-50	1	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	LOD	LOD	LOD	LOD	LOD	LOD	LOD
	2	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	LOD	LOD	LOD	LOD	LOD	LOD	LOD
	Mean	***N.C.***	***N.C.***	***N.C.***	***N.C.***	***N.C.***	***N.C.***	***LOD***	***LOD***	***LOD***	***LOD***	***LOD***	***LOD***	***LOD***
Total		***163***	***160***	***84.5***	***90.0***	***94.8***	***74.7***	***33.3***	***83.7***	***38.2***	***27.1***	***10.41***	***5.16***	***4.30***

N.D.: not detected, below method detection limit, N.A.: not analysed, DAT: Days after treatment
Values calculated in the summary are given in *italics*
[1] Value below LOQ, but higher than LOD

Table 7.1.2.2.1- 10: Residues of fluopyram (µg/kg) in field soil samples in Albaro, Italy

		DAT [days]												
Depths, cm	**Rep**	**0 (T1)**	**0 (T2)**	**15**	**28**	**55**	**101**	**151**	**210**	**270**	**367**	**479**	**598**	**731**
0-10	1	175	169	79.7	66.3	63.6	43.0	39.9	37.5	28.6	21.9	14.3	19.1	8.87
	2	176	173	76.3	65.7	61.1	42.9	38.8	35.6	29.9	22.4	13.6	19.0	9.84
	Mean	***176***	***171***	***78***	***66.0***	***62.4***	***43.0***	***39.4***	***36.6***	***29.3***	***22.2***	***14.0***	***19.1***	***9.36***
10-20	1	N.A.	N.A.	LOD	LOD	LOD	2.53[1]	LOD	LOD	LOD	LOD	LOD	LOD	LOD
	2	N.A.	N.A.	LOD	LOD	LOD	2.57[1]	LOD	LOD	LOD	LOD	LOD	LOD	LOD
	Mean	***N.C.***	***N.C.***	***LOD***	***LOD***	***LOD***	***2.55[1]***	***LOD***	***LOD***	***LOD***	***LOD***	***LOD***	***LOD***	***LOD***
20-30	1	N.A.	N.A.	LOD	LOD	2.64[1]	LOD	LOD	LOD	LOD	LOD	LOD	LOD	LOD
	2	N.A.	N.A.	LOD	LOD	3.33[1]	LOD	LOD	LOD	LOD	LOD	LOD	LOD	LOD
	Mean	***N.C.***	***N.C.***	***LOD***	***LOD***	***2.99[1]***	***LOD***	***LOD***	***LOD***	***LOD***	***LOD***	***LOD***	***LOD***	***LOD***
30-40	1	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	LOD	LOD	LOD	LOD	LOD	LOD	LOD
	2	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	LOD	LOD	LOD	LOD	LOD	LOD	LOD
	Mean	***N.C.***	***N.C.***	***N.C.***	***N.C.***	***N.C.***	***N.C.***	***LOD***	***LOD***	***LOD***	***LOD***	***LOD***	***LOD***	***LOD***
40-50	1	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	LOD	LOD	LOD	LOD	LOD	LOD	LOD
	2	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	LOD	LOD	LOD	LOD	LOD	LOD	LOD
	Mean	***N.C.***	***N.C.***	***N.C.***	***N.C.***	***N.C.***	***N.C.***	***LOD***	***LOD***	***LOD***	***LOD***	***LOD***	***LOD***	***LOD***
Total		***176***	***171***	***78***	***66.0***	***65.4***	***45.6***	***39.4***	***36.6***	***29.3***	***22.2***	***14.0***	***19.1***	***9.36***

N.D. = not detected, below method detection limit, N.A. = not analysed, DAT = Days after treatment
Values calculated in the summary are given in *italics*
[1] Value below LOQ, but higher than LOD

B. RESIDUES

The amount of fluopyram decreased from DAT-0 to study end (DAT-726) from 230 to 40.1 g/ha at Burscheid (Germany), from DAT-0 to DAT-240 from 266 to 62.4 g/ha at Little Shelford (UK), from DAT- to DAT-730 from 277 to 65.4 g/ha at Staffanstorp (Sweden), from DAT-0 to DAT-734 from 213 to 66.1 g/ha at Vatteville (France), from DAT-0 to DAT-729 from 230 to 79.9 g/ha at Vilobi d'Onyar (Spain) and from DAT-0 to DAT-731 from 209 to 16.2 g/ha at Albaro (Italy).

In general, it should be kept in mind that the presented field dissipation study is a rate and not a metabolism study. The study design does not allow calculation of a mass balance. Potential degradation products of fluopyram were not examined in the study.

C. KINETIC ANALYSIS

New kinetic calculations based on more recent guidance are necessary, therefore the information included in this study is not considered relevant. Evaluation of the rate of degradation is reported under KCA 7.1.2.2.1/19 (M-561908-01-1).

III. CONCLUSIONS

Quantifiable residues were detected to a maximum depth of 20 cm. Only in trial R 2005 0333/4 (Italy) slight amounts of fluopyram (between LOD and LOQ) were detected at a single sampling event in the 20-30 cm soil layer. Distinctly degradation of fluopyram was observed during the study resulting in fluopyram residues in soil of 9.2% to 26.5% of the applied amount at study completion.

3. Assessment and conclusion

Assessment and conclusion by applicant:
The study is considered to be valid and reliable.

Assessment and conclusion by RMS:
Outcome and conclusion of the study: RMS should indicate if they agree to the results and conclusions of the APPL.

Data Point:	KCA 7.1.2.2.1/02
Report Author:	[redacted]
Report Year:	2008
Report Title:	Kinetic evaluation of field dissipation studies after application of fluopyram (AE C656948) in Europe according to FOCUS using KinGui
Report No:	MEF-07/448
Document No:	M-297583-01-1
Guideline(s) followed in study:	not applicable
Deviations from current test guideline:	Current Guideline: not applicable (see justification)
Previous evaluation:	yes, evaluated and accepted DAR (2011)
GLP/Officially recognised testing facilities:	No, not conducted under GLP/officially recognised testing facilities
Acceptability/Reliability:	No

The kinetic evaluation of the field dissipation study with fluopyram (AE C656948) in Europe was performed according to FOCUS kinetics (2006): Guidance Document on Estimating Persistence and Degradation Kinetics from Environmental Fate Studies on Pesticides in EU Registration, EC Document Reference Sanco/10058/2005 version 1.0. To address most recent guideline updates a new kinetic evaluation was preformed and therefore this evaluation is not considered in the current dossier. The new evaluation can be found under KCA 7.1.2.2.1/10 (M-761908-01-1).

1. Information on the studies

Data Point:	KCA 7.1.2.2.1/03
Report Author:	[redacted]
Report Year:	2008
Report Title:	Terrestrial field dissipation of AE C656948 in a Washington soil, 2006
Report No:	MEMP065
Document No:	M-306817-01-2
Guideline(s) followed in study:	PMRA Data Code No.: 8.3.2 OECD Data Point: IIA 7.3, IIA 7.3.1, IIA 7.3.2, IIA 7.3.3, IIIA 9.2.1, IIIA 9.2.2, IIIA 9.2.3 EPA Guideline No.: 164-1 Terrestrial Field Dissipation; US EPA OPPTS Guideline No. 835.6100
Deviations from current test guideline:	Current Guideline: Guidance Document for Conducting Pesticide Terrestrial Field Dissipation Studies (2010) None
Previous evaluation:	yes, evaluated and accepted DAR (2011)
GLP/Officially recognised testing facilities:	Yes, conducted under GLP/Officially recognised testing facilities
Acceptability/Reliability:	Yes

Data Point:	KCA 7.1.2.2.1/04
Report Author:	[redacted]
Report Year:	2008
Report Title:	Terrestrial field dissipation of AE C656948 in a New York soil, 2006
Report No:	MEGMP084
Document No:	M-306809-01-2
Guideline(s) followed in study:	PMRA Data Code No.: 8.3.2 OECD Data Point: IIA 7.3, IIA 7.3.1, IIA 7.3.2, IIA 7.3.3, IIIA 9.2, IIIA 9.2.2, IIIA 9.2.3 EPA Guideline No.: 164-1 Terrestrial Field Dissipation; US EPA OPPTS Guideline No. 835.6100
Deviations from current test guideline:	Current Guideline: Guidance Document for Conducting Pesticide Terrestrial Field Dissipation Studies (2016) None
Previous evaluation:	yes, evaluated and accepted DAR (2011)
GLP/Officially recognised testing facilities:	Yes, conducted under GLP/Officially recognised testing facilities
Acceptability/Reliability:	Yes

Data Point:	KCA 7.1.2.2.1/05
Report Author:	[redacted]
Report Year:	2008
Report Title:	Terrestrial field dissipation of AE C656948 in a North Dakota soil, 2006
Report No:	MEGMP085
Document No:	M-306812-01-2
Guideline(s) followed in study:	PMRA Data Code No.: 8.3.2 OECD Data Point: IIA 7.3, IIA 7.3.1, IIA 7.3.2, IIA 7.3.3, IIIA 9.2.1, IIIA 9.2.2, IIIA 9.2.3 EPA Guideline No.: 164-1 Terrestrial Field Dissipation; US EPA OPPTS Guideline No. 835.6100
Deviations from current test guideline:	Current Guideline: Guidance Document for Conducting Pesticide Terrestrial Field Dissipation Studies (2016) None
Previous evaluation:	yes, evaluated and accepted DAR (2011)
GLP/Officially recognised testing facilities:	Yes, conducted under GLP/Officially recognised testing facilities
Acceptability/Reliability:	Yes

Data Point:	KCA 7.1.2.2.1/06
Report Author:	[redacted]
Report Year:	2008
Report Title:	Terrestrial field dissipation of AE C656948 in a Georgia soil, 2006
Report No:	MEGMP086
Document No:	M-306814-01-2
Guideline(s) followed in study:	PMRA Data Code No.: 8.3.2 OECD Data Point: IIA 7.3, IIA 7.3.1, IIA 7.3.2, IIA 7.3.3, IIIA 9.2, IIIA 9.2.2, IIIA 9.2.3 EPA Guideline No.: 164-1 Terrestrial Field Dissipation; US EPA OPPTS Guideline No. 835.6100
Deviations from current test guideline:	Current Guideline: Guidance Document for Conducting Pesticide Terrestrial Field Dissipation Studies (2016) None
Previous evaluation:	yes, evaluated and accepted DAR (2011)
GLP/Officially recognised testing facilities:	Yes, conducted under GLP/Officially recognised testing facilities
Acceptability/Reliability:	Yes

Data Point:	KCA 7.1.2.2.1/07
Report Author:	[redacted]
Report Year:	2008
Report Title:	Terrestrial field dissipation of AE C656948 in a California soil, 2006
Report No:	MEGMP087
Document No:	M-306820-01-2
Guideline(s) followed in study:	PMRA Data Code No.: 8.3.2 OECD Data Point: IIA 7.3, IIA 7.3.1, IIA 7.3.2, IIA 7.3.3, IIIA 9.2.1, IIIA 9.2.2, IIIA 9.2.3 EPA Guideline No.: 164-1 Terrestrial Field Dissipation; US EPA OPPTS Guideline No. 835.6100
Deviations from current test guideline:	Current Guideline: Guidance Document for Conducting Pesticide Terrestrial Field Dissipation Studies (2016) None
Previous evaluation:	yes, evaluated and accepted DAR (2011)
GLP/Officially recognised testing facilities:	Yes, conducted under GLP/Officially recognised testing facilities
Acceptability/Reliability:	Yes

2. Full summary of KCA 7.1.2.2.1/03, KCA 7.1.2.2.1/04, KCA 7.1.2.2.1/05, KCA 7.1.2.2.1/06 and KCA 7.1.2.2.1/07

Executive Summary

Terrestrial field dissipation studies of fluopyram were carried out on bare soil plots in Washington (WA), New York (NY), North Dakota (ND), Georgia (GA), and California (CA). All sites were located in ecoregions where the target markets could have been.

The target application rate in was 500 g a.s./ha, which corresponds to 100% of the maximum proposed label rate. Fluopyram SC 500 (Suspension Concentrate) was applied to the bare soil subplots as a liquid spray which is typical for the product. The applications were verified with solvent saturation pads and

soil pans, which showed an average recovery ranging from 80% to 97% and 57 to 107% of the nominal application rate, respectively.

The field dissipation studies were conducted for 673, 665, 499, 545, and 669 days at the WA, NY, ND, GA, and CA sites, respectively, with nominal soil sampling times of 0, 3, 7, 14, 30, 60, 90, 120, 180, 270, 365, and 540 days after treatment (DAT) for ND, and GA, and one additional sample was taken for WA, NY and CA sites at about 670 DAT. The actual sampling times varied with each site. Soil cores were collected at a depth of 0 to 48 inches (0 to 122 cm) in 6-inch (15-cm) segments. Soil layers were analyzed for fluopyram and its metabolites fluopyram-benzamide, fluopyram-7-hydroxy and fluopyram-pyridyl-carboxylic acid (PCA).

Fluopyram and its associated transformation products were extracted from soil using microwave extraction. The extract was fortified with isotopically labeled internal standards and diluted. The sample was analyzed by LC/MS/MS after a small aliquot of the diluted sample was evaporated and reconstituted. The soil residue analytical method was validated and the independent laboratory validation (ILV) was also conducted to confirm method performance. The limit of quantitation (LOQ) of the method was 1.0 µg/kg for fluopyram and its transformation products. The method detection limits (MDLs) determined for fluopyram, fluopyram-7-hydroxy, fluopyram-benzamide and fluopyram-PCA quantifier ions were 0.2, 0.2, 0.2, and 0.3 µg/kg, respectively.

The residues of fluopyram at the end of the study as the percentage of the zero-time concentration were 28% (WA), 41% (NY), 44% (ND), 27% (GA), and 21% (CA). The observed transformation products were fluopyram-7-hydroxy, fluopyram-benzamide, and fluopyram-PCA. The highest concentration of the transformation products fluopyram-7-hydroxy, fluopyram-benzamide, and fluopyram-PCA summed from each soil segment in the soil core was 3.0, 9.7, and 10.0 µg/kg at 6 DAT in CA, and the residues rapidly declined to at or below LOQ after 30 to 90 DAT. The maximum concentrations of fluopyram-7-hydroxy, fluopyram-benzamide, and fluopyram-pyridyl-carboxylic acid (PCA) from other study sites were below MDL to 2.8 µg/kg, below MDL to 6.0 µg/kg, and 1.0 to 4.2 µg/kg, respectively.

Although the field dissipation study design does not allow calculation of a mass balance, the total mass balance of fluopyram was evaluated at the one-year time point, based on available laboratory and field data. The major dissipation pathway was assumed to be biodegradation of fluopyram to fluopyram-7-hydroxy, then to fluopyram-benzamide, fluopyram-pyridyl-carboxylic acid (PCA), and non-extractable residues followed by mineralization to carbon dioxide. The total mass accountability varied from 76.3% to 89.8% for these five studies.

The double first order in parallel (DFOP) kinetics model explained the dissipation/degradation of fluopyram very well. The estimated degradation and half-life (DT_{50}) values ranged from 24.1 to 537 days.

I. MATERIALS AND METHODS

A. MATERIALS

1. Test Item

Fluopyram 500 SC (Suspension Concentrate)
Certificate of Analysis: BAR No.: 01174-00
Batch Number: 2005-004952

2. Test Sites

The sites were neither subjected to erosion, flooding nor run-off. The test plots were at slope 0-1%.
The identification, its locations and site details are presented in Table 7.1.2.2.1- 11.

Table 7.1.2.2.1- 11: Properties of the field soils

Characteristic	Washington	New York	North Dakota	Georgia	California
Report and Author	CA 7.1.2.2.1/03 Xu, T., 2008	CA 7.1.2.2.1/04 Xu, T., 2008	CA 7.1.2.2.1/05 Xu, T., 2008	CA 7.1.2.2.1/06; Xu, T., 2008	CA 7.1.2.2.1/07; Xu, T., 2008
Location:					
Province/State	Washington	New York	North Dakota	Georgia	California
Country	U.S.A.	U.S.A.	U.S.A.	U.S.A.	U.S.A.
Ecoregion	10.1.2	8.1.1	9.3.3	8.3.5	11.1.2
Slope gradient (%)	0 to 1%	0%	0%	0-1%	0-1%
Depth to ground water level	Greater than 30 feet	Greater than 7.5 feet	Greater than 20 feet	Greater than 7.5 feet	Greater than 50 feet
Soil					
Taxonomic class	Mixed, mesic Xeric Torripsam-ments, Quincy fine-sand grassland	Fine-silty, mixed, active, mesic Aeric Endoaqualfs	Coarse-silty, mixed, superactive, frigid Pachic Hapludolls	Fine-loamy, kaolinitic, thermic Plinthic Kandiudults	Fine-loamy, mixed, superactive, thermic Fluventic Haplocambids
Surface soil texture (USDA)	Sandy Loam	Loamy Sand	Loam	Loamy Sand	Sandy Loam
% Sand	80	87	34	84	57
% Silt	15	9.0	41	10	28
% Clay	6.0	5.0	26	7.0	16
CEC (meq/100 g)	9.3	7.0	21.9	4.5	9.7
pH: (1:1 soil:water)	8.1	6.2	7.0	5.9	7.8
pH: (0.01 M $CaCl_2$)	7.5	5.9	6.6	5.2	7.3
Organic matter (%)	0.8	2.2	5.8	0.8	1.1
Distance from weather station used for daily climatic measurements	Within 1 mile	On-site	Within 20 miles	On-site	~12 miles
Meteorological conditions compared to long-term average within normal levels (Yes/No)	No, the rainfall was not evenly distributed	No, the rainfall was not evenly distributed during the study period. 219% of 30-year after application in July 2006	No (June and July of 2006 were relatively dry, irrigation was applied to meet the target water input)	Yes (greater than normal)	Yes

B. STUDY DESIGN

1. Experimental Conditions

Fluopyram SC 500 was applied to the bare soil subplots at a rate of 500 g ai/ha (0.45 lb ai/A) as a liquid spray which is typical for the product and a nominal water rate of 54 gallons per acre.

Boom sprayers (12 to 30 ft) was equipped with flat-fan nozzles (6 to 18) spaced 18 to 20 inches apart and set at 18 to 24 inches above the ground. The tractor speed and nozzle output were calibrated prior

to application, and the sprayer yielded 51.6 to 59.3 gallons per acre during application. The control plots were located 50 feet to 550 feet distance from the treated plots. First soil samples were taken immediately after application.

Application to the treatment plots were verified using saturation pads and soil pans. Two Gelman Solvent Saturation Pads (5.4 inch x 8.7 inch or 13.7 cm x 22 cm) were placed staggered in each subplot (4 subplots x 2 = 8 pads total). Also, two pads were placed in the untreated control area. Immediately after application each pad was collected and placed in a labeled bottle. Each pad represented a separate sample. One disposable aluminum pan (9 inch x 13 inch; 23 cm x 33 cm on the top) containing a layer of pre-weighed, sieved air-dried control soil was placed in each subplot before the application for a total of four pans in the treated bare-ground plot. Immediately after application, soil from the pans was transferred to a labeled bottle. The soil and pad samples were stored frozen until analysis.

Supplemental weather data were collected either from a National Oceanic and Atmospheric Administration (NOAA) weather station or an on-site weather station. Supplemental irrigation was supplied by overhead irrigation to maintain at least 110% of long-term average rainfall for New York (126% of 30-yr average), North Dakota (177% of 10-yr average), and Georgia (149% of 10-yr average). For the highly irrigated areas of California and Washington, irrigation was carried out to meet water demand for a cropped field, although those were bare ground study. Actual evapotranspiration for bare soil is expected to be significantly lower than evapotranspiration for cropped soil. For WA, the total water input was 131% of the target evapotranspiration of apples (623% of 10-yr average rainfall). For CA the total water input was 125% of the target evapotranspiration of orchard (546% of 10-yr average rainfall, 391% of the bare ground evapotranspiration). The high actual water loading in comparison to bare ground ETc was visualized in Figure 7.1.2.2.1- 1.

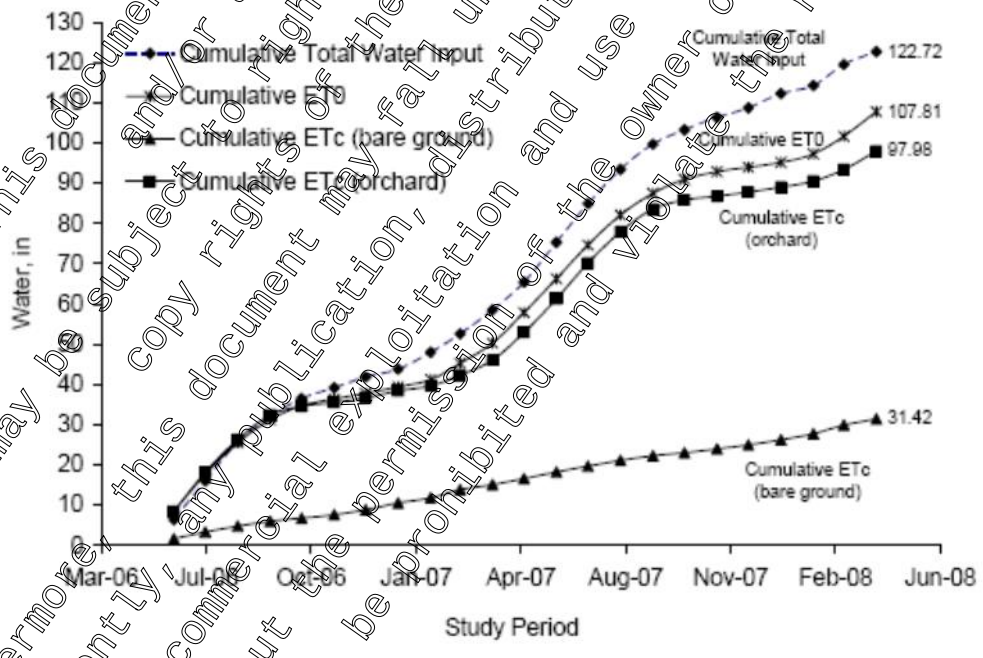


Figure 7.1.2.2.1- 1: Comparison of Cumulative Total Water Input (Rainfall and Irrigation) and Evapotranspiration (ET0 and ETc) through the Study Period

The field dissipation studies were conducted for 673, 665, 499, 545, and 669 days at the WA, NY, ND, GA, and CA sites, respectively.

2. Sampling

The test plot was divided into four equal sized areas called subplots. Each subplot was divided into sampling subsections.

Four cores from randomly selected subsections were sampled from each subplot at desired days after application. Soil samples were collected using a tractor mounted hydraulic sampler with acetate liners.

Each soil core consisted of two segments, a 0-6 inch (0-15 cm), 2.25 inch (5.7 cm) diameter core and a 6-48 inch (15-122 cm), 1.75 inch (4.4 cm) diameter core. Only 0-6 inch (0-15 cm) were collected for pre-application and day 0 samples.

All samples were frozen and shipped by freezer truck to the analytical laboratory except for the samples from the last sampling event (670 DAT) for Washington, New York and California which were shipped to the analytical laboratory by overnight delivery with dry ice. Samples were stored under freezer conditions at the analytical laboratories. The storage stability of fluopyram, fluopyram-7-hydroxy and fluopyram-pyridyl-carboxylic acid was assessed in untreated soil from North Dakota (loam) and New York (loamy sand). Residues were considered stable for at least 864 days of storage under frozen conditions (KCA 7.1.2.2.1/12, M-348402-01-1).

For each subplot, the 6-48 inch (15-122 cm) core was segmented starting with the upper 6 inches (15 cm) followed by every 6 inches (15 cm) to the depth of the core. Segments from the same depth from each subplot were composited into one sample per depth. The composited samples from each sampling interval were homogenized from the deepest to the shallowest soil depth. Each composited soil sample was milled with dry ice by a hammer mill into a clean plastic bag directly from the grinder. The milled sample was mixed using a bucket mixer equipped with fixed inner paddles.

The study was initially designed for 18 months. To better understand the dissipation of fluopyram, one additional sample was taken for Washington, New York and California sites. Soil samples at the five sites were taken on the following days:

1. Washington: 0, 3, 7, 14, 30, 64, 91, 120, 192, 273, 385, 497 and 673 DAT.
2. New York: 0, 3, 7, 14, 30, 58, 90, 120, 179, 267, 365, 545 and 665 DAT.
3. North Dakota: 0, 3, 7, 14, 30, 63, 93, 129, 316, 363, and 499 DAT.
4. Georgia: 0, 3, 7, 15, 30, 59, 90, 119, 182, 276, 372, and 545 DAT.
5. California: 0, 3, 6, 14, 30, 59, 90, 115, 189, 276, 361, 535 and 669 DAT.

3. Analytical Procedures

The application verification solvent saturation pads were analyzed for fluopyram only. The bottle containing a filter pad was extracted using 1000 mL of 50:50 v/v HPLC water:acetonitrile. The mixture was shaken for two hours, 0.4 mL aliquot of the solution was transferred into a 100 mL graduated cylinder and diluted to volume with 50:50 (v/v) HPLC water:acetonitrile. The diluted mixture was fortified with fluopyram-phenyl-$^{13}C_6$ as internal standard at concentration of 0.2 µg/mL, filtered and analyzed by LC/MS/MS.

Fluopyram and its associated transformation products were extracted from soil using Millstone® microwave extraction with acetonitrile:water (4:1 v/v) for 3 minutes at a maximum of 100 °C and a maximum of 250 watts. The extract was fortified with isotopically labeled internal standards of fluopyram-phenyl-$^{13}C_6$, [phenyl-$^{13}C_6$]fluopyram-benzamide, [phenyl-$^{13}C_6$]fluopyram-7-hydroxy, and [2,6-^{13}C, ^{15}N,carboxylic acid-^{13}C]fluopyram-pyridyl-carboxylic acid (PCA) prior to dilution.

About 1.5 mL of the extract was transferred to a centrifuge tube and centrifuged at approximately 12000 rpm for a minimum of 5 minutes to remove fine particles of soil. About 1 mL of the supernatant solution was transferred to a 50-mL polypropylene disposable centrifuge tube and solution was

evaporated to dryness using a Turbovap® LV evaporator set to a temperature of 30-35 °C. The residue was dissolved in 1 mL of a mixture of water/acetonitrile/acetic acid (900/100/5 v/v/v) and analyzed by LC/MS/MS.

The soil analytical residue method for fluopyram and its transformation products was developed in a separate study (M-287801-02-1). For the independent laboratory validation (ILV) of this method see M-299544-01-1. Following the ILV, the method was revised and given the method number GM-002-S07-01 (M-300037-01-1). Method or procedural recovery checks were also conducted with each sample set during analysis of field samples to confirm method performance. Full details and acceptable validation data to support the analytical method are presented within document M-CA 4, which comply with the EU regulatory requirements outlined within SANTE/2020/12830, Rev.1.

The LOQ of the method was 1.0 µg/kg for fluopyram and its transformation products. The method detection limits (MDLs) determined for fluopyram, fluopyram-7-hydroxy, fluopyram-benzamide and fluopyram-pyridyl-carboxylic acid (PCA) quantifier ions were 0.2, 0.2, 0.2, and 0.3 µg/kg, respectively.

II. RESULTS AND DISCUSSION

A. DATA

Application verification

The nominal application rate for the treatments corresponded to the maximum single application rate of 500 g a.s./ha. Application verification solvent saturation pads showed an average recovery ranging from 80% to 97% of the nominal application rate. The soil pans showed an average recovery of 57 to 107% of the nominal application rate. These deviations are considered acceptable since soil concentrations can vary considerably due to several uncertainties related to the first samplings after application. The following table summarizes the application verification results from each site.

Table 7.1.2.2.1- 12: Summary of recoveries from application verification saturation pads and soil pans

Site	Recovery from saturation pads (%)	Recovery from soil pans (%)
Washington	97.4	106.6
New York	95.8	94.2
North Dakota	94.5	70.6
Georgia	93.6	57.2
California	79.9	94.6

Analytical Results

Total concentrations (use actual value if less than LOQ) in each soil layer are added for convenience in representing dissipation in the soil column. The sum is not intended to express a concentration by depth, but rather approximate a concentration if all residues measured were confined to a single soil layer.

Table 7.1.2.2.1- 13: Analytical results of fluopyram [ng/g] in bare soil plots in Washington

Depths, inches	Rep	DAT [days]												
		0	**3**	**7**	**14**	**30**	**64**	**91**	**120**	**192**	**273**	**385**	**497**	**673**
0-6	1	284.64	244.78	250.89	228.07	220.84	161.97	117.02	108.47	127.90	93.83	66.12	18.84	31.18
	2	276.73	254.55	238.57	226.66	208.12	171.09	151.14	118.35	141.04	93.81	102.36	26.25	34.58
	3	300.79	245.74	260.82	245.09	179.48	166.21	157.01	157.54	147.86	120.41	104.93	65.35	16.55
	4	280.55	249.03	236.03	262.59	194.63	158.96	140.41	153.55	113.63	100.82	78.08	36.24	9.27
	Mean	**285.7**	**248.5**	**246.6**	**240.6**	**200.8**	**164.6**	**141.4**	**134.5**	**132.6**	**102.2**	**87.9**	**36.7**	**22.9**
6-12	1	N.A.	<LOQ (0.34)	2.87	<LOQ (0.29)	3.69	5.44	1.77	4.45	1.40	32.58	53.37	45.93	27.90
	2	N.A.	N.D.	<LOQ (0.24)	N.D.	2.58	1.99	4.20	17.97	15.59	24.11	9.99	23.43	39.58
	3	N.A.	<LOQ (0.47)	N.D	N.D	N.D.	N.D.	N.D.	N.D.	2.81	4.70	5.39	55.38	13.44
	4	N.A.	<LOQ (0.49)	<LOQ (0.53)	2.03	N.D.	5.15	N.D	21.07	6.02	27.41	29.13	42.93	11.60
	Mean	**N.A.**	**<LOQ (0.33)**	**<LOQ (0.91)**	**<LOQ (0.58)**	**1.57**	**4.40**	**1.49**	**10.9**	**5.96**	**22.2**	**24.2**	**41.9**	**23.1**
12-18	1	N.A.	N.D.	<LOQ (0.41)	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	1.69	30.75	2.40
	2	N.A.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	15.41	5.86
	3	N.A.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	<LOQ (0.96)	24.59
	4	N.A.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D	37.83
	Mean	**N.A.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**<LOQ (0.42)**	**11.8**	**17.7**
18-24	1	N.A.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
	2	N.A.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
	3	N.A.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	10.72
	4	N.A.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	29.26
	Mean	**N.A.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**9.99**
24-30	1	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.D.
	2	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	<LOQ (0.47)
	3	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	3.01
	4	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	12.19
	Mean	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**3.92**
30-36	1	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.D.
	2	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	2.43
	3	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	3.66
	4	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	<LOQ (0.75)
	Mean	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**1.71**
36-42	1	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.D.
	2	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.D.
	3	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.D.
	4	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.D.
	Mean	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.D.**
42-48	1	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.
	2	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.
	3	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.
	4	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.
	Mean	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.A.**
Total		285.7	248.8	247.5	241.2	202.3	169.0	142.9	145.4	138.6	124.4	112.5	90.4	79.3

N.D. = not detected, below method detection limit, N.A. = not analysed, DAT: Days after treatment

Table 7.1.2.2.1- 14: Analytical results of fluopyram [ng/g] in bare soil plots in New York

Depths, inches	Rep	DAT [days]												
		0	3	7	14	30	58	90	120	179	267	365	545	665
0-6	1	258.34	177.84	205.14	200.69	128.18	209.59	126.70	261.49	150.28	168.39	100.06	155.64	79.57
	1a	-	-	-	-	-	-	-	-	-	158.50	-	-	-
	2	288.34	179.52	243.27	202.02	168.22	186.56	164.45	197.27	174.67	134.08	131.29	84.38	55.95
	2a	-	-	-	-	-	-	-	-	-	123.85	-	-	-
	3	211.77	210.71	260.09	203.52	185.18	118.63	203.32	186.03	129.41	265.96	107.55	163.46	67.55
	3a	-	-	-	-	-	-	-	-	-	275.22	-	-	-
	4	291.86	221.17	229.43	155.45	137.85	97.45	127.79	112.02	108.73	143.78	126.64	86.84	119.70
	4a	-	-	-	-	-	-	-	-	-	144.59	-	-	-
	Mean	**262.6**	**197.3**	**234.5**	**190.4**	**154.9**	**153.1**	**155.6**	**189.2**	**140.8**	**176.8**	**116.4**	**117.6**	**80.6**
6-12	1	N.A.	N.D.	N.D.	N.D.	<LOQ (0.69)	1.56	<LOQ (1.03)	<LOQ (0.23)	N.D.	3.08	3.43	1.64	9.23
	2	N.A.	N.D.	1.84	N.D.	<LOQ (1.02)	<LOQ (0.56)	<LOQ (0.3)	N.D.	N.D.	N.D.	3.31	2.69	3.49
	3	N.A.	N.D.	N.D.	N.D.	<LOQ (0.39)	1.31	<LOQ (0.34)	N.D.	N.D.	1.73	N.D.	28.34	14.77
	4	N.A.	N.D.	N.D.	N.D.	<LOQ (0.52)	<LOQ (0.98)	<LOQ (0.49)	N.D.	N.D.	2.32	<LOQ (0.49)	<LOQ (1.02)	41.58
	Mean	**N.A.**	**N.D.**	**<LOQ (0.46)**	**N.D.**	**<LOQ (0.65)**	**1.09**	**<LOQ (0.54)**	**N.D.**	**N.D.**	**1.78**	**1.76**	**8.33**	**17.2**
12-18	1	N.A.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	<LOQ (1.1)	1.34	N.D.	2.51
	2	N.A.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	1.98	N.D.
	3	N.A.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	<LOQ (0.82)	1.63
	4	N.A.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	2.55	6.89
	Mean	**N.A.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**<LOQ (0.28)**	**<LOQ (0.33)**	**1.34**	**2.76**
18-24	1	N.A.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	<LOQ (0.74)	<LOQ (0.77)	N.D.	2.01
	2	N.A.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	5.13	N.D.
	3	N.A.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	2.09	<LOQ (0.4)
	4	N.A.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	12.84	4.17
	Mean	**N.A.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**5.01**	**1.64**
24-30	1	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.D.	<LOQ (1.02)
	2	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.D.	<LOQ (0.45)
	3	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.D.	<LOQ (0.9)
	4	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.D.	3.71
	Mean	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.D.**	**1.52**
30-36	1	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.D.	1.09
	2	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.D.	1.38
	3	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.D.	5.10
	4	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.D.	4.57
	Mean	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.D.**	**3.04**
36-42	1	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.D.	<LOQ (0.42)
	2	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.D.	N.D.
	3	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.D.	N.D.
	4	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.D.	N.D.
	Mean	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.D.**	**N.D.**
42-48	1	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.D.	N.D.
	2	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.D.	N.D.
	3	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.D.	N.D.

Depths, inches	Rep	DAT [days]												
		0	3	7	14	30	58	90	120	179	267	365	545	665
	4	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.D.	N.D.
	Mean	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.D.**	**N.D.**
Total		262.6	197.3	234.9	190.4	155.5	154.2	156.1	189.2	140.8	178.9	118.5	132.3	106.8

N.D. = not detected, below method detection limit, N.A. = not analysed, DAT: Days after treatment

Table 7.1.2.2.1- 15: Analytical results of fluopyram [ng/g] in bare soil plots in North Dakota

Depths, inches	Rep	DAT [days]										
		0	3	7	14	30	63	93	129	316	363	499
0-6	1	291.15	246.00	230.02	216.60	162.00	158.93	92.76	134.36	114.18	140.50	95.53
	2	233.28	239.37	206.27	200.25	156.31	117.51	131.80	130.95	132.54	112.30	114.87
	3	254.88	200.81	225.84	215.84	168.57	101.36	126.67	125.28	140.62	97.43	121.01
	4	249.77	243.80	220.40	205.72	178.53	115.57	123.65	144.46	115.29	119.78	120.80
	Mean	**257.3**	**232.5**	**220.6**	**209.6**	**166.4**	**123.3**	**118.7**	**133.8**	**125.7**	**117.5**	**113.1**
6-12	1	N.A.	1.91	<LOQ (1.17)	1.47	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
	2	N.A.	<LOQ (0.36)	N.D.	<LOQ (0.79)	N.D.	N.D.	N.D.	N.D.	N.D.	<LOQ (1.07)	N.D.
	3	N.A.	<LOQ (0.34)	<LOQ (1.27)	<LOQ (0.68)	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	<LOQ (0.65)
	4	N.A.	<LOQ (0.46)	6.14	<LOQ (0.48)	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
	Mean	**N.A.**	**<LOQ (0.77)**	**2.14**	**<LOQ (0.86)**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**<LOQ (0.27)**	**<LOQ (0.24)**
12-18	1	N.A.	N.D.	N.D.	<LOQ (0.27)	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
	2	N.A.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	<LOQ (0.51)	N.D.
	3	N.A.	N.D.	<LOQ (0.26)	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	<LOQ (0.36)	N.D.
	4	N.A.	N.D.	<LOQ (1.28)	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
	Mean	**N.A.**	**N.D.**	**<LOQ (0,38)**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**<LOQ (0.22)**	**N.D.**
18-24	1	N.A.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
	2	N.A.	N.D.	<LOQ (0.52)	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
	3	N.A.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
	4	N.A.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
	Mean	**N.A.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**
Total		257.3	233.3	223.3	210.5	166.4	123.3	118.7	133.8	125.7	118.0	113.4

N.D. = not detected, below method detection limit, N.A. = not analysed, DAT: Days after treatment

Table 7.1.2.2.1- 16: Analytical results of fluopyram [ng/g] in bare soil plots in Georgia

Depths, inches	Rep	DAT [days]											
		0	3	7	15	30	59	90	119	182	276	372	545
0-6	1	153.86	143.56	100.01	100.48	112.11	58.69	73.42	77.60	80.45	48.80	48.89	41.30
	1a	-	-	-	-	-	-	-	-	-	49.91	-	-
	2	158.86	123.29	134.80	97.26	92.04	71.34	71.00	56.69	71.39	46.15	48.69	26.82
	2a	-	-	-	-	-	-	-	-	-	45.57	-	-
	3	152.31	126.18	130.48	101.14	71.14	70.88	85.44	44.75	75.96	62.07	53.96	35.32
	3a	-	-	-	-	-	-	-	-	-	62.38	-	-
	4	150.66	131.19	114.41	81.19	83.86	47.88	73.12	59.14	46.65	59.14	56.01	44.69

Depths, inches	Rep	DAT [days]											
		0	3	7	15	30	59	90	119	182	276	372	545
	4a	-	-	-	-	-	-	-	-	-	60.65	-	-
	Mean	**153.9**	**131.1**	**119.9**	**95.0**	**89.8**	**62.2**	**75.7**	**59.6**	**68.6**	**54.3**	**51.9**	**37.0**
6-12	1	N.A.	24.81	<LOQ (0.48)	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	1.68	<LOQ (0.39)	11.70
	1a	-	22.05	-	-	-	-	-	-	-	-	-	-
	1b	-	23.09	-	-	-	-	-	-	-	-	-	-
	2	N.A.	153.52	N.D.	14.91	N.D.	N.D.	N.D.	N.D.	N.D.	<LOQ (0.24)	1.53	<LOQ (0.86)
	2a	-	132.06	-	-	-	-	-	-	-	-	-	-
	2b	-	138.13	-	-	-	-	-	-	-	-	-	-
	3	N.A.	117.85	<LOQ (0.86)	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	<LOQ (0.69)	N.D.
	3a	-	114.68	-	-	-	-	-	-	-	-	-	-
	3b	-	114.78	-	-	-	-	-	-	-	-	-	-
	4	N.A.	106.20	2.00	N.D.	1.12	N.D.	N.D.	N.D.	N.D.	N.D.	<LOQ (0.69)	<LOQ (0.47)
	4a	-	93.12	-	-	-	-	-	-	-	-	-	-
	4b	-	92.19	-	-	-	-	-	-	-	-	-	-
	Mean	**N.A.**	**94.37**	**<LOQ (0.83)**	**3.73**	**<LOQ (0.28)**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**<LOQ (0.48)**	**<LOQ (0.83)**	**3.26**
12-18	1	N.A.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
	2	N.A.	<LOQ (1.08)	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	1.34
	3	N.A.	2.07	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	<LOQ (0.31)
	4	N.A.	1.23	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	<LOQ (0.59)
	Mean	**N.A.**	**1.09**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**<LOQ (0.56)**
18-24	1	N.A.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
	2	N.A.	<LOQ (0.58)	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	2.38
	3	N.A.	<LOQ (0.8)	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	1.18
	4	N.A.	<LOQ (0.5)	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	1.37
	Mean	**N.A.**	**<LOQ (0.47)**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**1.23**
24-30	1	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.D.
	2	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.D.
	3	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.D.
	4	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.D.
	Mean	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.D.**
30-36	1	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.D.
	2	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.D.
	3	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.D.
	4	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.D.
	Mean	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.D.**
36-42	1	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.D.
	2	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	<LOQ (0.51)
	3	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.D.
	4	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.D.
	Mean	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.D.**
42-48	1	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.D.
	2	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.D.
	3	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.D.

Depths, inches	Rep	DAT [days]											
		0	3	7	15	30	59	90	119	182	276	372	545
	4	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.D.
	Mean	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.D.**
Total		153.9	227.0	120.8	98.8	90.1	62.2	75.7	59.6	68.6	54.8	52.7	46.9

N.D. = not detected, below method detection limit, N.A. = not analysed, DAT: Days after treatment

Table 7.1.2.2.1- 17: Analytical results of fluopyram [mg/g] in bare soil plots in California

Depths, inches	Rep	DAT [days]											
		0	3	6	14	30	59	90	115	189	276	361	535	669
0-6	1	79.75	180.85	170.96	72.52	110.20	65.59	37.31	52.85	43.66	32.37	14.46	16.87	10.48
	2	125.50	98.38	107.98	91.91	82.50	51.65	41.41	66.27	36.18	37.12	15.48	8.86	6.20
	3	111.09	129.47	97.25	71.02	62.34	45.35	37.88	53.91	46.97	24.70	25.05	3.89	3.59
	4	126.85	115.00	168.86	68.42	121.38	89.91	65.21	81.96	53.23	30.92	17.69	8.68	6.84
	Mean	**110.8**	**130.9**	**136.3**	**76.0**	**94.1**	**60.6**	**40.5**	**58.6**	**45.0**	**31.2**	**18.2**	**6.98**	**6.78**
6-12	1	N.A.	1.43	N.D.	<LOQ (0.57)	22.66	6.07	5.97	11.41	5.15	23.05	10.05	7.03	7.33
	2	N.A.	<LOQ (0.59)	N.D.	3.31	2.29	16.84	22.19	12.31	12.98	7.93	11.30	14.85	7.44
	3	N.A.	2.40	N.D.	N.D.	1.62	8.15	9.23	13.59	20.19	13.06	8.54	3.20	3.56
	4	N.A.	<LOQ (0.39)	<LOQ (0.33)	1.56	3.96	5.98	9.66	11.27	17.71	18.60	10.11	8.72	5.96
	Mean	**N.A.**	**1.20**	**N.D.**	**1.36**	**7.63**	**9.25**	**11.8**	**12.4**	**14.0**	**15.7**	**10.0**	**8.45**	**6.07**
12-18	1	N.A.	N.D.	N.D.	N.D.	N.D.	<LOQ (0.37)	2.00	4.42	N.D.	24.03	7.89	4.64	4.86
	2	N.A.	N.D.	N.D.	N.D.	N.D.	N.D.	9.12	2.77	9.58	1.61	10.28	11.48	4.56
	3	N.A.	N.D.	N.D.	N.D.	N.D.	<LOQ (0.19)	2.23	2.74	12.30	5.01	3.06	4.71	3.28
	4	N.A.	N.D.	N.D.	<LOQ (0.8)	N.D.	N.D.	1.15	1.16	3.86	9.13	4.06	4.99	4.40
	Mean	**N.A.**	**N.D.**	**N.D.**	**N.D.**	**1.91**	**<LOQ (0.22)**	**3.63**	**4.02**	**6.43**	**9.97**	**6.32**	**6.45**	**4.27**
18-24	1	N.A.	<LOQ (0.34)	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	2.74	6.73	3.67	<LOQ (0.75)
	2	N.A.	<LOQ (0.42)	N.D.	N.D.	N.D.	N.D.	3.78	N.D.	4.91	N.D.	10.27	5.26	2.42
	3	N.A.	N.D.	N.D.	N.D.	N.D.	N.D.	<LOQ (0.9)	N.D.	3.78	1.58	N.D.	5.36	3.57
	4	N.A.	N.D.	N.D.	N.D.	N.D.	N.D.	<LOQ (0.75)	<LOQ (0.25)	<LOQ (0.68)	4.10	1.56	5.25	2.20
	Mean	**N.A.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**1.36**	**N.D.**	**2.34**	**2.11**	**4.64**	**4.89**	**2.24**
24-30	1	N.A.	N.A.	N.A.	N.A.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	<LOQ (0.67)	4.05	<LOQ (0.39)
	2	N.A.	N.A.	N.A.	N.A.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	14.14	3.67	<LOQ (0.89)
	3	N.A.	N.A.	N.A.	N.A.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	1.62	4.29	3.88
	4	N.A.	N.A.	N.A.	N.A.	N.D.	N.D.	<LOQ (0.36)	N.D.	<LOQ (0.3)	N.D.	1.40	3.55	1.51
	Mean	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**4.46**	**3.89**	**1.67**
30-36	1	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.D.	N.D.	N.D.	4.33	N.D.	3.83	<LOQ (1.07)
	2	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.D.	N.D.	N.D.	N.D.	12.58	1.88	2.54
	3	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.D.	N.D.	N.D.	N.D.	1.78	4.50	4.73
	4	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.D.	N.D.	N.D.	N.D.	1.29	1.37	<LOQ (0.67)
	Mean	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.D.**	**N.D.**	**N.D.**	**1.08**	**3.91**	**2.89**	**2.25**

Depths, inches	Rep	DAT [days]												
		0	3	6	14	30	59	90	115	189	276	361	535	669
36-42	1	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.D.	N.D.	N.D.	5.42	N.D.	2.55	<LOQ (0.29)
	2	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.D.	N.D.	N.D.	N.D.	6.65	<LOQ (0.75)	1.60
	3	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.D.	N.D.	N.D.	N.D.	2.15	4.88	4.52
	4	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.D.	N.D.	N.D.	N.D.	1.23	<LOQ (0.5)	N.D.
	Mean	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.D.**	**N.D.**	**N.D.**	**1.35**	**2.51**	**2.17**	**1.66**
42-48	1	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.D.	N.D.	N.D.	1.32	N.A.
	2	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.D.	N.D.	3.05	<LOQ (0.57)	N.A.
	3	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.D.	N.D.	N.D.	6.18	N.A.
	4	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.D.	N.D.	<LOQ (0.5)	1.55	N.A.
	Mean	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.D.**	**N.D.**	**1.39**	**2.80**	**N.A.**
Total		110.8	132.3	136.4	77.5	103.6	70.1	57.3	75.1	67.8	61.4	51.2	38.1	15.3

N.D. = not detected, below method detection limit, N.A. = not analysed, DAT: Days after treatment

Table 7.1.2.2.1- 18: Analytical results of fluopyram-7-hydroxy [ng/g] in bare soil plots in Washington

Depths, inches	Rep	DAT [days]												
		0	3	7	14	30	64	91	120	192	273	385	497	673
0-6	1	N.D.	<LOQ (0.79)	<LOQ (0.99)	2.09	2.35	2.12	1.52	1.29	1.31	<LOQ (0.76)	<LOQ (0.52)	N.D.	<LOQ (0.32)
	2	N.D.	<LOQ (0.9)	1.03	1.34	1.82	1.92	1.96	1.38	1.49	<LOQ (0.79)	<LOQ (0.98)	N.D.	<LOQ (0.29)
	3	N.D.	<LOQ (0.75)	1.25	1.32	1.70	2.13	1.84	1.85	1.56	1.17	1.09	<LOQ (0.51)	N.D.
	4	N.D.	<LOQ (0.74)	1.09	1.74	1.84	1.69	1.68	1.99	1.13	1.14	<LOQ (0.85)	<LOQ (0.26)	N.D.
	Mean	**N.D.**	**<LOQ (0.8)**	**1.08**	**1.62**	**1.93**	**1.95**	**1.74**	**1.62**	**1.37**	**<LOQ (0.96)**	**<LOQ (0.86)**	**N.D.**	**N.D.**
6-12	1	N.A.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	<LOQ (0.24)	<LOQ (0.35)	N.D.	N.D.
	2	N.A.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	<LOQ (0.27)	N.D.	N.D.	N.D.
	3	N.A.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	<LOQ (0.27)	N.D.
	4	N.A.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	<LOQ (0.26)	N.D.	<LOQ (0.27)	N.D.	N.D.	N.D.
	Mean	**N.A.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**
12-18	1	N.A.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
	2	N.A.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
	3	N.A.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
	4	N.A.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
	Mean	**N.A.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**
18-24	1	N.A.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
	2	N.A.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
	3	N.A.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
	4	N.A.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
	Mean	**N.A.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**
24-30	1	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.D.

Depths, inches	Rep	DAT [days]												
		0	3	7	14	30	64	91	120	192	273	385	497	623
	2	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.D.
	3	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.D.
	4	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.D.
	Mean	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.D.**
30-36	1	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.D.
	2	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.D.
	3	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.D.
	4	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.D.
	Mean	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.D.**
36-42	1	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.D.
	2	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.D.
	3	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.D.
	4	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.D.
	Mean	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.D.**
42-48	1	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.D.
	2	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.D.
	3	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.D.
	4	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.D.
	Mean	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.A.**
Total		N.D.	<LOQ (0.8)	1.08	1.62	1.93	1.95	1.74	1.62	1.37	<LOQ (0.96)	<LOQ (0.86)	N.D.	N.D.

N.D. = not detected, below method detection limit; N.A. = not analysed, DAT: Days after treatment

Table 7.1.2.2.1- 19: Analytical results of fluopyram-7-hydroxy [ng/g] in bare soil plots in New York

Depths, inches	Rep	DAT [days]												
		0	3	7	14	30	58	90	120	179	267	365	545	665
0-6	1	N.D.	<LOQ (0.35)	<LOQ (0.95)	1.68	1.36	1.10	1.81	3.96	2.59	2.51	2.46	4.08	1.84
	1a	-	-	-	-	-	-	-	-	-	2.24	-	-	-
	2	N.D.	<LOQ (0.44)	<LOQ (0.83)	<LOQ (1.2)	1.52	2.05	2.23	2.83	2.06	1.58	2.39	1.37	<LOQ (1.03)
	2a	-	-	-	-	-	-	-	-	-	1.45	-	-	-
	3	N.D.	<LOQ (0.58)	<LOQ (0.81)	1.46	2.22	1.60	3.51	3.03	1.74	2.66	1.94	2.79	<LOQ (1.08)
	3a	-	-	-	-	-	-	-	-	-	2.74	-	-	-
	4	N.D.	<LOQ (0.46)	<LOQ (0.87)	<LOQ (0.83)	1.28	1.20	1.33	<LOQ (0.97)	1.50	1.51	1.87	1.34	1.47
	4a	-	-	-	-	-	-	-	-	-	1.37	-	-	-
	Mean	**N.D.**	**<LOQ (0.41)**	**<LOQ (0.86)**	**1.29**	**1.66**	**2.00**	**2.47**	**2.70**	**1.97**	**2.01**	**2.16**	**2.39**	**1.36**
6-12	1	N.A.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	<LOQ (0.53)	N.D.
	2	N.A.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
	3	N.A.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	<LOQ (0.39)	N.D.	<LOQ (0.97)	<LOQ (0.33)
	4	N.A.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	<LOQ (0.8)

Depths, inches	Rep	DAT [days]												
		0	3	7	14	30	58	90	120	179	267	365	545	665
	Mean	**N.A.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**<LOQ (0.37)**	**<LOQ (0.28)**
12-18	1	N.A.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
	2	N.A.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
	3	N.A.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
	4	N.A.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
	Mean	**N.A.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**
18-24	1	N.A.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
	2	N.A.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
	3	N.A.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
	4	N.A.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
	Mean	**N.A.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**
24-30	1	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.D.	N.D.
	2	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.D.	N.D.
	3	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.D.	N.D.
	4	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.D.	N.D.
	Mean	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.D.**	**N.D.**
30-36	1	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.D.	N.D.
	2	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.D.	N.D.
	3	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.D.	N.D.
	4	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.D.	N.D.
	Mean	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.D.**	**N.D.**
36-42	1	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.D.	N.D.
	2	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.D.	N.D.
	3	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.D.	N.D.
	4	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.D.	N.D.
	Mean	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.D.**	**N.D.**
42-48	1	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.D.	N.D.
	2	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.D.	N.D.
	3	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.D.	N.D.
	4	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.D.	N.D.
	Mean	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.D.**	**N.D.**
Total		N.D.	<LOQ (0.40)	>LOQ (0.86)	1.29	1.66	2.00	2.47	2.70	1.97	2.10	2.16	2.77	1.64

N.D. = not detected, below method detection limit, N.A. = not analysed, DAT: Days after treatment

Table 7.1.2.2.1- 20: Analytical results of fluopyram-7-hydroxy [ng/g] in bare soil plots in North Dakota

Depths, inches	Rep	DAT [days]										
		0	3	7	14	30	63	93	129	316	363	499
0-6	1	N.D.	<LOQ (0.5)	<LOQ (0.64)	<LOQ (0.83)	<LOQ (0.83)	<LOQ (1.16)	<LOQ (0.71)	<LOQ (1.07)	<LOQ (0.9)	<LOQ (0.86)	<LOQ (0.45)
	2	N.D.	<LOQ (0.49)	<LOQ (0.54)	<LOQ (0.75)	<LOQ (0.91)	<LOQ (0.84)	<LOQ (1.06)	<LOQ (1.01)	<LOQ (0.94)	<LOQ (0.66)	<LOQ (0.58)
	3	N.D.	<LOQ (0.32)	<LOQ (0.75)	<LOQ (0.68)	<LOQ (0.96)	<LOQ (0.81)	<LOQ (0.95)	<LOQ (0.91)	<LOQ (1.08)	<LOQ (0.59)	<LOQ (0.78)
	4	N.D.	<LOQ (0.65)	<LOQ (0.83)	<LOQ (1.01)	<LOQ (1.08)	<LOQ (0.86)	<LOQ (0.95)	<LOQ (1.03)	<LOQ (0.85)	<LOQ (0.74)	<LOQ (0.69)
	Mean	**N.D.**	**<LOQ (0.49)**	**<LOQ (0.69)**	**<LOQ (0.82)**	**<LOQ (0.95)**	**<LOQ (0.92)**	**<LOQ (0.91)**	**1.01**	**<LOQ (0.94)**	**<LOQ (0.71)**	**<LOQ (0.63)**
6-12	1	N.A.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
	2	N.A.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
	3	N.A.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
	4	N.A.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
	Mean	**N.A.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**
12-18	1	N.A.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
	2	N.A.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
	3	N.A.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
	4	N.A.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
	Mean	**N.A.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**
18-24	1	N.A.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
	2	N.A.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
	3	N.A.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
	4	N.A.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
	Mean	**N.A.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**
Total		-	<LOQ (0.49)	<LOQ (0.69)	<LOQ (0.82)	<LOQ (0.95)	<LOQ (0.92)	<LOQ (0.91)	1.01	<LOQ (0.94)	<LOQ (0.71)	<LOQ (0.63)

N.D. = not detected, below method detection limit; N.A. = not analysed, DAT = Days after treatment

Table 7.1.2.2.1- 21: Analytical results of fluopyram-7-hydroxy [ng/g] in bare soil plots in Georgia

Depths, inches	Rep	DAT [days]											
		0	3	7	15	30	59	90	119	182	276	372	545
0-6	1	N.D.	<LOQ (1.07)	<LOQ (0.83)	<LOQ (0.88)	1.36	<LOQ (0.7)	<LOQ (0.91)	<LOQ (0.8)	<LOQ (0.84)	<LOQ (0.77)	<LOQ (0.37)	<LOQ (0.35)
	1a	-	-	-	-	-	-	-	-	-	<LOQ (0.72)	-	-
	2	N.D.	<LOQ (0.56)	<LOQ (0.85)	<LOQ (0.7)	<LOQ (1.03)	<LOQ (0.54)	<LOQ (0.84)	<LOQ (0.65)	<LOQ (0.69)	<LOQ (0.63)	<LOQ (0.34)	N.D.
	2a	-	-	-	-	-	-	-	-	-	<LOQ (0.65)	-	-
	3	N.D.	<LOQ (0.78)	<LOQ (0.84)	<LOQ (0.88)	<LOQ (0.66)	<LOQ (0.55)	<LOQ (1.01)	<LOQ (0.45)	<LOQ (0.85)	<LOQ (0.92)	<LOQ (0.32)	<LOQ (0.25)
	3a	-	-	-	-	-	-	-	-	-	<LOQ (0.91)	-	-
	4	N.D.	<LOQ (0.72)	<LOQ (0.68)	<LOQ (0.51)	<LOQ (0.81)	<LOQ (0.47)	<LOQ (0.82)	<LOQ (0.58)	<LOQ (0.4)	<LOQ (0.77)	<LOQ (0.38)	<LOQ (0.36)
	4a	-	-	-	-	-	-	-	-	-	<LOQ (0.83)	-	-
	Mean	**N.D.**	**<LOQ (0.8)**	**<LOQ (0.8)**	**<LOQ (0.75)**	**<LOQ (1)**	**<LOQ (0.56)**	**<LOQ (0.9)**	**<LOQ (0.62)**	**<LOQ (0.7)**	**<LOQ (0.77)**	**<LOQ (0.35)**	**<LOQ (0.24)**
6-12	1	N.A.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
	1a	-	N.D.	-	-	-	-	-	-	-	-	-	-
	1b	-	N.D.	-	-	-	-	-	-	-	-	-	-

Depths, inches	Rep	DAT [days]											
		0	3	7	15	30	59	90	119	182	276	372	545
	2	N.A.	<LOQ (0.73)	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
	2a	-	<LOQ (0.79)	-	-	-	-	-	-	-	-	-	-
	2b	-	<LOQ (0.84)	-	-	-	-	-	-	-	-	-	-
	3	N.A.	<LOQ (0.62)	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
	3a	-	<LOQ (0.78)	-	-	-	-	-	-	-	-	-	-
	3b	-	<LOQ (0.8)	-	-	-	-	-	-	-	-	-	-
	4	N.A.	<LOQ (0.57)	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
	4a	-	<LOQ (0.64)	-	-	-	-	-	-	-	-	-	-
	4b	-	<LOQ (0.64)	-	-	-	-	-	-	-	-	-	-
	Mean	**N.A.**	**<LOQ (0.54)**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**
12-18	1	N.A.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
	2	N.A.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
	3	N.A.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
	4	N.A.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
	Mean	**N.A.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**
18-24	1	N.A.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
	2	N.A.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
	3	N.A.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
	4	N.A.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
	Mean	**N.A.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**
24-30	1	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.D.
	2	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.D.
	3	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.D.
	4	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.D.
	Mean	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.D.**
30-36	1	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.D.
	2	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.D.
	3	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.D.
	4	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.D.
	Mean	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.D.**
36-42	1	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.D.
	2	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.D.
	3	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.D.
	4	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.D.
	Mean	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.D.**
42-48	1	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.D.
	2	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.D.
	3	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.D.
	4	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.D.
	Mean	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.D.**
Total		N.D.	<LOQ (1.4)	<LOQ (0.8)	<LOQ (0.75)	<LOQ (1.0)	<LOQ (0.56)	<LOQ (0.9)	<LOQ (0.62)	<LOQ (0.7)	<LOQ (0.77)	<LOQ (0.35)	<LOQ (0.24)

N.D. = not detected, below method detection limit, N.A. = not analysed, DAT: Days after treatment

Table 7.1.2.2.1- 22: Analytical results of fluopyram-7-hydroxy [ng/g] in bare soil plots in California

Depths, inches	Rep	DAT [days]												
		0	3	6	14	30	59	90	115	189	276	361	535	669
0-6	1	N.D.	2.11	2.96	2.20	2.26	1.25	<LOQ (0.63)	<LOQ (0.99)	<LOQ (0.87)	<LOQ (0.57)	N.D.	N.D.	N.D.
	2	N.D.	2.09	2.78	2.57	1.97	<LOQ (0.96)	<LOQ (0.72)	1.20	<LOQ (0.65)	<LOQ (0.72)	N.D.	N.D.	N.D.
	3	N.D.	1.64	2.51	1.69	1.35	<LOQ (0.74)	<LOQ (0.63)	<LOQ (0.84)	<LOQ (0.94)	<LOQ (0.48)	<LOQ (0.33)	N.D.	N.D.
	4	N.D.	1.92	3.80	154	2.20	1.43	<LOQ (0.71)	<LOQ (1.02)	<LOQ (0.91)	<LOQ (0.58)	<LOQ (0.39)	N.D.	N.D.
	Mean	**N.D.**	**1.94**	**3.01**	**2.00**	**1.94**	**1.09**	**<LOQ (0.67)**	**1.01**	**<LOQ (0.84)**	**<LOQ (0.59)**	**N.D.**	**N.D.**	**N.D.**
6-12	1	N.A.	N.D.	N.D.	N.D.	<LOQ (0.44)	N.D.	N.D.	N.D.	N.D.	<LOQ (0.29)	N.D.	N.D.	N.D.
	2	N.A.	N.D.	N.D.	N.D.	N.D.	<LOQ (0.34)	<LOQ (0.32)	N.D.	<LOQ (0.29)	N.D.	N.D.	N.D.	N.D.
	3	N.A.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	<LOQ (0.24)	<LOQ (0.54)	<LOQ (0.23)	N.D.	N.D.	N.D.
	4	N.A.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	<LOQ (0.28)	<LOQ (0.37)	<LOQ (0.32)	N.D.	N.D.	N.D.
	Mean	**N.A.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**<LOQ (0.30)**	**<LOQ (0.21)**	**N.D.**	**N.D.**	**N.D.**
12-18	1	N.A.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
	2	N.A.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
	3	N.A.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	<LOQ (0.27)	N.D.	N.D.	N.D.	N.D.
	4	N.A.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
	Mean	**N.A.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**
18-24	1	N.A.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
	2	N.A.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
	3	N.A.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
	4	N.A.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
	Mean	**N.A.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**
24-30	1	N.A.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	<LOQ (0.43)	N.D.
	2	N.A.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
	3	N.A.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
	4	N.A.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
	Mean	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**
30-36	1	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
	2	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
	3	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
	4	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
	Mean	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**
36-42	1	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
	2	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
	3	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
	4	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
	Mean	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**
42-48	1	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.D.		N.D.	N.D.	N.D.

Depths, inches	Rep	DAT [days]												
		0	3	6	14	30	59	90	115	189	276	361	535	669
	2	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.D.	N.D.	N.D.	N.D.	N.D.
	3	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.D.	N.D.		N.D.	N.D.
	4	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.D.	N.D.	N.D.	N.D.	N.D.
	Mean	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**NA**
Total		N.D.	1.94	3.01	2.00	1.94	1.09	<LOQ (0.67)	1.01	<LOQ (0.14)	<LOQ (0.80)	N.D.	N.D.	N.D.

N.D. = not detected, below method detection limit, N.A. = not analysed, DAT: Days after treatment

Table 7.1.2.2.1- 23: Analytical results of fluopyram-benzamide [ng/g] in bare soil plots in Washington

Depths, inches	Rep	DAT [days]												
		0	3	7	14	30	64	91	120	192	273	385	497	673
0-6	1	N.D.	<LOQ (0.94)	<LOQ (0.69)	<LOQ (0.27)	<LOQ (0.44)	<LOQ (0.37)	<LOQ (0.31)	N.D.	<LOQ (0.25)	N.D.	N.D.	N.D.	N.D.
	2	N.D.	<LOQ (0.76)	<LOQ (0.73)	N.D.	N.D.	N.D.	N.D.	N.D.	<LOQ (0.25)	N.D.	N.D.	N.D.	N.D.
	3	N.D.	<LOQ (0.79)	<LOQ (0.82)	N.D.	<LOQ (0.36)	N.D.	<LOQ (0.38)	<LOQ (0.33)	N.D.	N.D.	N.D.	N.D.	N.D.
	4	N.D.	<LOQ (0.84)	<LOQ (0.59)	N.D.	<LOQ (0.51)	<LOQ (0.4)	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
	Mean	**N.D.**	**<LOQ (0.83)**	**<LOQ (0.71)**	**N.D.**	**<LOQ (0.33)**	**<LOQ (0.24)**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**
6-12	1	N.A.	N.D.	N.D.	N.D.	N.D.	1.15	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
	2	N.A.	N.D.	N.D.	N.D.	N.D.	N.D.	<LOQ (0.26)	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
	3	N.A.	N.D.	N.D.	N.D.	N.D.	N.D.	<LOQ (0.25)	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
	4	N.A.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
	Mean	**N.A.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**<LOQ (0.29)**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**
12-18	1	N.A.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
	2	N.A.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
	3	N.A.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
	4	N.A.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
	Mean	**N.A.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**
18-24	1	N.A.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
	2	N.A.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
	3	N.A.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
	4	N.A.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
	Mean	**N.A.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**
24-30	1	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.D.
	2	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.D.
	3	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.D.
	4	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.D.
	Mean	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.D.**
30-36	1	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.D.
	2	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.D.
	3	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.D.
	4	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.D.
	Mean	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.D.**
36-42	1	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.D.

Depths, inches	Rep	DAT [days]												
		0	3	7	14	30	64	91	120	192	273	385	497	673
	2	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.D.
	3	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.D.
	4	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.D.
	Mean	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.D.**
42-48	1	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.
	2	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.
	3	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.
	4	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.
	Mean	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.A.**
Total		N.D.	<LOQ (0.83)	<LOQ (0.71)	N.D.	<LOQ (0.33)	<LOQ (0.53)	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.

N.D. = not detected, below method detection limit, N.A. = not analysed, DAT: Days after treatment

Table 7.1.2.2.1- 24: Analytical results of fluopyram-benzamide [ng/g] in bare soil plots in New York

Depths, inches	Rep	DAT [days]												
		0	3	7	14	30	58	90	120	179	267	365	545	665
0-6	1	N.D.	1.46	1.22	<LOQ (0.33)	N.D.	<LOQ (0.25)	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
	1a	-.	-	-	-	-	-	-	-	-	N.D.	-	-	-
	2	N.D.	1.34	<LOQ (1.2)	<LOQ (0.36)	N.D.	<LOQ (0.22)	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
	2a	-	-	-	-	-	-	-	-	-	N.D.	-	-	-
	3	N.D.	1.40	1.38	<LOQ (0.66)	<LOQ (0.22)	N.D.	N.D.	N.D.	N.D.	<LOQ (0.41)	N.D.	N.D.	N.D.
	3a	-	-	-	-	-	-	-	-	-	N.D.	-	-	-
	4	N.D.	1.72	2.19	<LOQ (0.44)	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	-	N.D.
	4a	-	-	-	-	-	-	-	-	-	N.D.	-	-	-
	Mean	**N.D.**	**1.48**	**1.55**	**<LOQ (0.45)**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**
6-12	1	N.A.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
	2	N.A.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
	3	N.A.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
	4	N.A.	N.D.	N.D.	N.D.	N.D.	N.D.	<LOQ (0.31)	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
	Mean	**N.A.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**
12-18	1	N.A.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
	2	N.A.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
	3	N.A.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
	4	N.A.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
	Mean	**N.A.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**
18-24	1	N.A.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
	2	N.A.	N.D.	N.D.	N.D.	N.D.	N.D.	<LOQ (0.43)	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
	3	N.A.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
	4	N.A.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
	Mean	**N.A.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**
24-30	1	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.D.	N.D.
	2	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.D.	N.D.
	3	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.D.	N.D.

Depths, inches	Rep	DAT [days]												
		0	3	7	14	30	58	90	120	179	267	365	545	665
	4	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.D.	N.D.
	Mean	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.D.**	**N.D.**
30-36	1	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.D.	N.D.
	2	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.D.	N.D.
	3	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.D.	N.D.
	4	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.D.	N.D.
	Mean	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.D.**	**N.D.**
36-42	1	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.D.	N.D.
	2	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.D.	N.D.
	3	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.D.	N.D.
	4	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.D.	N.D.
	Mean	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.D.**	**N.D.**
42-48	1	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.D.	N.D.
	2	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.D.	N.D.
	3	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.D.	N.D.
	4	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.D.	N.D.
	Mean	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.D.**	**N.D.**
Total		N.D.	1.48	1.55	<LOQ (0.45)	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.

N.D. = not detected, below method detection limit, N.A. = not analysed, DAT: Days after treatment

Table 7.1.2.2.1- 25: Analytical results of fluopyram-benzamide [mg/g] in bare soil plots in North Dakota

Depths, inches	Rep	DAT [days]										
		0	3	7	14	30	63	98	129	316	363	499
0-6	1	N.D.	2.88	4.34	6.32	<LOQ (0.35)	<LOQ (0.29)	N.D.	N.D.	N.D.	N.D.	N.D.
	2	N.D.	3.44	4.67	5.80	<LOQ (0.55)	N.D.	<LOQ (0.3)	N.D.	N.D.	N.D.	N.D.
	3	N.D.	4.35	5.77	6.50	1.40	<LOQ (0.3)	<LOQ (0.26)	N.D.	<LOQ (0.32)	N.D.	N.D.
	4	N.D.	3.34	4.42	5.41	<LOQ (0.43)	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
	Mean	**N.D.**	**3.00**	**4.55**	**6.01**	**<LOQ (0.68)**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**
6-12	1	N.A.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
	2	N.A.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
	3	N.A.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
	4	N.A.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
	Mean	**N.A.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**
12-18	1	N.A.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
	2	N.A.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
	3	N.A.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
	4	N.A.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
	Mean	**N.A.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**
18-24	1	N.A.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
	2	N.A.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
	3	N.A.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
	4	N.A.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
	Mean	**N.A.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**
Total			3.00	4.55	6.01	<LOQ (0.68)	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.

N.D. = not detected, below method detection limit, N.A. = not analysed, DAT: Days after treatment

Table 7.1.2.2.1- 26: Analytical results of fluopyram-benzamide [ng/g] in bare soil plots in Georgia

Depths, inches	Rep	DAT [days]											
		0	3	7	15	30	59	90	119	182	276	372	545
0-6	1	N.D.	3.58	1.59	1.37	<LOQ (0.64)	<LOQ (0.35)	<LOQ (0.37)	<LOQ (0.25)	<LOQ (0.26)	N.D.	N.D.	N.D.
	1a	-	-	-	-	-	-	-	-	-	N.D.	-	-
	2	N.D.	2.11	3.50	<LOQ (1.07)	<LOQ (0.62)	<LOQ (0.32)	<LOQ (0.32)	N.D.	N.D.	N.D.	N.D.	N.D.
	2a	-	-	-	-	-	-	-	-	-	N.D.	-	-
	3	N.D.	2.67	2.75	1.30	<LOQ (0.35)	<LOQ (0.32)	<LOQ (0.31)	<LOQ (0.3)	<LOQ (0.22)	N.D.	N.D.	N.D.
	3a	-	-	-	-	-	-	-	-	-	N.D.	-	-
	4	N.D.	2.74	1.84	<LOQ (0.59)	<LOQ (0.43)	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
	4a	-	-	-	-	-	-	-	-	-	<LOQ (0.23)	-	-
	Mean	**N.D.**	**2.77**	**2.42**	**1.08**	**<LOQ (0.51)**	**<LOQ (0.25)**	**<LOQ (0.25)**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**
6-12	1	N.A.	<LOQ (0.5)	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
	1a	-	<LOQ (0.4)	-	-	-	-	-	-	-	-	-	-
	1b	-	<LOQ (0.46)	-	-	-	-	-	-	-	-	-	-
	2	N.A.	2.54	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
	2a	-	2.80	-	-	-	-	-	-	-	-	-	-
	2b	-	3.01	-	-	-	-	-	-	-	-	-	-
	3	N.A.	1.76	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
	3a	-	2.28	-	-	-	-	-	-	-	-	-	-
	3b	-	2.38	-	-	-	-	-	-	-	-	-	-
	4	N.A.	1.62	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
	4a	-	2.01	-	-	-	-	-	-	-	-	-	-
	4b	-	2.10	-	-	-	-	-	-	-	-	-	-
	Mean	**N.A.**	**1.82**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**
12-18	1	N.A.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
	2	N.A.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
	3	N.A.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
	4	N.A.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
	Mean	**N.A.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**
18-24	1	N.A.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
	2	N.A.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
	3	N.A.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
	4	N.A.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
	Mean	**N.A.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**
24-30	1	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.D.
	2	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.D.
	3	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.D.
	4	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.D.
	Mean	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.D.**
30-36	1	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.D.
	2	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.D.
	3	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.D.
	4	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.D.
	Mean	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.D.**
36-42	1	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.D.
	2	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.D.
	3	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.D.

Depths, inches	Rep	DAT [days]											
		0	3	7	15	30	59	90	119	182	276	372	545
	4	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.D.
	Mean	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.D.**
42-48	1	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.D.
	2	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.D.
	3	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.D.
	4	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.D.
	Mean	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.D.**
Total		N.D.	4.59	2.42	1.08	<LOQ (0.51)	<LOQ (0.25)	<LOQ (0.25)	N.D.	N.D.	N.D.	N.D.	N.D.

N.D. = not detected, below method detection limit, N.A. = not analysed, DAT: Days after treatment

Table 7.1.2.2.1- 27: Analytical results of fluopyram-benzamide [ng/g] in bare soil plots in California

Depths, inches	Rep	DAT [days]												
		0	3	6	14	30	59	90	115	189	276	361	535	669
0-6	1	N.D.	7.31	5.15	2.97	N.D.	N.D.	N.D.	<LOQ (0.26)	N.D.	N.D.	N.D.	N.D.	N.D.
	2	N.D.	8.65	10.81	2.45	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
	3	N.D.	7.69	9.04	1.37	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
	4	N.D.	7.86	11.38	1.59	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
	Mean	**N.D.**	**7.87**	**9.32**	**2.07**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**
6-12	1	N.A.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
	2	N.A.	N.D.	<LOQ (0.23)	<LOQ (0.42)	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
	3	N.A.	N.D.	<LOQ (0.91)	<LOQ (0.46)	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
	4	N.A.	N.D.	<LOQ (0.24)	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
	Mean	**N.A.**	**N.D.**	**<LOQ (0.34)**	**<LOQ (0.22)**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**
12-18	1	N.A.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
	2	N.A.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
	3	N.A.	N.D.	N.D.	<LOQ (0.4)	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
	4	N.A.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
	Mean	**N.A.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**
18-24	1	N.A.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
	2	N.A.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
	3	N.A.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
	4	N.A.	N.D.	N.D.	N.D.	<LOQ (0.76)	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
	Mean	**N.A.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**
24-30	1	N.A.	N.A.	N.A.	N.A.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
	2	N.A.	N.A.	N.A.	N.A.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
	3	N.A.	N.A.	N.A.	N.A.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
	4	N.A.	N.A.	N.A.	N.A.	<LOQ (0.28)	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
	Mean	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**
30-36	1	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
	2	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
	3	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
	4	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
	Mean	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**
36-42	1	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.

Depths, inches	Rep	DAT [days]												
		0	3	6	14	30	59	90	115	189	276	361	535	669
	2	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
	3	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
	4	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
	Mean	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**
42-48	1	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.D		N.D
	2	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.D	N.D	N.D
	3	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.D	N.D	
	4	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.D	N.D	N.D
	Mean	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**
Total		N.D.	N.D.	7.87	9.66	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.

N.D. = not detected, below method detection limit, N.A. = not analysed, DAT = Days after treatment

Table 7.1.2.2.1- 28: Analytical results of fluopyram-PCA [ng/g] in bare soil plots in Washington

Depths, inches	Rep	DAT [days]												
		0	3	7	14	30	64	91	120	192	273	385	497	673
0-6	1	N.D.	<LOQ (0.9)	1.09	1.17	<LOQ (0.77)	<LOQ (0.77)	N.D.	N.D.	N.D.	N.D.	N.D.	<LOQ (0.53)	N.D.
	2	N.D.	<LOQ (0.87)	1.02	<LOQ (0.75)	<LOQ (0.7)	<LOQ (0.89)	<LOQ (0.38)	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
	3	N.D.	<LOQ (0.95)	1.12	<LOQ (0.78)	<LOQ (0.74)	<LOQ (0.85)	<LOQ (0.35)	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
	4	N.D.	<LOQ (0.88)	<LOQ (0.86)	<LOQ (0.4)	<LOQ (0.55)	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
	Mean	**N.D.**	**<LOQ (0.9)**	**1.02**	**<LOQ (0.77)**	**<LOQ (0.69)**	**<LOQ (0.63)**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**
6-12	1	N.A.	N.D.	N.D.	N.D.	<LOQ (0.34)	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
	2	N.A.	N.D.	N.D.	<LOQ (0.36)	<LOQ (0.77)	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
	3	N.A.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
	4	N.A.	N.D.	N.D.	<LOQ (0.46)	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
	Mean	**N.A.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**
12-18	1	N.A.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
	2	N.A.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
	3	N.A.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
	4	N.A.	N.D.	N.D.	<LOQ (0.37)	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
	Mean	**N.A.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**
18-24	1	N.A.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
	2	N.A.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
	3	N.A.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
	4	N.A.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
	Mean	**N.A.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**
24-30	1	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.D.
	2	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.D.
	3	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.D.
	4	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.D.
	Mean	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.D.**
30-36	1	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.D.
	2	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.D.
	3	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.D.
	4	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.D.
	Mean	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.D.**

Depths, inches	Rep	DAT [days]												
		0	3	7	14	30	64	91	120	192	273	385	497	673
36-42	1	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.D.
	2	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.D.
	3	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.D.
	4	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.D.
	Mean	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.D.**
42-48	1	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.
	2	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.
	3	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.
	4	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.
	Mean	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.A.**
Total		N.D.	<LOQ (0.9)	1.02	<LOQ (0.77)	<LOQ (0.69)	<LOQ (0.63)	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.

N.D. = not detected, below method detection limit, N.A. = not analysed, DAT: Days after treatment

Table 7.1.2.2.1- 29: Analytical results of fluopyram PCA [ng/g] in bare soil plots in New York

Depths, inches	Rep	DAT [days]												
		0	3	7	14	30	58	90	120	179	267	365	545	665
0-6	1	N.D.	<LOQ (0.6)	<LOQ (0.87)	N.D.	<LOQ (0.39)	N.D.	N.D.	N.D.	N.D.	N.D.	<LOQ (0.6)	<LOQ (0.87)	<LOQ (0.41)
	1a	-	-	-	-	-	-	-	-	-	N.D.	-	-	-
	2	N.D.	<LOQ (0.75)	<LOQ (0.89)	<LOQ (0.43)	<LOQ (0.43)	N.D.	N.D.	N.D.	N.D.	N.D.	<LOQ (0.43)	N.D.	N.D.
	2a	-	-	-	-	-	-	-	-	-	N.D.	-	-	-
	3	N.D.	<LOQ (0.7)	<LOQ (1.03)	N.D.	<LOQ (0.33)	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
	3a	-	-	-	-	-	-	-	-	-	N.D.	-	-	-
	4	N.D.	<LOQ (0.87)	1.33	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
	4a	-	-	-	-	-	-	-	-	-	N.D.	-	-	-
	Mean	**N.D.**	**<LOQ (0.72)**	**1.06**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**
6-12	1	N.A.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
	2	N.A.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
	3	N.A.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
	4	N.A.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
	Mean	**N.A.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**
12-18	1	N.A.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
	2	N.A.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
	3	N.A.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
	4	N.A.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
	Mean	**N.A.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**
18-24	1	N.A.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
	2	N.A.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
	3	N.A.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
	4	N.A.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
	Mean	**N.A.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**
24-30	1	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.D.	N.D.
	2	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.D.	N.D.
	3	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.D.	N.D.
	4	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.D.	N.D.
	Mean	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.D.**	**N.D.**
30-36	1	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.D.	N.D.
	2	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.D.	N.D.

Depths, inches	Rep	DAT [days]												
		0	3	7	14	30	58	90	120	179	267	365	545	665
	3	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.D.	N.D.
	4	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.D.	N.D.
	Mean	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.D.**	**N.D.**
36-42	1	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.D.	N.D.
	2	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.D.	N.D.
	3	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.D.	N.D.
	4	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.D.	N.D.
	Mean	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.D.**	**N.D.**
42-48	1	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.D.	N.D.
	2	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.D.	N.D.
	3	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.D.	N.D.
	4	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.D.	N.D.
	Mean	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.D.**	**N.D.**
Total		N.D.	<LOQ (0.72)	1.06	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.

N.D. = not detected, below method detection limit, N.A. = not analysed, DAT: Days after treatment

Table 7.1.2.2.1- 30: Analytical results of fluopyram PCA [ng/g] in bare soil plots in North Dakota

Depths, inches	Rep	DAT [days]										
		0	3	7	14	30	63	93	129	316	363	499
0-6	1	N.D.	1.11	3.28	3.80	<LOQ (0.76)	<LOQ (0.99)	N.D.	N.D.	<LOQ (0.38)	<LOQ (0.9)	N.D.
	2	N.D.	2.16	3.32	3.41	<LOQ (0.85)	<LOQ (0.61)	<LOQ (0.77)	N.D.	N.D.	<LOQ (0.71)	N.D.
	3	N.D.	1.66	4.00	4.08	1.53	<LOQ (0.86)	<LOQ (0.74)	<LOQ (0.44)	<LOQ (0.9)	<LOQ (0.67)	N.D.
	4	N.D.	2.32	3.31	3.48	<LOQ (0.91)	<LOQ (0.91)	<LOQ (0.51)	N.D.	N.D.	<LOQ (0.71)	N.D.
	Mean	**N.D.**	**2.06**	**3.48**	**3.68**	**1.01**	**<LOQ (0.83)**	**<LOQ (0.5)**	**N.D.**	**<LOQ (0.32)**	**<LOQ (0.75)**	**N.D.**
6-12	1	N.A.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
	2	N.A.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	<LOQ (0.59)	N.D.
	3	N.A.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	<LOQ (0.45)	N.D.
	4	N.A.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
	Mean	**N.A.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**
12-18	1	N.A.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
	2	N.A.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
	3	N.A.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
	4	N.A.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
	Mean	**N.A.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**
18-24	1	N.A.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
	2	N.A.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
	3	N.A.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
	4	N.A.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
	Mean	**N.A.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**
Total			2.06	3.48	3.68	1.01	<LOQ (0.83)	<LOQ (0.5)	N.D.	<LOQ (0.32)	<LOQ (0.75)	N.D.

N.D. = not detected, below method detection limit, N.A. = not analysed, DAT: Days after treatment

Table 7.1.2.2.1- 31: Analytical results of fluopyram-PCA [ng/g] in bare soil plots in Georgia

Depths, inches	Rep	DAT [days]											
		0	3	7	15	30	59	90	119	182	276	372	545
0-6	1	N.D.	2.58	1.10	1.89	<LOQ (0.6)	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
	1a	-	-	-	-	-	-	-	-	-	N.D.	-	
	2	N.D.	2.47	2.76	<LOQ (0.89)	<LOQ (0.35)	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
	2a	-	-	-	-	-	-	-	-	-	N.D.		
	3	N.D.	3.22	3.39	1.67	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
	3a	-	-	-	-	-	-	-	-	-	N.D.	-	-
	4	N.D.	2.87	1.27	<LOQ (0.67)	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
	4a	-	-	-	-	-					N.D.	-	-
	Mean	**N.D.**	**2.78**	**2.13**	**1.28**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**
6-12	1	N.A.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
	1a	-	<LOQ (0.59)	-				-			-		
	1b	-	<LOQ (0.45)	-	-	-	-	-	-	-	-	-	-
	2	N.A.	2.09	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
	2a	-	2.19	-							-	-	-
	2b	-	2.25	-	-	-	-	-	-	-	-	-	-
	3	N.A.	1.58	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
	3a	-	1.92	-				-				-	-
	3b	-	1.87	-				-			-	-	-
	4	N.A.	1.31	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
	4a	-	1.56	-	-	-	-	-	-		-	-	-
	4b	-	1.77	-				-			-	-	-
	Mean	**N.A.**	**1.46**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**
12-18	1	N.A.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
	2	N.A.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
	3	N.A.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
	4	N.A.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
	Mean	**N.A.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**
18-24	1	N.A.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
	2	N.A.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
	3	N.A.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
	4	N.A.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
	Mean	**N.A.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**
24-30	1	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.D.
	2	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	<LOQ (0.52)
	3	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.D.
	4	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.D.
	Mean	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.D.**
30-36	1	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.D.
	2	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.D.
	3	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.D.
	4	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.D.
	Mean	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.D.**
36-42	1	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.D.
	2	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.D.
	3	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.D.
	4	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.D.
	Mean	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.D.**
42-48	1	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.D.

Depths, inches	Rep	DAT [days]											
		0	3	7	15	30	59	90	119	182	276	372	545
	2	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.D.
	3	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.D.
	4	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.D.
	Mean	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.D.**
Total		N.D.	4.24	2.13	1.28	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.

N.D. = not detected, below method detection limit, N.A. = not analysed, DAT: Days after treatment

Table 7.1.2.2.1- 32: Analytical results of fluopyram-PCA [ng/g] in bare soil plots in California

Depths, inches	Rep	DAT [days]											
		0	3	6	14	30	59	90	115	189	276	361	535	669
0-6	1	N.D.	4.91	5.22	8.55	<LOQ (0.75)	<LOQ (0.44)	N.D.	N.D.	<LOQ (0.46)	N.D.	N.D.	N.D.	<LOQ (0.44)
	2	N.D.	6.83	10.18	7.02	1.38	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
	3	N.D.	6.03	10.65	3.40	<LOQ (0.46)	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
	4	N.D.	6.13	11.01	5.18	<LOQ (0.84)	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
	Mean	**N.D.**	**5.98**	**9.27**	**6.04**	**<LOQ (0.85)**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**
6-12	1	N.A.	N.D.	<LOQ (0.56)	<LOQ (0.84)	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
	2	N.A.	N.D.	<LOQ (0.85)	<LOQ (0.96)	<LOQ (1.44)	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
	3	N.A.	N.D.	1.41	<LOQ (0.55)	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
	4	N.A.	N.D.	N.D.	<LOQ (0.35)	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
	Mean	**N.A.**	**N.D.**	**<LOQ (0.7)**	**<LOQ (0.68)**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**
12-18	1	N.A.	N.D.	N.D.	<LOQ (0.44)	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
	2	N.A.	N.D.	N.D.	N.D.	<LOQ (0.93)	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
	3	N.A.	N.D.	N.D.	<LOQ (0.78)	<LOQ (0.36)	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
	4	N.A.	N.D.	N.D.	<LOQ (0.38)	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
	Mean	**N.A.**	**N.D.**	**N.D.**	**<LOQ (0.39)**	**<LOQ (0.32)**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**
18-24	1	N.A.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
	2	N.A.	N.D.	N.D.	N.D.	<LOQ (0.38)	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
	3	N.A.	N.D.	N.D.	<LOQ (0.62)	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
	4	N.A.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
	Mean	**N.A.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**
24-30	1	N.A.	N.A.	N.A.	N.A.	-	-	<LOQ (0.35)	N.D.	N.D.	N.D.	N.D.	3.07	N.D.
	2	N.A.	N.A.	N.A.	N.A.	-	-	N.D.	N.D.	N.D.	N.D.	N.D.	<LOQ (0.37)	N.D.
	3	N.A.	N.A.	N.A.	N.A.	-	-	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
	4	N.A.	N.A.	N.A.	N.A.	-	-	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
	Mean	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**<LOQ (0.86)**	**N.D.**
30-36	1	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
	2	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.

Depths, inches	Rep	DAT [days]												
		0	3	6	14	30	59	90	115	189	276	361	535	669
	3	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
	4	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
	Mean	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**
36-42	1	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
	2	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
	3	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
	4	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
	Mean	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**
42-48	1	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	-	N.D.	N.D.	N.D.	N.A.
	2	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.D.	N.D.	N.D.	N.D.	N.A.
	3	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.D.	-	N.D.	N.D.	N.A.
	4	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	N.D.	N.D.	N.D.	N.D.	N.A.
	Mean	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.A.**	**N.D.**	**N.D.**	**N.D.**	**N.D.**	**N.A.**
Total		N.D.	5.98	9.97	7.24	<LOQ (0.17)	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	<LOQ (0.86)	N.D.

N.D. = not detected, below method detection limit, N.A. = not analysed, DAT: Days after treatment

B. RESIDUES

Residues of fluopyram and its transformation products

The total recoveries of fluopyram in these field studies are limited to the recovery of the analytes of concern which are parent, fluopyram-7-hydroxy, fluopyram-benzamide, and fluopyram-pyridyl-carboxylic acid (PCA). Average residues in bare ground soil samples and total residue recovered for each sampling interval from each study site are summarized in Table 7.1.2.2.1-13 to Table 7.1.2.2.1-32.

The average time zero concentration of fluopyram in the 0-6 inch (15 cm) soil segment was 286 µg/kg (WA), 263 µg/kg (NY), 257 µg/kg (ND), 154 µg/kg (GA), and 111 µg/kg (CA). The average time zero concentration of fluopyram in the 0-6 inch (0-15 cm) soil segment for CA was 111 µg/kg which was equivalent 267 g a.s./ha, in contrast to the other sites, where it is approximately 500 g a.s./ha. The residue of fluopyram at the end of the study as the percentage of the zero-time concentration were 28% (673 DAT, WA), 41% (665 DAT, NY), 44% (499 DAT, ND), 27% (545 DAT, GA), and 21% (669 DAT, CA).

The observed transformation products were fluopyram-7-hydroxy, fluopyram-benzamide, and fluopyram-pyridyl-carboxylic acid (PCA). The highest concentration of fluopyram-7-hydroxy summed from each soil segment in the soil core was 3.0 µg/kg at 6 days after treatment in CA, and rapidly declined to at or below LOQ after 59 DAT. The maximum concentration of fluopyram-7-hydroxy for other study sites were 2.0 µg/kg (WA, 64 DAT), 2.8 µg/kg (NY, 545 DAT) and 1.0 µg/kg (ND, 129 DAT), no residue of fluopyram-7-hydroxy above LOQ was detected in GA. The highest concentration of fluopyram-benzamide summed from each soil segment in the soil core was 9.7 µg/kg at 6 days after treatment in CA, and rapidly declined to below the method detection limit after 30 DAT. The maximum concentration of fluopyram-benzamide for other study sites were 1.6 µg/kg (NY, 7 DAT) and 6.0 µg/kg (ND, 14 DAT), 4.6 µg/kg (GA, 3 DAT), and no residue of fluopyram-benzamide above LOQ was detected in WA. The highest concentration of fluopyram-PCA summed from each soil segment in the soil core was 10.0 µg/kg at 6 days after treatment in CA, and rapidly declined to below the method detection limit after 59 DAT. The maximum concentration of fluopyram-PCA for other study sites were 1.0 µg/kg (WA, 7 DAT), 1.1 µg/kg (NY, 7 DAT) and 3.7 µg/kg (ND, 14 DAT), and 4.2 µg/kg (GA, 3 DAT).

Leaching potential
Most residues of fluopyram were found in the 0-6 and 6-12 inch (0-15 and 15-30 cm) soil segment of each study.

In the ND study, only one finding above LOQ was detected below 6 inches (15 cm), and there were no detections below 12 inches. In GA, residues of fluopyram above LOQ were detected once at 12-18 inches (30-46 cm; 1.09 µg/kg, 3 DAT) and once at 18-24 inches (46-61 cm; 1.23 µg/kg, 545 DAT). Both of the detected residues below 12 inches (30 cm) were <1% of the initial concentration. In NY, residues of fluopyram remained in the upper 12 inches (30 cm) during the first year of the study. Some movement to lower depths was observed in the following year with ca. 2.5% of the initial residue detected between 12 and 24 inches (30 and 61 cm) at 545 DAT and <2% of the initial residue between 24 and 36 inches (61 and 91 cm) detected at 665 DAT. In WA, residues of fluopyram remained in the upper 12 inches (30 cm) of the soil profile for the first year. In the second year, some movement to lower depths was observed such that at the end of the study (673 DAT) ca. 10% of the initial residue was detected between 12 and 24 inches (30 and 61 cm) and a farther 2% between 24 and 36 inches (61 and 91 cm). In CA, residues of fluopyram were detected below 36 inches (91 cm) from 276 DAT until the end of the study. However, the maximum amount detected below this depth at 535 DAT was equivalent to only 4.1% of the zero-time residue. By 669 DAT this had declined to only 1.5% of the zero-time residue. The downward movement of residues is driven by the large input of irrigation water applied to the treated area (particularly in CA and WA). As required by the guideline, for WA, the total water input was 131% of the target evapotranspiration of apples, however this was equivalent to 623% of 10-yr average rainfall. For CA the total water input was 125% of the target evapotranspiration of orchard, but was 546% of 10-yr average rainfall and, more importantly in the context of this study, 391% of the bare ground evapotranspiration.

No residue of transformation products was detected above LOQ below top 6 inches (15 cm) with exception of fluopyram-benzamide and fluopyram-PCA, which were detected once above the LOQ in the 12 to 18 inches (30-46 cm) segment in GA.

Mass accounting
Although the field dissipation study design does not allow calculation of a mass balance, the total mass balance of fluopyram was evaluated by reviewing physicochemical properties, radiolabeled soil metabolism studies and residue data from the field dissipation trials. The routes of dissipation considered includes residues of fluopyram, and its transformation products fluopyram-7-hydroxy, fluopyram-benzamide and fluopyram-pyridyl-carboxylic acid (PCA), biodegradation to soil bound residue and mineralization to CO_2, leaching, volatilization, plant uptake, and run off.

Fluopyram is not volatile as indicated by a vapor pressure of 3.1×10^{-6} Pa at 25 °C (see overview on physico-chemical properties in MCA section 2, M-265174-02-1). Therefore, volatilization is not a major dissipation route. Plant uptake was not the object of this study and was not measured. Run-off was not measured since the test plot had a slope of 0-1%.

Available results of radiolabeled soil metabolism study at the time of writing this report showed that mineralization of fluopyram to CO_2 was a major dissipation route. Up to 27.2% of the applied radioactivity was mineralized to CO_2 after one year (see KCA 7.1.1.1/03, M-299548-02-1). Formation of non-extractable residue can also account for up to 14.9% of total applied radioactivity after one year of incubation (see KCA 7.1.1.1/03, M-299548-02-1).

Degradation of fluopyram to fluopyram-7-hydroxy, fluopyram-benzamide and fluopyram-pyridyl-carboxylic acid (PCA) was observed in the field dissipation studies. After an equivalent time interval with radiolabeled soil metabolism study in this terrestrial field dissipation study (about one year), the total mass accountability was evaluated. Biodegradation of fluopyram to fluopyram-7-hydroxy, then to fluopyram-benzamide, fluopyram-pyridyl-carboxylic acid (PCA) and formation of non-extractable

residues followed by mineralization to carbon dioxide was the major dissipation pathway. This premise was supported by radiolabeled aerobic soil metabolism studies and this terrestrial field dissipation study. The dissipation routes and resultant conceptual model are summarized in Table 7.1.2.2.1- 33.

Table 7.1.2.2.1- 33: Dissipation routes and conceptual model for fluopyram and transformation products in soil

Route of Dissipation	WA (385 DAT)	NY (365 DAT)	ND (363 DAT)	GA (372 DAT)	CA (361 DAT)
Soil residue of fluopyram as percentage of zero-time concentration	39.4%	45.1%	45.9%	34.3%	46.2%
Transformation Products[1]					
Fluopyram-7-hydroxy	0.3%	0.8%	0.3%	0.1%	0%
Fluopyram-benzamide	0%	0%	0%	0%	0%
Fluopyram-PCA	0%	0%	0.5%	0%	0.6%
Leaching, if measured	0.0% - Residues were not found below 18 inches (46 cm)	0.0% - Residues were not found below 18 inches (46 cm)	0.0% - Residues were not found below 18 inches (46 cm)	0.0% - Residues were not found below 24 inches (61 cm)	1.1% - fluopyram residue was 1.1% of the zero time concentration at 42-48 inches (107 -122 cm)
Mineralization to CO_2[2]	27.2% - Radiolabeled soil metabolism studies: 27.2% of applied radioactivity was liberated as CO2 after one year				
Non-extractable residues[2]	14.9% - Radiolabeled soil metabolism studies: 14.7% of applied radiolabeled fluopyram was unextractable after exhaustive extraction.				
Volatilization, if measured	0.0% - fluopyram is non-volatile product with a vapor pressure of 3.1 x 10^{-6} Pa at 25°C				
Plant uptake, if measured	0.0% - Not measured				
Run off, if measured	0.0% - Not measured since the test plots had a slope of 0-1%.				
Total accountability	81.6%	87.0%	88.6%	76.3%	89.8%

[1]: Percentage of concentrations of transformation products in parent equivalent to the initial residue of fluopyram at day 0.
[2] see M-299548-02-1

C. KINETIC ANALYSIS

New kinetic calculations based on more recent guidance are necessary, therefore the information included in this study is not considered relevant. The kinetic evaluation following current FOCUS guidance was conducted separately and is summarised under KCA 7.1.2.2.1/20 for trigger endpoints and KCA 7.1.2.2.1/16 for modelling endpoints. The representativeness of the tested US soils for European agricultural areas was assessed separately and is summarised under KCA 7.1.2.2.1/13 and KCA 7.1.2.2.1/09.

III. CONCLUSIONS

The residue of fluopyram at the end of the study as the percentage of the zero-time concentration were 28% (673 DAT, WA), 41% (665 DAT, NY), 44% (499 DAT, ND), 27% (545 DAT, GA), and 21% (669 DAT, CA).At one site fluopyram residues were observed below 36 inches, which was due to the excessive input of water to the bare soil plots. No residue of transformation products was detected above LOQ below top 6 inches (15 cm).

The observed transformation products were fluopyram-7-hydroxy, fluopyram-benzamide, and fluopyram-pyridyl-carboxylic acid (PCA). The highest concentration of fluopyram-7-hydroxy summed from each soil segment in the soil core was 3.0 µg/kg at 6 days after treatment in CA, and rapidly declined to at or below LOQ after 59 DAT. The maximum concentration of fluopyram-7-hydroxy for other study sites were 2.0 µg/kg (WA, 64 DAT), 2.8 µg/kg (NY, 545 DAT) and 1.0 µg/kg (ND, 129 DAT), no residue of fluopyram-7-hydroxy above LOQ was detected in GA. The highest concentration of fluopyram-benzamide summed from each soil segment in the soil core was 9.7 µg/kg at 6 days after treatment in CA, and rapidly declined to below the method detection limit after 30 DAT. The maximum concentration of fluopyram-benzamide for other study sites were 1.6 µg/kg (NY, 7 DAT) and 6.0 µg/kg (ND, 14 DAT), 4.6 µg/kg (GA, 3 DAT), and no residue of fluopyram-benzamide above LOQ was detected in WA. The highest concentration of fluopyram-PCA summed from each soil segment in the soil core was 10.0 µg/kg at 6 days after treatment in CA, and rapidly declined to below the method detection limit after 59 DAT. The maximum concentration of fluopyram-PCA for other study sites were 1.0 µg/kg (WA, 7 DAT), 1.1 µg/kg (NY, 7 DAT) and 3.7 µg/kg (ND, 14 DAT), and 4.2 µg/kg (GA, 3 DAT).

3. Assessment and conclusion

Assessment and conclusion by applicant: The study and its data are considered to be valid and reliable for use in risk assessment.

Assessment and conclusion by RMS: Outcome and conclusion of the study: RMS should indicate if they agree to the results and conclusions of the APPL.

Data Point:	KCA 7.1.2.2.1/08
Report Author:	[redacted]
Report Year:	2012
Report Title:	Evaluation of fluopyram field dissipation studies conducted in US for derivation of modeling endpoints used in european exposure assessment
Report No:	ENSR-12-0484
Document No:	M-428459-01-1
Guideline(s) followed in study:	not specified
Deviations from current test guideline:	Current Guideline (not applicable, see justification)
Previous evaluation:	yes, evaluated and accepted Addendum 2 to the RAR (2012)
GLP/Officially recognised testing facilities:	No, not conducted under GLP/Officially recognised testing facilities
Acceptability/Reliability:	No

The analysis of the representativeness of US field studies for European conditions under consideration of soil and climate data does not meet current standard anymore and can be regarded as outdated. A new Ecoregion crosswalk using the GIS-based software 'Europe-North America Soil Geographic Information for Pesticide Studies' (ENASGIPS) 3.0 was conducted and is presented under KCA 7.1.2.2.1/13 (M-754876-01-1).

1. Information on the study

Data Point:	KCA 7.1.2.2.1/09
Report Author:	[redacted]
Report Year:	2012
Report Title:	Reply to EFSA request concerning the evaluation of EU and US terrestrial field dissipation studies according to Ctb checklist
Report No:	EnSa-12-0195
Document No:	M-428545-01-1
Guideline(s) followed in study:	not specified
Deviations from current test guideline:	Current Guideline: not applicable (response to technical authority request)
Previous evaluation:	yes, evaluated and accepted Addendum 1 to the DAR (2012)
GLP/Officially recognised testing facilities:	No, not conducted under GLP/Officially recognised testing facilities
Acceptability/Reliability:	Yes

2. Full summary of KCA 7.1.2.2.1/09

On 24th January 2012 Bayer CropScience received a request for additional information from EFSA within the Peer Review of the Draft Assessment Report (DAR) on the active substance fluopyram. This request dealt with the formal check of available field data according to criteria as defined by Dutch ctb and is underlined below: "Applicant to provide a new kinetic evaluation […*including assessment against the 'ctb checklist' that aims to ensure degradation and not dissipation endpoints are derived […]*."

Details of the CtB-checklist were used for assessing whether the field studies can be used to estimate transformation rates in soil. Results for the various field dissipation studies and the respective checks are shown in detail below.

According to the CtB-checklist, all points should be checked and reported. A conclusion should be drawn whether from the field study the dissipation DT_{50} can be attributed to transformation only. In the light of all available information in the dossier it should be determined whether the field DT_{50} can be used to predict leaching of the compound.

1. 'Ctb Checklist' Point 1:
Check that only a non-significant fraction of the dose can have leached out of the soil layers that were sampled (consider the amount of rainfall and concentration measured in the deepest sampled layer):

EU Field dissipation tests (KCA 7.1.2.2.1/01, M-293999-01-1):
The tests included six sites in the EU performed and reported as one document. The four sites Burscheid (D), Little Shelford (UK), Staffanstorp (SWE) and Vatteville (F) represent Ecoregion EU North and the two sites Vilobi d'Onyar (SP) and Albaro (ITA) represent EU South. Ecoregions in the EU context refer mainly to climates, i.e representing temperate climates of the northern and central zone and Mediterranean climate for the south. There have not been defined yet ecological regions in the EU in contrast to the existing NAFTA regions. No additional irrigation was performed at the EU sites during the tests except for site Vilobi d'Onyar (Spain).

Deviations from long-term averages occurred for limited periods of time (usually on a monthly scale) during the tests at some of the sites. However, the overall extent of deviation in terms of precipitation and temperature was very limited and thus with no significance for the overall outcome of the study. It should also be noted that the variable soil temperature and soil moisture, including deviations from the

long-term averages, are compensated during the DT_{50} calculation by the normalisation to 20°C and pF 2 moisture.

Residue concentrations across the soil profile were measured up to 50 cm soil depth in the course of the study, indicating no mobility of residues of fluopyram into deeper layers of soil beyond the top 30 cm plough layer in an EU field situation within 726 to 734 days after treatment.

US Field dissipation tests (M-306817-01-2, M-306809-01-2, M-306812-01-2, M-306814-01-2, M-306820-01-2, KCA 7.1.2.2.1/03 to KCA 7.1.2.2.1/07):
The tests included five sites in the US performed and reported as five documents in total. The five sites represented the following Ecological Region of North America: 10.1.2 (Washington), 8.1.1 (New York), 9.3.3 (North Dakota), 8.3.5 (Georgia) and 11.1.2 (California). For the five US sites additional irrigation was done throughout the study period for sites Georgia and California and during the vegetation period for sites Washington, New York and North Dakota.

For the five US sites supplemental irrigation during the study was significant at all US tests sites resulting in a total water input of 126% (New York) to 547% (California) of the annual basis. In order to fulfil US-specific requirements the total water input target rate was based on crop requirements for Washington and California.

Supplemental irrigation was significant at all US tests sites resulting in a total water input of

- 131% of the crop (apples) requirement through the total study period for site Washington. This is significantly more (i.e. 442%, annual basis, June 2006 to May 2007) than the 'normal annual rainfall' of 235 mm on bare soil at the same time. Irrigation was particularly high during months of summer (June through September). It should be noted that the test was performed on bare soil with evapotranspiration being significantly lower than from a cropped soil.
- 126% of the long term average (30 years) rainfall through the total study period for site New York. This applies, in particular, for the first experimental year (June 2006 to May 2007).
- 177% of the long-term average (10 years) rainfall through the total study period for site North Dakota. In particular, the first two months (June to July 2006) were very dry, being significantly below the long-term average of 'normal annual rainfall'.
- 149% of the 30-years long-term average rainfall through the total study period for site Georgia. However, rainfall was 21% below the long-term average of 'normal annual rainfall' for the first experimental year (August 2006 to July 2007).
- 391% of the bare soil evaporation for site California. This is significantly more (i.e. 547%, annual basis, June 2006 to May 2007) than the 'normal annual rainfall' of 304 mm on bare soil at the same time. As a result, irrigation significantly exceeded evapotranspiration for bare soil. Total inputs were higher than evapotranspiration in the total course of the study with factors between 3 and more than 6 during 14 out of 23 months of total study period. Since total water input was significantly higher than losses from evapotranspiration, this enforced the transport of fluopyram residues into deeper soil layers.

In contrast to EU sites irrigation was significant compared to long-term averages of rainfall. This had a predominant influence at those US sites that had received supplemental irrigation to simulate conditions of cropped soils, i.e. sites Washington and California, while the actual test plot was bare. This surplus of moisture in soil enforced leaching into deeper layers of soil at later sampling intervals under the conditions of the test. While this effect is most obvious for site California, this could be also observed at sites Washington, New York and Georgia.

Residue concentrations were measured up to 122 cm soil depth in course of study.

For site California, leaching of a significant portion of fluopyram residues cannot be excluded. The results of this site are therefore not regarded as valid for an accurate estimation of the transformation rate of fluopyram in soil.

For US sites Washington, New York and Georgia the results indicate some movement into deeper layers of soil but no indications for losses beyond the deepest soil layers analysed during a study period of 673 days, 665 days and 545 days, respectively. For US site North Dakota the results indicate no mobility of residues of fluopyram into deeper layers of soil beyond the top 30 cm plough layer during a study period of 499 days.

2. 'Ctb Checklist' Point 2:
Check that only a non-significant fraction of the dose disappeared via processes at the soil surface such as volatilisation or photochemical transformation (consider the period between spraying and the first significant rainfall event; check additionally that there is no initial fast decline followed by a slower decline; a recovery in the field that is much lower than the dose is also an indication of losses at the soil surface) EU and US Field dissipation tests:

Volatilization was not measured in any of the field studies. However, considering a vapour pressure of 1.2 x 10^{-6} Pa at 20°C or, 3.1 x 10^{-6} Pa at 25°C, no relevant volatilisation of fluopyram is expected under conditions of field testing. Thus, volatilization did not influence the results of tests performed with fluopyram under field conditions.

The behaviour of fluopyram under conditions of photochemical transformation on soil surfaces has been investigated in a laboratory study (KCA 7.1.1.2.01, M-286872-01-1). The study revealed stability of fluopyram under the conditions of the test. Photochemical transformation processes at soil surfaces therefore do not contribute to the degradation of fluopyram under field conditions.

The assessment provided in the report for this point is outdated due to new kinetic evaluations.

3. 'Ctb Checklist' Point 3:
Check that the decrease of the total amount with time corresponds reasonably well with first-order kinetics (either via curve-fitting or via applying a simulation model); if there is much scatter in the relationship between total amount with time (probably due to an inadequate sampling strategy) the estimation of a transformation rate in soil may be not acceptable:

The assessment provided in the report for this point is outdated due to new kinetic evaluations.

4. 'Ctb Checklist' Point 4
Check whether the soil has been characterised (organic matter, clay etc.) EU and US Field dissipation tests:

Soil of each test site has been characterised by analysis for texture, pH, cation exchange capacity and organic matter and was adequately characterised for all EU and US field test sites.

5. 'Ctb Checklist' Point 5
Check whether the location can be considered representative with respect to soil type and climate for Dutch (*here: EU*) conditions EU Field dissipation tests:

The assessment provided in the report for this point is outdated due to new ecoregion crosswalk comparison.

6. 'Ctb Checklist' Point 6:

Check whether meteorological data are available, and whether a correction for the difference between the actual soil temperature (mean temperature measured during the day in top soil layer) and 20°C has been made (an acceptable alternative is temperature during the day in air measured on location, or nearby whether station):

Meteorological data have been reported adequately for EU field sites while neither daily sunshine hours nor data of global radiation have been reported for the US sites. Corrections for the difference between the actual soil temperature and 20°C have been made for the top layer in any of the field tests being subject of kinetic evaluation of the field data.

7. 'Ctb Checklist' Point 7:
Check whether the dose is reported and whether the formulated product is relevant (no granulate or slow release):

Nominal and applied doses have been reported for all field sites. The formulated product applied as a suspension concentrate is regarded as relevant. The product tested was not a granule or slow release formulation.

8. 'Ctb Checklist' Point 8:
If inverse modelling was used, check whether the model used is acceptable (see focus document: soil persistence models and EU registration 1996) within the reporting of EU or US field data, no inverse modelling was used or presented.

This point is not relevant for study reports of field testing.

9. 'Ctb Checklist' Point 9:
Check whether analytical procedure was documented well and whether recovery was acceptable:

For EU and US field sample analysis analytical procedures have been documented well including acceptable recoveries.

10. 'Ctb Checklist' Point 10:
Check history of pesticide use on plot. In preceding years, no active ingredient or structure analogue should be used:

History of pesticide use has been reported for all but one field test sites in the EU and the US. For fluopyram or other carboxamides there are no publications or reporting known about an enhanced degradation in the field following repeated application.

11. 'Ctb Checklist' Point 11:
Check method of application. Pesticide should not be applied below soil surface For EU and US field dissipation tests the product containing the test substance fluopyram was applied by spraying onto bare soil:

For EU and US field dissipation tests the product containing the test substance fluopyram was applied by spraying onto bare soil. There was no incorporation into soil. The method of application reflected conditions of intended agricultural use of fluopyram. These do not include applications below soil surfaces.

12. 'Ctb Checklist' Point 12:
Check method of sampling:

The method of sampling and processing is regarded adequate for both, EU and US field dissipation tests.

13. 'Ctb Checklist' Point 13:
Check influence of crop. Uptake of pesticide by crop should be negligible EU Field dissipation tests:

Both, EU and US tests started by application to bare soil assuring that the dose applied directly reached the ground, thus excluding any plant interception. Grass (sown on EU-soils) being a model for a minimum crop situation was regarded as a standard in field testing minimizing uptake of residues followed by their 'recycling' as a result from mulching during the tests.

CONCLUSIONS

Overall, the European trials can be considered for estimation of the degradation rate of fluopyram in soil according to the CtB-checklist. Heavy irrigation during the US California trial enforced leaching into deeper layers of soil at later sampling intervals under the conditions of the test. This effect is very most obvious for site California, therefore it should be excluded for modelling purpose.

3. Assessment and conclusion

Assessment and conclusion by applicant: The European trials can be considered for estimation of the degradation rate of fluopyram in soil according to the CtB-checklist. For the US-trials it is concluded that California site data have to be excluded for modelling purpose.

Assessment and conclusion by RMS: Outcome and conclusion of the study: RMS should indicate if they agree to the results and conclusions of the APPL.

Data Point:	KCA 7.1.2.2.1/10
Report Author:	[redacted]
Report Year:	2010
Report Title:	Kinetic evaluation of field dissipation studies according to FOCUS after application of fluopyram+AE C656948 in Europe - Use of Q10 = 2.58
Report No:	MEF-10/389
Document No:	M-385171-01-1
Guideline(s) followed in study:	not applicable
Deviations from current test guideline:	Current Guideline: not applicable (see justification)
Previous evaluation:	yes, evaluated and accepted Addendum 1 to the DAR (2012)
GLP/Officially recognised testing facilities:	No, not conducted under GLP/Officially recognised testing facilities
Acceptability/Reliability:	no

In the field study, which was the basis for the kinetic evaluation, grass was grown on the fields during the trial period which should be avoided, when endpoints are intended to be used in exposure modelling, according to EFSA Guidance to obtain $DegT_{50}$ values in soil (2014). Therefore, the kinetic evaluation of the field dissipation study to derive endpoints for modelling purposes is considered as not appropriate anymore.

Data Point:	KCA 7.1.2.2.1/11
Report Author:	[redacted]
Report Year:	2012
Report Title:	Fluopyram - Peer review of new active substances - Request for additional information - Environmental fate - EFSA letter ref D(2012)HF/JS/al/620079, dated January 24, 2012
Report No:	M-428680-01-1
Document No:	M-428680-01-1
Guideline(s) followed in study:	not specified
Deviations from current test guideline:	Current Guideline: not applicable (see justification)
Previous evaluation:	No, not previously submitted
GLP/Officially recognised testing facilities:	not applicable
Acceptability/Reliability:	No

Request from the previous evaluation summarised in this document, were addressed at the respective data points within the dossier if still relevant. A few requests belonged to studies which are considered as not appropriate anymore. Therefore, this document is outdated and will be not submitted.

1. Information on the study

Data Point:	KCA 7.1.2.2.1/12
Report Author:	Freitag, J.; Schoening, R.
Report Year:	2009
Report Title:	Determination of the storage stability of AE C656948 and its metabolites AE C656948-benzamide (AE F148815), AE C656948-7-hydroxy (BCS-AA-10065) and AE C656948-pyridyl-carboxylic acid (AE C657188) in soil
Report No:	MR-09/062
Document No:	M-348402-01-1
Guideline(s) followed in study:	EU: Annex II part A, section 6 and Annex III, part A, section 8 of Council Directive 91/414/EEC; EC DGA: Appendix H, 7032/VI/95 rev. 5 of 22 July 1997; US EPA: OPPTS 860.1380, EPA 712-C-95-177 of August 1996
Deviations from current test guideline:	Current Guideline: EC Guideline 7032/VI/95 (1997); Appendix H of working document 1607/VI/97 rev. 2 (1999) None
Previous evaluation:	No, not previously submitted
GLP/Officially recognised testing facilities:	Yes, conducted under GLP/Officially recognised testing facilities
Acceptability/Reliability:	Yes

2. Full summary of KCA 7.1.2.2.1/12

Executive Summary

The purpose of this study was to determine the stability of fluopyram and its metabolites fluopyram-benzamide (AE F148815), fluopyram-7-hydroxy (BCS-AA-10065) and fluopyram-pyridyl-carboxylic acid (AE C657188) in soil under frozen storage conditions.

Untreated soil from North Dakota, USA (loam) and New York, USA (loamy sand) was used for this storage stability study. Soil samples were fortified separately with 20 µg/kg of fluopyram, 20 µg/kg of fluopyram-benzamide and fluopyram-pyridyl-carboxylic acid each and with 20 µg/kg of fluopyram-7-hydroxy.

Soil samples were analysed on day 0, day 323, day 547 and after 864 days of storage in the freezer at <-18 °C or below.

Soil samples were analysed for fluopyram, fluopyram-benzamide, fluopyram-7-hydroxy and fluopyram-pyridyl-carboxylic acid according to method 01023.

Identification and quantitation of the test item was done by high performance liquid chromatography using MS/MS detection in the Multiple Reaction Monitoring mode. Possible matrix effects of fluopyram and its metabolites were eliminated by using an internal standard solution of isotopically labelled reference item. This solution was added to the sample solutions after extraction. Aliquots of the extracts were directly injected into the HPLC-MS/MS.

The limit of quantitation (LOQ) for the method was 1.0 µg/kg and the limit of detection (LOD) was 0.3 µg/kg for fluopyram and its metabolites.

The mean concurrent recovery during analyses of the samples was 102 % for fluopyram, fluopyram-benzamide 100 %, fluopyram-7-hydroxy 106 %, and fluopyram-pyridyl-carboxylic acid 100 %.

At all sampling intervals an average of more than 70 % of the initially fortified amount of fluopyram, fluopyram-benzamide, fluopyram-7-hydroxy, and fluopyram-pyridyl-carboxylic acid was recovered from the stored samples. The mean recovered amounts in two soils after 864 days of freezer storage ranged from 88 % to 121 %.

Fluopyram, fluopyram-benzamide, fluopyram-7-hydroxy, and fluopyram-pyridyl-carboxylic acid residues in soil are considered to be stable for at least 864 days of storage under frozen conditions.

I. MATERIALS AND METHODS

A. Materials

1. Test Materials

Common name: Fluopyram
Certificate number: AZ 14764
Purity: 99.4 %

Common name: Fluopyram-benzamide
Certificate number: AZ 20596 and AZ 21923
Purity: 99.0%

Common name: Fluopyram-7-hydroxy
Certificate number: AZ 14321
Purity: 99.0%

Common name: Fluopyram-pyridyl-carboxylic acid
Certificate number: AZ 14882
Purity: 97.2%

2. Soil Samples

Untreated soil from North Dakota, USA (loam) and New York, USA (loamy sand) was used for this storage stability study. The different soils were used in order to assess a possible influence of different soil characteristics. The soil samples were classified according to USDA specifications.

Table 7.1.2.2.1- 34: Soil characteristics

Soil	North Dakota, USA	New York, USA
Description	0-15 cm soil layer	0-15 cm soil layer
pH (in $CaCl_2$ solution)	6.4	6.0
pH (in H_2O)	6.8	6.3
Organic Matter (%) [1]	6.1	2.4
Cation Exchange Capacity (meq / 100 g dry soil)	23.7	7.1
Textural Class (USDA) **Sand [50 µm – 2 mm]** **Silt [2 µm – 50 µm]** **Clay [< 2 µm]**	loam 33 42 25	loamy sand 87 8 5

USDA: United States Department for Agriculture
[1] organic matter = organic carbon x 1.72

B. STUDY DESIGN

1. Sample Handling

Portions of 20 g of the homogenized soils were weighed into 125 mL glass containers with plastic lids. The reference items were dissolved in acetonitrile. Standard solutions of 2.0 mg/L were prepared by appropriate dilution with acetonitrile. This fortification standard solutions were used to treat the control soil samples. For the preparation of the storage stability samples 0.2 mL of the 2 mg/L fortification standard solution was added to each of the corresponding sets of soil samples. The resulting concentration in all soil samples was approximately 20 µg/kg soil. A certain number of untreated soil samples were used as control samples, samples to be spiked for the determination of concurrent recoveries, and reserve samples.

After fortification, the soil samples were transferred to the cold storage depot and were stored at –18 °C or below. After specified storage intervals one sample set was taken out of the cold storage depot for analysis. One control sample (C) and four fortified soil samples (T) were analysed. A second control sample was used for the determination of the concurrent recovery (R).

2. Analytical procedures

Samples were analysed according to the analytical procedure 01023 described in 'Analytical Method 01023 for the Determination of Residues of AE C656948 and its Metabolites AE C656948-benzamide (AE F148815), AE C656948-7-hydroxy (BCS AA-10065) and AE C656948-PCA in Soil by HPLC-MS/MS (M-287801-02-1). Full details and acceptable validation data to support the analytical method are presented within document M-CA 4, which comply with the EU regulatory requirements outlined within SANTE/2020/12830, Rev.1.

Identification and quantitation of the test item was done by high performance liquid chromatography using MS/MS detection in the Multiple Reaction Monitoring mode. Possible matrix effects of fluopyram and its metabolites were eliminated by using an internal standard solution of isotopically labelled reference item. This solution was added to the sample solutions after extraction. Aliquots of the extracts were directly injected into the HPLC-MS/MS.

The limit of quantitation (LOQ) for the method was 1.0 µg/kg and the limit of detection (LOD) was 0.3 µg/kg for fluopyram and its metabolites.

II. RESULTS AND DISCUSSION

A. DATA

The following tables show the levels for fluopyram, fluopyram-benzamide, fluopyram-7-hydroxy, and fluopyram-pyridyl-carboxylic acid measured in the stored spiked samples of soil North Dakota and New York. In each table, the recoveries determined in the stored spiked samples are shown 'uncorrected' first. The fortification level was 20 µg/kg for all analytes. In further columns, the results are normalized to day 0 or corrected by the average concurrent recoveries from freshly fortified samples. Mean values were calculated with rounded values. Therefore, minor deviations may occur when the values given in the table are used.

Table 7.1.2.2.1- 35: Storage stability data and concurrent recovery data for fluopyram in soil North Dakota

Storage Period (days)	Residue Level in Stored Samples			Residue Level in Fresh Concurrent Recoveries	day-0 Normalized Average
	µg/kg	% of nominal spiking level	Average % recovery	% recovery (Single Values)	
0	19.8	99	99	105	100
	19.8	99			
	20.8	104			
	18.8	94			
323	22.0	110	98	102	n.d.
	20.2	101			
	17.5	88			
	18.5	93			
547	18.8	94	93	98	n.d.
	18.2	91			
	19.4	97			
	18.1	91			
864	24.6	123	121	112	122
	24.4	122			
	23.7	119			
	23.9	120			

Table 7.1.2.2.1- 36: Storage stability data and concurrent recovery data for fluopyram in soil New York

Storage Period (days)	Residue Level in Stored Samples			Residue Level in Fresh Concurrent Recoveries	day-0 Normalized Average
	µg/kg	% of nominal spiking level	Average % recovery	% recovery (Single Values)	
0	17.5	88	92	93	100
	18.0	90			
	18.2	91			
	20.0	100			
323	20.6	103	101	95	n.d.
	20.2	101			
	20.1	101			
	20.0	100			
547	19.9	100	97	101	n.d.
	19.8	99			
	18.9	95			
	19.3	97			
864	23.3	117	116	114	125
	22.9	115			
	23.0	115			
	23.2	116			

Table 7.1.2.2.1- 37: Storage stability data and concurrent recovery data for fluopyram-benzamide in soil North Dakota

Storage Period (days)	Residue Level in Stored Samples			Residue Level in Fresh Concurrent Recoveries	day-0 Normalized Average
	µg/kg	% of nominal spiking level	Average % recovery	% recovery (Single Values)	
0	19.2	96	90	90	100
	18.1	91			
	17.4	87			
	17.4	87			
323	18.3	92	88	93	n.d.
	17.4	87			
	17.5	88			
	17.0	85			
547	21.5	108	105	110	n.d.
	19.7	99			
	21.4	107			
	21.2	106			
864	20.4	102	102	104	113
	19.9	100			
	21.0	105			
	20.3	102			

Table 7.1.2.2.1- 38: Storage stability data and concurrent recovery data for fluopyram-benzamide in soil New York

Storage Period (days)	Residue Level in Stored Samples			Residue Level in Fresh Concurrent Recoveries	day-0 Normalized Avarage
	µg/kg	% of nominal spiking level	Average % recovery	% recovery (Single Values)	
0	18.8	94	96	92	100
	19.9	100			
	18.2	91			
	19.8	99			
323	19.4	97	91	93	n.d.
	17.7	89			
	18.6	93			
	17.3	87			
547	21.4	107	106	111	n.d.
	20.3	102			
	21.5	108			
	21.8	109			
864	22.0	110	108	108	113
	21.5	108			
	21.4	107			
	21.6	108			

Table 7.1.2.2.1- 39: Storage stability data and concurrent recovery data for fluopyram-7-hydroxy in soil North Dakota

Storage Period (days)	Residue Level in Stored Samples			Residue Level in Fresh Concurrent Recoveries	day-0 Normalized Avarage
	µg/kg	% of nominal spiking level	Average % recovery	% recovery (Single Values)	
0	18.6	93	103	101	100
	22.1	111			
	22.4	112			
	19.5	98			
323	26.4	132	109	117	n.d.
	16.1	81			
	21.3	107			
	23.0	115			
547	20.0	100	105	103	n.d.
	21.6	108			
	20.7	104			
	21.3	107			
864	22.8	114	114	117	110
	22.3	112			
	22.8	114			
	22.9	115			

Table 7.1.2.2.1- 40: Storage stability data and concurrent recovery data for fluopyram-7-hydroxy in soil New York

Storage Period (days)	Residue Level in Stored Samples			Residue Level in Fresh Concurrent Recoveries	day-0 Normalized Avarage
	µg/kg	% of nominal spiking level	Average % recovery	% recovery (Single Values)	
0	23.8	119	105	91	100
	16.9	85			
	23.2	116			
	20.2	101			
323	16.9	85	105	101	n.d.
	23.7	119			
	19.1	96			
	24.0	120			
547	20.5	103	101	106	n.d.
	19.9	100			
	21.5	108			
	19.2	96			
864	22.8	114	116	114	110
	23.8	119			
	23.5	118			
	22.7	114			

Table 7.1.2.2.1- 41: Storage stability data and concurrent recovery data for fluopyram-pyridyl-carboxylic acid in soil North Dakota

Storage Period (days)	Residue Level in Stored Samples			Residue Level in Fresh Concurrent Recoveries	day-0 Normalized Avarage
	µg/kg	% of nominal spiking level	Average % recovery	% recovery (Single Values)	
0	19.9	100	100	96	100
	19.8	99			
	20.3	102			
	20.3	102			
323	18.8	94	94	99	n.d.
	18.7	94			
	18.8	94			
	18.7	94			
547	20.0	100	107	110	n.d.
	21.6	108			
	21.8	109			
	21.8	109			
864	18.1	91	92	96	91
	18.5	93			
	18.6	93			
	18.2	91			

Table 7.1.2.2.1- 42: Storage stability data and concurrent recovery data for fluopyram-pyridyl-carboxylic acid in soil New York

Storage Period (days)	Residue Level in Stored Samples			Residue Level in Fresh Concurrent Recoveries	day-0 Normalized Avarage
	µg/kg	% of nominal spiking level	Average % recovery	% recovery (Single Values)	
0	19.8	99	99	98	100
	19.7	99			
	19.5	98			
	20.0	100			
323	18.5	93	92	99	n.d.
	18.2	91			
	18.4	92			
	18.4	92			
547	20.0	100	98	109	n.d.
	19.7	99			
	19.4	97			
	19.5	98			
864	17.7	89	88	97	89
	17.6	88			
	17.4	87			
	17.8	89			

B. STORAGE STABILITY

The mean concurrent recovery during analyses of the samples was 102% for fluopyram, 100% for fluopyram-benzamide, 106% for fluopyram-7-hydroxy and 100% for fluopyram-pyridyl-carboxylic acid 100 %.

At all sampling intervals an average of more than 81% of the initially fortified amount of fluopyram, fluopyram-benzamide, fluopyram-7-hydroxy, and fluopyram-pyridyl-carboxylic acid was recovered from the stored samples. The mean recovered amounts in two soils after 864 days of freezer storage ranged from 88 % to 121 %.

III. CONCLUSIONS

Fluopyram, fluopyram-benzamide, fluopyram-7-hydroxy, and fluopyram-pyridyl-carboxylic acid residues in soil are considered to be stable for at least 864 days of storage under frozen conditions.

3. Assessment and conclusion

Assessment and conclusion by applicant:
The study is considered to be valid and reliable.

Assessment and conclusion by RMS:
Outcome and conclusion of the study: RMS should indicate if they agree to the results and conclusions of the APPL.

1. Information on the study

Data Point:	KCA 7.1.2.2.1/13
Report Author:	[redacted].
Report Year:	2020
Report Title:	Fluopyram (FLU): Ecoregion crosswalk - Representativeness of environmental conditions at five North American terrestrial field dissipation trial sites for Europe
Report No:	EnSa-19-0396
Document No:	M-754876-01-1
Guideline(s) followed in study:	not applicable
Deviations from current test guideline:	Current Guideline: not applicable (calculation)
Previous evaluation:	No, not previously submitted
GLP/Officially recognised testing facilities:	No, not conducted under GLP/Officially recognised testing facilities
Acceptability/Reliability:	Yes

2. Full summary of KCA 7.1.2.2.1/13

Executive Summary

The environmental conditions at 5 North American field dissipation trial sites were compared to European environmental conditions. It was assessed whether the conditions at North American fluopyram terrestrial field dissipation trial sites (M-306809-01-2; M-306812-01-2; M-306817-01-2; M-306820-01-2; M-306814-01-2; KCA 7.1.2.2.1/03 to KCA 7.1.2.2.1/07) are representative for Europe according to a refined ENASGIPS evaluation. In case of similar conditions, results from North American field dissipation trials might be used to derive degradation half-live values ($DegT_{50}$) for European risk assessments.

The concept of ecoregions build the basis of the comparison. Ecoregions are delineated with respect to similar location, climate, soil, vegetation, hydrology, terrain, wildlife, and land use and form distinct geographical areas. The ENASGIPS software is recommended by the OECD Guidance Document for Conducting Pesticide Terrestrial Field Dissipation Studies to identify comparable North American and European ecoregions. It uses the concept of ecoregions under the assumption that pesticide degradation should be similar in ecoregions with similar environmental properties.

The similarity model within ENASGIPS merely considers mean annual climate parameters (temperature, precipitation) and selected soil parameters (soil texture, organic carbon, pH). However, climate is often characterised by seasonal variations and pesticide degradation cannot solely be attributed to selected soil properties, i.e topsoil texture, organic carbon content, and pH. Therefore, a refinement of the ENASGIPS approach was proposed, which took into account more holistic indicators, such as climate seasonality and soil types.

Trial sites North Rose, New York and Kerman, California were considered representative for European climate conditions and soil properties according to the ENASGIPS approach.
For the site Ephrata, Washington a refined comparison was conducted which takes into account the conditions at the trial site (including irrigation) rather than of the ecoregion because the site is not well represented by the ecoregion. According to this comparison, it can be concluded that the site Ephrata, Washington is representative for Europe.

No similar European ecoregions could be identified by ENASGIPS for trial site Sycamore, Georgia, which exhibits a strong subtropical climate, and Northwood, North Dakota, which has a pronounced continental climate.

I. METHODS

The environmental conditions at the five North American trial sites used for the North American fluopyram terrestrial field dissipation trial sites North Rose, New York; Northwood, North Dakota; Ephrata, Washington; Kerman, California and Sycamore, Georgia (KCA 7.1.2.2.1/03 to KCA 7.1.2.2.1/07; M-306809-01-2, M-306812-01-2, M-306817-01-2, M-306820-01-2, M-306814-01-2) were compared to European environmental conditions.

The GIS-based software 'Europe-North America Soil Geographic Information for Pesticide Studies' (ENASGIPS) 3.0 was developed by the Pest Management Regulatory Agency – Health Canada and the US Environmental Protection Agency in collaboration with Agriculture and Agri-Food Canada and the EC Joint Research Centre. The development was part of the OECD project 'Harmonized International Guidance for Pesticide Terrestrial Field Dissipation Studies and Crosswalk of North American and European Eco-regions'.

The tool includes a database with ecoregion boundaries as defined by WWF and a distribution for five environmental parameters and crop information for each ecoregion. The considered environmental parameters are

- mean annual temperature,
- mean annual precipitation,
- mean soil pH,
- mean soil organic carbon and
- soil texture.

Their distribution was derived by an overlay of the ecoregions with MARS FOODSEC Meteodata and Harmonized World Soil Database. It is assumed that these parameters are normally distributed and the distributions are described by mean value and standard deviation. In case of soil texture, the textural classes were mapped onto an integer scale from heavy clay (1) to sand (13).

Ecoregions are compared by calculating a similarity score between a root ecoregion and other ecoregions. The score for a parameter in an ecoregion is 100% if the parameter of ecoregion does not differ more than one standard deviation from the mean of the root ecoregion. The ENASGIPS tool can either be used with the so-called 'Holistic Ecoregion Similarity' approach which takes into account all five parameters with equal weights or the 'Weights of Evidence Ecoregion Similarity' which uses only selected parameters for its comparison.

The results of ENASGIPS were amended with a refined assessment of climate seasonality and occurring soil types. The climate of an ecoregion is typically characterised by seasonal variation. The descriptions of the North American ecoregions paraphrases the climatic conditions as e.g. 'The climate is marked by warm summers and very cold winters' or 'The ecoregion has a severe, mid-latitude, humid continental climate, marked by hot summers and severe winters', sometimes with a temperature or precipitation range given. The European ecoregions contain several climate parameters for a specific month, such as maximum temperature in September and October, rain days in November and December, precipitation in June and October, etc.

A pronounced seasonality of temperature or precipitation distribution in an ecoregion is characteristic of a climate type but is not reflected by the climate parameters used in the ENASGIPS similarity models (mean annual temperature and annual precipitation). North-American climate was considered similar to EU conditions in a specific MARS grid, if all relevant indicators are contained in the interval for this

indicator given in the ecoregion classification for a specific field trial site. If similar climate occurs in Europe, the analysis was refined with additional information on soil types and land use.

II. RESULTS

A North Rose, New York

The trial site North Rose, New York, is located within WWF ecoregion Southern Great Lakes forests in ENASGIPS and the North American ecoregion Eastern Great Lakes Lowlands.

Long-term monthly climate data from the nearby weather station Sodus are illustrated in Figure 7.1.2.2.1- 2. General climate parameters of the trial site and corresponding ecoregions are given in Table 7.1.2.2.1- 43. The site's climate can be classified as temperate continental forest according to Köppen-Trewartha climate types (FAO 2012a) and is characterised by warm summers, cold winters, and overall humid conditions.

During the trial, the plot was irrigated (438.2 mm during the study duration, total water input corresponds to 126% of the 30 year (1977 – 2006) average annual rainfall. However, irrigation is not explicitly considered in the ecoregion crosswalk analysis. This analysis focuses on the long-term climate influencing the formation of ecoregion characteristics (e.g. via vegetation and soil genesis) and thus overall conditions for degradation, whereas the influence of short-term weather and irrigation on degradation during the trial duration are addressed via temperature and moisture normalization. The sum of irrigated water and precipitation at the site is at the upper tail of the precipitation distribution of the root ecoregion. Therefore, the comparison based on the Eastern Great Lakes Lowland ecoregion would cover the trial site conditions even if irrigation was considered.

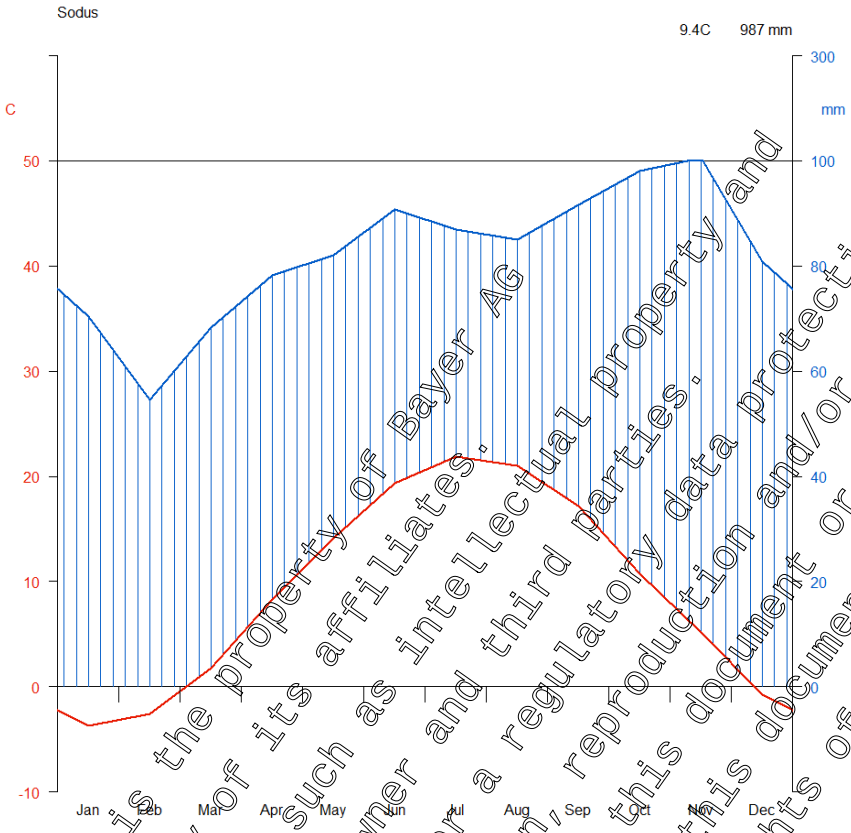


Figure 7.1.2.2.1- 2: Climate diagram according to Walter & Lieth of weather station Sodus (NCEI2019d). Shown are long-term monthly averages of temperature and precipitation from 1981 to 2010

Table 7.1.2.2.1- 43: Climate parameters near trial site North Rose, New York (NCEI weather station Sodus) and in corresponding ecoregions

	No. of months > 10°C	Average temperature			Average precipitation		
		Annual (°C)	Summer (°C)	Winter (°C)	Annual (mm)	Summer (mm)	Winter (mm)
Trial site North Rose, New York	6	9.4	20.5	-2.4	987	263	206
CEC ecoregion 8.1.1 Eastern Great Lakes Lowlands	5[1]	5 – 9	16.7 – 20.7[1]	-9.1 – -2.0[1]	720 – 1200	198 – 386[1]	186 – 260[1]
ENASGIPS ecoregion[2] NA0414 Southern Great Lakes forests	6	9.3 ± 1.2	20.8	-2.5	970 ± 133	256	207

[1] derived from spatial overlay with MARS FOODSEC data
[2] mean value ± standard deviation (corresponding to range with 100% similarity score)

The terrain of ecoregion Eastern Great Lakes Lowlands is covered with a wide variety of deep glacial and marine deposits. Typical soil types are Alfisols, Inceptisols or Spodosols. The soil series at the trial site is Niagara silt loam. The physical properties of the upper 30 cm are summarised in Table 7.1.2.2.1-44. The soil series belongs to the taxonomic class of Endoaqualfs, a subgroup of Alfisols. The soil

corresponds to an Arenosol in the World Reference Base of Soil Resources which covers about 2 % of the EU's surface.

Table 7.1.2.2.1- 44: Summary of topsoil characteristics at trial site North Rose, New York

Soil Series	Depth (cm)	USDA texture class	Soil texture			pH H_2O (-)	OC (%)
			Sand (%)	Silt (%)	Clay (%)		
Niagara	0 – 15	Loamy sand	87	9	5	6.2	1.28
	15 – 30	Sandy loam	83	14	4	5.4	0.52

The ENASGIPS holistic similarity query with a similarity threshold of 80% identifies 9 similar ecoregions in Europe which are displayed in Figure 7.1.2.2.1- 3. These ecoregions are mostly found in Central Europe, the United Kingdom and selected mountainous regions such as the Pyrenees, Carpathian Mountains, and Apennine Mountains. Similarity scores range from 80% to 92%.

The site's climate and soil conditions fit very well with the root ecoregion, as well as with most of the European ecoregions which were identified as similar by ENASGIPS. An exception is organic carbon content, which is on the upper tail of the root ecoregion's distribution, but within the range of most of the similar European ecoregions. It can be concluded that root ecoregion Southern Great Lakes forests is representative for the trial site.

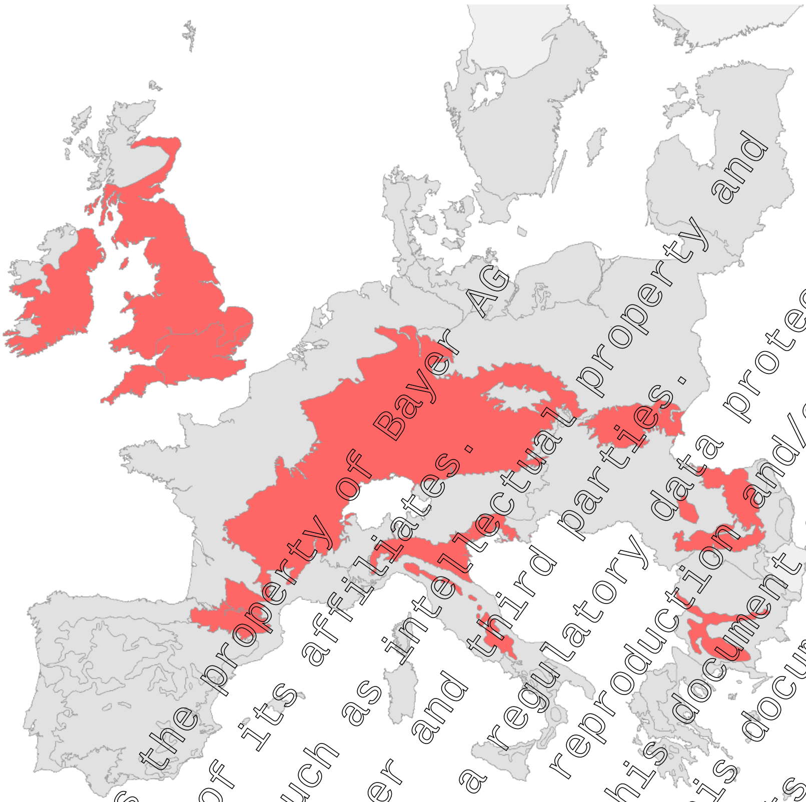


Figure 7.1.2.2.1- 3: European Ecoregions similar to Southern Great Lakes forests according to ENASGIPS (holistic similarity model with threshold 80%); similar ecoregions are marked red

The ENASGIPS approach does not take into account the pronounced seasonal character of the site's continental climate. As temperature and precipitation are major factors influencing degradation in soil, the MARS-AGRI4CAST database was queried to identify regions with similar climate properties in Europe. The query was based on average summer and winter temperature, as well as average annual precipitation because of the site's climate with warm summers and cold winters. Parameter ranges for the query were taken from the North American ecoregion Eastern Great Lakes Lowlands (Table 7.1.2.2.1- 43). The query yields grid cells in Baltic countries and southern Poland with matching climate parameters. The analysis shows that average winter temperature is the most restricting property with regard to trial site similarity (Figure 7.1.2.2.1- 4). The identified climate cells also cover the trial site's soil type which can mostly be found in the Baltic countries and Central Europe.

In conclusion, climate conditions at the trial site are well represented by the root ecoregions' properties. Several European ecoregions were identified as similar to the North American ecoregion by ENASGIPS. When taking into account the trial site's continental climate a comparison with summer and winter temperature as well as annual precipitation yields similar conditions in Europe, but in different regions (Eastern Europe, especially Baltic countries) compared to the ENASGIPS result. The trial site's soil type has a limited coverage in Europe but the existing areas are relevant for European agriculture. Overall, the trial site North Rose, New York, is considered representative for European conditions.

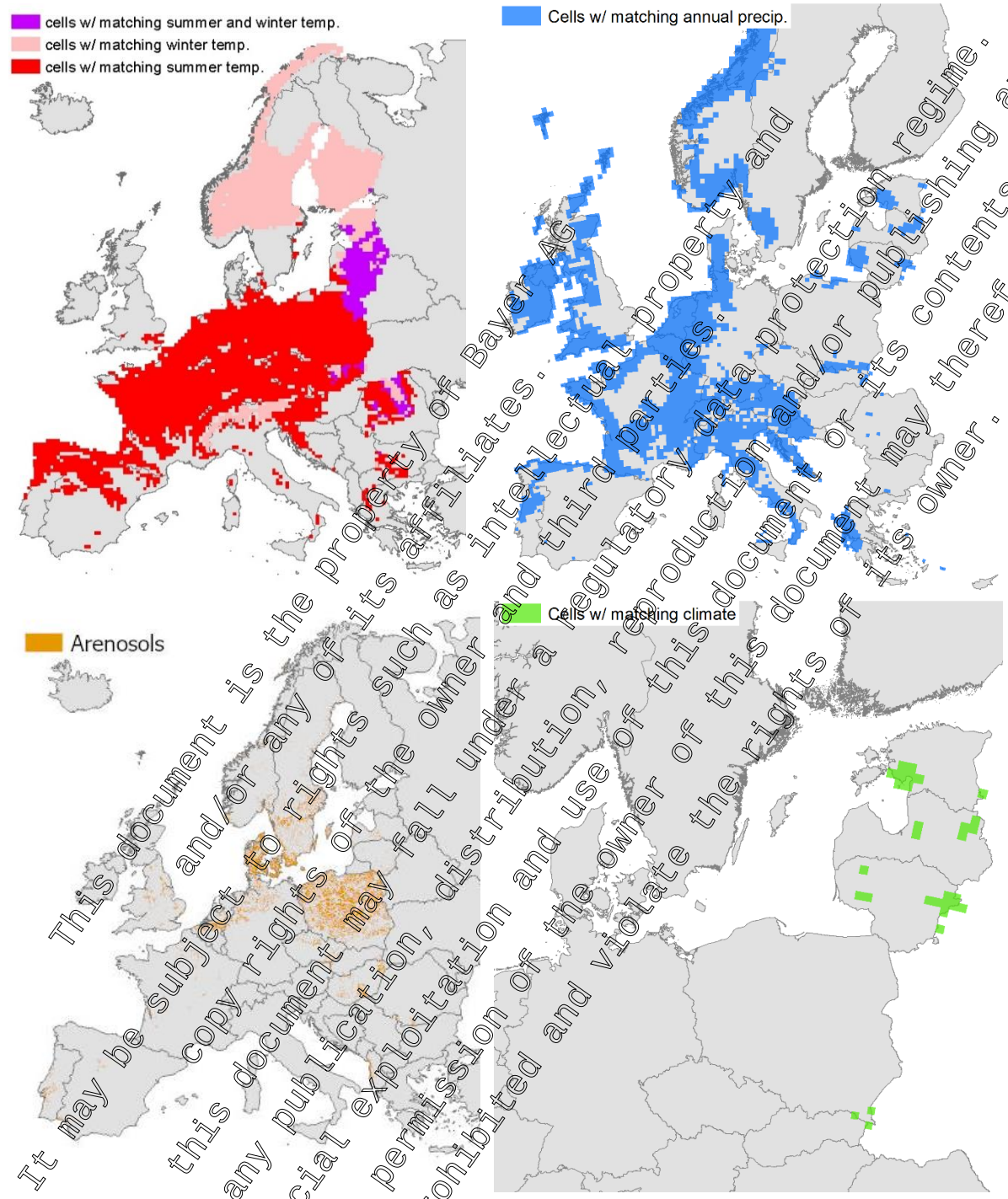


Figure 7.1.2.2.1- 4: Areas in Europe with similar summer and winter temperature (upper left) and precipitation (upper right) as CEC ecoregion Eastern Great Lakes Lowlands as well as soil type Arenosols[2] (lower left) ; overlap of both similar temperature and climate in Baltic countries and Poland (lower right)

[2] The spatial extent displayed in the map represents soil mapping units which normally contain different soils, i.e. only a fraction (on average 33%) of the area is covered by Arenosols

B Northwood, North Dakota

The trial site Northwood, North Dakota, is located within WWF ecoregion Northern Tall Grasslands in ENASGIPS or the Lake Manitoba and Lake Agassiz Plain, respectively.

Long term monthly climate data from the nearby weather station Grand Forks International Airport are illustrated in Figure 7.1.2.2.1- 5. General climate parameters of the trial site and corresponding ecoregions are given in Table 7.1.2.2.1- 45. The site's climate can be classified as temperate continental according to Köppen-Trewartha climate types and is a humid climate characterized by hot summers and very cold winters.

During the trial the plot was irrigated during summer month (870.9 mm during study duration, total water input corresponds to 177% of the historical 10 year (1995 – 2004) average annual rainfall. However, irrigation is not explicitly considered in the ecoregion crosswalk analysis. This analysis focuses on the long-term climate influencing the formation of ecoregion characteristics (e.g. via vegetation and soil genesis) and thus overall conditions for degradation, whereas the influence of short-term weather and irrigation on degradation during the trial duration are addressed via temperature and moisture normalization. Nevertheless, for the refined analysis with a direct query of similar summer precipitation ranges in Europe the ecoregion summer precipitation range has been enlarged to cover irrigation as well (Figure 7.1.2.2.1- 6).

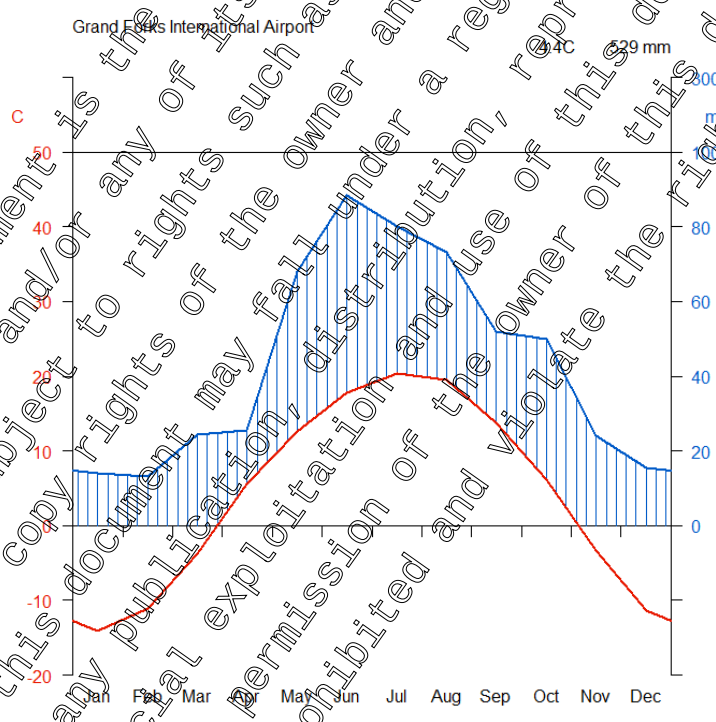


Figure 7.1.2.2.1- 5: Climate diagram according to Walter & Lieth of weather station Grand Forks International Airport (NCEI 2019a). Shown are long-term monthly averages of temperature and precipitation from 1981 to 2010

Table 7.1.2.2.1- 45: Climate parameters near trial site Northwood, North Dakota (NCEI weather station Grand Forks International Airport) and in corresponding ecoregions

	No. of months > 10°C	Average temperature			Average precipitation		
		Annual (°C)	Summer (°C)	Winter (°C)	Annual (mm)	Summer (mm)	Winter (mm)
Trial site Northwood, North Dakota	5	4.4	19.2	-12.2	529	242	41
CEC ecoregion 9.2.2 Lake Manitoba and Lake Agassiz Plain	5[1]	2 – 6	17 (17.1 – 21[1])	-10 (-14.1 – -9.6[1])	450 – 700	227 – 292[1]	64 – 72[1]
ENASGIPS ecoregion[2] NA0812 Northern tall grasslands	5	4.1 ± 1.2	19.1	-12.2	623 ± 38	257	68

[1] derived from spatial overlay with MARS FOODSEC data
[2] mean value ± standard deviation (corresponding to range with 100% similarity score)

Ecoregion Lake Manitoba and Lake Agassiz Plain typically has Mollisols and Vertisols soils with mean annual soil temperatures between 0°C and 8°C, but remarkable soil temperature differences between summer and winter (frigid soil temperature regime) and rather wet moisture conditions (aquic and udic). The soil at the trial site is a Hapludoll (great group of Udolls which is suborder of Mollisols) with the typical soil series Gardena, a deep, coarse-silty, well drained soil. The physical properties at the site of the upper 30 cm are summarised in Table 7.1.2.2.1- 46. In the World Reference Base for Soil Resources Mollisols would correspond to Chernozems. According to Amelung et al. (2008) Chernozems cover less than 5% of Europe's arable land.

Table 7.1.2.2.1- 46: Summary of topsoil characteristics at trial site Northwood, North Dakota

Soil Series	Depth (cm)	USDA texture class	Soil texture			pH H_2O (-)	OC (%)
			Sand (%)	Silt (%)	Clay (%)		
Gardena	0 – 15	loam	34	41	26	7.0	3.36
	15 – 30	loam	32	42	26	7.0	2.9

The ENASGIPS holistic similarity query with a similarity threshold of 80% identifies no similar ecoregions in Europe.

While the site's annual average temperature, its soil pH and soil texture are within the ranges of the root ecoregion, the site's precipitation is lower and its soil organic carbon content is considerably higher. However, the ENASGIPS ecoregion precipitation range is very narrow, especially compared to the corresponding CEC ecoregion, and the absolute difference between precipitation at the site and in the ecoregion used for the comparison is not too large.

The ENASGIPS approach does not take into account the pronounced seasonal character of the site's continental climate. As temperature and precipitation are major factor influencing degradation in soil,

the MARS-AGRI4CAST database was queried to identify regions with similar climate properties in Europe. The query was based on average summer and winter temperature, as well as average summer and winter precipitation because of the site's climate with warm, wet summers and cold winters with less precipitation. Parameter ranges for the query were taken from the North American ecoregion Lake Manitoba and Lake Agassiz Plain (Table 7.1.2.2.1- 45). An additional query for summer precipitation + irrigation has been conducted.

The query yields no cells with both similar temperature and precipitation seasonality. While cold winter temperatures comparable to the Lake Manitoba and Lake Agassiz Plain can only be found in northern Scandinavia, similar summer temperatures occur in central Europe. There are only very few locations with a comparably dry winter, in eastern Spain, in the rain shadow of the Carpathian mountains in Romania and the Ore mountains and the Bohemian-Moravian Highlands in Czech Republic. Including higher summer precipitation to account for irrigation at the trial site does not yield an overlap either (Figure 7.1.2.2.1- 6).

In conclusion, climate and soil conditions at the trial site are partly represented by the root ecoregions' properties. No European ecoregions were identified as similar to the North American ecoregion by ENASGIPS. An additional query against European climate data taking into account the climate seasonality does neither result in regions with similar continental and dry climate. Therefore, the trial site Northwood, North Dakota, is considered not representative for European conditions.

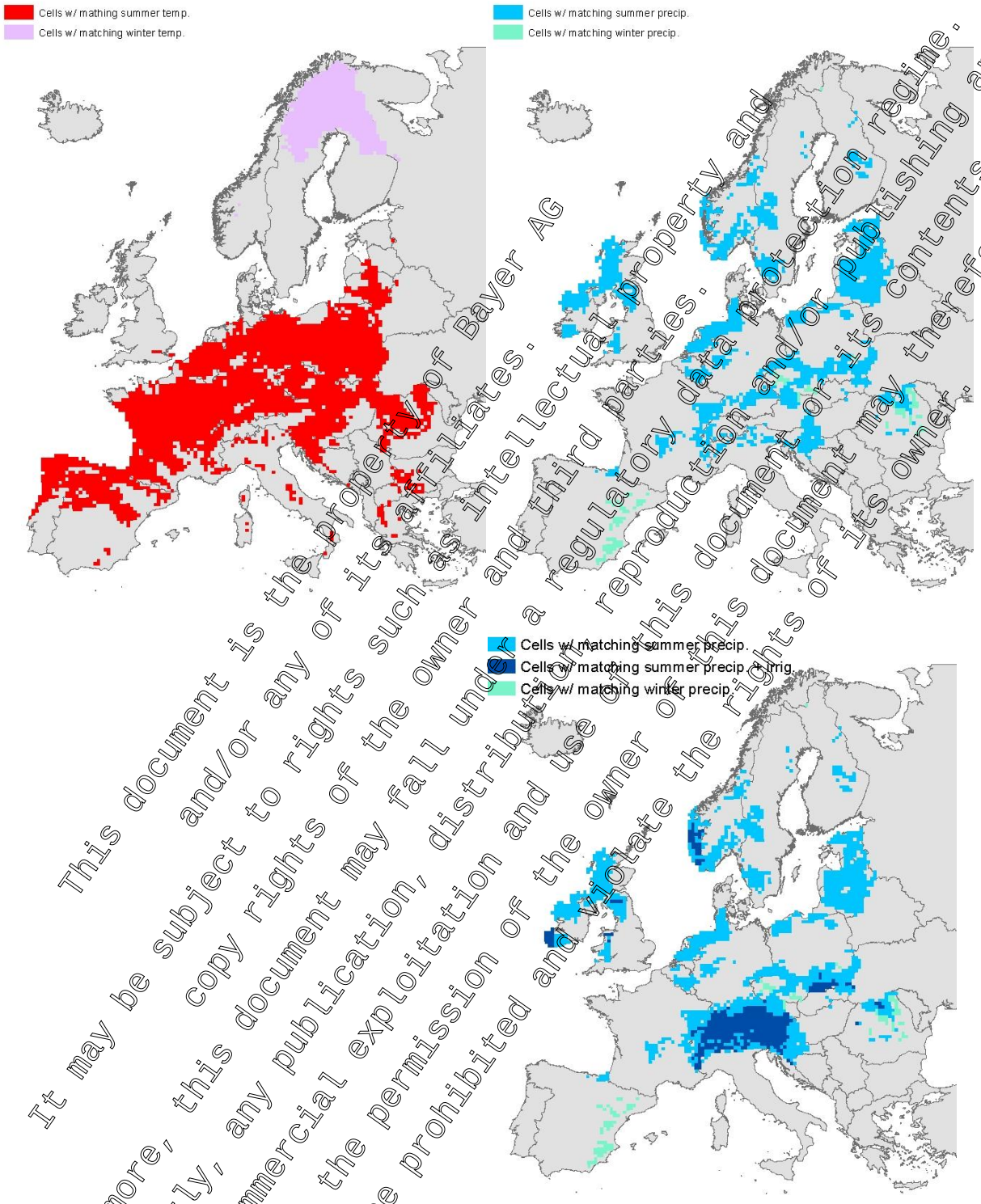


Figure 7.1.2.2.1-6: Areas in Europe with similar summer and winter temperature (left) and precipitation (right) as CEC ecoregion Lake Manitoba and Lake Agassiz Plain (JRC 2017); no overlap of areas with a similar pronounced climate seasonality; irrigation was added to the summer precipitation range leading to additional matching cells in mountainous regions, but still no overlap with winter precipitation (bottom right)

C Ephrata, Washington

The trial site Ephrata, Washington, is located within WWF ecoregion Snake-Columbia shrub steppe in ENASGIPS, which corresponds to the North American ecoregion Columbia Plateau.

Long term monthly climate data from the nearby weather station Quincy are illustrated in Figure 7.1.2.2.1- 7. General climate parameters of the trial site and corresponding ecoregions are given in Table 7.1.2.2.1- 47. The site's climate can be classified as temperate continental forest according to Köppen-Trewartha climate types and is characterized by warm summers, cold winters, and arid conditions from spring to autumn.

During the trial, the plot was irrigated (1962.4 mm during the study, water input corresponds to 131% of ET for apples. However, irrigation is not explicitly considered in the ecoregion crosswalk analysis. This analysis focuses on the long-term climate influencing the formation of ecoregion characteristics (e.g. via vegetation and soil genesis) and thus overall conditions for degradation, whereas the influence of short-term weather and irrigation on degradation during the trial duration are addressed via temperature and moisture normalization. Nevertheless, for the refined analysis with a direct query of similar summer precipitation ranges in Europe the ecoregion summer precipitation range has been enlarged to cover irrigation as well (Figure 7.1.2.2.1- 9).

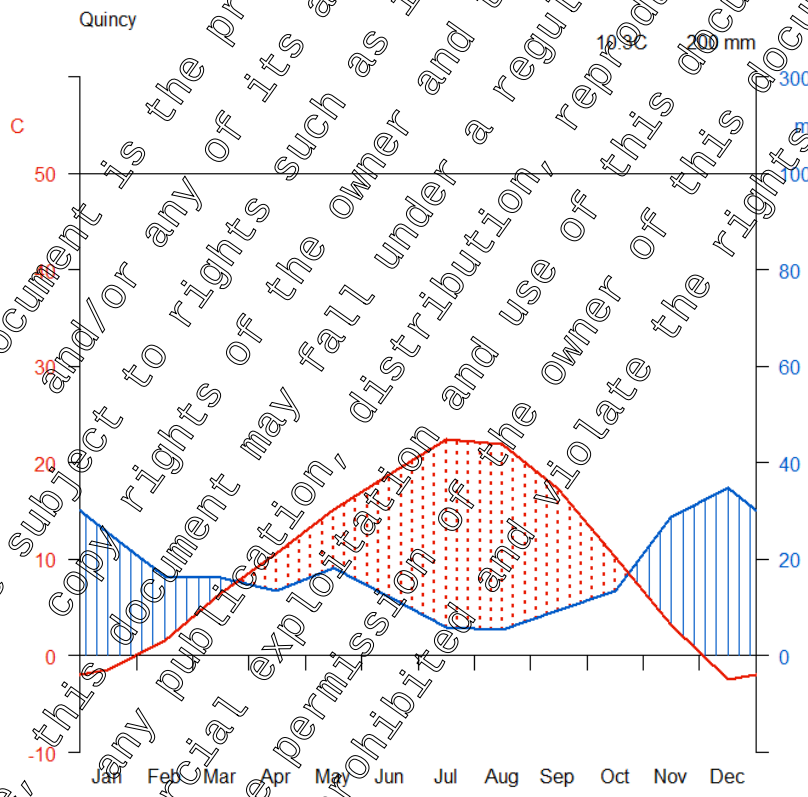


Figure 7.1.2.2.1- 7: Climate diagram according to Walter & Lieth of weather station Quincy (NCEI 2019b). Shown are long-term monthly averages of temperature and precipitation from 1981 to 2010

Table 7.1.2.2.1- 47: Climate parameters near trial site Ephrata, Washington (NCEI weather station Quincy) and in corresponding ecoregions

	No. of months > 10°C	Average temperature			Average precipitation		
		Annual (°C)	Summer (°C)	Winter (°C)	Annual (mm)	Summer (mm)	Winter (mm)
Trial site Ephrata, Washington	7	10.3	21.4	-0.8	200	23	77
CEC ecoregion 10.1.2 Columbia Plateau	5[1]	7 - 12	16.5 – 22.6[1]	-3.5 – 1.8[1]	150 – 600	29 – 115[1]	144 – 331[1]
ENASGIPS ecoregion[2] NA1309 Snake-Columbia shrub steppe	5	8.6 ± 2.2	20.5	-2.2	464 ± 104	52	160

[1] derived from spatial overlay with MARS FOODSEC data
[2] mean value ± standard deviation (corresponding to range with 100% similarity score)

The Columbia Plateau is largely covered with deep loess soils. The trial site's physical properties of the upper 30 cm soil are summarised in Table 7.1.2.2.1- 48. The soil series at the site is Quincy, a Torripsamment. This would correspond to Arenosols according to the World Reference Base of Soil Resources which cover about 2 % of EU's arable land.

Table 7.1.2.2.1- 48: Summary of topsoil characteristics at trial site Ephrata, Washington

Soil Series	Depth (cm)	USDA texture class	Soil texture			pH H_2O (-)	OC (%)
			Sand (%)	Silt (%)	Clay (%)		
Quincy	0 – 15	Sandy loam	80	15	6	8.1	0.46
	15 – 30	Loamy sand	85	11	4	8.2	0.17

The ENASGIPS holistic similarity query with a similarity threshold of 80% identifies 7 similar ecoregions in Europe which are displayed in Figure 7.1.2.2.1- 8. The ecoregions are located in the Mediterranean area and at the eastern borders of Romania and Bulgaria. Similarity scores range from 80% to 87%. The soil properties of the identified ecoregions are very similar to the root ecoregions soil properties, whereas the climatic conditions show a much lower similarity with higher mean annual temperature and more precipitation in most similar ecoregions.

The comparison between the study site and the root ecoregion shows that the site is not well represented by the root ecoregion especially with regard to precipitation which is 200 mm per year at the site compared to an average of 464 mm per year in the ecoregion. However, at the site roughly 1000 mm irrigation was applied per year. This results in water amounts much larger than the precipitation range of the ecoregion. Topsoil organic carbon is very low at the study site (< 0.5%). The high similarity score is due to the broad OC range in the root ecoregion. It was shown that OC is considerably higher in all European ecoregions that were identified as similar by ENASGIPS.

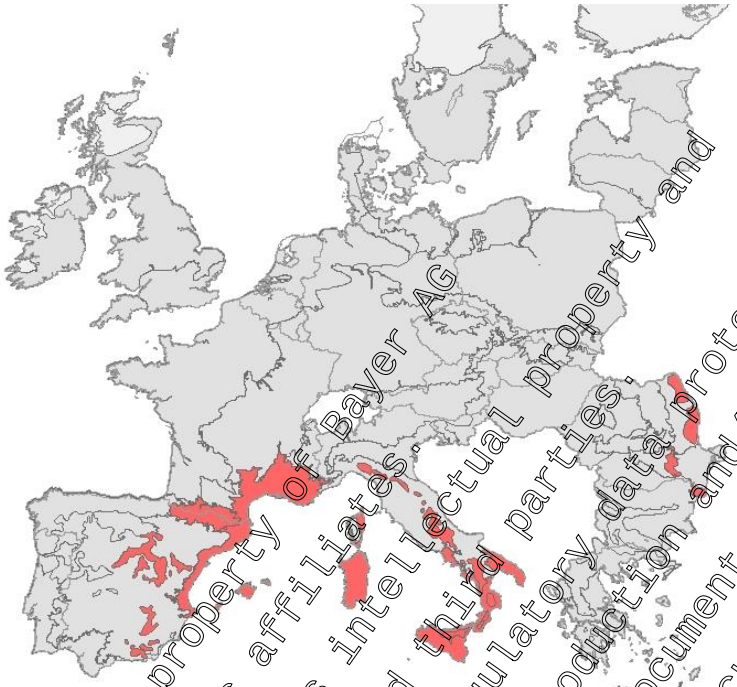


Figure 7.1.2.2.1- 8: European Ecoregions similar to Snake-Columbia shrub steppe according to ENASGIPS (holistic similarity model with threshold 80%); similar ecoregions are marked red

The ENASGIPS approach does not take into account the pronounced seasonal character of the site's continental climate. In addition, annual precipitation in the identified European ecoregions differs drastically from conditions at the study site. To take these aspects into account, the MARS-AGRI4CAST database was queried to identify regions with similar climate properties in Europe. The query was based on average summer and winter temperature and annual precipitation ranges of the ecoregion Columbia plateau (Table 7.1.2.2.1- 47) because of the site's climate with hot summers and very cold winters and the dry conditions at the study site. Additionally, the precipitation range has been enlarged to cover the annual irrigation at the study site as well. In Figure 7.1.2.2.1- 9 the spatial occurrence of similar climate conditions is mapped which can be found in large regions in Eastern Europe. Especially the precipitation range covering the irrigated water amounts additionally to precipitation cover almost entire Europe. Besides the climate also soil type Arenosol is mapped in Figure 7.1.2.2.1- 9. Its occurrence is small but spread throughout Europe.

In conclusion, climate and soil conditions at the trial site are not adequately represented by the root ecoregions' properties. Therefore, the similarity of the 7 European ecoregions that were identified as similar to the root ecoregion by ENASGIPS should be considered with caution with regard to the study site. However, given the large amount of irrigation at the site makes it reasonable to compare the overall water amount (precipitation + irrigation) to European precipitation. The refined query with parameters similar to the study site against MARS climate data yields that large parts of Eastern Europe have a climate similar to the root ecoregion and also similar to the study site considering irrigation. Overall, site Ephrata, Washington, is considered representative for European conditions.

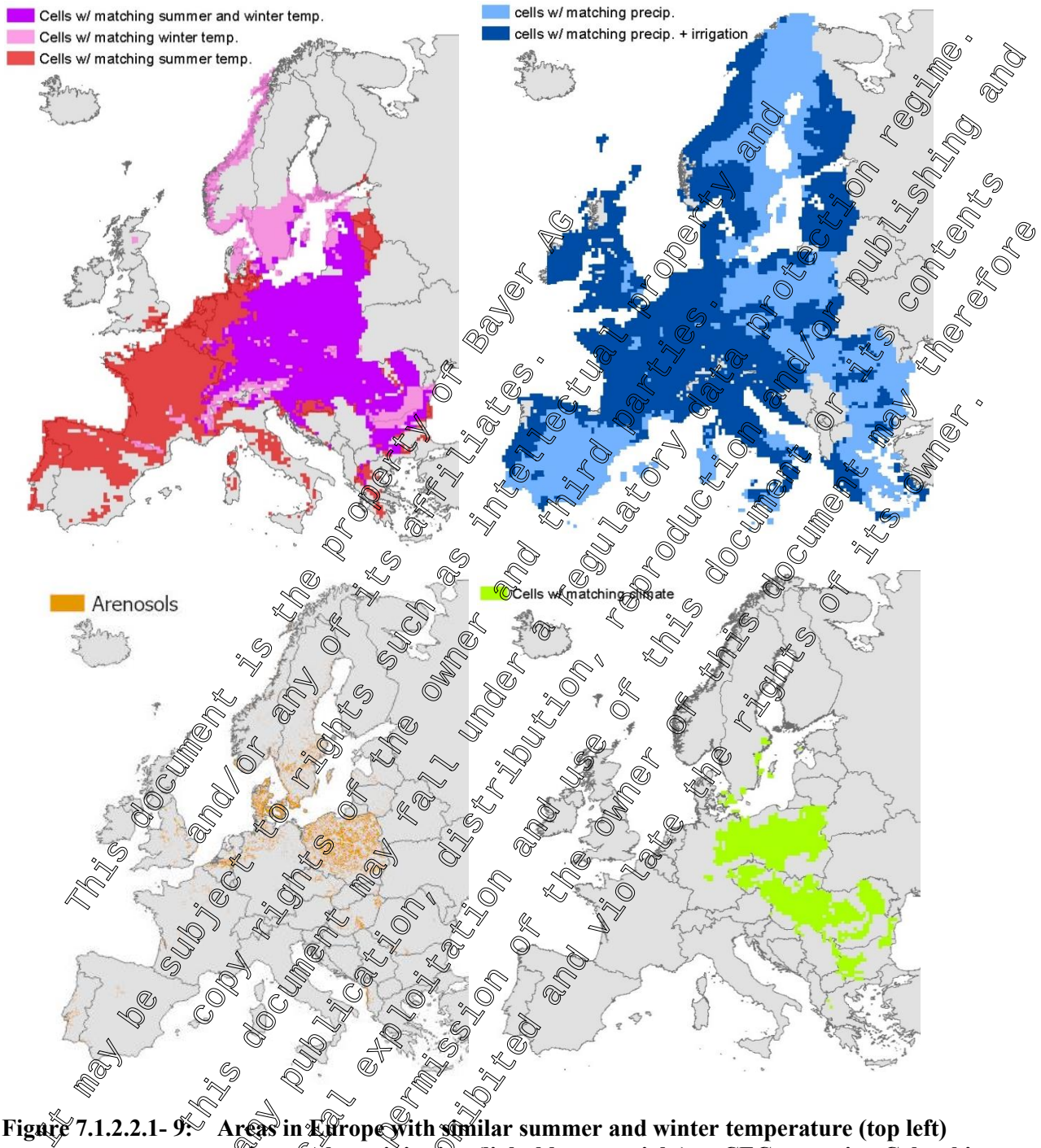


Figure 7.1.2.2.1- 9: Areas in Europe with similar summer and winter temperature (top left) and annual precipitation (light blue, top right) as CEC ecoregion Columbia Plain (JRC 2017); additionally precipitation similar to CEC ecoregion Columbia Plain + irrigation at study site is illustrated (dark blue, top right); large areas where both similar temperature seasonality and similar precipitation are identified (bottom right); Arenosols soil type can be found to small extents throughout Europe (bottom left)[3]

[3] [3] The spatial extent displayed in the map represents soil mapping units which normally contain different soils, i.e. only a fraction (on average 33%) of the area is covered by Arenosols

D Kerman, California
The trial site Kerman, California, is located within WWF ecoregion California Central Valley grasslands in ENASGIPS and the North American ecoregion Central California Valley.

Long term monthly climate data from the nearby weather station Fresno Yosemite International Airport are illustrated in Figure 7.1.2.2.1- 10. General climate parameters of the trial site and corresponding ecoregions are given in Table 7.1.2.2.1- 49. The site's climate can be classified as subtropical dry forest according to Köppen-Trewartha climate types (FAO 2012a) and is characterised by hot, dry summers and winter rains.

During the trial, the plot was irrigated (2753.1 mm during the study, water input corresponds to 114% of reference ET. However, irrigation is not explicitly considered in the ecoregion crosswalk analysis. This analysis focuses on the long-term climate influencing the formation of ecoregion characteristics (e.g. via vegetation and soil genesis) and thus overall conditions for degradation, whereas the influence of short-term weather and irrigation on degradation during the trial duration are addressed via temperature and moisture normalization.

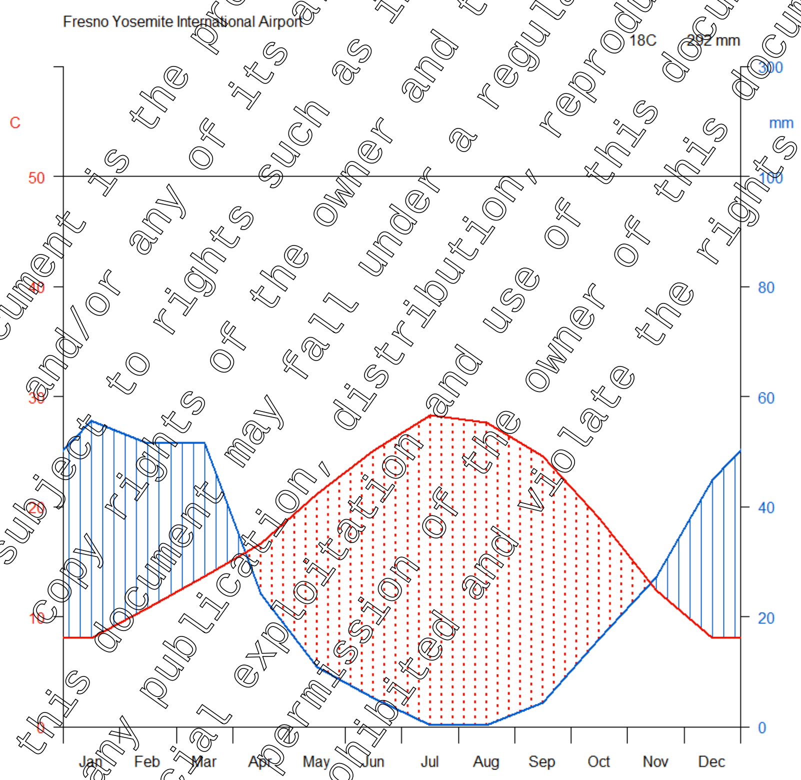


Figure 7.1.2.2.1- 10: Climate diagram according to Walter & Lieth of weather station Fresno Yosemite International Airport. Shown are long-term monthly averages of temperature and precipitation from 1981 to 2010

Table 7.1.2.2.1- 49: Climate parameters near trial site Kerman, California (NCEI weather station Fresno Yosemite International Airport) and in corresponding ecoregions

	No. of months > 10°C	Average temperature			Average precipitation		
		Annual (°C)	Summer (°C)	Winter (°C)	Annual (mm)	Summer (mm)	Winter (mm)
Trial site Kerman, California	10	18.0	27.0	9.0	292	6	152
CEC ecoregion 11.1.2 Central California Valley	9[1]	15 – 19	18.4 – 22.1[1]	6.5 – 9.4[1]	125 – 760	4 – 22[1]	164 – 466[1]
ENASGIPS ecoregion[2] NA0801 California Central Valley grasslands	9	16.5 ± 1.3	25.0	8.3	538 ± 197	10	302

[1] derived from spatial overlay with MARS FOODSEC data
[2] mean value ± standard deviation (corresponding to range with 100% similarity score)

Ecoregion Central California Valley consists of a wide variety of soil types which are generally deep, well drained, and loamy or clayey. The soil series at the trial site is classified as Cerini clay loam. The physical properties of the upper 30 cm are summarised in Table 7.1.2.2.1- 50. The soil series belongs to the great group Haplocambids which belongs to the soil order of Aridisols. The soil is classified as Calcaric Fluvisol in the World Reference Base for Soil Resources and covers 2.6% of EU's arable land.

Table 7.1.2.2.1- 50: Summary of topsoil characteristics at trial site Kerman, California

Soil Series	Depth (cm)	USDA texture class	Soil texture			pH H_2O (-)	OC (%)
			Sand (%)	Silt (%)	Clay (%)		
Cerini	0 – 15	Sandy loam	57	28	16	7.8	0.64
	15 – 30	Sandy loam	57	28	16	7.4	0.29

The ENASGIPS holistic similarity query with a similarity threshold of 80% identifies 8 European ecoregions similar to California Central Valley grasslands which are displayed in Figure 7.1.2.2.1- 11. The ecoregions are located in Southern Europe and cover most parts of Portugal, Spain, Italy, and Greece. Similarity scores range from 83% to 97%.

Compared to the root ecoregion the temperature at the trial site is at the upper tail of the temperature distribution, whereas precipitation is at the lower tail of the precipitation distribution. Similarly, the soil properties at the site reflect the extremes of the root ecoregion's parameter distribution with low organic carbon content and comparably high soil pH and coarse texture. It can be concluded that root ecoregion California Central Valley grasslands is representative for the trial site, however the site's properties are at the tails of the ecoregions' properties distributions.

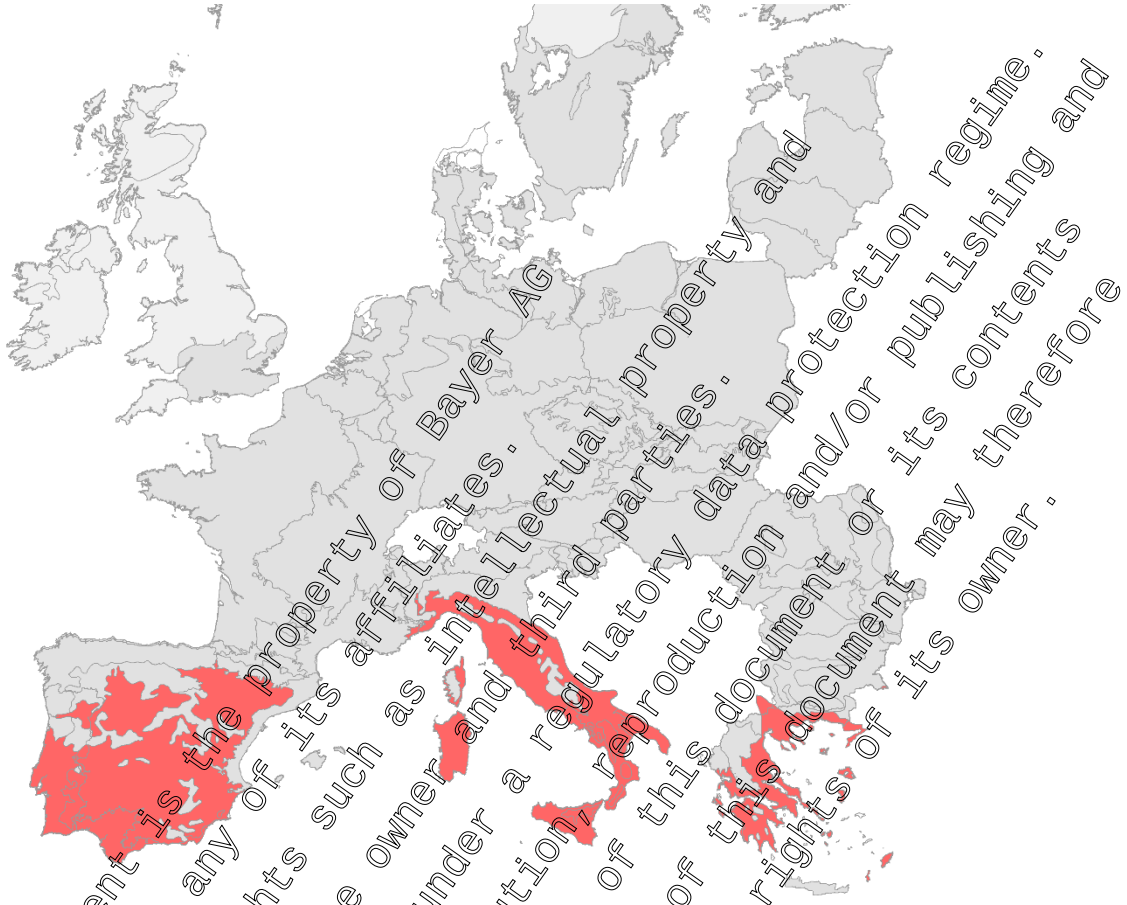


Figure 7.1.2.2.1- 11: European Ecoregions similar to California Central Valley grasslands according to ENASGIPS (holistic similarity model with threshold 80%); similar ecoregions are marked red

The ENASGIPS approach does not take into account the pronounced seasonal character of the site's subtropical, summer dry climate. As temperature and precipitation are major factor influencing degradation in soil, the MARS-AGRI4CAST database was queried to identify regions with similar climate properties in Europe. The query was based on average summer and winter temperature, as well as average summer and winter precipitation because of the site's climate with hot, dry summers and a winter rain season. Parameter ranges for the query were taken from the North American ecoregion Central California Valley (Table 7.1.2.2.1- 49). The query yields several grid cells in Southern Spain with matching climate parameters near the Mediterranean. The analysis shows that winter temperature and the amount of summer precipitation are the most restricting properties with regard to trial site similarity (Figure 7.1.2.2.1-12). Fluvisols occur under comparable climate conditions in Europe and are present on a significant share of European surface area. The identified climate cells do not cover the trial site's soil types but the region is relevant for European agriculture. In addition, the trial site is irrigated throughout the study (except for 3 winter month in 2007/2008) with large water amounts. Enlarging the precipitation range used for the query against the MARS data would lead to a much larger area with similar precipitation.

In conclusion, climate conditions at the trial site are adequately represented by the root ecoregions' properties. Several European ecoregions were identified as similar to the North American ecoregions by ENASGIPS. Although the trial site was classified as a subtropical climate with dry and wet seasons, similar environmental conditions are present in parts of Southern Europe which are relevant to European agriculture. Therefore, the trial site Fresno, California, is considered representative for European conditions.

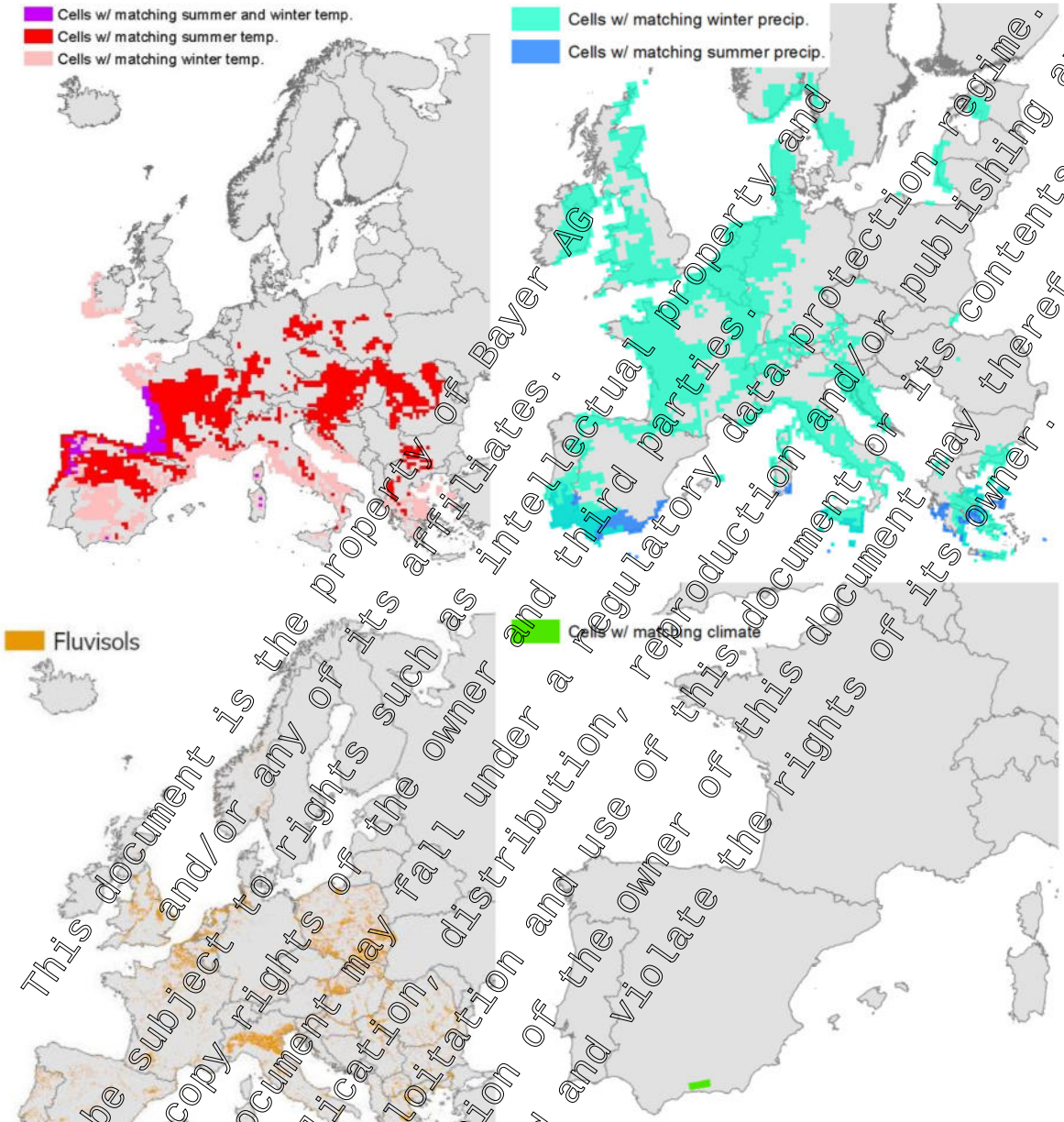


Figure 7.1.2.2.1- 12: Areas in Europe with similar climate as CEC ecoregion Central California Valley and similar Soil Reference Group (Fluvisols in general, not only calcaric Fluvisols)[4] as the trial site

E Sycamore, Georgia

The trial site Sycamore (Denham road), Georgia, is located in WWF ecoregion Southeastern conifer forests in ENASGIPS and the North American ecoregion Southeastern Plains.

[4] The spatial extent displayed in the map represents soil mapping units which normally contain different soils, i.e. only a fraction (on average 60%) of the area is covered by Fluvisols

Long term monthly climate data from the nearby weather station Ashurn are illustrated in Figure 7.1.2.2.1- 13. General climate parameters of the trial site and corresponding ecoregions are given in Table 7.1.2.2.1- 51. The site's climate can be classified as subtropical humid forest according to Köppen-Trewartha climate types (FAO 2012a) and is characterised by overall warm and humid conditions without any dry seasons.

During the trial, the plot was irrigated (1174.2 mm during the study, total water input corresponds to 149% of 30 year average annual rainfall). However, irrigation is not explicitly considered in the ecoregion crosswalk analysis. This analysis focuses on the long-term climate influencing the formation of ecoregion characteristics (e.g. via vegetation and soil genesis) and thus overall conditions for degradation, whereas the influence of short-term weather and irrigation on degradation during the trial duration are addressed via temperature and moisture normalization.

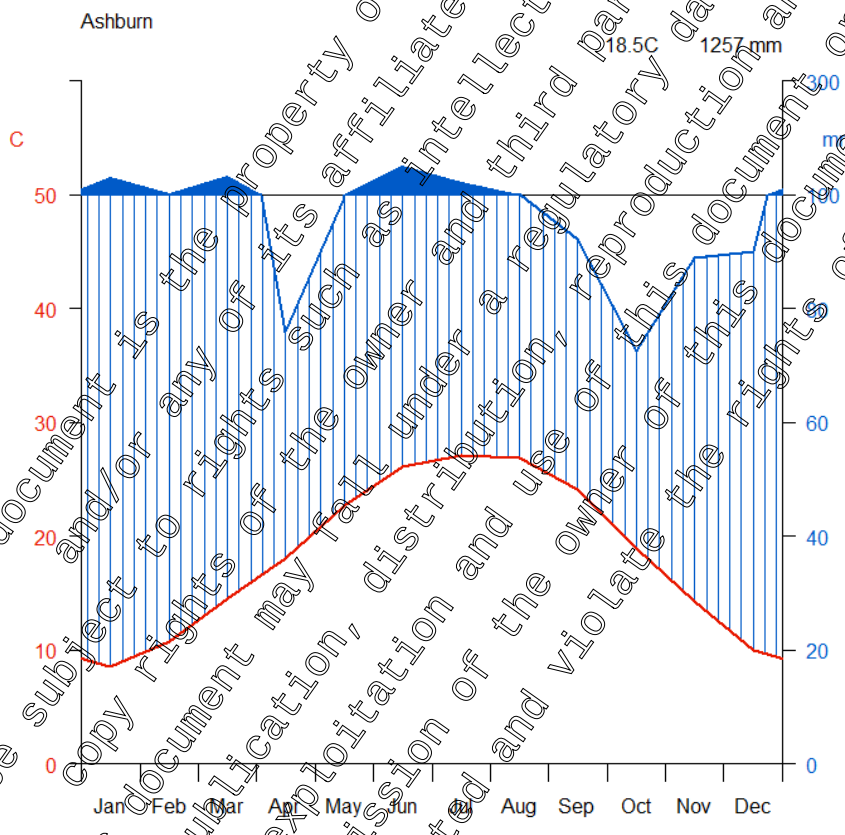


Figure 7.1.2.2.1- 13: Climate diagram according to Walter & Lieth of weather station Ashburn (NCEI 2019c). Shown are long-term monthly averages of temperature and precipitation from 1981 to 2010

Table 7.1.2.2.1- 51: Climate parameters near trial site Sycamore, Georgia (NCEI weather station Ashburn) and in corresponding ecoregions

	No. of months > 10°C	Average temperature			Average precipitation		
		Annual (°C)	Summer (°C)	Winter (°C)	Annual (mm)	Summer (mm)	Winter (mm)
Trial site Sycamore, Georgia	10	18.5	26.7	9.8	1257	372	322
CEC ecoregion 8.3.5 Southeastern Plains	9[1]	13 – 19	24.6 – 27.1[1]	3.4 – 11.9[1]	1140 – 1520	293 – 541[1]	215 – 341[1]
ENASGIPS ecoregion[2] NA0529 Southeastern conifer forests	12	20.5 ± 1.4	26.7	13.6	1266 ± 102	548	205

[1] derived from spatial overlay with MARS FOODSEC data
[2] mean value ± standard deviation (corresponding to range with 100% similarity score)

The predominant landform in ecoregion Southeastern Plains are dissected, rolling to smooth plains. The soil series at the trial site is classified as Tifton loamy sand, belonging to the taxonomic class of kaolinitic, thermic Plinthic Kandiudults (Ultisol with low-activity clays). The physical soil properties of the upper 30 cm are summarised in Table 7.1.2.2.1- 52. The soil order of Ultisols corresponds to the World Resource Base soil groups of Acrisols. According to Amelung et al. (2008) comparable soils do not occur in EU.

Table 7.1.2.2.1- 52: Summary of topsoil characteristics at trial site Sycamore, Georgia; soil samples were collected from bare ground plot

Soil Series	Depth (cm)	USDA texture class	Soil texture			pH H2O (-)	OC (%)
			Sand (%)	Silt (%)	Clay (%)		
Tifton	0 – 15	Loamy sand	84	10	7	5.9	0.46
	15 – 30	Sandy loam	85	9	7	6.0	0.52

The ENASGIPS holistic similarity query with a similarity threshold of 80% identifies no similar ecoregions in Europe.

The site's parameters fit well with the root ecoregion with respect to precipitation and soil texture. Temperature at Sycamore is on the lower tail of the root ecoregion's temperature distribution but well within the range of the corresponding CEC ecoregion Southeastern Plains. On the other hand, pH is substantially higher at the trial site and organic carbon content is on the lower tail of the root ecoregion's distribution. It can be concluded that root ecoregion Southern conifer forests is appropriately representative for the trial site with regard to climate and soil properties despite some observable differences.

The MARS-AGRI4CAST database was queried to identify regions with similar climate properties in Europe, also taking into account the seasonal character. The query was based on average summer and winter temperature, as well as annual precipitation because of the site's pronounced subtropical climate

with very high temperatures in summer and high precipitation amounts. Parameter ranges for the query were taken from the North American ecoregion Southeastern Plains (Table 7.1.2.2.1- 51). The irrigated water amount was not added to the query as the queried precipitation range is anyhow on the upper tail of Europe's precipitation distribution. The MARS-AGRI4CAST query yields no grid cells with matching climate conditions in Europe. The analysis shows that regions with comparable summer temperatures are only found in coastal regions along the Mediterranean and in south-western Spain (Figure 7.1.2.2.1- 14). In contrast to that, regions with similar precipitation are restricted to mountainous regions in Central Europe and the west coasts of Spain, Ireland, Great Britain, and Norway.

In conclusion, no European ecoregions similar to the root ecoregion were identified by ENASGIPS. The site's soil type is virtually non-existent in European soils and its subtropical climate conditions are not present within Europe. Therefore, the trial site Sycamore, Georgia, is considered not representative for European conditions.

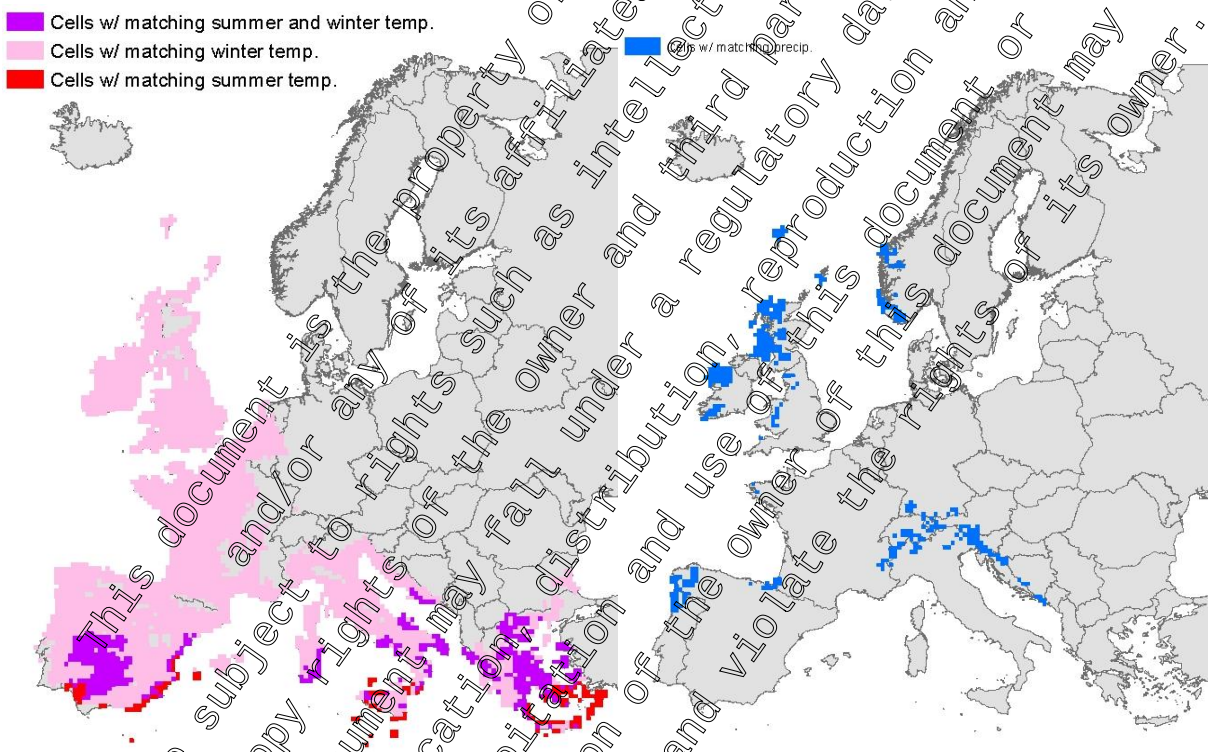


Figure 7.1.2.2.1- 14: Areas in Europe with similar climate as CEC ecoregion Southeastern Plains

III. CONCLUSIONS

Conditions at the three trial locations North Rose (New York), Kerman (California) and Ephrata (Washington) were considered representative for Europe with regard to climate and soil properties according to the refined ENASGIPS approach. Similar ecoregions could not be identified by ENASGIPS for the two locations Sycamore (Georgia) and Northwood (North Dakota).

3. Assessment and conclusion

Assessment and conclusion by applicant: The crosswalk evaluation is considered valid and reliable.

Assessment and conclusion by RMS: Outcome and conclusion of the study: RMS should indicate if they agree to the results and conclusions of the APPL.

1. Information on the study

Data Point:	KCA 7.1.2.2.1/14
Report Author:	[redacted]
Report Year:	2020
Report Title:	Terrestrial field dissipation study following single application of fluopyram SC 500 to bare ground - Agricultural regions of Northern and Southern Europe - Interim final report
Report No:	683226
Document No:	M-758582-01-1
Guideline(s) followed in study:	OECD 13, Series on Principles of Good Laboratory Practice and Compliance Monitoring. Consensus Document of the Working Group on Good Laboratory Practice. The application of the OECD principles of GLP to the Organisation and Management of Multi-Site Studies (June 2002) OECD Environment Health and Safety Publications, Series on Testing and Assessment No. 232, Series on Pesticides No. 82, Guidance Document for Conducting Pesticide Terrestrial Field Dissipation Studies, ENV/JM/MONO(2016)6, 2016-02-29 Regulation (EC) No. 1107/2009 of the European Parliament and of the Council of 21 October 2009 EC Guideline 7029/VI/95 Rev 5 General Recommendations for the Design, Preparation and Realisation of Residue Trials (July 1997). EFSA Journal 2014;12(5):3662, EFSA Guidance Document for evaluating laboratory and field dissipation studies to obtain DegT50 values of active substances of plant protection products and transformation products of these active substances in soil SANCO/825/00 Rev. 8.1, Guideline on Pesticide Residue Analytical Methods. (November 2010) SANCO/3029/99/Revision 4, Residues: Guidance for Generating and Reporting Methods of Analysis in Support of Pre-Registration Data Requirements for Annex II (Part A, Section 4) and Annex III (Part A, Section 5) of Directive 91/414 (July 2000) OECD Guideline 106, Adsorption/Desorption Using a Batch Equilibrium Method (2000)
Deviations from current test guideline:	Current Guideline: Guidance Document for Conducting Pesticide Terrestrial Field Dissipation Studies (2016) None
Previous evaluation:	No, not previously submitted
GLP/Officially recognised testing facilities:	Yes, conducted under GLP/Officially recognised testing facilities
Acceptability/Reliability:	Yes

2. Full summary of KCA 7.1.2.2.1/14

Executive Summary

Degradation of fluopyram and its movement into soil is investigated after application of fluopyram SC 500 on bare soil in six trial sites around Europe (United Kingdom; France; Greece; Poland; Spain and Italy). The sites were located in the ecoregions Europe, North and South. The study is not completed yet. Results which are available so far are summarised herewith.

Fluopyram SC 500 was sprayed once onto field plots at a rate of 0.5 L/ha, corresponding to nominal 250 g a.i./ha fluopyram. Immediately after the application of the test item, 3-5 mm of sand was applied evenly across the treated plot to minimise surface processes like soil photolysis. The plots received at least 10 mm water between DAT-0 (after sampling) and before the DAT-3 sampling events. The control plot was at least 10 m away from the treated plots. Soil samples were taken to a maximum depth of 100 cm.

Soil core samples up to 450 days after treatment from all 6 trials were taken so far. The analysis for this study covers up to 270 days after treatment from the following trials: Trial 1 (LO), Trial 2 (AM), Trial 3 (UB), Trial 4 (CR), Trial 5 (SI). The final report will cover both field and analysis up until the final sampling day of 720 DAT.

Sub-samples of homogenized 10-cm soil layers were extracted in a microwave extractor with a mixture of acetonitrile/water (4/1; v/v). Potential matrix effects were eliminated by using an internal standard solution. Quantitation of the analyte was performed by high performance liquid chromatography using MS/MS detection in the multiple reaction monitoring mode. The limit of quantitation (LOQ) was 5.0 µg/kg and the limit of detection (LOD) was 1.5 µg/kg for fluopyram.

The aged sorption properties of fluopyram under field conditions were also investigated from the same six trials in the course of the study. No results of this part are available so far. A detailed description of the procedure and the results will be presented in the final report and the respective summary.

At Trial 1 (LO) the mean amount of fluopyram at day 0 was 217.7 g/ha, representing 87.1% of the nominal application rate. fluopyram in the top soil layer declined from 217.7 g Fluopyram /ha in soil at day 0 to 127.9 g/ha at day 270. Residues of fluopyram were found mainly in 0-10 cm soil. At Trial 2 (AM) the mean amount of fluopyram at day 0 was 265.3 g/ha, representing 106 % of the nominal application rate. fluopyram in the top soil layer declined from 265.3 g fluopyram /ha in soil at day 0 to 216.1 g/ha at day 270. Residues of fluopyram were found mainly in 0-10 cm soil. At Trial 3 (UB) the mean amount of fluopyram at day 0 was 282.1 g/ha, representing 113% of the nominal application rate. fluopyram in the top soil layer declined from 282.1 g fluopyram /ha in soil at day 0 to 178.3 g/ha at day 270. Residues of Fluopyram were found mainly in 0-10 cm soil. At Trial 4 (CR) the mean amount of fluopyram at day 0 was 252.7 g/ha, representing 101% of the nominal application rate. Fluopyram in the top soil layer declined from 252.7 g fluopyram /ha in soil at day 0 to 144.8 g/ha at day 270. Residues of fluopyram were found mainly in 0-10 cm soil. At Trial 5 (SI) the mean amount of fluopyram at day 0 was 172.8 g/ha, representing 69.1% of the nominal application rate. fluopyram in the top soil layer declined from 172.8 g Fluopyram /ha in soil at day 0 to 153.6 g/ha at day 270. Residues of fluopyram were found mainly in 0-10 cm soil.

At Trial 7 (PZ) the collected soil sample weights significantly exceed the maximum theoretical sample size, the excessive weights generate inaccurate g/ha residue results and for this reason only the field procedures will be presented in this interim report. Analytical data is not presented while further review of this issue is on-going. The outcome will be presented in the Final report.

I. MATERIALS AND METHODS

A. MATERIALS

1. Test Item

Fluopyram SC 500 (500 g/L)	(Suspension concentrate)
Certificate of Analysis	FAR No.: 30138-00
Batch Number	2016-012182-01
Content a.s.	Nominal: 500 g/L; actual: 494 g/L

2. Test Sites

The sites selected are typical for the ecoregions of Europe, North and South. The site was neither subjected to erosion, flooding nor to run-off. The test plots had no significant slope and was largely free of stones. Their locations and site details are presented in the table below.

Table 7.1.2.2.1- 53: Geographic Location, Site Description and Climatic Data at the Study Sites

	Trial Site – LQ	Trial Site – AM	Trial Site – UB
Details	Trial 1	Trial 2	Trial 3
Location	Malton, YO17 6QA, North Yorkshire, UK	Auchy-les-Mines, 62138, Hauts de France, France	Urbanowice, 47-270, Opole, Poland
Plot Size [sqm]	Untreated Plot: 36 sqm Treated Plots (for each replicate): 180 sqm	Untreated Plot: 36 sqm Treated Plots (for each replicate): 180 sqm	Untreated Plot: 36 sqm Treated Plots (for each replicate): 180 sqm
Ecoregion	Northern Europe	Northern Europe	Northern Europe
Distance from weather station used for climatic measurements	At trial location (on site)	At trial location (*ca* 194 m)	At trial location (275 m)
Meteorological conditions compared to long-term average within normal levels (Yes/No)	Yes	Yes	Yes
Other details, if any	Bare soil plots located in a field that was in commercial use prior to study use. The site was flat and level, allowed soil sampling down to 100 cm and free from flooding risk	Bare soil plots located in a commercial representative field. The site was flat and level, allowed soil sampling down to 100 cm and free from flooding risk	Bare soil plots located in a field that was in commercial use prior to study use. The site was flat and level, allowed soil sampling down to 100 cm and free from flooding risk

	Trial Site – CR	Trial Site – SI	Trial Site – PZ
Details	Trial 4	Trial 5	Trial 7[1]
Location	Alpicat, 25110, Catalunya, Spain	Sindos, GR 57022, Central Macedonia, Greece	San Zenone al Lambro, 20070, Lombardia, Italy
Plot Size [sqm]	Untreated Plot: 36 sqm Treated Plots (for each replicate): 180 sqm	Untreated Plot: 36 sqm Treated Plots (for each replicate): 144 sqm	Untreated Plot: 36 sqm Treated Plots (for each replicate): 180 sqm
Ecoregion	Southern Europe	Southern Europe	Southern Europe
Distance from weather station used for climatic measurements	At trial location (*ca* 18 m)	At trial location (on site)	At trial location (less than 500 feet)
Meteorological conditions compared to long-term average	Yes	Yes	Yes

within normal levels (Yes/No)			
Other details, if any	Bare soil plots located in a field that was in commercial use prior to study use. The site was flat and level, allowed soil sampling down to 100 cm and free from flooding risk	Bare soil plots located in a field that was in commercial use prior to study use. The site was flat and level, allowed soil sampling down to 100 cm and free from flooding risk	Bare soil plots located in a field that was only for experimental use prior to study use. The site was flat and level, allowed soil sampling down to 100 cm and free from flooding risk

[1] Trial 7 replaces the terminated Trail 6. The Trial 6 soil site did not allow consistent sampling and was therefore terminated and replaced with Trial 7. Trial 7 sample weights exceed the maximum theoretical sample size the excessive weights generate inaccurate g/ha residue results and further review of this issue is on-going. For this reason only the field procedures are presented here. The outcome will be addressed in the final report.

B. STUDY DESIGN

1. Experimental Conditions

Fluopyram SC 500 is a suspension concentrate formulation containing 500 g fluopyram/L. The product was sprayed once with an application rate of 0.5 L/ha and 600 L/ha water, corresponding to 250 g fluopyram/ha.

The product was sprayed on bare soil with two passages in opposite directions at each 50% of the total test item rate. 3-5 mm of sand was applied evenly to the treated plots after application.

The application devices were calibrated prior to the application. The applications were accepted if the deviation from the nominal rate was less than 5 % and the visual spraying pattern was adequate. This criteria was met at all trial with the exception of Trial 2, AM (at Replicate I the test item was over-applied (7.1%) however in average of the three plots the application rate was within margin and it was therefore considered of no concern to the study). The formulated fluopyram SC 500 was applied mimicking local practice.

Air temperature, humidity, wind speed, Global (solar) radiation, precipitation, evapotranspiration data (ETO), soil temperature and soil moisture data were recorded during the field trials. Irrigation was applied during the field phase, the combined rainfall and irrigation targeted 110-120% of the long-term average rainfall amount. Irrigation was not applied during winter months and wet periods if the addition of irrigation risked flooding or pooling of water on the surface of the trial.

Soil dissipation data discussed in this interim report includes data up to 270 days after application.

2. Sampling

The treated area of each trial was divided into three plots, each with 200 sub-plots. 10 random subplots were collected and combined per each 10-cm depth. The randomisation from the three sub-plots ensured each sample was representative of the treated plot area.

The samples were taken as follows (nominal sampling timings): 0 (pre application) and 0 (post application) to a depth of 10 cm, 3, 7, 14, 35 (0-40 cm depth), 60, 120, 180 (each 0-60 cm depth), 270 and 360 (both 0-85/90 cm depth) and 450 (0-100 cm depth). The sampling occasions 600 DAT and 720 DAT (each 0-100 cm depth) are still to be collected and will be reported in the Final Report. Samples to a depth of 10 cm were removed by hand using a suitable implement after placing a metal ring (inner diameter 9.5 cm) into the ground. Samples from 10 to 100 cm soil depth were collected using a mechanical corer.

From the control plot samples were taken on day 0 DAT (pre application) and is scheduled to be taken on the final sampling occasion 720 days after treatment. In addition, prior to application, the soil characterisation samples were taken from the treated plots to a depth of 100 cm (10 soil cores).

On the day of application ca. 50 mL of application solution was removed from the spray mix prior to the application being made and a further ca. 50 mL of application solution was removed from the spray mix after application. Samples were protected from light as soon as possible after collection and placed into cool boxes with ice/ice packs during transit between the field and the test site.

Two soil filled trays were placed in each plot prior to application, placed at opposite ends of the treated plot and not within 0.5 m of the sides or the end of the plots. After application, the trays were removed and sealed in plastic bags. Recovery trays were protected from light as soon as possible after collection.

3. Analytical Procedures

The analytical method 01591 (M-658192-01-1) was developed for the determination of fluopyram and the metabolites fluopyram-benzamide, fluopyram-7-hydroxy and fluopyram-PCA residues in/on soil. In this study only fluopyram was analysed.

Soil samples of 5 g were extracted in a microwave extractor with 10 mL of acetonitrile/water (4/1; v/v). The extracts were centrifuged to remove fine particles. Possible matrix effects were eliminated by using an internal standard solution of isotope labelled reference item. Identification and quantitation of fluopyram was done by high performance liquid chromatography using MS/MS detection in the multiple reaction monitoring mode. Residues of fluopyram were quantified using external calibration with standards in solvent containing stable isotope labelled standard (ISTD).

Aged sorption determination was performed by equilibrating 5 g soil samples from the top 10 cm layer using 20 mL of aqueous 0.01 M $CaCl_2$ (Solution ratio 1:4) during a ca 48 hour period while being shaken horizontally at ca 100 rpm. At the end of this period, the samples were centrifuged (3000 g for roughly 30 minutes). The supernatants (liquid fraction) were decanted and made up to the volume of 20 mL with water. The soil fractions were also analysed based on analytical method mentioned above. Possible matrix effects of fluopyram were eliminated by using an internal standard solution of isotopic labelled reference item. Identification and quantitation of fluopyram was done by high performance liquid chromatography using MS/MS detection in the multiple reaction monitoring mode.

The limit of quantitation (LOQ) for fluopyram was 5.0 µg/kg in soil. The limit of determination (LOD) for fluopyram was 1.5 µg/kg. The maximum period of storage of sample extracts was seven days until analysis.

Full details and acceptable validation data to support the analytical method are presented within document M-CA 4, which comply with the EU regulatory requirements outlined within SANTE/2020/12830, Rev 1.

II. RESULTS AND DISCUSSION

A. DATA

The measured initial mean concentration of fluopyram was 172.8 g/ha to 282.1 g/ha, representing 69% to 113% of the intended dose rate. It should be kept in mind that the presented field dissipation study is a rate and not a route study. The study design does not allow the calculation of a mass balance.

At Trial 1 (LO) the mean amount of fluopyram at day 0 was 217.7 g/ha, representing 87.1% of the nominal application rate. At Trial 2 (AM) the mean amount of fluopyram at day 0 was 265.3 g/ha, representing 106% of the nominal application rate and thus slightly higher than the acceptable deviation from the nominal rate of 5%. Only at replicate I (of III) the test item was over-applied (7.1%). At Trial

3 (UB) the mean amount of fluopyram at day 0 was 282.1 g/ha, representing 113% of the nominal application rate. At Trial 4 (CR) the mean amount of fluopyram at day 0 was 252.7 g/ha, representing 101 % of the nominal application rate. At Trial 5 (SI) the mean amount of fluopyram at day 0 was 172.8 g/ha, representing 69.1% of the nominal application rate. Trial 7 replaces the terminated Trail 6. Trial 7 sample weights exceed the maximum theoretical sample size further explanation is presented in Section 5 and for this reason only the field procedures from this trial will be presented in this interim report summary.

Table 7.1.2.2.1- 54: Analytical results of fluopyram, whole column values (g/ha) - Trial 1 – LO

	DAT (days)												
Rep.	**0 (post)**	**3**	**7**	**14**	**36**	**63**	**122**	**184**	**273**	**359**	**452**	**600**	**720**
I	216.7	189.8	195.1	204.8	158.5	206.6	111.2	118.9	124.3	-	-	-	-
II	260	264.1	209.9	228.4	182.3	237.7	149.8	153.4	132.6	-	-	-	-
III	176.3	171.2	177.7	232.6	164.4	205.5	133.2	104.4	138.2	-	-	-	-
Mean	**217.7**	**208.4**	**194.2**	**221.9**	**168.4**	**216.6**	**131.4**	**125.6**	**131.7**	**-**	**-**	**-**	**-**
Min	176.3	171.2	177.7	204.8	158.5	205.5	111.2	104.4	124.3	-	-	-	-
Max	260	264.1	209.9	232.6	182.3	237.7	149.8	153.4	138.2	-	-	-	-
n	3	3	3	3	3	3	3	3	3	-	-	-	-

DAT = Days after treatment; Rep = Replicate; n = Number of data sets contributing to the Mean, Min and Max values.
Data presented is a total detected residue (>LOD) summed at each sampling interval from each replicate treated plot.
DAT 359 to 720 DAT are still under processing or were not sampled yet.

Table 7.1.2.2.1- 55: Analytical results of fluopyram, whole column values (g/ha) - Trial 2 – AM

	DAT (days)												
Rep.	**0 (post)**	**2**	**6**	**13**	**36**	**61**	**119**	**183**	**265**	**357**	**455**	**600**	**720**
I	285	236.1	269.5	223.7	209.1	245.6	228.1	244.2	254.6	-	-	-	-
II	253.1	220.9	198.4	225	210	211	205.8	205.2	190.8	-	-	-	-
III	257.8	229.3	240.7	245.1	222.3	251.5	205.1	174.3	228.5	-	-	-	-
Mean	**265.3**	**228.8**	**236.2**	**231.3**	**213.8**	**236**	**213**	**207.9**	**224.6**	**-**	**-**	**-**	**-**
Min	253.1	220.9	198.4	223.7	209.1	211	205.1	174.3	190.8	-	-	-	-
Max	285	236.1	269.5	245.1	222.3	251.5	228.1	244.2	254.6	-	-	-	-
n	3	3	3	3	3	3	3	3	3	-	-	-	-

DAT = Days after treatment; Rep = Replicate; n = Number of data sets contributing to the Mean, Min and Max values.
Data presented is a total detected residue (>LOD) summed at each sampling interval from each replicate treated plot.
DAT 357 to 720 DAT are still under processing or were not sampled yet.

Table 7.1.2.2.1- 56: Analytical results of fluopyram, whole column values (g/ha) - Trial 3 – UB

	DAT (days)												
Rep	**0 (post)**	**4**	**7**	**15**	**36**	**64**	**126**	**185**	**270**	**363**	**454**	**600**	**720**
I	277	263	261.7	274.6	299.7	248	223.3	249.6	101.8	-	-	-	-
II	290.9	226.3	291.9	251.1	240.8	204.9	252.2	279.8	242.5	-	-	-	-
III	278.4	238.4	267.2	223.8	242.8	240.7	217.5	278.3	193.9	-	-	-	-
Mean	**282.1**	**242.6**	**273.6**	**249.8**	**261.1**	**231.2**	**231**	**269.2**	**179.4**	**-**	**-**	**-**	**-**
Min	277	226.3	261.7	223.8	240.8	204.9	217.5	249.6	101.8	-	-	-	-
Max	290.9	263	291.9	274.6	299.7	248	252.2	279.8	242.5	-	-	-	-
n	3	3	3	3	3	3	3	3	3	-	-	-	-

DAT = Days after treatment; Rep = Replicate; n = Number of data sets contributing to the Mean, Min and Max values.
Data presented is a total detected residue (>LOD) summed at each sampling interval from each replicate treated plot.
DAT 363 to 720 DAT are still under processing or were not sampled yet.

Table 7.1.2.2.1- 57: Analytical results of fluopyram, whole column values (g/ha) - Trial 4 – CR

	DAT (days)												
Rep	**0 (post)**	**2**	**7**	**15**	**35**	**55**	**122**	**180**	**273**	**364**	**450**	**600**	**720**
I	245.3	236.5	366.6	213.9	358.1	207.2	227.6	184.6	172.5	-	-	-	-
II	247.3	241.5	346.9	201	250.8	224	196.9	183.8	156.7	-	-	-	-
III	265.7	291	429.4	214.1	360.8	302	192.7	209.4	131.8	-	-	-	-
Mean	**252.7**	**256.3**	**381**	**209.7**	**316.5**	**244.4**	**205.8**	**192.6**	**153.7**	**-**	**-**	**-**	**-**
Min	245.3	236.5	346.9	201	250.8	207.2	192.7	183.8	131.8	-	-	-	-
Max	265.7	291	429.4	214.1	360.8	302	227.6	209.4	172.5	-	-	-	-
n	3	3	3	3	3	3	3	3	3	-	-	-	-

DAT = Days after treatment; Rep = Replicate; n = Number of data sets contributing to the Mean, Min and Max values.
Data presented is a total detected residue (>LOD) summed at each sampling interval from each replicate treated plot.
DAT 364 to 720 DAT are still under processing or were not sampled yet.

Table 7.1.2.2.1- 58: Analytical results of fluopyram, whole column values (g/ha) - Trial 5 – SI

	DAT (days)												
Rep	**0 (post)**	**3**	**8**	**15**	**35**	**65**	**128**	**179**	**275**	**365**	**450**	**600**	**720**
I	166	173	196.5	176.9	179.9	212.2	177.8	230.4	129.2	-	-	-	-
II	167.3	191.6	184.5	190.2	139.9	151.9	173.2	161	155.1	-	-	-	-
III	185.1	134.2	171.1	150.5	173.1	187.2	138.8	176.4	176.6	-	-	-	-
Mean	**172.8**	**166.2**	**184**	**172.6**	**164**	**183.7**	**163.3**	**189.3**	**153.6**	**-**	**-**	**-**	**-**
Min	166	134.2	171.1	150.5	139.9	151.9	138.8	161	129.2	-	-	-	-
Max	185.1	191.6	196.5	190.2	179.9	212.2	177.8	230.4	176.6	-	-	-	-
n	3	3	3	3	3	3	3	3	3	-	-	-	-

DAT = Days after treatment; Rep = Replicate; n = Number of data sets contributing to the Mean, Min and Max values.
Data presented is a total detected residue (>LOD) summed at each sampling interval from each replicate treated plot.
DAT 365 to 720 DAT are still under processing or were not sampled yet.

Table 7.1.2.2.1- 59: Detailed analytical results of fluopyram (µg/kg), dry soil - Trial 1 – LO

		DAT (days)												
Depth (cm)	**Rep.**	**0**	**3**	**7**	**14**	**35**	**60**	**120**	**180**	**270**	**360**	**450**	**600**	**720**
0-10	I	182.4	197.8	189.9	176.3	127.1	160.1	107.8	144.4	103.9	-	-	-	-
	II	203.0	283.3	173.5	200.6	168.9	193.1	117.5	174.1	112.7	-	-	-	-
	III	153.9	175.2	168.9	220.2	137.3	197.6	121.2	108.7	125.2	-	-	-	-
	Mean[1]	**179.8**	**218.8**	**177.4**	**199.0**	**144.4**	**183.6**	**115.5**	**142.4**	**113.9**	-	-	-	-
10-20	I	-	[4.211]	[3.898]	<LOD	<LOD	11.92	9.334	[4.562]	<LOD	-	-	-	-
	II	-	11.40	<LOD	[4.867]	<LOD	6.560	6.251	[2.828]	<LOD	-	-	-	-
	III	-	[4.845]	<LOD	[3.401]	<LOD	<LOD	[5.061]	[6.077]	[5.927]	-	-	-	-
	Mean[1]	**-**	**6.818**	**[1.799]**	**[3.006]**	**<LOD**	**6.409**	**6.882**	**[4.489]**	**[2.476]**	-	-	-	-
20-30	I	-	<LOD	<LOD	[4.250]	<LOD	<LOD	<LOD	<LOD	[1.944]	-	-	-	-
	II	-	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	-	-	-	-
	III	-	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	-	-	-	-
	Mean[1]	**-**	**<LOD**	**<LOD**	**[1.917]**	**<LOD**	**<LOD**	**<LOD**	**<LOD**	**<LOD**	-	-	-	-
30-40	I	-	-	-	<LOD	-	<LOD	<LOD	<LOD	<LOD	-	-	-	-
	II	-	-	-	<LOD	-	<LOD	<LOD	<LOD	<LOD	-	-	-	-
	III	-	-	-	<LOD	-	<LOD	<LOD	<LOD	<LOD	-	-	-	-
	Mean[1]	**-**	**-**	**-**	**<LOD**	**-**	**<LOD**	**<LOD**	**<LOD**	**<LOD**	-	-	-	-
40-50	I	-	-	-	-	-	[3.181]	<LOD	<LOD	<LOD	-	-	-	-
	II	-	-	-	-	-	<LOD	<LOD	<LOD	<LOD	-	-	-	-
	III	-	-	-	-	-	<LOD	<LOD	<LOD	<LOD	-	-	-	-
	Mean[1]	**-**	**-**	**-**	**-**	**-**	**<LOD**	**<LOD**	**<LOD**	**<LOD**	-	-	-	-
50-60	I	-	-	-	-	-	<LOD	-	-	-	-	-	-	-
	II	-	-	-	-	-	<LOD	-	-	-	-	-	-	-
	III	-	-	-	-	-	<LOD	-	-	-	-	-	-	-
	Mean[1]	**-**	**-**	**-**	**-**	**-**	**<LOD**	**-**	**-**	**-**	-	-	-	-
Total		**156.2**	**189.6**	**153.2**	**172.2**	**120.5**	**166.2**	**105.6**	**121.0**	**95.75**	-	-	-	-

DAT = Days after treatment; Rep = Replicate, values in brackets are between LOD and LOQ
[1] for mean calculations 0.75 µg/kg (1/2 LOD) was used where at least one value was >LOD
DAT 360 to 720 DAT are still under processing or were not sampled yet.

Table 7.1.2.2.1- 60: Detailed analytical results of fluopyram (µg/kg), dry soil - Trial 2 – AM

		DAT (days)												
Depth (cm)	**Rep.**	**0**	**3**	**7**	**14**	**35**	**60**	**120**	**180**	**270**	**360**	**450**	**600**	**720**
0-10	I	213.9	202.1	216.0	181.7	152.9	199.4	181.6	197.5	206.6	-	-	-	-
	II	196.7	178.4	160.2	177.8	181.4	184.5	158.1	172.4	162.3	-	-	-	-
	III	206.0	187.6	193.3	201.9	183.0	208.7	167.8	167.3	211.6	-	-	-	-
	Mean[1]	**205.5**	**189.4**	**189.8**	**187.1**	**172.4**	**197.5**	**169.2**	**179.1**	**193.5**	-	-	-	-
10-20	I	-	[2.343]	[2.256]	[1.914]	<LOD	7.486	14.94	[5.997]	[4.358]	-	-	-	-
	II	-	[5.660]	<LOD	[4.327]	<LOD	8.652	14.85	[4.456]	8.066	-	-	-	-
	III	-	<LOD	<LOD	[4.198]	<LOD	11.03	14.61	[4.343]	7.654	-	-	-	-
	Mean[1]	**-**	**[2.918]**	**<LOD**	**[3.480]**	**<LOD**	**9.056**	**14.80**	**[4.932]**	**6.693**	-	-	-	-
20-30	I	-	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	[2.538]	<LOD	-	-	-	-
	II	-	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	[2.180]	-	-	-	-
	III	-	[4.728]	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	-	-	-	-
	Mean[1]	**-**	**[2.076]**	**<LOD**	**<LOD**	**<LOD**	**<LOD**	**<LOD**	**<LOD**	**<LOD**	-	-	-	-
30-40	I	-	<LOD	-	-	-	<LOD	<LOD	<LOD	<LOD	-	-	-	-
	II	-	<LOD	-	-	-	<LOD	<LOD	<LOD	<LOD	-	-	-	-
	III	-	<LOD	-	-	-	<LOD	<LOD	<LOD	<LOD	-	-	-	-
	Mean[1]	**-**	**<LOD**	**-**	**-**	**-**	**<LOD**	**<LOD**	**<LOD**	**<LOD**	-	-	-	-
40-50	I	-	-	-	-	-	<LOD	<LOD	<LOD	<LOD	-	-	-	-
	II	-	-	-	-	-	<LOD	<LOD	<LOD	<LOD	-	-	-	-
	III	-	-	-	-	-	<LOD	<LOD	<LOD	<LOD	-	-	-	-
	Mean[1]	**-**	**-**	**-**	**-**	**-**	**<LOD**	**<LOD**	**<LOD**	**<LOD**	-	-	-	-
50-60	I	-	-	-	-	-	-	-	-	-	-	-	-	-
	II	-	-	-	-	-	-	-	-	-	-	-	-	-
	III	-	-	-	-	-	-	-	-	-	-	-	-	-
	Mean[1]	**-**	**-**	**-**	**-**	**-**	**-**	**-**	**-**	**-**	-	-	-	-
Total		**205.5**	**195.1**	**191.3**	**191.3**	**173.9**	**208.8**	**186.2**	**186.9**	**202.4**		-	-	-

DAT = Days after treatment; Rep = Replicate, values in brackets are between LOD and LOQ
[1] for mean calculations 0.75 µg/kg (1/2 LOD) was used where at least one value was >LOD
DAT 360 to 720 DAT are still under processing or were not sampled yet.

Table 7.1.2.2.1- 61: Detailed analytical results of fluopyram (µg/kg), dry soil - Trial 3 – UB

		DAT (days)												
Depth (cm)	**Rep.**	**0**	**3**	**7**	**14**	**35**	**60**	**120**	**180**	**270**	**360**	**450**	**600**	**720**
0-10	I	193.4	187.2	182.0	181.8	197.1	146.1	151.0	148.1	56.2	-	-	-	-
	II	200.1	150.2	199.7	165.8	155.3	121.9	165.8	173.8	140.3	-	-	-	-
	III	194.5	166.7	172.5	153.3	148.0	151.6	144.4	169.0	109.1	-	-	-	-
	Mean[1]	**196.0**	**168.0**	**184.7**	**167.0**	**166.8**	**139.9**	**153.73**	**163.6**	**102.4**	-	-	-	-
10-20	I	-	<LOD	<LOD	<LOD	<LOD	8.439	<LOD	[3.371]	<LOD	-	-	-	-
	II	-	<LOD	<LOD	<LOD	<LOD	6.274	<LOD	[3.920]	[2.395]	-	-	-	-
	III	-	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	[1.885]	<LOD	-	-	-	-
	Mean[1]	**-**	**<LOD**	**<LOD**	**<LOD**	**<LOD**	**[5.154]**	**<LOD**	**[3.059]**	**<LOD**	-	-	-	-
20-30	I	-	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	-	-	-	-
	II	-	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	-	-	-	-
	III	-	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	-	-	-	-
	Mean[1]	**-**	**<LOD**	**<LOD**	**<LOD**	**<LOD**	**<LOD**	**<LOD**	**<LOD**	**<LOD**	-	-	-	-
30-40	I	-	-	-	-	-	<LOD	<LOD	<LOD	<LOD	-	-	-	-
	II	-	-	-	-	-	<LOD	<LOD	<LOD	<LOD	-	-	-	-
	III	-	-	-	-	-	<LOD	<LOD	<LOD	<LOD	-	-	-	-
	Mean[1]	**-**	**-**	**-**	**-**	**-**	**<LOD**	**<LOD**	**<LOD**	**<LOD**	-	-	-	-
40-50	I	-	-	-	-	-	<LOD	<LOD	<LOD	<LOD	-	-	-	-
	II	-	-	-	-	-	<LOD	<LOD	<LOD	<LOD	-	-	-	-
	III	-	-	-	-	-	<LOD	<LOD	<LOD	<LOD	-	-	-	-
	Mean[1]	**-**	**-**	**-**	**-**	**-**	**<LOD**	**<LOD**	**<LOD**	**<LOD**	-	-	-	-
50-60	I	-	-	-	-	-	-	-	-	-	-	-	-	-
	II	-	-	-	-	-	-	-	-	-	-	-	-	-
	III	-	-	-	-	-	-	-	-	-	-	-	-	-
	Mean[1]	**-**	**-**	**-**	**-**	**-**	**-**	**-**	**-**	**-**	-	-	-	-
Total		**196.0**	**169.5**	**186.2**	**168.5**	**168.3**	**147.3**	**156.7**	**168.9**	**105.4**	-	-	-	-

DAT = Days after treatment; Rep = Replicate, values in brackets are between LOD and LOQ
[1] for mean calculations 0.75 µg/kg (1/2 LOD) was used whereat least one value was >LOD
DAT 360 to 720 DAT are still under processing or were not sampled yet.

Table 7.1.2.2.1- 62: Detailed analytical results of fluopyram (µg/kg), dry soil - Trial 4 – CR

		DAT (days)												
Depth (cm)	**Rep.**	**0**	**3**	**7**	**14**	**35**	**60**	**120**	**180**	**270**	**360**	**450**	**600**	**720**
0-10	I	196.5	202.2	292.2	201.5	277.4	192.5	204.9	148.9	156.4	-	-	-	-
	II	184.4	203.2	260.6	199.0	207.1	203.0	173.9	151.2	154.7	-	-	-	-
	III	222.9	224.2	314.8	218.6	290.1	269.1	172.1	178.0	117.6	-	-	-	-
	Mean[1]	**201.3**	**209.9**	**289.2**	**206.4**	**258.2**	**221.5**	**183.6**	**159.4**	**142.9**	-	-	-	-
10-20	I	-	<LOD	<LOD	<LOD	<LOD	<LOD	7.842	9.375	[4.651]	-	-	-	-
	II	-	<LOD	[1.847]	<LOD	[2.723]	<LOD	7.895	7.605	[6.245]	-	-	-	-
	III	-	8.011	[5.246]	<LOD	[3.322]	7.254	12.67	13.65	9.871	-	-	-	-
	Mean[1]	**-**	**[3.170]**	**[2.614]**	**<LOD**	**[2.265]**	**[2.918]**	**9.468**	**10.21**	**6.922**	-	-	-	-
20-30	I	-	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	-	-	-	-
	II	-	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	-	-	-	-
	III	-	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	[3.042]	<LOD	-	-	-	-
	Mean[1]	**-**	**<LOD**	**<LOD**	**<LOD**	**<LOD**	**<LOD**	**<LOD**	**<LOD**	**<LOD**	-	-	-	-
30-40	I	-	-	-	-	-	<LOD	<LOD	<LOD	<LOD	-	-	-	-
	II	-	-	-	-	-	<LOD	<LOD	<LOD	<LOD	-	-	-	-
	III	-	-	-	-	-	<LOD	<LOD	<LOD	<LOD	-	-	-	-
	Mean[1]	**-**	**-**	**-**	**-**	**-**	**<LOD**	**<LOD**	**<LOD**	**<LOD**	-	-	-	-
40-50	I	-	-	-	-	-	<LOD	<LOD	<LOD	<LOD	-	-	-	-
	II	-	-	-	-	-	<LOD	<LOD	<LOD	<LOD	-	-	-	-
	III	-	-	-	-	-	<LOD	<LOD	<LOD	<LOD	-	-	-	-
	Mean[1]	**-**	**-**	**-**	**-**	**-**	**<LOD**	**<LOD**	**<LOD**	**<LOD**	-	-	-	-
50-60	I	-	-	-	-	-	-	-	-	-	-	-	-	-
	II	-	-	-	-	-	-	-	-	-	-	-	-	-
	III	-	-	-	-	-	-	-	-	-	-	-	-	-
	Mean[1]	**-**	**-**	**-**	**-**	**-**	**-**	**-**	**-**	**-**	-	-	-	-
Total		**201.3**	**213.8**	**292.6**	**207.9**	**261.2**	**226.7**	**195.3**	**172.6**	**152.1**	-	-	-	-

DAT = Days after treatment; Rep = Replicate, values in brackets are between LOD and LOQ
[1] for mean calculations 0.75 µg/kg (1/2 LOD) was used where at least one value was >LOD
DAT 360 to 720 DAT are still under processing or were not sampled yet.

Table 7.1.2.2.1- 63: Detailed analytical results of fluopyram (µg/kg), dry soil - Trial 1 – SI

		DAT (days)												
Depth (cm)	**Rep.**	**0**	**3**	**7**	**14**	**35**	**60**	**120**	**180**	**270**	**360**	**450**	**600**	**720**
0-10	I	142.0	165.9	167.3	135.8	166.4	185.4	161.3	221.6	103.9	-	-	-	-
	II	135.4	196.2	167.9	170.8	141.5	134.6	154.4	151.1	130.5	-	-	-	-
	III	155.9	132.7	159.3	132.4	156.3	173.2	122.8	172.2	135.7	-	-	-	-
	Mean[1]	144.5	164.9	164.8	146.3	154.7	164.4	146.2	181.6	123.4	-	-	-	-
10-20	I	-	<LOD	<LOD	[1.902]	<LOD	[2.920]	7.221	10.04	<LOD	-	-	-	-
	II	-	<LOD	<LOD	<LOD	<LOD	<LOD	[3.445]	[2.515]	<LOD	-	-	-	-
	III	-	<LOD	<LOD	<LOD	<LOD	7.360	<LOD	<LOD	<LOD	-	-	-	-
	Mean[1]	-	<LOD	<LOD	<LOD	<LOD	[3.680]	[3.806]	[4.234]	<LOD	-	-	-	-
20-30	I	-	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	-	-	-	-
	II	-	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	-	-	-	-
	III	-	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	-	-	-	-
	Mean[1]	-	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	-	-	-	-
30-40	I	-	-	-	-	-	<LOD	<LOD	<LOD	<LOD	-	-	-	-
	II	-	-	-	-	-	<LOD	<LOD	<LOD	<LOD	-	-	-	-
	III	-	-	-	-	-	<LOD	<LOD	<LOD	<LOD	-	-	-	-
	Mean[1]	-	-	-	-	-	<LOD	<LOD	<LOD	<LOD	-	-	-	-
40-50	I	-	-	-	-	-	<LOD	<LOD	<LOD	<LOD	-	-	-	-
	II	-	-	-	-	-	<LOD	<LOD	<LOD	<LOD	-	-	-	-
	III	-	-	-	-	-	<LOD	<LOD	<LOD	<LOD	-	-	-	-
	Mean[1]	-	-	-	-	-	<LOD	<LOD	<LOD	<LOD	-	-	-	-
50-60	I	-	-	-	-	-	-	-	-	-	-	-	-	-
	II	-	-	-	-	-	-	-	-	-	-	-	-	-
	III	-	-	-	-	-	-	-	-	-	-	-	-	-
	Mean[1]	-	-	-	-	-	-	-	-	-	-	-	-	-
Total		144.5	166.4	166.3	147.8	156.2	170.3	152.3	188.3	126.4	-	-	-	-

DAT = Days after treatment; Rep = Replicate; values in brackets are between LOD and LOQ
[1] for mean calculations 0.75 µg/kg (1/2 LOD) was used where at least one value was >LOD
DAT 360 to 720 DAT are still under processing or were not sampled yet

B. RESIDUES

Results obtained for control samples show that fluopyram was < LOD for all samples taken.

The amount of fluopyram decreased from DAT-0 until the last analysed samples of this interim study report (DAT-270).

At Trial 1 (LO) the mean amount of fluopyram in the top soil layer declined from 217.7 g fluopyram /ha in soil at day 0 to 127.9 g/ha at day 270. Residues of fluopyram were found mainly in 0-10 cm soil. At Trial 2 (AM) the mean amount of fluopyram in the top soil layer declined from 265.3 g fluopyram /ha in soil at day 0 to 216.1 g/ha at day 270. Residues of fluopyram were found mainly in 0-10 cm soil. At Trial 3 (UB) the mean amount of fluopyram in the top soil layer declined from 282.1 g fluopyram /ha in soil at day 0 to 178.3 g/ha at day 270. Residues of fluopyram were found mainly in 0-10 cm soil. At Trial 4 (CR) the mean amount of fluopyram in the top soil layer declined from 252.7 g fluopyram /ha in soil at day 0 to 144.8 g/ha at day 270. Residues of fluopyram were found mainly in 0-10 cm soil. And at Trial 5 (SI) the mean amount of fluopyram in the top soil layer declined from 172.8 g fluopyram /ha in soil at day 0 to 153.6 g/ha at day 270. Residues of fluopyram were found mainly in 0-10 cm soil.

C. KINETIC ANALYSIS

The kinetic evaluation following current FOCUS guidance was conducted separately and is summarised under KCA 7.1.2.2.1/21 for trigger endpoints and KCA 7.1.2.2.1/17 for modelling endpoints.

III. CONCLUSIONS

Under field conditions, fluopyram is declining at varying rates in the five monitored trials. The analysis is on-going and this summary of the interim report presents the data up to and including the Day 270 samples. The field and analytical data relating to the Day 360, 450, 600 and 720 samples will be

presented in the final report and the summary thereof. Additionally, the analytical results from the Trial 7 (PZ) will be presented in the final report if the sample weight issue can be understood and resolved.

3. Assessment and conclusion

Assessment and conclusion by applicant: The study and its data available so far are considered to be valid and reliable for use in risk assessment.

Assessment and conclusion by RMS: Outcome and conclusion of the study: RMS should indicate if they agree to the results and conclusions of the APPL.

The study is still ongoing, and the final report of this field dissipation study will be provided at the latest by end of February 2022.

1. Information on the study

Data Point:	KCA 7.1.2.2.1/15
Report Author:	[redacted]
Report Year:	2021
Report Title:	Terrestrial field dissipation study with fluopyram SC 500 in Germany, United Kingdom, N-France, S-France, Italy and Spain - Interim report
Report No:	IF19-04831340
Document No:	M-758589-01-1
Guideline(s) followed in study:	Regulation (EC) No. 1107/2009 of the European Parliament and of the Council of 21 October 2009. OECD Environment, Health and Safety Publications, Series on Testing and Assessment No. 232, Series on Pesticides No. 82, Guidance Document for Conducting Pesticide Terrestrial Field Dissipation Studies, ENV/JM/MONO(2016)6, March 2016. EFSA Panel on Plant Protection Products; Guidance Document for evaluating laboratory and field dissipation studies to obtain DegT50 values of active substances of plant protection products and transformation products of these active substances in soil. EFSA Journal 2014; 12(5):3662, 37pp. This Study will be conducted in accordance with the OECD Principles of Good Laboratory Practice and the GLP Principles of the German "Chemikaliengesetz" (Chemicals Act). The OECD Principles of Good Laboratory Practice (as Revised in 1997), OECD Series on Principles of GLP and Compliance Monitoring Number 1, ENV/MC/CHEM(98)17. The OECD principles of GLP to the Organisation and Management of Multi-site studies will be applied (ENV/JM/MONO(2002)9, June 2002). National relevant GLP requirements of countries, where trials are conducted.
Deviations from current test guideline:	Current Guideline: Guidance Document for Conducting Pesticide Terrestrial Field Dissipation Studies (2016) None
Previous evaluation:	No, not previously submitted
GLP/Officially recognised testing facilities:	Yes, conducted under GLP/Officially recognised testing facilities
Acceptability/Reliability:	Yes

2. Full summary of KCA 7.1.2.2.1/15

Executive Summary

The aim of this GLP terrestrial field dissipation (TFD) study was to investigate soil dissipation of fluopyram (FLU) under European field conditions. Furthermore, the time-dependent sorption behaviour of selected soil specimens (soil specimens of 0-10 cm of the sampling events 0, 14, 35, 60, 120, 180, 360 and 720 DAA (days after application) should be determined.

This summary is of an interim report and the study was still ongoing at the time of writing this summary. All work conducted and all results obtained up to the nominal 360 DAA sampling event are reported for soil residue analysis specimens and up to 180 DAA for time-dependent sorption analysis specimens.

The field trials were carried out in Germany, UK, Northern France, Southern France, Italy and Spain covering Northern and Southern European ecoregions. Fluopyram was applied as suspension concentrate (SC) formulation (Fluopyram 500 SC) containing 500 g a.s./L.

One application of Fluopyram 500 SC was conducted on bare soil using a boom sprayer (knapsack or monocycle) and passing over the plot twice in opposite directions. The target application rate was

500 mL product/ha and 600 L water/ha, corresponding to 250 g a.s./ha. Directly after application, the treated soil surface was covered with sand (~ 6-10 mm thickness) by using a sand spreader passing around the plot several times or driving over the plot once. The tractor tracks were clearly marked, and the specimens were taken from in between the tractor tracks only. The first soil specimens for residue analysis were collected just after spraying and covering with sand. The control plots were at least 10 m away from the treated plots.

Soil specimens were collected at the following nominal sampling events up to maximum 85 cm depth: 0 DAA, 3 DAA, 7±1 DAA, 14±2 DAA, 35±3 DAA, 60±3 DAA, 120±3 DAA, 180±5 DAA, 270±5 DAA and 360±5 DAA. Further specimens were taken but in this Interim Report sampling events and residue results up to the 360±5 DAA sampling interval are reported, only. Untreated specimens were taken from subplot 1B of the control plot at nominal 0-7 DBA (days before application).

The time intervals between application, sampling and deep-freezing was kept as short as practically possible. The specimens taken at the 0 DAA sampling event were placed on dry ice or freezer trucks directly on-site and immediately after sampling. The specimens of the 3 DAA sampling event onwards were stored deep frozen at the test sites within less than 8 hours. The soil cores were cut into 10 cm soil layers, bulked soil layers were homogenized and finally analysed for fluopyram. The first three segments were analysed in general, deeper segments were only analysed for the plots were residues above the LOD were found in the deepest segment analysed. The deepest analysed segment was 40-50 cm.

Sub-samples of homogenized soil were extracted with organic solvent. Potential matrix effects were eliminated by using an internal standard solution of isotopically labelled reference item added to sample extracts. Following separation of fine particles from soil extracts by centrifugation and filtration the identification and quantitation of the analytes was performed by high performance liquid chromatography using MS/MS detection in the multiple reaction monitoring mode. The analytical method used for the time-dependent sorption specimens is the same method than for the residue analysis soil specimens, with one additional extraction step with an aqueous $CaCl_2$ solution. The limit of quantitation (LOQ) was 5.0 µg/kg and the limit of detection (LOD) was 1.5 µg/kg of wet soil. The detailed method is described in the interim analytical phase report.

The target dose rate was calculated from residues of fluopyram in the recovery trays. The target dose rate was calculated to be 93% for HS, 100% for HT, 96% for LT, 86% for BS, 93% for BB and 95% for AE, respectively. It should be kept in mind that the presented field dissipation study is by its character a rate and not a metabolism study. The study design does not allow for the determination of full mass balances.

At HS (Germany), the mean amount of fluopyram at day 0 was 268 g/ha, representing 107% of the nominal application rate. Fluopyram declined from 268 g/ha in soil at day 0 to 170 g/ha at day 360.

At HT (United Kingdom), the mean amount of fluopyram at day 0 was 275 g/ha, representing 110% of the nominal application rate. Fluopyram declined from 275 g/ha in soil at day 0 to 175 g/ha at day 362.

At LT (France), the mean amount of fluopyram at day 0 was 194 g/ha, representing 78% of the nominal application rate. Fluopyram declined from 194 g/ha in soil at day 0 to 67.7 g/ha at day 358.

At BS (France), the mean amount of fluopyram at day 0 was 266 g/ha, representing 106% of the nominal application rate. Fluopyram declined from 266 g/ha in soil at day 0 to 121 g/ha at day 359.

At BB (Italy), the mean amount of fluopyram at day 0 was 231 g/ha, representing 92% of the nominal application rate. Fluopyram declined from 231 g/ha in soil at day 0 to 74.4 g/ha at day 365.

At AE (Spain), the mean amount of fluopyram at day 0 was 257 g/ha, representing 103% of the nominal application rate. Fluopyram declined from 257 g/ha in soil at day 0 to 107 g/ha at day 371.

I. MATERIALS AND METHODS

A. MATERIALS

1. Test Item

Fluopyram 500 SC (suspension concentrate)
Certificate of Analysis: FAR30138-00
Batch Number: NK43GX1710
Content a.s.: Nominal: 500 g/L actual: 494.4 g/L

2. Test Sites

Field trials were carried out at test sites in six different countries, covering Northern and Southern European ecoregions. The test system was bare soil with sand coverage. Each trial comprised one untreated plot (plot 1) and one treated plot (plot 2). The untreated plot was located in >10 m distance to the treated plot. The treated plot was subdivided into three subplots (2A, 2B and 2C) to give triplicates. Their location and site details are presented in the table below.

Table 7.1.2.2.1-64: Properties of field soils

Characteristic	Trial 19-00024-01	Trial 19-00024-02	Trial 19-00024-03
Location	49685 Emstek-Hoeltinghausen (HS)	Hornton OX15 6BZ (HT)	08190 Le Thour (LT)
Country	Germany	United Kingdom	France
Ecoregion	Northern EU	Northern EU	Northern EU
Plot Size [sqm]	306 m² treated 18 m² control	306 m² treated 18 m² control	306 m² treated 18 m² control
Soil			
Surface soil texture (USDA)[1]	Loamy fine sand	Silt loam	Silt loam
% Sand[1]	83.7	29.2	18.0
% Silt[1]	13.4	51.9	78.4
% Clay[1]	2.9	18.9	3.5
CEC (meq/100 g)[1]	6.5	24.3	18.3
pH: (water suspension)[1]	6.40	6.67	8.00
pH: (0.01 M $CaCl_2$)[1]	5.56	6.11	7.50
Organic carbon (%)[1]	0.8	2.2	2.5
Distance from weather station used for daily climatic measurements	At trial location	At trial location	At trial location
Meteorological conditions compared to long-term average within normal levels	The sum of precipitation over the study period met the LTA, whereas the average temperature over the study period was comparatively warmer than the LTA data.	The sum of precipitation over the study period was higher than the LTA, mainly due to comparatively wet autumn and winter month, whereas the air temperature was comparable.	The sum of precipitation over the study period was higher than the LTA, mainly due to comparatively wet autumn and winter months, and the air temperature was slightly higher than the LTA.
Distance of LTA weather station to test field	Distance approx. 18 km	Distance approx. 16 km	Distance approx. 5.5 km

[1] upper soil layer (0-10 cm)

Characteristic	Trial 19-00024-04	Trial 19-00024-05	Trial 19-00024-06
Location	33124 Brannens (BS)	20060 Balbiano (BB)	29740 Torre del Mar (field called 'Almayate East'; AE)
Country	France	Italy	Spain
Ecoregion	Southern EU	Southern EU	Southern EU
Plot Size	306 m² treated 18 m² control	306 m² treated 18 m² control	306 m² treated 18 m² control
Soil			
Surface soil texture (USDA)[1]	Sandy loam	Loam	Silt loam
% Sand[1]	55.4	47.4	27.6
% Silt[1]	37.9	34.9	55.4
% Clay[1]	6.8	17.8	17.1
CEC (meq/100 g)[1]	5.8	15.8	17.0
pH: (water suspension)[1]	5.07	7.77	8.27
pH: (0.01 M $CaCl_2$)[1]	4.44	7.20	7.74
Organic carbon (%)[1]	0.8	2.0	1.4
Distance from weather station used for daily climatic measurements	At trial location	At trial location	At trial location
Meteorological conditions compared to long-term average within normal levels	The sum of precipitation over the study period was higher than the LTA, mainly due to comparatively wet autumn and winter months, and the air temperature was slightly higher than the LTA.	The sum of precipitation over the study period was slightly lower than the LTA, whereas the average air temperature was slightly warmer than the LTA.	The sum of precipitation over the study period was slightly lower than the LTA, whereas the average air temperature met the LTA
Distance of LTA weather station to test field	Distance approx. 6.8 km	Distance approx. 3 km	Distance approx. 7.3 km

[1] upper soil layer (0-10 cm)

The selected fields had not been treated with fungicides that share the mode of action of SDH inhibitors within the last three years before commencing the trials. No soil disinfectants were used within the previous year.

B. STUDY DESIGN

1. Experimental Conditions

Prior to spraying the product onto the bare soil, the plots were ploughed or tilled in order to loosen the top soil and then tightened by rolling, harrowing or grubbing. Stones and plant debris were removed and a fine seedbed was prepared.

Fluopyram was applied as a suspension concentrate formulation (fluopyram 500 SC) containing 500 g a.s./L. One application of the test item was conducted on bare soil using a boom sprayer (knapsack or monocycle) and passing over the plot twice in opposite directions to gain a homogeneous distribution. The target application rate was 500 mL product/ha and 600 L water/ha, corresponding to 250 g a.s./ha.

Directly after application and sampling of deposition tray specimens, the treated soil surface was covered with ~6-10 mm sand using a tractor mounted sand spreader. After application and 0 DAA sampling of soil residue specimens, but before the 3 DAA sampling event, the treated plots were irrigated with approximately 10 mm of water, in case no rain of approximately 10 mm occurred until then.

The application equipment was calibrated prior to the application. The applications were accepted if the deviation from the target rate was less than 5% and the visual spraying pattern was adequate. This was the case in all applications except subplot 2A of trial 19-00024-03 in Le Thour (LT), N-France. There, the deviation from the target rate was 12.8% and therefore this subplot was cancelled. A new subplot 2A was prepared and the application was repeated on this freshly prepared subplot. The deviation from the target rate was -5.4% and the application was accepted. Fluopyram 500 SC was applied according to the local application practice.

General agricultural maintenance practices were implemented. The growth of weeds was controlled by means of regular applications of Glyphosate, Oxyfluorfen or Flumioxazin on treated and untreated plots. The treated subplots were irrigated in case of drier than normal conditions with the aim to achieve 110% of the LTA precipitation in any month during the field phase.

2. Sampling

Untreated soil specimens were taken from subplot 1A of the control plot for the purpose of laboratory studies. Untreated soil specimens for residue analysis and control soil purposes were taken from subplot 1B of the control plot at 0-3 days before application (-3BA).

Treated soil specimens were collected from the treated subplots 2A, 2B and 2C at the following nominal sampling events: 0 DAA, 3 DAA, 7±1 DAA, 14±2 DAA, 35±3 DAA, 60±3 DAA, 120±3 DAA, 180±5 DAA, 270±5 DAA and 360±5 DAA. Further specimens were taken but in the Interim Report sampling events and residue results up to the 360±5 DAA sampling interval are reported, only. At each sampling event, 10 soil cores per subplot were taken up to a depth of approx. 85 cm according to the following procedure:

Soil specimens of 0-10 cm depth were taken using metal collars of 11 cm diameter, which are pressed into the ground. The 0-10 cm soil segments were transferred into plastic bags and pooled per subplot. The soil specimens were double-bagged to exclude contamination. To prevent surface soil from falling into the hole, the collars remained in the ground during the entire sampling time (until subsequent coring of deeper soil layers was finished) and were covered with matching lids.

The deeper soil cores were taken using acetate tubes of 4.6 cm diameter (with exception of the UK Test Site that used 4.4 cm diameter), which were pushed into the ground by a hydraulic corer (e.g. Geotool). The cores were taken from within the existing 0-10 cm holes.

Samples at 0 DAA were stored on dry ice immediately after sampling and then transferred into freezers later on and the soil specimens of the following sampling events were stored in deep freezers upon return to the test site less than 8 hours after sampling. The soil cores were cut into 10-cm soil layers, bulked soil layers were homogenized.

3. Analytical Procedures

The analytical method used in this study was based on method 01591 (M-658192-01-1). Soil specimens were extracted with a mixture of acetonitrile/water using a microwave extractor. The final determination of fluopyram was performed by HPLC-MS/MS.

Possible matrix effects of fluopyram were eliminated by using an internal standard solution of isotope labelled reference item. Residues of fluopyram were quantified using a calibration with standards in solvent containing stable isotope labelled standard (IS).

Generally, all residue determinations were performed according to the extraction procedure described above (one replicate) and analysed with a single injection. In the case of questionable results extraction and determination of residues were repeated to confirm the results.

The limit of quantitation (LOQ) was 5 µg/kg wet soil for fluopyram. The limit of detection (LOD) was 1.5 µg/kg wet soil.

The maximum period of storage of specimen final volumes was six days until analysis. Fluopyram was found to be stable in soil extracts for at least 18 days when stored in a fridge (M-658192-01-1). In the case of re-measurement the procedural recoveries of the respective set of analysis were measured together with the specimens of interest to prove the stability of the used extracts/solutions.

Full details and acceptable validation data to support the analytical method are presented within document M-CA 4, which comply with the EU regulatory requirements outlined within SANTE/2020/12830, Rev.1.

4. Preparation Method used for the Determination of Time-dependent Sorption of Fluopyram in Field Soil Specimens

At six events (0, 14, 35, 60, 120 and 180 DAA) a second set of specimens (0-10 cm) were investigated to determine time-dependent sorption. A second aliquot (10 g) of the regular residue specimens of the respective sampling events were extracted with 0.01 mol/L aqueous $CaCl_2$ solution prior to the regular extraction steps according to method 01591 (see above), and then analysed. Soil / $CaCl_2$ solution ratio was 1/4. An aliquot of 10 g of specimen were weighed into a 250 mL centrifuge bottle, 40 mL of 0.01 mol/L $CaCl_2$ solution (pH neutral) were added and shaken for 48 hours at 100 rpm. The specimens were centrifuged for about 30 min at approx. 3000 rpm. Shaking and centrifuging was conducted at 20 ± 1°C. The supernatant was decanted into a 50 mL centrifuge vial. An aliquot of the extract was diluted with a mixture of acetonitrile/water (4/1, v/v). Internal standard solution was added at this point so that the concentration corresponds to the concentration in the calibration standards. The obtained extract was centrifuged for 5 min at 10000 rpm before the measurement.

No procedural recoveries could be carried out for the determination of desorbable fluopyram residues with aqueous $CaCl_2$ solution.

Desorbable fluopyram residues were determined in the aqueous extracted sediments. Sediments in the centrifuge bottle were loosened and transferred into a test tube. The centrifuge bottles were rinsed with 5 mL of acetonitrile/water (4/1, v/v) four times. The acetonitrile/water (4/1, v/v) aliquots were combined in the test tube. After addition of the magnetic stirrers, the specimens were extracted according to the method 01591 (see above) respecting the ratio of soil and solvent.

The aqueous and organic extractable residues in the soil were calculated.

5. Recoveries

For each analytical batch consisting of a maximum of 24 specimens, a minimum of two concurrent recovery experiments were performed by spiking control specimens of the current study with the analyte. A summary of the recovery data can be found in the table below.

Table 7.1.2.2.1-65: Overall recoveries for fluopyram

Analyte	Matrix	Overall Recovery [1] [%]	RSD [%]	n
Fluopyram	Soil	97	6.0	106
Fluopyram	Soil (Time-dependent Sorption)	95	5.1	12
Fluopyram	Spray Mixture	103	4.8	6

[1] The overall recovery values were generated by calculation with the exact single values.

II. RESULTS AND DISCUSSION

A. DATA

The data was calculated from g/kg wet soil to g/ha if LOQ: 5 µg/kg, LOD: 1.5 µg/kg (wet soil). For values <LOD in the µg/kg tables no transformation to g/ha values was done and the respective values are reported as zero; for values >LOD and <LOQ, the transformation was done and calculated values are depicted in square brackets. Calculations were based on the total amount of residues and the respective surface area of the individual soil layers.

Table 7.1.2.2.1-66: Analytical results of fluopyram [g/ha] as arithmetic mean of three subplots

Trial 19-00024-01, HS, Germany

DAA	0	3	7	15	34	57	121	175	269	360
0-10 cm	268	237	227	207	193	178	132	157	155	147
10-20 cm	0	0	0	0	0	0	0	0	[6.52]	22.8
20-30 cm	0	0	0	0	0	0	0	0	0	0
Sum 0-30 cm	**268**[1]	**237**	**227**	**207**	**193**	**178**	**132**	**157**	**161**	**170**

[1] corresponding to 107% of the target application rate of 250 g/ha.
DAA = days after application; n.a. = not analysed; values are given as 0 if the corresponding value in µg/kg was <LOD and in brackets if the corresponding value in µg/kg was >LOD and <LOQ.

Trial 19-00024-02, HT, UK

DAA	0	3	6	12	33	57	121	180	268	362
0-10 cm	275	249	245	233	222	223	204	167	168	159
10-20 cm	0	0	0	0	0	0	[1.07]	[4.13]	9.68	14.3
20-30 cm	0	0	0	0	0	0	0	0	[1.28]	[1.75]
30-40 cm	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	0[1]	0[1]	0[1]
40-50 cm	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	0[1]	0[1]	0[1]
Sum 0-50 cm	**275**[2]	**249**	**245**	**233**	**223**	**223**	**205**	**172**	**179**	**175**

[1]value not analysed for all subplots, mean of analysed subplots is shown
[2] corresponding to 110% of the target application rate of 250 g/ha.
DAA = days after application; n.a. = not analysed; values are given as 0 if the corresponding value in µg/kg was <LOD and in brackets if the corresponding value in µg/kg was >LOD and <LOQ.

Trial 19-00024-03, LT, France

DAA	0	3	7	14	38	63	121	182	274	358
0-10 cm	190	191	203	212	158	150	89.2	67.5	58.4	62.3
10-20 cm	[2.36]	0	[3.06]	[1.84]	[6.13]	[4.87]	[3.06]	[1.82]	[5.15]	[5.40]
20-30 cm	[1.53]	0	0	0	0	0	0	0	0	0
30-40 cm	0[1]	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
40-50 cm	0[1]	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
Sum 0-30 cm	**194**[2]	**191**	**207**	**214**	**164**	**155**	**92.3**	**69.3**	**63.6**	**67.7**

[1]value not analysed for all subplots, mean of analysed subplots is shown
[2] corresponding to 77% of the target application rate of 250 g/ha.
DAA = days after application; n.a. = not analysed; values are given as 0 if the corresponding value in µg/kg was <LOD and in brackets if the corresponding value in µg/kg was >LOD and <LOQ.

Trial 19-00024-04, BS, France

DAA	0	3	7	14	28	58	120	189	266	359
0-10 cm	266	250	242	205	184	161	117	98.3	68.1	59.7
10-20 cm	0	[2.54]	[0.94]	[3.26]	[8.14]	14.0	[7.55]	22.9	25.4	33.2
20-30 cm	0	0	0	0	[1.73]	[1.22]	[7.44]	14.5	13.5	17.8
30-40 cm	n.a.	n.a.	n.a.	n.a.	0[1]	0[1]	0	[4.34]	[7.03]	[6.74]
40-50 cm	n.a.	n.a.	n.a.	n.a.	0[1]	0[1]	0	0	[3.73]	[4.18]
Sum 0-50 cm	**266**[2]	**252**	**243**	**208**	**194**	**176**	**132**	**140**	**118**	**121**

[1]value not analysed for all subplots, mean of analysed subplots is shown
[2] corresponding to 106% of the target application rate of 250 g/ha.
DAA = days after application; n.a. = not analysed; values are given as 0 if the corresponding value in µg/kg was <LOD and in brackets if the corresponding value in µg/kg was >LOD and <LOQ.
Segments below 50 cm where the residue result is >LOD will be analysed until one residue free segment is detected, and the results will be reported in the Final Report.

Trial 19-00024-05, BB, Italy

DAA	0	3	8	15	35	63	120	184	269	365
0-10 cm	230	195	225	206	220	138	94.4	96.8	73.7	52.8
10-20 cm	0	[4.52]	[7.24]	11.3	10.4	25.8	16.6	17.1	29.5	13.8
20-30 cm	0	0	0	0	0	11.3	[4.07]	[3.58]	[5.91]	[7.77]
30-40 cm	n.a.	n.a.	n.a.	n.a.	n.a.	0	0[1]	0[1]	[2.45] [1]	n.a.
40-50 cm	n.a.	n.a.	n.a.	n.a.	n.a.	0	0[1]	[1.51] [1]	[1.06] [1]	n.a.
Sum 0-50 cm	**231**[2]	**199**	**232**	**217**	**230**	**175**	**115**	**119**	**113**	**74.4**

[1]value not analysed for all subplots, mean of analysed subplots is shown
[2] corresponding to 92% of the target application rate of 250 g/ha.
DAA = days after application; n.a. = not analysed; values are given as 0 if the corresponding value in µg/kg was <LOD and in brackets if the corresponding value in µg/kg was >LOD and <LOQ.
Segments below 50 cm where the residue result is >LOD will be analysed until one residue free segment is detected, and the results will be reported in the Final Report.

Trial 19-00024-06, AE, Spain

DAA	0	3	6	15	35	62	121	181	268	371
0-10 cm	253	232	213	194	152	158	135	128	118	94.4
10-20 cm	[3.95]	17.7	9.15	[3.99]	13.8	8.57	15.2	7.39	[4.22]	13.0
20-30 cm	0	0	0	0	0	0	0	0	0	0
Sum 0-30 cm	**257**[1]	**250**	**222**	**198**	**166**	**166**	**150**	**136**	**123**	**107**

[1] corresponding to 103% of the target application rate of 250 g/ha.
DAA = days after application; n.a. = not analysed; values are given as 0 if the corresponding value in µg/kg was <LOD and in brackets if the corresponding value in µg/kg was >LOD and <LOQ.

Table 7.1.2.2.1-67: Analytical results of aqueous and organic desorbable fluopyram residues

Trial 19-00024-01, HS, Germany

DAA	Sub-plot	FLU in $CaCl_2$ shaking solution [µg/mL]	Aqueous desorbable FLU [µg/kg wet weight]	Organic desorbable FLU [µg/kg wet weight]	Sum aqueous and organic desorbable FLU [µg/kg wet weight]	Total FLU determined via standard method [µg/kg wet weight]
0	2 A	0.0160	63.6	103	167	206
0	2 B	0.0200	80.3	110	190	228
0	2 C	0.0187	74.3	95.3	170	185
15	2 A	0.0133	52.9	92.6	145	158
15	2 B	0.0137	54.7	83.9	139	151
15	2 C	0.0143	57.3	83.4	141	162
34	2 A	0.0113	45.2	92.7	138	163
34	2 B	0.0136	54.4	93.5	148	129
34	2 C	0.0126	50.5	85.4	136	154
57	2 A	0.00852	34.2	94.5	129	132
57	2 B	0.00850	34.1	85.3	119	143
57	2 C	0.00980	39.0	90.5	130	137
121	2 A	0.00590	23.7	66.8	90.6	104
121	2 B	0.00669	26.7	61.9	88.6	101
121	2 C	0.00602	24.1	56.1	80.3	94.1
175	2 A	0.00535	21.4	70.3	91.7	89.7
175	2 B	0.00621	24.8	72.5	97.2	112
175	2 C	0.00694	27.8	84.1	112	131

DAA = days after application

Trial 19-00024-02, HT, UK

DAA	Sub-plot	FLU in $CaCl_2$ shaking solution [µg/mL]	Aqueous desorbable FLU [µg/kg wet weight]	Organic desorbable FLU [µg/kg wet weight]	Sum aqueous and organic desorbable FLU [µg/kg wet weight]	Total FLU determined via standard method [µg/kg wet weight]
0	2 A	0.0173	69.3	149	219	254
0	2 B	0.0204	81.5	152	234	255
0	2 C	0.0158	63.3	128	191	204
12	2 A	0.0124	49.8	123	173	177
12	2 B	0.0169	67.6	162	229	220
12	2 C	0.0136	54.1	122	176	167
33	2 A	0.0101	40.5	117	157	161
33	2 B	0.0100	40.1	112	152	146
33	2 C	0.0119	47.2	132	180	224
57	2 A	0.0100	39.7	125	165	178
57	2 B	0.0113	45.2	118	163	175

DAA	Sub-plot	FLU in $CaCl_2$ shaking solution [µg/mL]	Aqueous desorbable FLU [µg/kg wet weight]	Organic desorbable FLU [µg/kg wet weight]	Sum aqueous and organic desorbable FLU [µg/kg wet weight]	Total FLU determined via standard method [µg/kg wet weight]
57	2 C	0.0113	45.0	140	185	171
121	2 A	0.00868	34.6	148	182	183
121	2 B	0.00785	31.4	133	164	168
121	2 C	0.00828	32.9	137	170	173
180	2 A	0.00673	26.8	115	141	138
180	2 B	0.00500	20.0	92.7	113	123
180	2 C	0.00619	24.6	106	131	130

DAA = days after application

Trial 19-00024-03, LT, France

DAA	Sub-plot	FLU in the $CaCl_2$ shaking solution [µg/mL]	Aqueous desorbable FLU [µg/kg wet weight]	Organic desorbable FLU [µg/kg wet weight]	Sum aqueous and organic desorbable FLU [µg/kg wet weight]	Total FLU determined via standard method [µg/kg wet weight]
0	2 A	0.0291	116	174	290	288
0	2 B	0.0146*	58.2*	80.5*	139	153
0	2 C	0.0233	93.3	122	216	222
14	2 A	0.0330	131	208	339	321
14	2 B	0.0271	108	149	257	226
14	2 C	0.0272	109	152	261	266
38	2 A	0.0159	63.5	118	181	192
38	2 B	0.0167	66.6	110	176	212
38	2 C	0.0185	73.9	120	194	220
63	2 A	0.0167	66.7	148	215	223
63	2 B	0.0145	57.9	107	165	170
63	2 C	0.0128	51.1	97.0	148	154
121	2 A	0.00459	18.3	51.4	69.7	75.2
121	2 B	0.00524[1]	20.9[1]	60.0[1]	80.9	80.3
121	2 C	0.00343	13.6	38.7	52.4	53.8
182	2 A	0.00295	11.8	42.0	53.8	45.5
182	2 B	0.00508	20.3	45.5	65.8	63.1
182	2 C	0.00327	13.1	37.6	50.7	49.4

DAA = days after application
[1] Mean value of two determinations

Trial 19-00024-04, BS, France

DAA	Sub-plot	FLU in the $CaCl_2$ shakuing solution [µg/mL]	Aqueous desorbable FLU [µg/kg wet weight]	Organic desorbable FLU [µg/kg wet weight]	Sum aqueous and organic desorbable FLU [µg/kg wet weight]	Total FLU determined via standard method [µg/kg wet weight]
0	2 A	0.0383	154	81.7	236	245
0	2 B	0.0286	115	61.0	176	190
0	2 C	0.0303	121	80.4	201	219
14	2 A	0.0198	79.1	51.5	131	143
14	2 B	0.0193	77.2	60.0	137	141
14	2 C	0.0224	89.4	64.5	151	182
28	2 A	0.0183	72.8	55.4	128	135
28	2 B	0.0195	78.0	88.4	166	185
28	2 C	0.0165	65.7	58.3	124	135
58	2 A	0.0161	64.2	61.8	126	148
58	2 B	0.0170	67.9	57.6	126	139
58	2 C	0.0150	60.3	55.1	116	119
120	2 A	0.0101	40.3	37.1	77.3	84.4
120	2 B	0.00975	39.2	45.0	84.2	84.8
120	2 C	0.00939	37.7	37.5	75.3	76.4
189	2 A	0.00551	21.9	38.3	60.2	65.6
189	2 B	0.00636	25.2	33.7	59.0	68.7
189	2 C	0.00626	25.1	31.1	56.2	56.4

DAA = days after application

Trial 19-00024-05, BB, Italy

DAA	Sub-plot	FLU in the $CaCl_2$ shaking solution [µg/mL]	Aqueous desorbable FLU [µg/kg wet weight]	Organic desorbable FLU [µg/kg wet weight]	Sum aqueous and organic desorbable FLU [µg/kg wet weight]	Total FLU determined via standard method [µg/kg wet weight]
0	2 A	0.0198	78.9	123	202	193
0	2 B	0.0240	95.3	134	229	239
0	2 C	0.0227	90.8	149	240	226
15	2 A	0.0128	50.8	90.6	141	134
15	2 B	0.0160	63.4	108	171	184
15	2 C	0.0130	51.8	94.7	147	162
35	2 A	0.0158	62.8	127	190	183
35	2 B	0.0152	60.8	114	175	180
35	2 C	0.0164	65.5	122	187	216
63	2 A	0.00712	28.3	80.6	109	113
63	2 B	0.00738	29.5	78.4	108	116
63	2 C	0.00619	24.7	67.7	92.4	90.9

DAA	Sub-plot	FLU in the $CaCl_2$ shaking solution [µg/mL]	Aqueous desorbable FLU [µg/kg wet weight]	Organic desorbable FLU [µg/kg wet weight]	Sum aqueous and organic desorbable FLU [µg/kg wet weight]	Total FLU determined via standard method [µg/kg wet weight]
120	2 A	0.00390	15.5	51.5	67.0	66.6
120	2 B	0.00428	17.0	61.2	78.2	74.2
120	2 C	0.00429	17.1	68.7	85.8	86.2
184	2 A	0.00397	15.8	52.1	67.9	76.3
184	2 B	0.00345	13.8	55.4	69.2	63.3
184	2 C	0.00425	16.9	55.5	72.4	79.3

DAA = days after application

Trial 19-00024-06, AE, Spain

DAA	Sub-plot	FLU in the $CaCl_2$ shaking solution [µg/mL]	Aqueous desorbable FLU [µg/kg wet weight]	Organic desorbable FLU [µg/kg wet weight]	Sum aqueous and organic desorbable FLU [µg/kg wet weight]	Total FLU determined via standard method [µg/kg wet weight]
0	2 A	0.0166	65.8	119	184	205
0	2 B	0.0251	100	119	219	268
0	2 C	0.0217	86.5	106	193	238
15	2 A	0.0192	76.3	111	187	180
15	2 B	0.0181	72.1	105	177	170
15	2 C	0.0174	69.1	97.3	166	171
35	2 A	0.0139	55.8	84.0	140	155
35	2 B	0.0118	47.2	69.1	116	117
35	2 C	0.0146	58.4	77.8	136	144
62	2 A	0.0131	52.3	88.1	140	142
62	2 B	0.0109	43.7	103	147	144
62	2 C	0.0123	48.9	82.9	132	138
121	2 A	0.0125	50.0	75.5	126	111
121	2 B	0.0121	48.0	74.3	122	112
121	2 C	0.0146	58.5	86.1	145	146
181	2 A	0.0127	50.5	78.6	129	117
181	2 B	0.0123	49.0	76.5	125	120
181	2 C	0.00912	36.4	72.8	109	90.7

DAA = days after application

B. RESIDUES

1. Results of application monitors

The spray mixture specimens were analysed for their content of fluopyram. The results ranged from 354 mg to 410 mg FLU/L, being 85% to 98% of the target concentration of 417 mg FLU/L.

The deposition trays were analysed for their contents of fluopyram, being in a range of 54 to 117%, with average recoveries per trial (average of 6 recovery trays) of 93% for trial 19-00024-01 (HS, Germany), 100% for trial 19-00024-02 (HT, UK), 96% for trial 19-00024-03 (LT, France), 86% for trial 19-00024-04 (BS, France), 93% for trial 19-00024-05 (BB, Italy) and 95% for trial 19-00024-06 (AE, Spain). These results indicate a correct application procedure, which is also confirmed by the 0 DAA residue specimen recoveries.

2. Storage stability

Information on the frozen storage stability was determined in a separate study (KCA 7.1.2.2.1/12, M-348402-01-1). According to the results of that study fluopyram is stable in soil for at least 864 days of storage under frozen conditions.

3. Analytical results of control specimens

Results obtained for control specimens, which were analysed with regard to blank values in [µg/kg] are based on the concentration of the analyte in wet soil. From these results it can be concluded that residues of fluopyram in control specimens were < LOD for all specimens taken from all trials.

4. Results of soil residue specimens

The actual applied dose rate of fluopyram measured in 0 DAA specimens compared to the target rate of 250 g fluopyram per hectare was calculated to be 268 g/ha (107%) for trial 19-00024-01 (HS, Germany), 275 g/ha (110%) for trial 19-00024-02 (HT, UK), 194 g/ha (77%) for trial 19-00024-03 (LT, France), 266 g/ha (106%) for trial 19-00024-04 (BS, France), 231 g/ha (93%) for trial 19-00024-05 (BB, Italy) and 257 g/ha (103%) for trial 19-00024-06 (AE, Spain), in average of the three treated replicates, respectively.

Up to the nominal 360 DAA sampling event, residues for fluopyram were detected so far down to a soil depth of 50 cm of the soil profile. Soil segments will be analysed until at least one residue free horizon is shown. This will be done and reported in the Final Report.

C. KINETIC ANALYSIS

The kinetic evaluation following current FOCUS guidance was conducted separately and is summarised under KCA 7.1.2.2.1/22 for trigger endpoints and KCA 7.1.2.2.1/18 for modelling endpoints.

III. CONCLUSIONS

Under field conditions, fluopyram is declining at varying rates in the six monitored trials. Soil specimens were collected at the following nominal sampling events: 0 DAA, 3 DAA, 7±1 DAA, 14±2 DAA, 35±3 DAA, 60±3 DAA, 120±3 DAA, 180±5 DAA, 270±5 DAA and 360±5 DAA. Further specimens were taken but in the interim report sampling events and residue results up to the 360±5 DAA sampling interval are reported, only. The analysis is on-going and additional results will be shown in the final report.

3. Assessment and conclusion

Assessment and conclusion by applicant: The study and its data available so far are considered to be valid and reliable for use in risk assessment.

Assessment and conclusion by RMS: Outcome and conclusion of the study: RMS should indicate if they agree to the results and conclusions of the APPL.

The study is still ongoing, and the final report of this field dissipation study will be provided latest by end of February 2022.

1. Information on the study

Data Point:	KCA 7.1.2.2.1/16
Report Author:	[redacted]
Report Year:	2020
Report Title:	Fluopyram (FLU): Kinetic evaluation of field dissipation studies in USA according to FOCUS Kinetics and EFSA TFD guidance for modelling purpose using KinGUI 2.1
Report No:	EnSa-20-0249
Document No:	M-761975-01-1
Guideline(s) followed in study:	EFSA 2014
Deviations from current test guideline:	Current Guideline: EFSA 2014 none
Previous evaluation:	No, not previously submitted
GLP/Officially recognised testing facilities:	No, not conducted under GLP/Officially recognised testing facilities
Acceptability/Reliability:	Yes

2. Full summary of KCA 7.1.2.2.1/16

Executive Summary

Normalised (20°C, 100% field capacity) degradation $DT_{50\,matrix}$ values of fluopyram (FLU) in the soil matrix under US field conditions were derived for modelling purpose, using the software tool KinGUI 2.1. Processes potentially occurring at the soil surface, e.g. photo-degradation and volatilisation, during the field study should be eliminated to result finally in a $DT_{50\,matrix}$ representing the degradation in the soil. The identification of the appropriate kinetic model followed the recommendations given by FOCUS Kinetics and EFSA guidance on field dissipation studies. The modelling analysis is based on residue data from terrestrial field dissipation studies conducted at the field sites located in New York and Washington.

The $DegT_{50,matrix}$ normalised values for fluopyram (modelling endpoints) were calculated to be between 257.4 and 281.7 days for both soils while the $DT_{50,actual}$ values were between 144.8 and 281.7 days.

I. METHODS

Normalised (20°C, 100% field capacity) degradation $DT_{50\,matrix}$ values of fluopyram (FLU) in the soil matrix under US field conditions were derived for modelling purpose, using the software tool KinGUI 2.1. Processes potentially occurring at the soil surface, e.g. photo-degradation and volatilisation, during the field study should be eliminated to result finally in a $DT_{50\,matrix}$ representing the degradation in the soil. The identification of the appropriate kinetic model followed the recommendations given by FOCUS Kinetics (FOCUS, 2006, 2014a) and EFSA guidance on field dissipation studies (EFSA 2014) based on a detailed statistical analysis including visual assessment, χ^2 statistic, significance t-test and correlation analysis, using correspondingly pre-processed residue data. Additionally, the Scaled Weighted Area under Residue Curve (SWARC) was used as a further indicator for the visual assessment and to choose the appropriate model.

The modelling analysis is based on residue data from terrestrial field dissipation studies conducted at the field sites located in New York (KCA 7.1.2.2.1/04, M-306809-01-2) and Washington (KCA 7.1.2.2.1/03, M-306817-01-2).

In the experimental studies, the active substance has been applied to bare soil onto 4 subplots per site at a nominal rate of 500 g FLU/ha in summer 2006. Throughout the study period no cultivation activities were carried out. Herbicides were applied to maintain bare soil conditions. Supplemental irrigation events were conducted.

Simulated (with PEARL) daily soil temperatures and moisture contents, based on local weather data, were used to normalise degradation parameters to reference conditions according to FOCUS groundwater assumptions (Arrhenius equation, Q_{10} = 2.58; Walker equation, pF2) (European Commission 2014; FOCUS 2014b). The residue data together with the transformed incubation times (transformed time approach, time step normalisation) were kinetically and statistically evaluated.

In the attempt to separate soil surface degradation processes, such as photo-degradation and volatilisation, from bulk soil degradation, an important threshold to start a kinetic evaluation might be the time point, when the sum of precipitation and irrigation equals or exceeds 10 mm (EFSA 2014). Then, it is assumed that the active substance is sufficiently deep washed into the soil matrix. Following the EFSA guideline, data points in the field studies before 10 mm of rain or irrigation were excluded for SFO degradation. In addition, biphasic breakpoints (DFOP, HS) are considered valid only, when they do occur after 10 mm of rain/irrigation have been fallen.

In laboratory degradation studies of fluopyram long-term sorption kinetics (TDS) was observed (e.g. KCA 7.1.1.1/02, M-298296-01-1). Although this leads to biphasic decline in theory, this effect is typically, as in the case of fluopyram, rather weak and visually hardly distinguishable from SFO behaviour. For TFD studies, especially legacy studies, we therefore attribute bi-phasic behaviour rather to surface processes than to TDS. Consequently, to avoid double interpretation of a biphasic behaviour, the standard evaluation method (according box 3, EFSA, 2014) was followed here.

Table 7.1.2.2.1-68: Precipitation (rain + irrigation) conditions on trial sites

Site	Weather station for precipitation	10 mm precip. reached at natural day	10 mm precip. reached at normalised day	Precip. amount until this day (mm)	Natural day of next sample	Normalised day of next sample	Data points excluded (natural day)
North Rose, New York	ACDS Research, East Farm weather station, No. 650	6 [1]	5.75	22.8	7	6.99	0, 3
Ephrata, Washington	Quails Agriculture Laboratory (QAL) weather station	2	1.60	40.6	3	2.20	0

[1] day 0: 20.8 mm rain started at 2 am., while application was at 10 am. Sampling was at 11 am. Thus, 10 mm criterion not reached at day 0. (Personal communication and raw data, Xu 2013)

Concentrations of the metabolites of fluopyram remained very low throughout the study, e.g. for fluopyram-7-hydroxy. Therefore, in the following kinetic evaluation only the dissipation of the parent compound was considered. It was assumed the parent directly degraded in the sink.

II. RESULTS

Degradation of fluopyram

Results of the kinetic evaluation for modelling purpose based on residue data from the terrestrial field dissipation studies in the USA are summarised in the tables below.

Table 7.1.2.2.1-69: Fluopyram (M-306809-01-2): kinetic and statistical results of degradation in field soil North Rose, New York

Kinetic model	DT_{50} actual	DT_{90} actual	DT_{50} mod	VA	χ^2 err / SWARC	k_1	k_2	g / t_b	t-test k_1 / k_2	95th CI of k_1	95th CI of k_2
	(d)	(d)	(d)		(% / -)	(1/d)	(1/d)	(- / d)	(-)	(1/d)	(1/d)
SFO	281.7	936	**281.7**	+	12.5 / 12.2	0.00246	-	- / -	<0.001	0.00153 to 0.004	-
DFOP	181.2	>1000	396.3	+	10.5 / 8.13	0.1039	0.00174	0.3135 / 20.0	0.084 / 0.007	0.04167 to 0.249	0.00042 to 0.003
HS	171.7	853	293.2	+	11.4 / 14.3	0.05233	0.00236	0.2598 / 5.75 [fix]	0.002 / <0.001	0.01817 to 0.086	0.00131 to 0.003

$DT_{50\ mod}$ = half-lives for modelling; DFOP, HS: DT_{50} of slow phase
VA = visual assessment, + = good, o = acceptable, - = poor
SWARC = Scaled Weighted Area under Residue Curve
CI = confidence intervall

Modelling Endpoints: SFO fit is statistically (χ^2-err < 15%, t-test) and visually good. SWARC value < 40 confirms SFO degradation. Consequently, SFO degradation model is appropriate for modelling endpoints.

SFO (data points before 10 mm of rain/irrigation excluded)

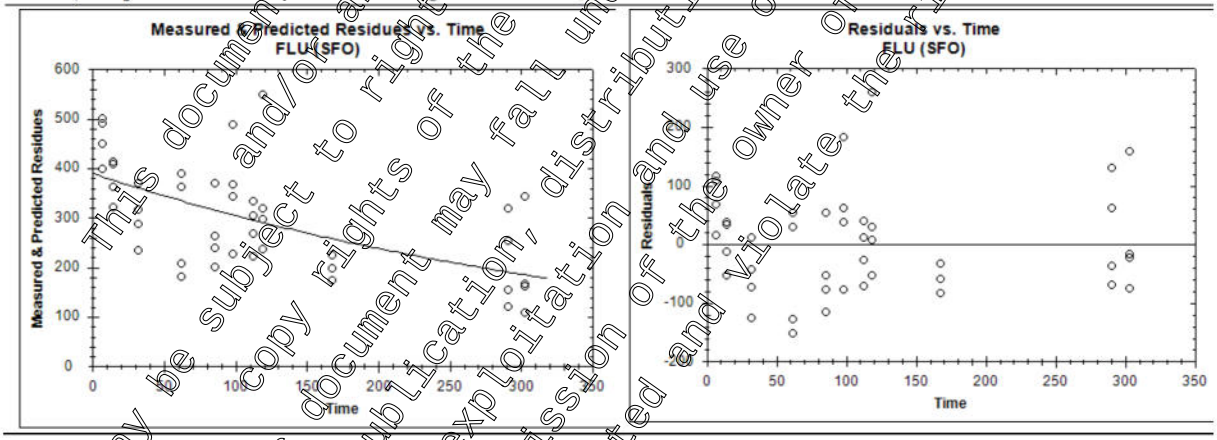


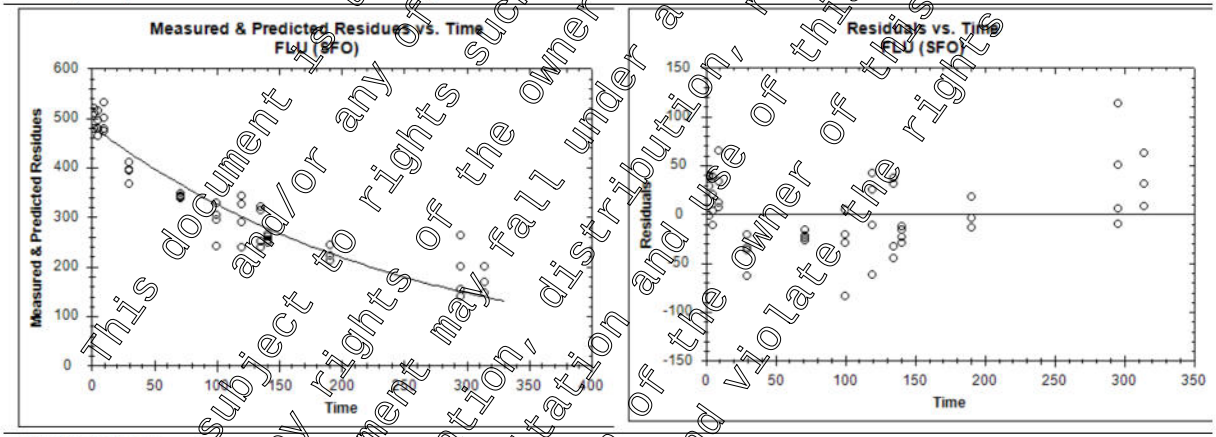
Table 7.1.2.2.1-70: Fluopyram (M-306817-01-2): kinetic and statistical results of degradation in soil Ephrata, Washington

Kinetic model	DT_{50} actual	DT_{90} actual	DT_{50} mod	VA	χ^2 err / SWARC	k_1	k_2	g / t_b	t-test k_1 / k_2	95th CI of k_1	95th CI of k_2
	(d)	(d)	(d)		(% / -)	(1/d)	(1/d)	(- / d)	(-)	(1/d)	(1/d)
SFO	174	578	174	o	6.18 / 66.5	0.003984	-	- / -	<0.001	0.00355 to 0.004	-
DFOP	144.8	742	**257.4**	+	3.03 / 1.92	0.04457	0.002693	0.3021 / 46.7	0.006 / <0.001	0.01154 to 0.0178	0.00201 to 0.0033
HS	144.4	548	173.98	o	5.89 / 57.7	0.07762	0.003984	0.1168 / 1.60 fix	0.001 / <0.001	0.02998 to 0.125	0.00356 to 0.004

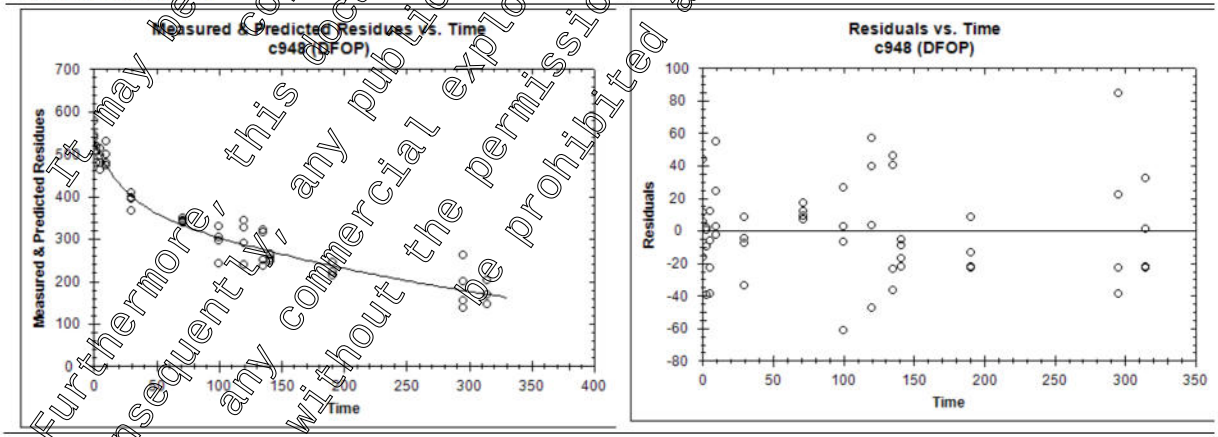
$DT_{50\ mod}$ = half-lives for modelling; DFOP, HS: DT_{50} of slow phase
VA = visual assessment, + = good, o = acceptable, - = poor
SWARC = Scaled Weighted Area under Residue Curve
CI = confidence intervall

Modelling Endpoints: SFO fit is statistically (χ^2err, t-test) good, and visually moderately acceptable. SWARC value slightly > 40 indicates that decline might be biphasic. Therefore, DFOP was tested, meeting the criteria of g <0.75, $k_{1\ fast}$ and $k_{2\ slow}$ significantly different (95th confidence intervals no overlap) and 10 mm precipitation reached at breakpoint t_b. The DFOP fit is statistically (χ^2err, t-test) and visually good. Consequently, **DFOP** degradation model using $k_{2\ slow}$ is appropriate for modelling endpoints.

SFO (data points before 10 mm of rain/irrigation excluded)



DFOP (full dataset)



III. CONCLUSIONS

The normalised modelling endpoints of field dissipation studies of fluopyram based on residue data from two US trials are summarised in the table below.

Table 7.1.2.2.1-71: Fluopyram: Field matrix degradation endpoints for modelling purpose; normalised to 20°C, 100% field capacity, Q_{10} = 2.58; US sites

Fluopyram	Field conditions								
Soil type (USDA) [4]	**Location**		**pH ($CaCl_2$)** [4]	**Depth (cm)**	**DT_{50} actual (d)**	**DT_{90} actual (d)**	**St. (χ^2) (%)**	**DegT_{50} matrix (d) norm.** [3]	**Method of calculation**
Loamy sand, bare [1]	North Rose New York, USA		5.9	15	281.7	936	12.5	281.7	SFO
Sandy loam, bare [2]	Ephrata Washington, USA		7.5	15	144.8	742	3.03	$DT_{50,slow}$: 257.4	DFOP

[1] M-306809-01-2
[2] M-306817-01-2
[3] normalised using a Q10 of 2.58 and Walker equation coefficient of 0.7, values correspond with $DT_{50,mod}$ of selected kinetic models
[4] analysed in topsoil

3. Assessment and conclusion

Assessment and conclusion by applicant:
The kinetic evaluation followed FOCUS Guidance on degradation kinetics (2006, 2014) and EFSA guidance on field dissipation studies (2014) and is considered to be valid and reliable.

Assessment and conclusion by RMS:
Outcome and conclusion of the study: RMS should indicate if they agree to the results and conclusions of the APPL.

1. Information on the study

Data Point:	KCA 7.1.2.2.1/17
Report Author:	[redacted]
Report Year:	2020
Report Title:	Fluopyram (FLU): Interim kinetic evaluation of a field dissipation study in Europe (Doig, 2020) according to FOCUS kinetics and EFSA TFD guidance for modelling purpose using KinGUI 2.1
Report No:	EnSa-20-0855
Document No:	M-761974-01-1
Guideline(s) followed in study:	EFSA 2014
Deviations from current test guideline:	Current Guideline: EFSA 2014 none
Previous evaluation:	No, not previously submitted
GLP/Officially recognised testing facilities:	No, not conducted under GLP/Officially recognised testing facilities
Acceptability/Reliability:	Yes

2. Full summary of KCA 7.1.2.2.1/17

Executive Summary

Normalised (20°C, 100% field capacity) degradation $DT_{50\ matrix}$ values of fluopyram (FLU) in the soil matrix under European field conditions were derived for modelling purpose, using the software tool KinGUI 2.1. Since processes potentially occurring at the soil surface, e.g. photo-degradation and volatilisation, were eliminated during the field study performance the measured data should result in a $DT_{50\ matrix}$ representing the degradation kinetics in soil. The identification of the appropriate kinetic model followed the recommendations given by FOCUS Kinetics and EFSA guidance on field dissipation studies. The modelling analysis is based on interim residue data from a terrestrial field dissipation study conducted at the field sites located in Little Oliver (Malton, UK), Auchy les Mines (France), Urbanowice (Poland), Charles River Farm (Alpicat, Lleida, Spain) and Sindos (Greece).

Concentrations of the metabolites of fluopyram were not analysed. Therefore, only the degradation of the parent compound was considered.

The $DegT_{50,matrix}$ normalised values for fluopyram (modelling endpoints) were calculated to be between 153.8 and >1000 days for all six soils. The $DT_{50\ actual}$ values were between 153.8 and >1000 days as well.

I. METHODS

Normalised (20°C, 100% field capacity) degradation $DT_{50\ matrix}$ values of fluopyram (FLU) in the soil matrix under European field conditions were derived for modelling purpose, using the software tool KinGUI 2.1. Processes potentially occurring at the soil surface, e.g. photo-degradation and volatilisation during the field study should be eliminated to result finally in a $DT_{50\ matrix}$ representing the degradation in the soil. The identification of the appropriate kinetic model followed the recommendations given by FOCUS Kinetics (FOCUS, 2006, 2014a) and EFSA guidance on field dissipation studies (EFSA 2014) based on a detailed statistical analysis including visual assessment, χ^2 statistic, significance t-test and correlation analysis, using correspondingly pre-processed residue data. Additionally, the Scaled Weighted Area under Residue Curve (SWARC) was used as a further indicator for the visual assessment and to choose the appropriate model.

The modelling analysis is based on interim residue data from a terrestrial field dissipation study conducted at the field sites located in Little Oliver (Malton, UK), Auchy les Mines (France), Urbanowice

(Poland), Charles River Farm (Alpicat, Lleida, Spain) and Sindos (Greece) (KCA 7.1.2.2.1/14, M-758583-01-1).

In the 5 experimental trials, the active substance has been applied to bare soil at 3 subplots per site at a nominal rate of 250 g/ha fluopyram in spring 2019. After application, 3 - 5 mm of sand was applied evenly to the treated plots, to exclude surface processes of the active compound, e.g. photo-degradation, volatilisation. The sand cover was in place at least until the sum of precipitation exceeded 10 mm which was reached 3 days after application for all sites. Therefore, the full dataset was used for evaluation (EFSA 2014). No cultivation activities were carried out throughout the study period. Herbicides were applied to maintain bare soil conditions. Supplemental irrigation events were conducted.

Simulated (with PEARL) daily soil temperatures and moisture contents, based on local weather data, were used to normalise degradation parameters to reference conditions according to FOCUS groundwater assumptions (Arrhenius equation, Qc = 2.58; Walker equation, pF2) (European Commission 2014; FOCUS 2014b). The residue data together with the transformed incubation times (transformed time approach, time step normalisation) were kinetically and statistically evaluated.

In laboratory degradation studies of fluopyram long-term sorption kinetics (TDS) was observed (e.g. KCA 7.1.1.1/05, M-681092-01-1, amended report M-681092-02-1). Although this leads to biphasic decline in theory, this effect is typically, as in the case of fluopyram, rather weak and visually hardly distinguishable from SFO behaviour. For TFD studies, especially legacy studies, we therefore attribute bi-phasic behaviour rather to surface processes than to TDS. Consequently, to avoid double interpretation of a biphasic behaviour, the standard evaluation method (according box 3, EFSA, 2014) was followed here.

Concentrations of the metabolites of fluopyram were not analysed. It was assumed the parent directly degraded into sink.

II. RESULTS

Degradation of fluopyram

Results of the kinetic evaluation for modelling purpose based on residue data from the terrestrial field dissipation studies in Europe are summarised in the tables below.

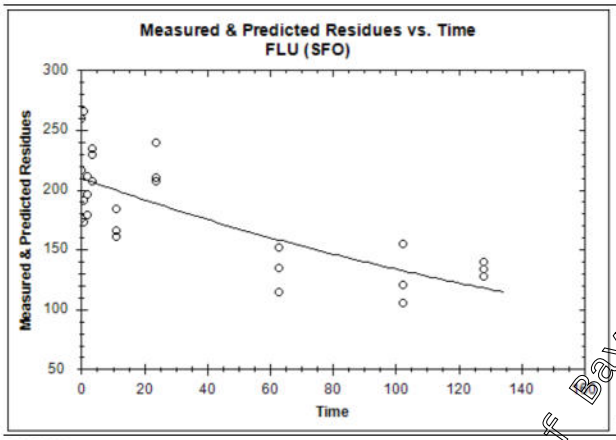
Table 7.1.2.2.1-72: Fluopyram: kinetic and statistical results of degradation in field soil Little Oliver, UK

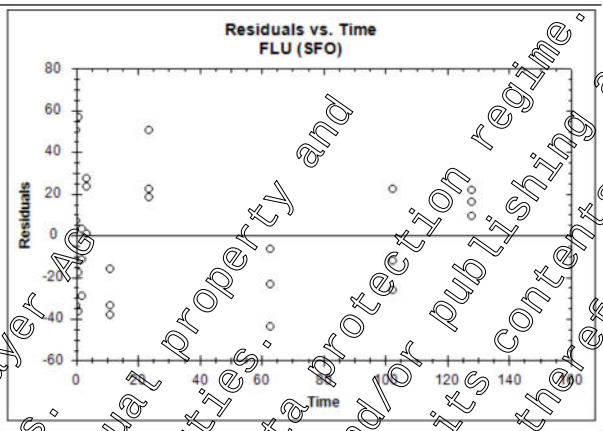
Kinetic model	DT_{50} actual	DT_{90} actual	DT_{50} slow phase	VA	χ^2err / SWARC	k_1	k_2	g / t_b	t-test k_1 / k_2	95th CI of k_1	95th CI of k_2
	(d)	(d)	(d)		(% / -)	(1/d)	(1/d)	(- / d)	(-)	(1/d)	(1/d)
SFO	153.8	510.8	**153.8**	o	8.31 / 14.7	0.004508	-	- / -	<0.001	0.00281 to 0.006	-
DFOP	>1000	>1000	>1000	o	9.01 / 6.31	0.01461	2.3 E-14	0.4888 / 142	0.433 / 0.5	-0.15380 to 0.183	-0.07006 to 0.07
HS	148.1	519.6	160.0	o	9.23 / 13.9	0.05338	0.004332	0.0548 / 1.06	0.376 / <0.001	-0.27370 to 0.38	0.00243 to 0.006

VA = visual assessment, + = good, o = acceptable, - = poor
SWARC = Scaled Weighted Area under Residue Curve
CI = confidence intervall

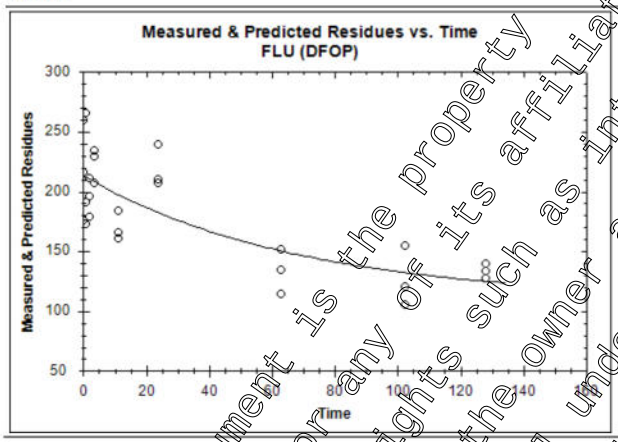
Modelling Endpoints: SFO fit is statistically good (χ^2err <15%, t-test < 0.05) and visually acceptable. SWARC value < 40 confirms SFO degradation. DFOP and HS fits do not result in better χ^2err. Consequently, **SFO** degradation model is appropriate for modelling endpoints.

SFO





DFOP



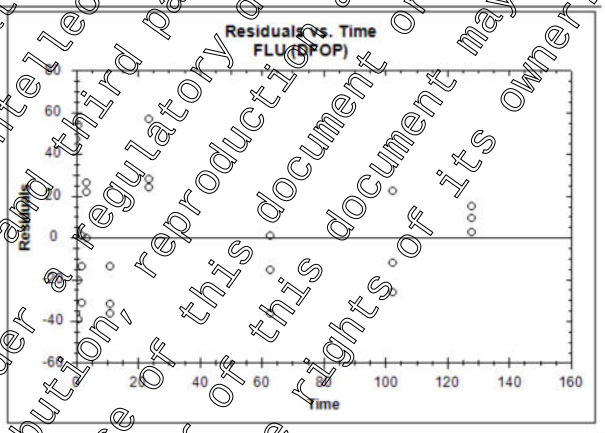


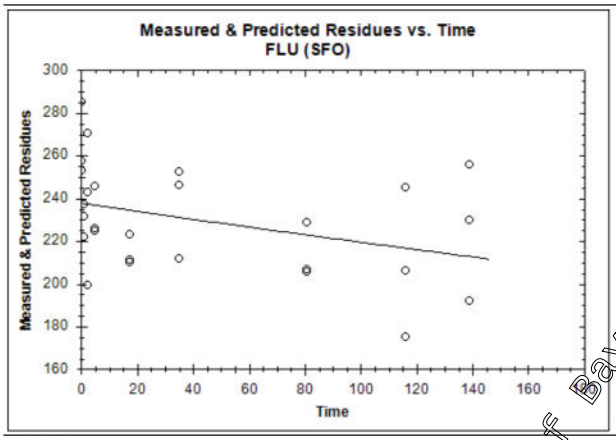
Table 7.1.2.2.1-73: Fluopyram: kinetic and statistical results of degradation in field soil Auchy les Mines, France

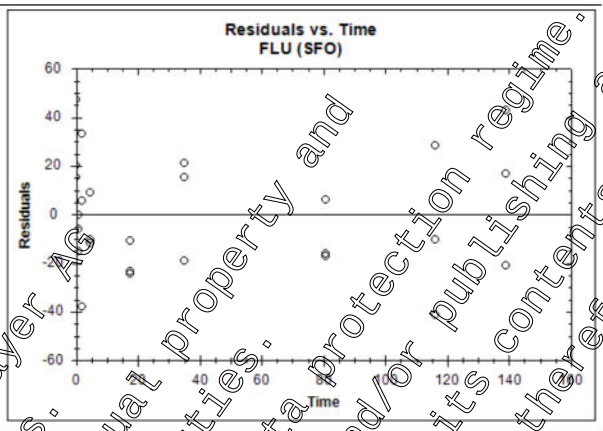
Kinetic model	DT_{50} actual	DT_{90} actual	DT_{50} slow phase	VA	χ^2 err / SWARC	k_1	k_2	g / t_b	t-test k_1 / k_2	95th CI of k_1	95th CI of k_2
	(d)	(d)	(d)		(%) / -	(1/d)	(1/d)	(- / d)	(-)	(1/d)	(1/d)
SFO	871.6	>1000	**871.6**	o	4.59 / 5.93	0.00079	-	- / -	0.030 / -	0 to 0.002	-
DFOP	1095	>1000	>1000	o	3.21 / 3.29	20180	0.00050 6	0.1302 / <0.001	<0.001 / 0.107	20180 to 20176	-0.00027 to 0.001
HS	>1000	>1000	>1000	o	2.92 / 3.22	0.05168	0.00037 5	0.1126 / 2.31	0.097 / 0.225	-0.02398 to 0.127	-0.00058 to 0.001

VA = visual assessment, + = good, o = acceptable, - = poor
SWARC = Scaled Weighted Area under Residue Curve
CI = confidence interval

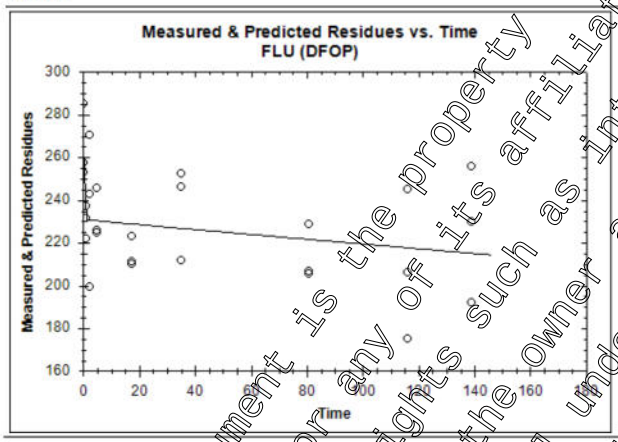
Modelling Endpoints: SFO fit is statistically (χ^2err <15%, t-test < 0.05) good and visually acceptable. SWARC value < 40 confirms SFO degradation. Consequently, **SFO** degradation model is appropriate for modelling endpoints.

SFO





DFOP



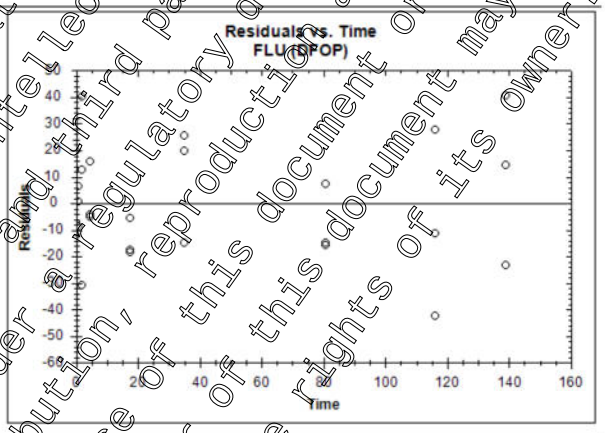


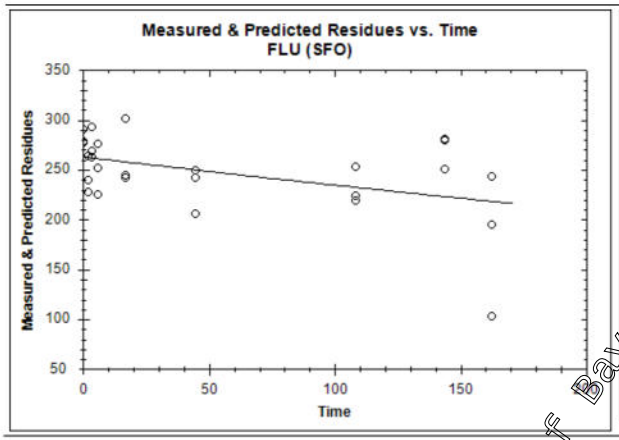
Table 7.1.2.2.1-74: Fluopyram: kinetic and statistical results of degradation in field soil Urbanowice, Poland

Kinetic model	DT_{50} actual	DT_{90} actual	DT_{50} slow phase	VA	χ^2 err / SWARC	k_1	k_2	g / t_b	t-test k_1 / k_2	95th CI of k_1	95th CI of k_2
	(d)	(d)	(d)		(% / -)	(1/d)	(1/d)	(- / d)	(-)	(1/d)	(1/d)
SFO	605.3	>1000	**605.3**	o	7.60 / 4.86	0.00114	-	- / -	0.012 / -	0.00021 to 0.002	-
DFOP	605.3	>1000	605.4	o	8.57 / 4.86	0.00114 5	0.00114 5	1.0000 / 1816	0.004 / <0.001	0.00038 to 0.002	0.00115 to 0.001
HS	608.0	>1000	697.3	o	8.16 / 7.33	0.07076	0.00099 4	0.0861 / 1.27	0.018 / 0.032	0.00840 to 0.133	-0.00001 to 0.002

VA = visual assessment, + = good, o = acceptable, - = poor
SWARC = Scaled Weighted Area under Residue Curve
CI = confidence interval

Modelling Endpoints: SFO fit is statistically (χ^2err <15%, t-test < 0.05) good and visually acceptable. SWARC value < 40 confirms SFO degradation. Consequently, **SFO** degradation model is appropriate for modelling endpoints.

SFO



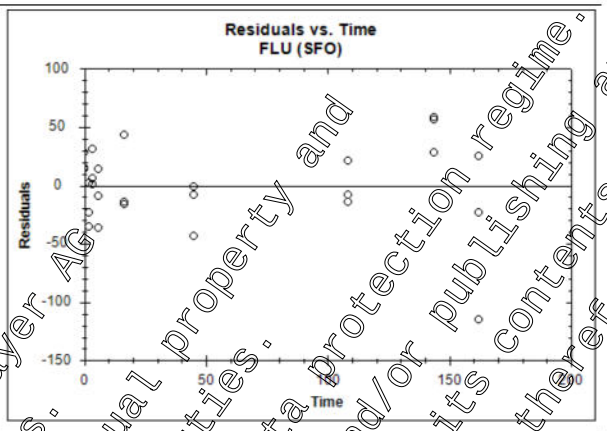


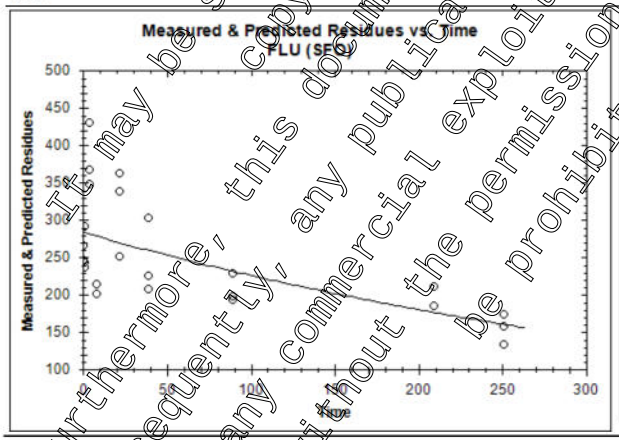
Table 7.1.2.2.1-75: Fluopyram: kinetic and statistical results of degradation in field soil Charles River Farm, Lleida, Spain

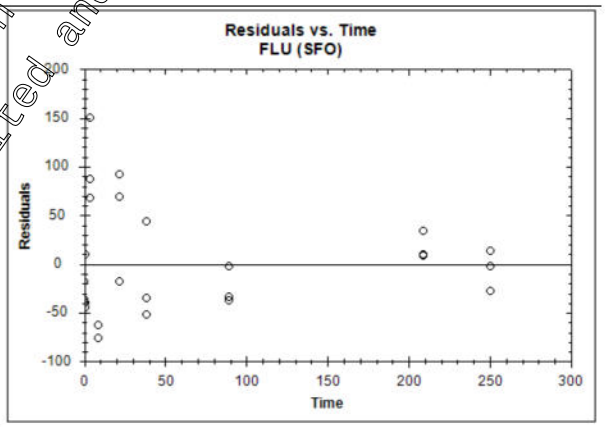
Kinetic model	DT_{50} actual	DT_{90} actual	DT_{50} slow phase	VA	χ^2err / SWARC	k_1	k_2	g / t_b	t-test k_1 / k_2	95th CI of k_1	95th CI of k_2
	(d)	(d)	(d)		(% / -)	(1/d)	(1/d)	(- / d)	(-)	(1/d)	(1/d)
SFO	306.2	1017	**306.2**	o	15.2 / 4.16	0.00226 3	-	- / -	0.001	0.00102 to 0.004	-
DFOP	356.7	>1000	892.7	o	17.1 / 3.06	0.00658 9	0.00077 707	0.3894 / 316	0.451 / 0.494	-0.26410 to 0.277	-0.09241 to 0.094
HS	301.7	954.1	2819	o	17.1 / 5.17	0.00173 5	0.00246 7	- / 21.9	0.495 / 0.009	-0.02298 to 0.023	0.00057 to 0.004

VA = visual assessment, + = good, o = acceptable, - = poor
SWARC = Scaled Weighted Area under Residue Curve
CI = confidence interval

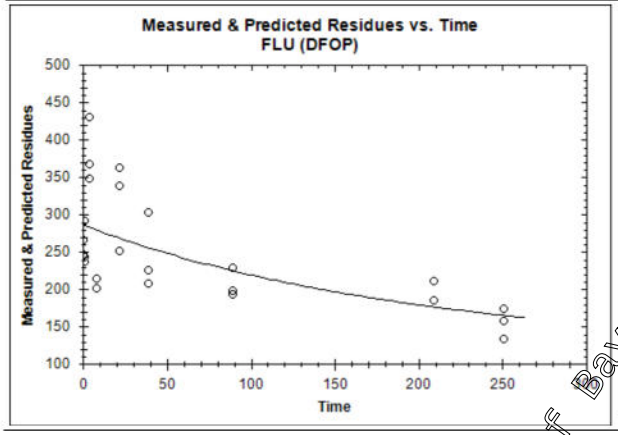
Modelling Endpoints: SFO fit is statistically (χ^2err ~15%, t-test < 0.05) and visually acceptable. SWARC value < 40 confirms SFO degradation. Consequently, **SFO** degradation model is appropriate for modelling endpoints.

SFO





DFOP



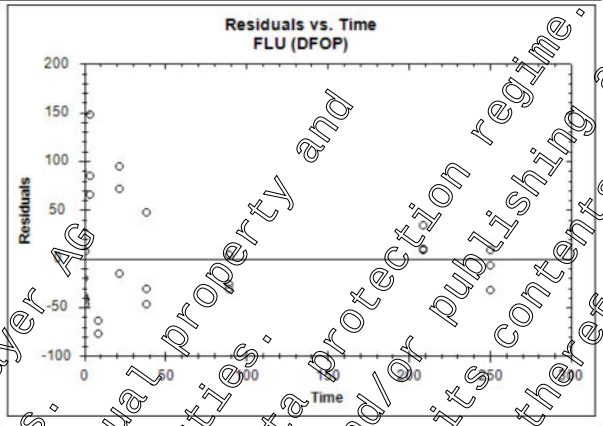


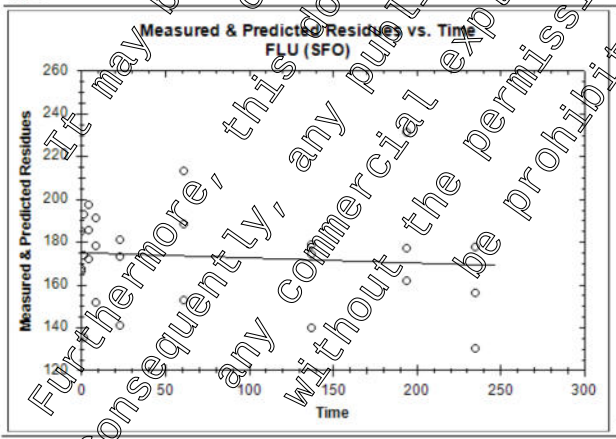
Table 7.1.2.2.1-76: Fluopyram: kinetic and statistical results of degradation in field soil Sindos, Greece

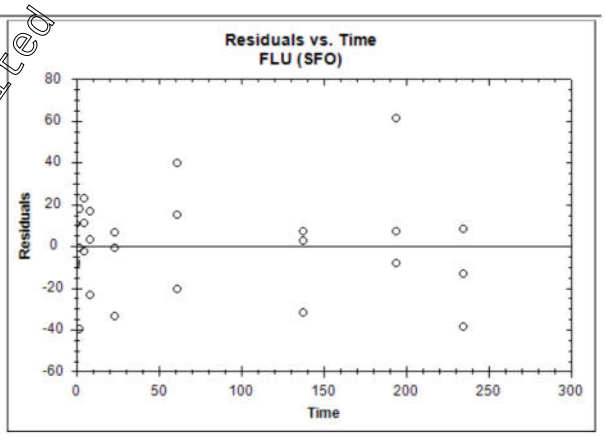
Kinetic model	DT_{50} actual	DT_{90} actual	DT_{50} slow phase	VA	χ^2err / SWARC	k_1	k_2	g / t_b	t-test k_1 / k_2	95th CI of k_1	95th CI of k_2
	(d)	(d)	(d)		(% / -)	(1/d)	(1/d)	(- / d)	(-)	(1/d)	(1/d)
SFO	>1000	>1000	**1000**	o	4.99 / 0.737	0.00069 1	-	- / -	0.324	-0.00046 to 0.001	-
DFOP	>1000	>1000	1000	o	5.63 / 0.737	0.00014 1	<0.0001	1.0 / 0.737	0.284 / <0.001	-0.00034 to 0.001	2.2 E-14 to <0.0005
HS	>1000	>1000	1000	o	5.63 / 0.737	0.01961	0.00014 1	- / 3.1 E-14	<0.001 / 0.336	0.01961 to 0.02	-0.00050 to 0.001

VA = visual assessment, + = good, o = acceptable, - = poor
SWARC = Scaled Weighted Area under Residue Curve
CI = confidence intervall

Modelling Endpoints: SFO fit is visually acceptable, χ^2err is acceptable, but t-test failed. SWARC value is < 40, not indicating a biphasic decline. DFOP and HS fits were alternatively tested. No visual nor statistical improvement could be reached with biphasic models. Consequently, **SFO** model can be accepted for modelling endpoints, leading to a default DT_{50} of 1000 d anyway.

SFO





III. CONCLUSIONS

The normalised modelling endpoints of field dissipation studies of fluopyram based on residue data from European soils are summarised in the table below.

Table 7.1.2.2.1-77: Fluopyram: Field matrix degradation endpoints for modelling purpose; normalised to 20°C, 100% field capacity, Q_{10} = 2.58; European sites

Fluopyram	Field conditions							
Soil type (USDA) [2]	**Location**	**pH ($CaCl_2$) [2]**	**Depth (cm)**	**$DT_{50\ actual}$ (d)**	**$DT_{90\ actual}$ (d)**	**St. (χ^2) (%)**	**$DegT_{50\ matrix}$ (d) norm. [1]**	**Method of calculation**
Sandy clay loam	Little Oliver, UK	5.3	20	153.8	510.8	8.31	153.8	SFO
Loam	Auchy les Mines, N-France	7.3	20	871.6	>1000	4.59	871.6	SFO
Silt loam	Urbanowice, Poland	5.2	20	605.3	>1000	7.60	605.3	SFO
Clay	Charles River Farm, Lleida, ES	7.8	20	306.2	>1000	15.2	306.2	SFO
Loam	Sindos, GR	6.6	20	>1000	>1000	4.99	1000 (default)	SFO

[1] normalised using a Q10 of 2.58 and Walker equation coefficient of 0.7, values correspond with $DT_{50\ mod}$ of selected kinetic models

[2] analysed in topsoil (M-758583-01-1)

3. Assessment and conclusion

Assessment and conclusion by applicant:
The kinetic evaluation followed FOCUS Guidance on degradation kinetics (2006, 2014) and EFSA guidance on field dissipation studies (2014) and is considered to be valid and reliable.

Assessment and conclusion by RMS:
Outcome and conclusion of the study: RMS should indicate if they agree to the results and conclusions of the APPI.

A final kinetic evaluation will be conducted when the final report of study M-758583-01-1 is available and will be provided at the latest by end of February 2022.

1. Information on the study

Data Point:	KCA 7.1.2.2.1/18
Report Author:	[redacted]
Report Year:	2021
Report Title:	Fluopyram (FLU): Interim kinetic evaluation of a field dissipation study in Europe (Gut, 2021) according to FOCUS Kinetics and EFSA TFD guidance for modelling purpose using KinGUI 2.1
Report No:	EnSa-20-0800
Document No:	M-762154-01-1
Guideline(s) followed in study:	EFSA 2014
Deviations from current test guideline:	Current Guideline: EFSA 2014 none
Previous evaluation:	No, not previously submitted
GLP/Officially recognised testing facilities:	No, not conducted under GLP/Officially recognised testing facilities
Acceptability/Reliability:	Yes

2. Full summary of KCA 7.1.2.2.1/18

Executive Summary

Normalised $DegT_{50matrix}$ values of fluopyram (FLU) in soil were derived for modelling purposes using the software tool KinGUI 2.1. The identification of the appropriate kinetic model following the recommendations given by FOCUS Kinetics and EFSA guidance on field dissipation studies. The analysis is based on interim residue data of a terrestrial field dissipation study conducted on six European field sites (M-758589-01-1).

The degradation $DegT_{50\ matrix}$ values for fluopyram were between 83.91 and 453.9 days in the tested soils.

I. METHODS

A kinetic modelling analysis of terrestrial field dissipation residue data of fluopyram was conducted in order to derive kinetic parameters suitable for modelling purpose ($DegT_{50matrix}$, normalised to 20°C and 100% field capacity) using the software tool KinGUI 2.1. The identification of the appropriate kinetic model followed the recommendations given by FOCUS Kinetics (FOCUS, 2006, 2014a) and EFSA guidance on field dissipation studies (EFSA, 2014) based on a detailed statistical analysis including visual assessment, χ^2 statistic, significance t-test and correlation analysis, using correspondingly pre-processed residue data. Additionally, the Scaled Weighted Area under Residue Curve (SWARC) was used as a further indicator for the visual assessment and to choose the appropriate model.

The modelling analysis is based on residue data from a terrestrial field dissipation study conducted at six European field sites located in Hoefinghausen (Emstek, Germany), Hornton (Banbury, UK), Le Thour (N-France), Brannens (S-France), Balbiano (Italy), and Almayate East (Spain).

In the 6 experimental trials, the active substance has been applied to bare soil at 3 subplots per site at a nominal rate of 250 g FLU/ha in spring 2019. After application, 6 – 10 mm of sand was applied evenly to the treated plots, to exclude surface processes of the active compound, e.g. photo-degradation, volatilisation. The sand cover was in place at least until the sum of precipitation exceeded 10 mm, which was reached within 4 days after application for all sites. Therefore, the full dataset was used for evaluation (EFSA 2014). No cultivation activities were carried out throughout the study period.

Herbicides were applied to maintain bare soil conditions. Supplemental irrigation events were conducted.

Simulated (with PEARL) daily soil temperatures and moisture contents, based on local weather data, were used to normalise degradation parameters to reference conditions according to FOCUS groundwater assumptions (Arrhenius equation, Q10 = 2.58; Walker equation, pF2) (European Commission 2014; FOCUS 2014b). The residue data together with the transformed incubation times (transformed time approach, time step normalisation) were kinetically and statistically evaluated.

In laboratory degradation studies of fluopyram long-term sorption kinetics (TDS) was observed (e.g. Yuan and Kasel, 2020). Although this leads to biphasic decline in theory, this effect is typically, as in the case of fluopyram, rather weak and visually hardly distinguishable from SFO behaviour. For TFD studies, especially legacy studies, we therefore attribute bi-phasic behaviour rather to surface processes than to TDS. Consequently, to avoid double interpretation of a biphasic behaviour, the standard evaluation method (according box 3, EFSA, 2014) was followed here.

Concentrations of the metabolites of fluopyram were not analysed. Therefore, in the following kinetic evaluation only the degradation of the parent compound into a sink was considered.

II. RESULTS

Degradation of fluopyram

Results of the kinetic evaluation for modelling purpose based residue data from a terrestrial field dissipation study conducted in six European field sites are summarised in the tables below.

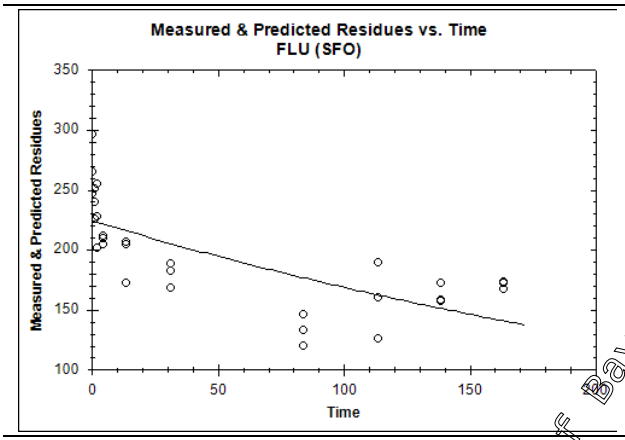
Table 7.1.2.2.1-78: Fluopyram: kinetic and statistical results of degradation in field soil Hoeltinghausen, Germany

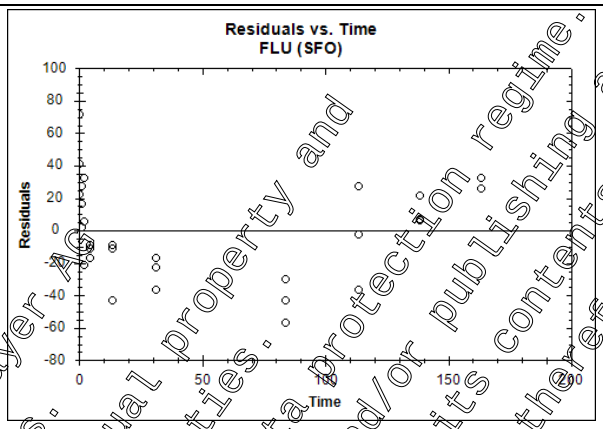
Kinetic model	DT_{50} actual	DT_{90} actual	DT_{50} slow phase	VA	χ^2 err / SWARC	k_1	k_2	g / t_b	t-test k_1 / k_2	95th CI of k_1	95th CI of k_2
	(d)	(d)	(d)		(% / -)	(1/d)	(1/d)	(- / d)	(-)	(1/d)	(1/d)
SFO	243.0	807	243.0	-	10.5 / 329	0.002852	-	- / -	<0.001	0.00179 to 0.004	-
DFOP	>1000	>1000	>1000	o	5.87 / 8.16	0.09065	2.3 E-14	0.3682 / 22.9	0.029 / 0.5	0.00096 to 0.18	-0.00192 to 0.002
HS	244.3	>1000	**453.9**	o	6.82 / 68.0	**0.08109**	**0.001527**	**0.2784 / 4.02**	0.016 / 0.002	0.01109 to 0.151	0.00056 to 0.002

VA = visual assessment, + = good, o = acceptable, - = poor
SWARC = Scaled Weighted Area under Residue Curve
CI = confidence intervall

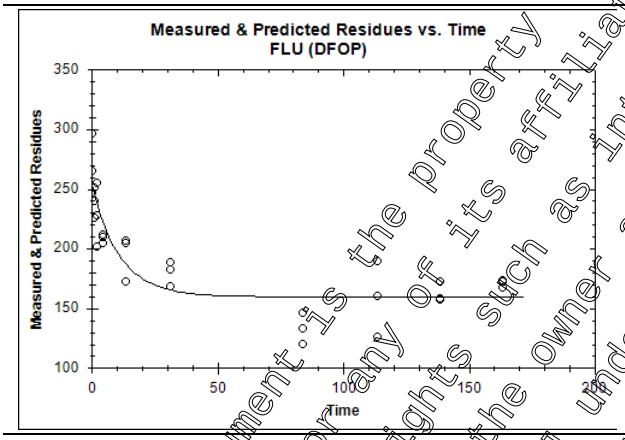
Modelling Endpoints: SFO fit is statistically (χ^2err, t-test) acceptable, but visually poor. SWARC value > 40 indicates that decline might be biphasic. Therefore, DFOP was tested, providing a visually acceptable fit and meeting the criteria of g > 0.75. However, $k_{1\ fast}$ and $k_{2\ slow}$ are not significantly different (95th confidence intervals overlap) and t-test for $k_{2\ slow}$ failed. Thus, reliability of the DFOP degradation rates is questionable. Hence, HS was tested. The HS fit is statistically (χ^2err, t-test) and visually acceptable. Thus, **HS** model is appropriate for modelling endpoints, using either conservatively the slow phase (k_2, $DT_{50\ slow}$) or the full HS parameter set (k_1, k_2, t_b, or equivalent recalculated **g 0.2784, or $DT_{50\ fast}$ 8.548 d, $DT_{50\ slow}$ 453.9 d**), as surface processes are already excluded by sand cover.

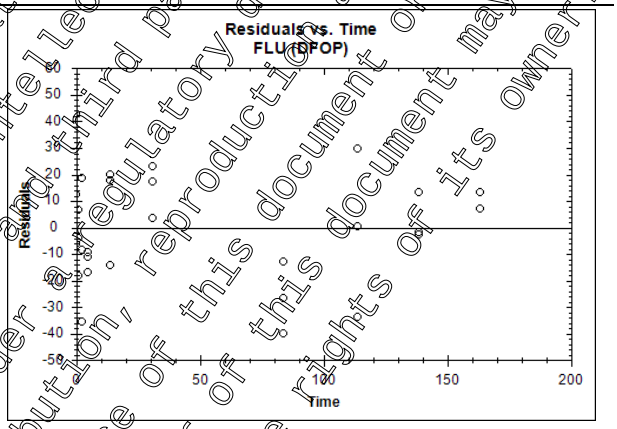
SFO



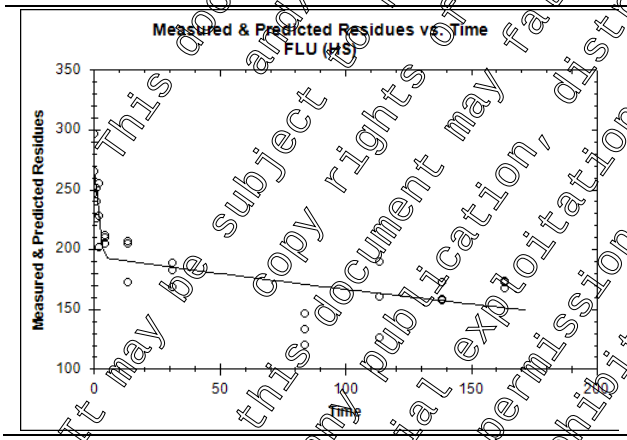


DFOP





HS



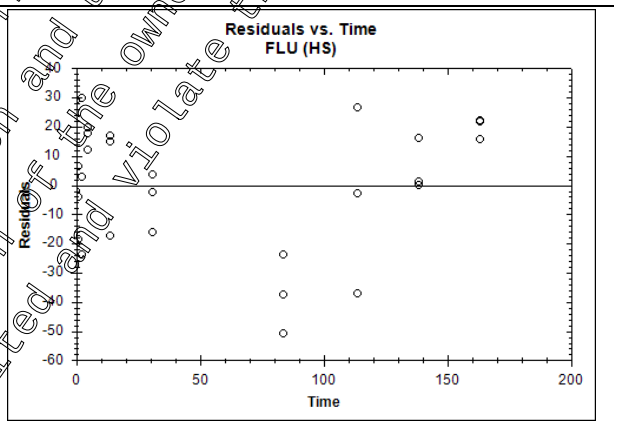


Table 7.1.2.2.1-79: Fluopyram: kinetic and statistical results of degradation in field soil Hornton, UK

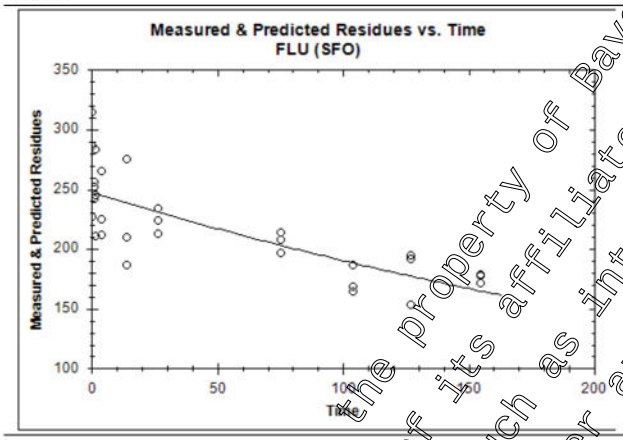
Kinetic model	DT_{50} actual	DT_{90} actual	DT_{50} slow phase	VA	χ^2 err / SWARC	k_1	k_2	g / t_b	t-test k_1 / k_2	95th CI of k_1	95th CI of k_2
	(d)	(d)	(d)		(% / -)	(1/d)	(1/d)	(- / d)	(-)	(1/d)	(1/d)
SFO	263.7	875.9	**263.7**	+	4.63 / 10.0	0.002629	-	- / -	<0.001	0.00177 to 0.003	-

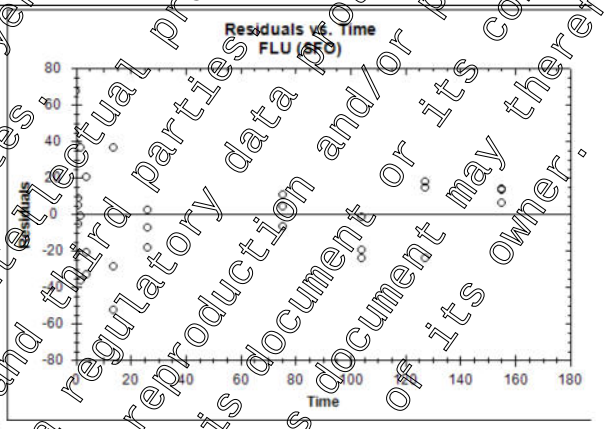
DFOP	255.9	1038	337.0	+	2.38 / 3.08	0.791156	0.002057	0.1534 / 2.63	0.139 / <0.001	-0.61013 to 2.192	0.00102 to 0.003
HS	257.9	1031	332.9	+	2.55 / 3.00	0.06969	0.002082	0.1487 / 2.31	0.069 / <0.001	-0.01961 to 0.159	0.00111 to 0.003

VA = visual assessment, + = good, o = acceptable, - = poor
SWARC = Scaled Weighted Area under Residue Curve
CI = confidence intervall

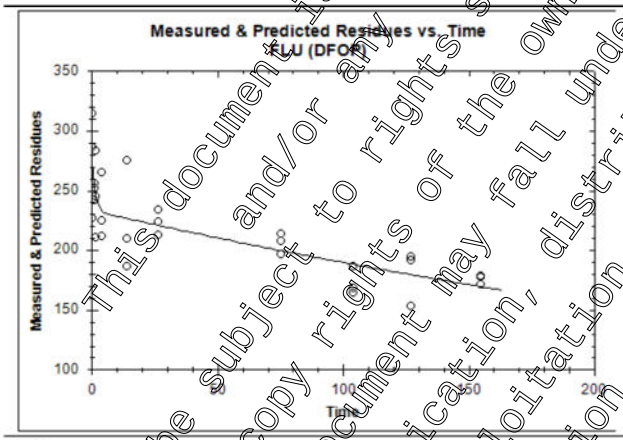
Modelling Endpoints: SFO fit is statistically (χ^2err, t-test) and visually good. SWARC value < 40 confirms SFO degradation. Consequently, **SFO** degradation model is appropriate for modelling endpoints.

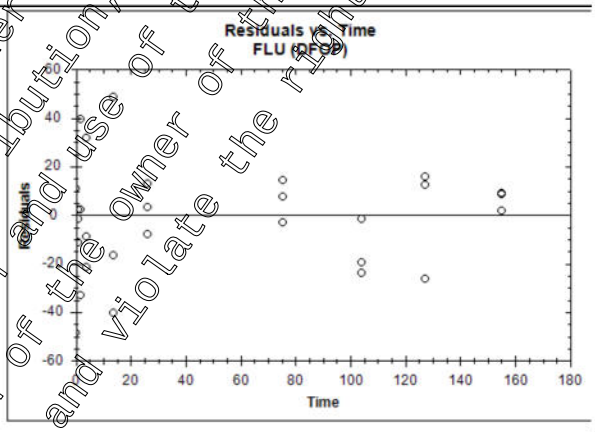
SFO



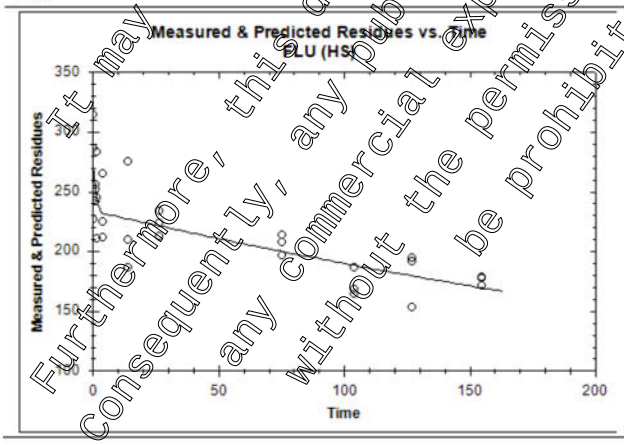


DFOP





HS



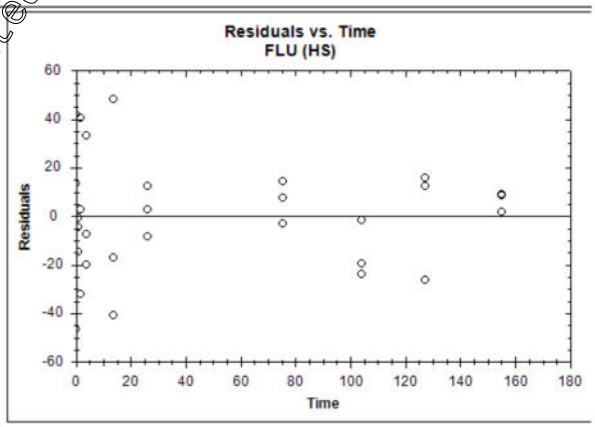


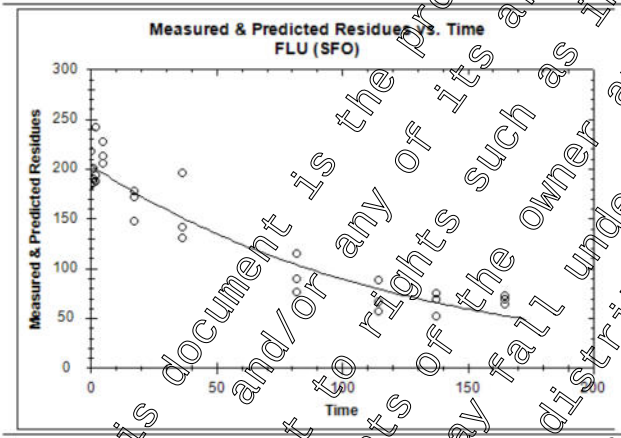
Table 7.1.2.2.1-80: Fluopyram: kinetic and statistical results of degradation in field soil Le Thour, France

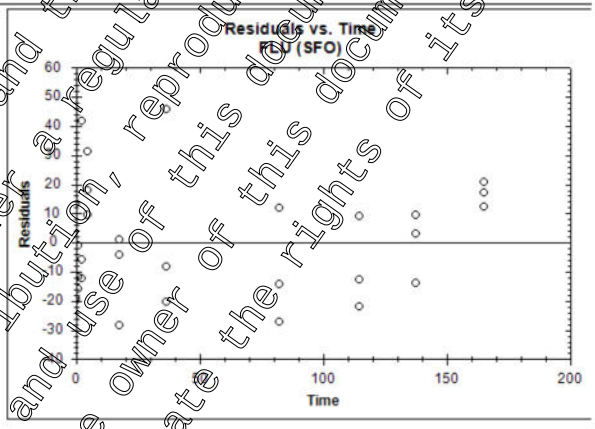
Kinetic model	DT_{50} actual	DT_{90} actual	DT_{50} slow phase	VA	χ^2 err / SWARC	k_1	k_2	g / t_b	t-test k_1 / k_2	95th CI of k_1	95th CI of k_2
	(d)	(d)	(d)		(% / -)	(1/d)	(1/d)	(- / d)	(-)	(1/d)	(1/d)
SFO	83.91	278.7	**83.91**	+	6.16 / 18.6	0.008261	-	- / -	<0.001	0.00969 to 0.01	-
DFOP	76.21	>1000	>1000	+	6.32 / 8.77	0.01251	2.3 E-14	0.8137 / 166	0.287 / 0.5	-0.03049 to 0.056	-0.07539 to 0.075
HS	86.35	275.7	81.55	+	6.45 / 13.5	3.95 E-14	0.0085	- / 4.80	0.5 / <0.001	-0.05363 to 0.054	0.00662 to 0.01

VA = visual assessment, + = good, o = acceptable, - = poor
SWARC = Scaled Weighted Area under Residue Curve
CI = confidence intervall

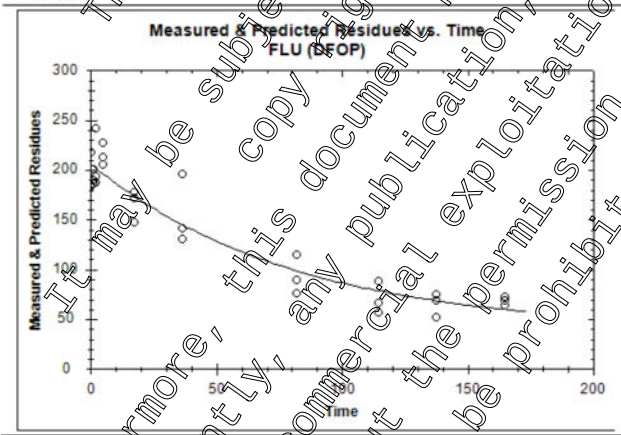
Modelling Endpoints: SFO fit is statistically (χ^2err, t-test) and visually good. SWARC value < 40 confirms SFO degradation. Consequently, **SFO** degradation model is appropriate for modelling endpoints.

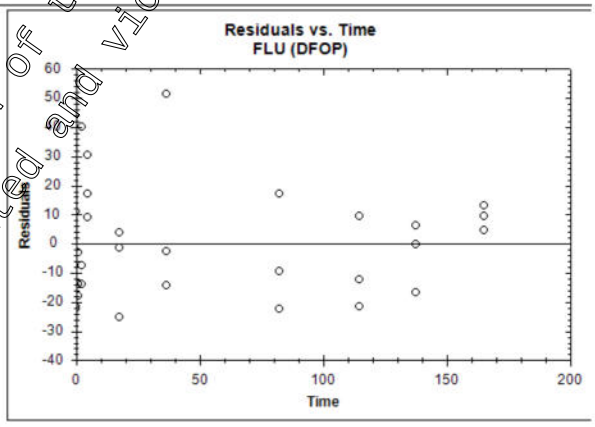
SFO



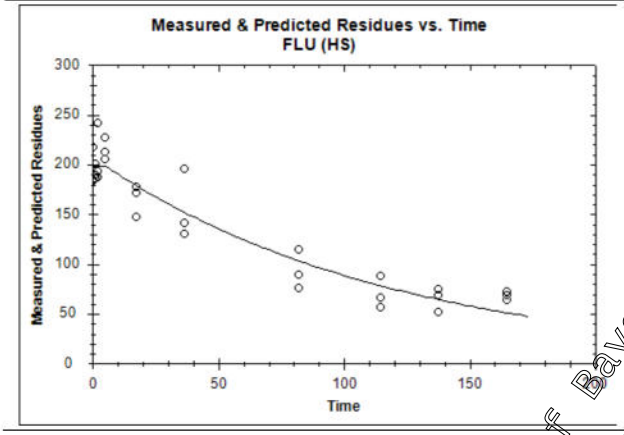


DFOP





HS



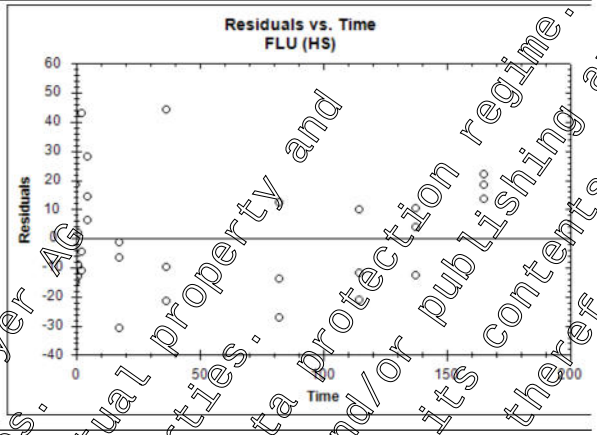


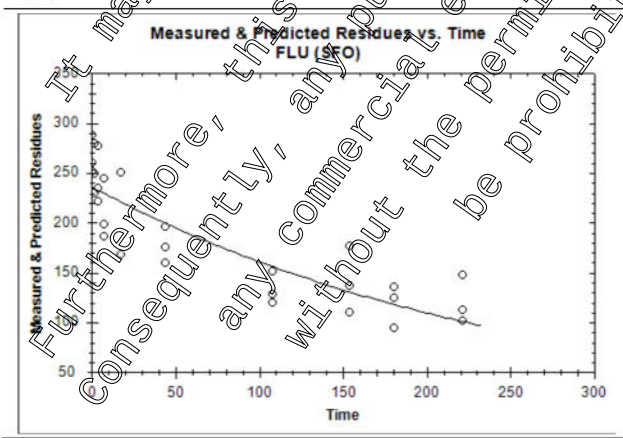
Table 7.1.2.2.1-81: Fluopyram: kinetic and statistical results of degradation in field soil Brannens, France

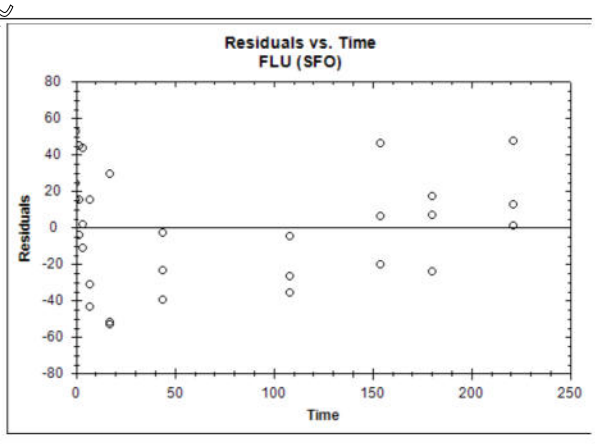
Kinetic model	DT_{50} actual	DT_{90} actual	DT_{50} slow phase	VA	χ^2err / SWARC	k_1	k_2	g / t_b	t-test k_1 / k_2	95th CI of k_1	95th CI of k_2
	(d)	(d)	(d)		(% / -)	(1/d)	(1/d)	(- / d)	(-)	(1/d)	(1/d)
SFO	180.5	599.6	**180.5**	o	8.61 / 109	0.00384	-	- / -	<0.001	0.00284 to 0.005	-
DFOP	150.8	8544	302.9		3.55 / 0.94	0.01241	0.00228	0.2940 / 16.8	0.059 / 0.002	-0.02608 to 0.274	0.00086 to 0.004
HS	151.4	776.8	269.4	+	3.54 / 0.59	0.01205	0.00257 3	0.2812 / 10^{-5}	0.006 / <0.001	0.00908 to 0.055	0.00146 to 0.004

VA = visual assessment, + = good, o = acceptable, - = poor
SWARC = Scaled Weighted Area under Residue Curve
CI = confidence interval

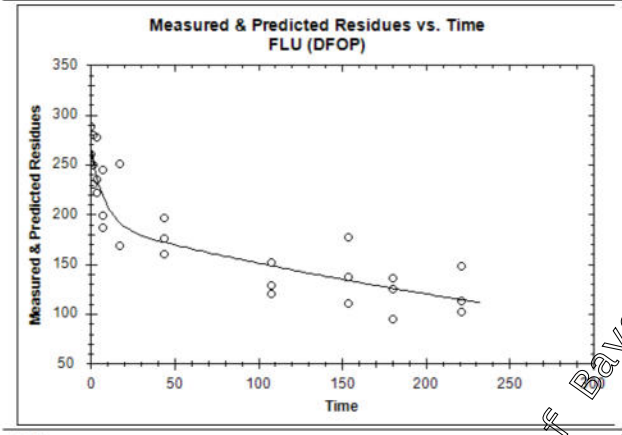
Modelling Endpoints: SFO fit is statistically goodness-err, t-test) and visually considered still acceptable, although SWARC is > 40. Biphasic fits have been tested and HS is statistically reliable. However, weight of evidence still supports SFO, and surface effects are already excluded in this TFD trial. Even more, the predicted mass remaining at time of HS DT_{90} using the SFO rate k is 5.1 % of HS M_0. If this mass is ≥ 5 %, a biphasic fit is considered not sufficiently better than SFO. SFO kinetic is prefered for modelling endpoints and describes the degradation sufficiently well. Consequently, **SFO** degradation model is appropriate for modelling endpoints.

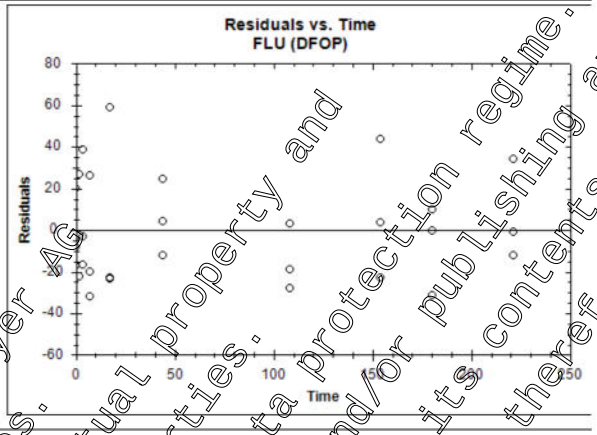
SFO



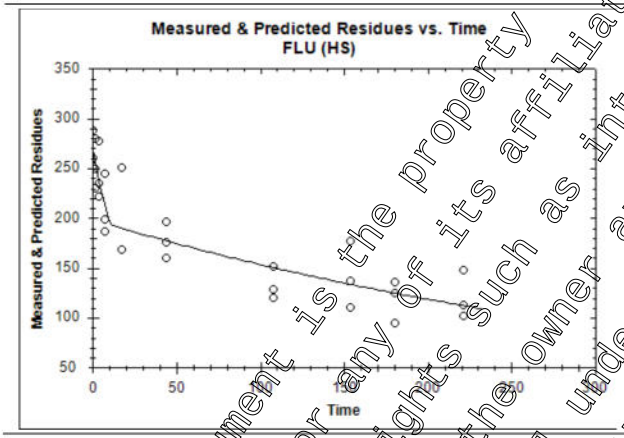


DFOP





HS



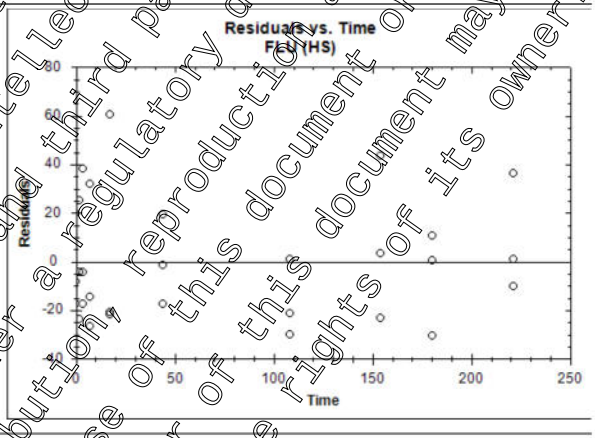


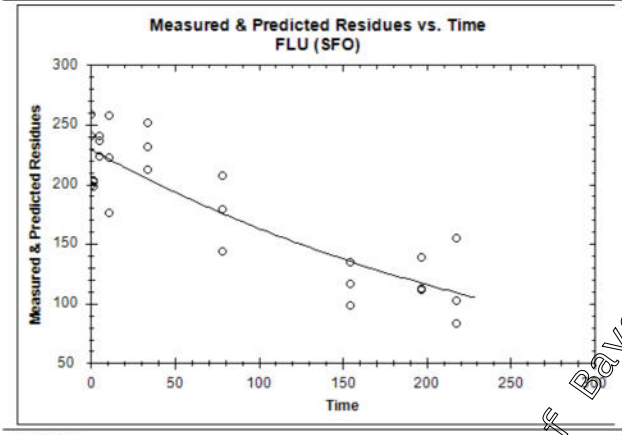
Table 7.1.2.2.1-82: Fluopyram: kinetic and statistical results of degradation in field soil Balbiano, Italy

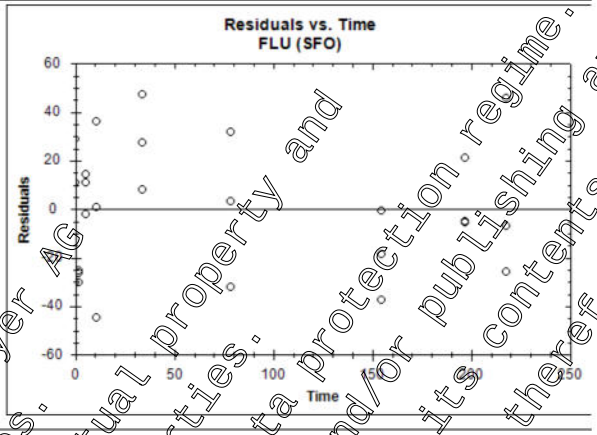
Kinetic model	DT_{50} actual	DT_{90} actual	DT_{50} slow phase	VA	χ^2 err / SWARC	k_1	k_2	g / t_b	t-test k_1 / k_2	95th CI of k_1	95th CI of k_2
	(d)	(d)	(d)		(%) / -	(1/d)	(1/d)	(- / d)	(-)	(1/d)	(1/d)
SFO	203.0	674.2	**203.0**	+	6.47 / 5.70	0.003415	-	- / -	<0.001	0.00256 to 0.004	-
DFOP	203.0	674.2	203.0 [1]	+	7.30 / 5.70	0.003415 [2]	2.2 E-14 [2]	1.00 / -	0.224 / 0.005	-0.00528 to 0.012	0.0 to 6.5 E-15
HS	199.4	674.8	204.7	+	4.27 / 5.83	0.239855	0.003386	0.0180 / 0.076	<0.001 / <0.001	0.14731 to 0.332	0.00246 to 0.004

VA = visual assessment, + = good, o = acceptable, - = poor
SWARC = Scaled Weighted Area under Residue Curve
CI = confidence interval
[1] = DT50 of fast phase, due to g = 1 is slow phase of no relevance.
[2] = fast and slow rate k1, k2 were exchanged here, compared to KinGui output, to deliver the correct g, which has to be related to the fast phase (g fast = 1 – g slow).

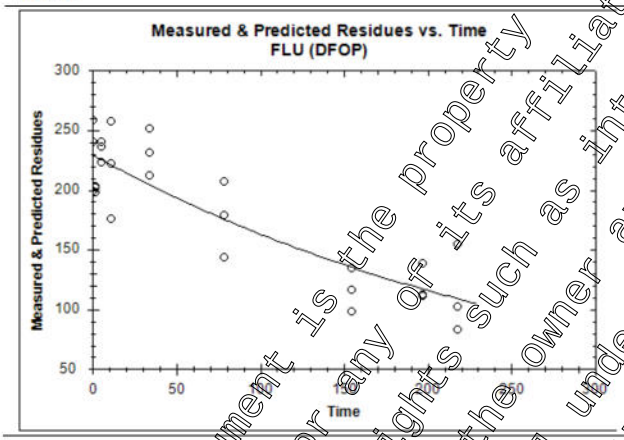
Modelling Endpoints: SFO fit is statistically (χ^2err, t-test) and visually good. SWARC value < 40 confirms SFO degradation. Consequently, **SFO** degradation model is appropriate for modelling endpoints.

SFO





DFOP



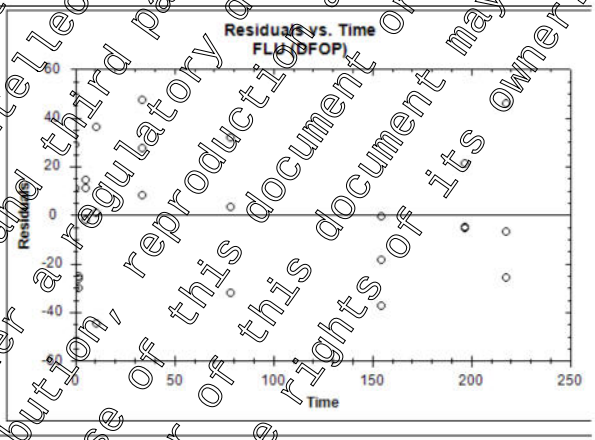


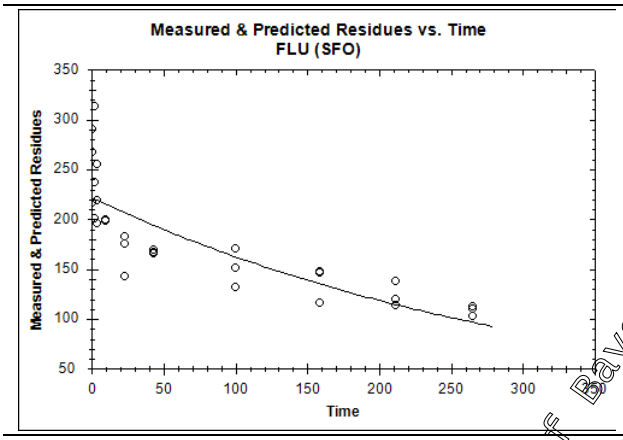
Table 7.1.2.2.1-83: Fluopyram: kinetic and statistical results of degradation in field soil Almayate East, Spain

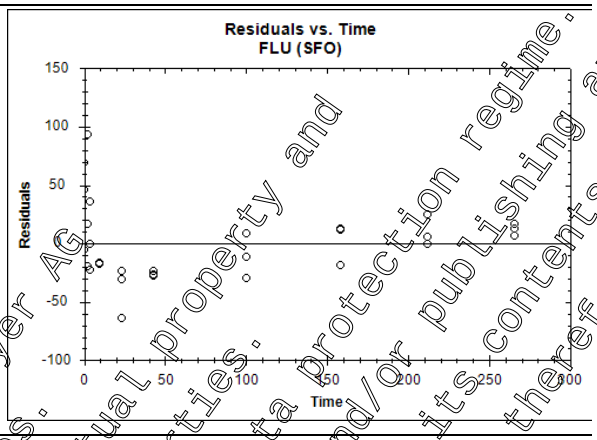
Kinetic model	DT_{50} actual	DT_{90} actual	DT_{50} (low phase)	VA	χ^2 err / SWARC	k_1	k_2	g / t_b	t-test k_1 / k_2	95th CI of k_1	95th CI of k_2
	(d)	(d)	(d)		(% / -)	(1/d)	(1/d)	(- / d)	(-)	(1/d)	(1/d)
SFO	221.9	735.3	**221.3**	o	10.2 / 56.8	0.00313	-	- / -	<0.001	0.00218 to 0.004	-
DFOP	173.1	>1000	405.6	+	2.11 / 6.67	0.01381	0.00170 9	0.3279 / 15.1	0.024 / 0.001	0.00715 to 0.269	0.00070 to 0.003
HS	181.7	>1000	395.9	+	4.85 / 5.42	0.03051	0.00175 1	0.3282 / 13.0	0.002 / <0.001	0.01220 to 0.049	0.00084 to 0.003

VA = visual assessment, + = good, o = acceptable, - = poor
SWARC = Scaled Weighted Area under Residue Curve
CI = confidence interval

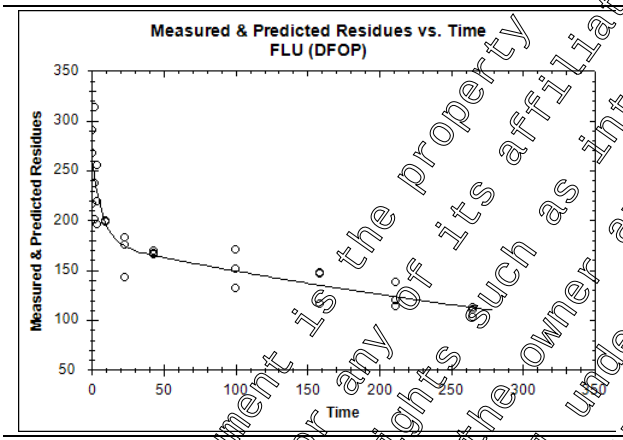
Modelling Endpoints: SFO fit is statistically good (χ^2err, t-test) and visually considered still acceptable, although SWARC is slightly > 40. Biphasic fits have been tested and are statistically reliable. However, weight of evidence still supports SFO, and surface effects are already excluded in this TFD trial. SFO kinetic is prefered for modelling endpoints and describes the degradation sufficiently well. Consequently, **SFO** degradation model is appropriate for modelling endpoints.

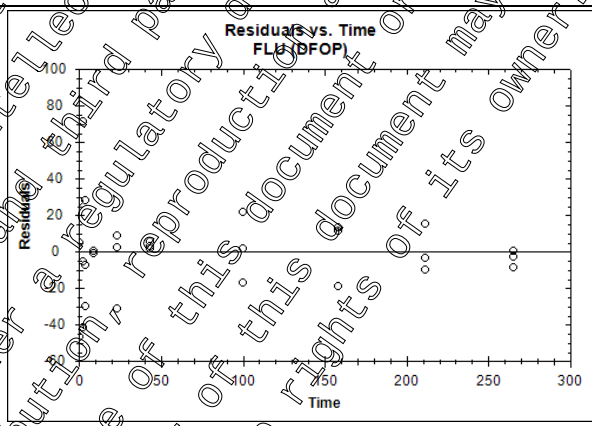
SFO



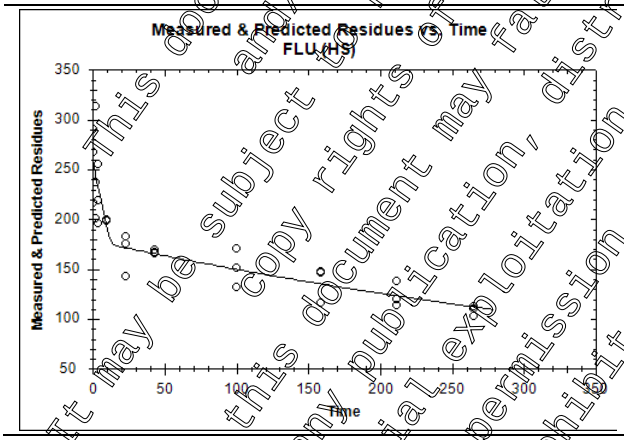


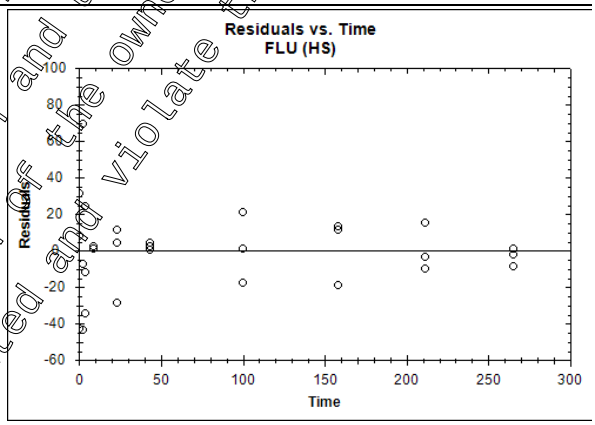
DFOP





HS





III. CONCLUSIONS

The field matrix degradation endpoints ($DegT_{50matrix}$) of fluopyram for modelling purpose based on residue data of European soils are summarised in the table below.

Table 7.1.2.2.1-84: Fluopyram: Field matrix degradation endpoints for modelling purpose; normalised to 20°C, 100% field capacity, Q_{10} = 2.58; European sites

Fluopyram	Aerobic conditions							
Soil type (USDA) [2]	**Location**	**pH ($CaCl_2$) [2]**	**Depth (cm)**	**DT_{50} actual (d)**	**DT_{90} actual (d)**	**St. (χ²) (%)**	**$DegT_{50}$ matrix (d) norm. [1]**	**Method of calculation**
Loamy fine sand	Hoeltinghausen, Emstek, Germany	5.56	20	244.3	>1000	6.82	$DT_{50\ fast}$ 8.548 d, $DT_{50\ slow}$ 433.9 d, tb 4.02 d = g 0.2784	HS
Silt loam	Hornton, Banbury, UK	6.11	20	263.7	876.9	4.63	263.7	SFO
Silt loam	Le Thour, N-France	7.50	20	83.91	278.7	6.16	83.91	SFO
Sandy loam	Brannens, S-France	4.44	30	180.5	599.6	8.61	180.5	SFO
Loam	Balbiano, Italy	7.20	40	203.0	674.2	6.47	203.0	SFO
Silt loam	Almayate East, Es	7.74	20	221.3	735.3	10.2	221.3	SFO

[1] normalised using a Q10 of 2.58 and Walker equation coefficient of 0.7, values correspond with DT_{50mod} of selected kinetic models
[2] analysed in topsoil, M-758589-01-0

3. Assessment and conclusion

Assessment and conclusion by applicant:
The kinetic evaluation followed FOCUS Guidance on degradation kinetics (2006, 2014) and EFSA guidance on field dissipation studies (2014) and is considered to be valid and reliable.

Assessment and conclusion by RMS:
Outcome and conclusion of the study - RMS should indicate if they agree to the results and conclusions of the APPL.

A final kinetic evaluation will be conducted when the final report of study M-758589-01-1 is available and will be provided at the latest by end of February 2022.

1. Information on the study

Data Point:	KCA 7.1.2.2.1/19
Report Author:	[redacted]
Report Year:	2020
Report Title:	Fluopyram (FLU): Kinetic evaluation of field dissipation studies in Europe (Heinemann and Telscher, 2007) according to FOCUS Kinetics for trigger purpose using KinGUI 2.1
Report No:	EnSa-20-0460
Document No:	M-761908-01-1
Guideline(s) followed in study:	not applicable
Deviations from current test guideline:	Current Guideline: not applicable (kinetic evaluation)
Previous evaluation:	No, not previously submitted
GLP/Officially recognised testing facilities:	No, not conducted under GLP/Officially recognised testing facilities
Acceptability/Reliability:	Yes

2. Full summary of KCA 7.1.2.2.1/19

Executive Summary

Non-normalised dissipation DT_{50} values of fluopyram (FLU) in soil under European field conditions were derived for trigger purpose, using the software tool KinGUI 2.1 following the recommendations given by FOCUS Kinetics. The trigger analysis is based on residue data from a terrestrial field dissipation study conducted at the field sites located in Höfchen, Burscheid (Germany), Little Shelford (United Kingdom), Staffanstorp (Sweden), Vatteville (France), Vilobi d'Onyar (Spain) and Albaro (Italy) (KCA 7.1.2.2.1/01, M-293999-01-1). The non-normalized $DisT_{50}$ values for fluopyram (trigger endpoints) were between 99.32 and 376.9 days in the tested soils.

I. METHODS

Non-normalised dissipation DT_{50} values of fluopyram (FLU) in soil under European field conditions were derived for trigger purpose, using the software tool KinGUI 2.1. The identification of the appropriate kinetic model followed the recommendations given by FOCUS Kinetics (FOCUS, 2006, 2014) based on a detailed statistical analysis including visual assessment, χ^2 statistic, significance t-test and correlation analysis, using correspondingly pre-processed residue data. Additionally, the Scaled Weighted Area under Residue Curve (SWARC) was used as a further indicator for the visual assessment and to choose the appropriate model.

The trigger analysis is based on residue data from a terrestrial field dissipation study conducted at the field sites located in Höfchen, Burscheid (Germany), Little Shelford (United Kingdom), Staffanstorp (Sweden), Vatteville (France), Vilobi d'Onyar (Spain) and Albaro (Italy) (KCA 7.1.2.2.1/01,M-293999-01-1).

In the 6 experimental trials, the active substance has been applied at a nominal rate of 250 g/ha fluopyram in spring/summer 2005. Grass was sown onto the plots before application except for trial Albaro (Italy) where grass was sown 10 days after application. In Vilobi d'Onyar (Spain), a herbicide other than fluopyram was applied and supplemental irrigation was conducted.

No metabolites of fluopyram were analysed throughout the study. It was assumed the parent directly degraded in the sink.

II. RESULTS

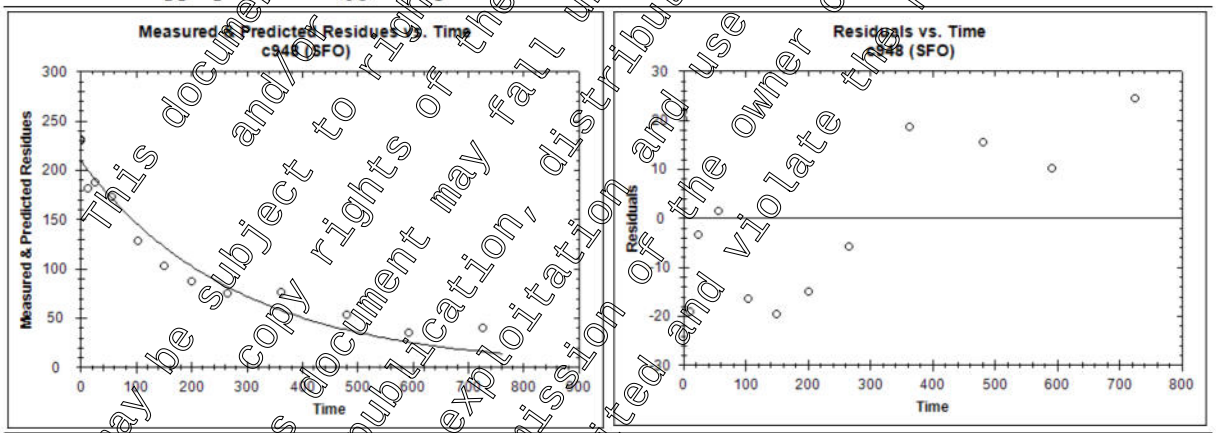
Dissipation of fluopyram

Table 7.1.2.2.1-85: Fluopyram: kinetic and statistical results of dissipation in soil Höfchen, Burscheid, Germany

Kinetic model	DT_{50} actual	DT_{90} actual	VA	χ^2err / SWARC	k_1 / α	k_2 / β	g / t_b	t-test k_1 / k_2	95th CI of k_1	95th CI of k_2
	(d)	(d)		(% / -)	(1/d / -)	(1/d / d)	(- / d)	(-)	(1/d)	(1/d)
SFO	194.2	645	-	11.3 / 156	0.00357	-	-/-	<0.001	0.00278 to 0.004	
DFOP	**137.5**	**1030**	+	7.43 / 4.65	0.01214	0.00157	0.4952 / 171	0.037 / 0.035	0.00034 to 0.024	0.00007 to 0.003
FOMC	138.6	>1000	+	7.14 / 5.42	0.90520	120.429	- / -	- / -	-	
HS	164.1	699	o	9.19 / 87.0	0.11070	0.00301	0.0853 / 1.85	<0.001 / <0.001	0.06118 to 0.160	0.00237 to 0.004

VA = visual assessment, + = good, o = acceptable, - = poor
SWARC = Scaled Weighted Area under Residue Curve
CI = confidence intervall

Trigger Endpoints: SFO fit is statistically (χ^2err, t-test) acceptable, but visually poor. DFOP, FOMC and HS fits were alternatively tested. For FOMC, DT_{90} is extrapolated far beyond study end and the fit therefore not suitable, especially for accumulation assessments. DFOP shows proper χ^2err and SWARC value in combination with a good visual fit and passed t-tests. Consequently, **DFOP** degradation model is appropriate for trigger endpoints.



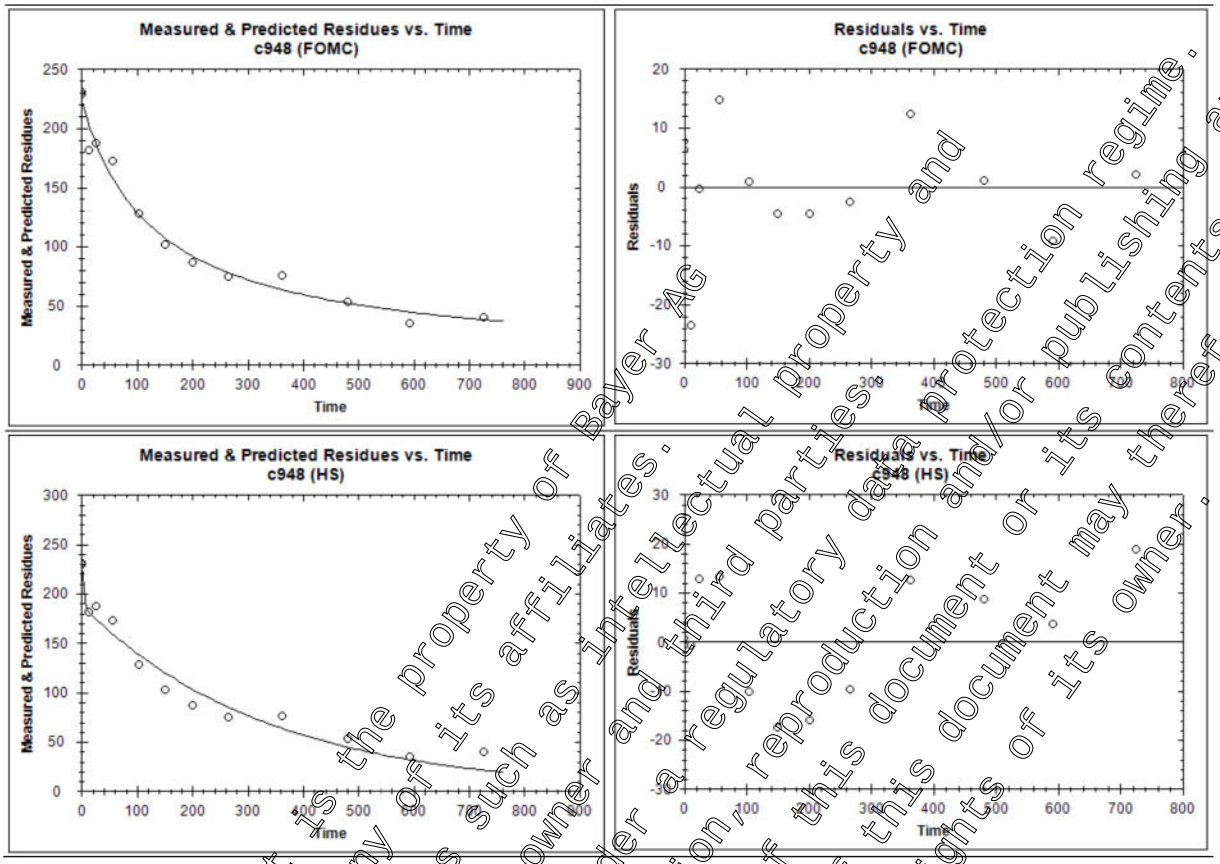
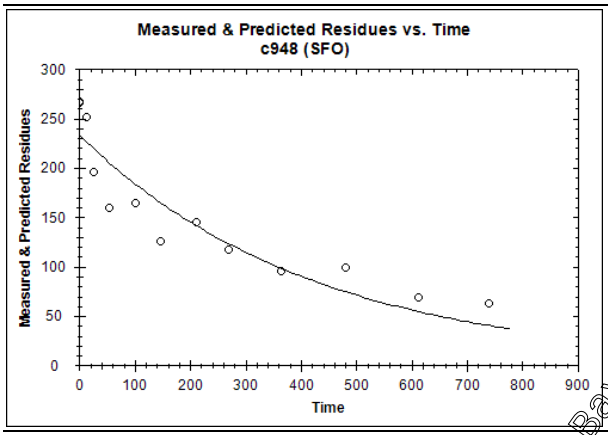


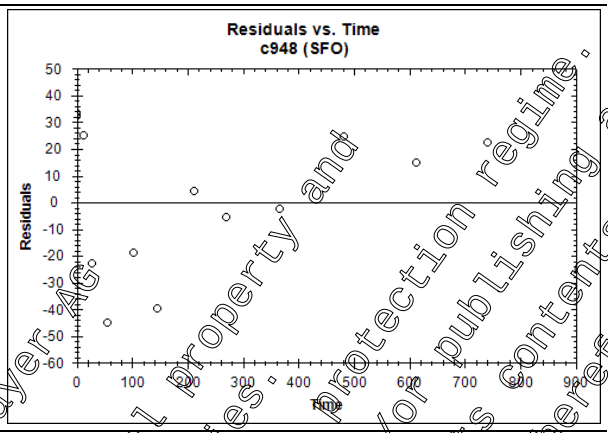
Table 7.1.2.2.1-86: Fluopyram: kinetic and statistical results of dissipation in soil Little Shelford, United Kingdom

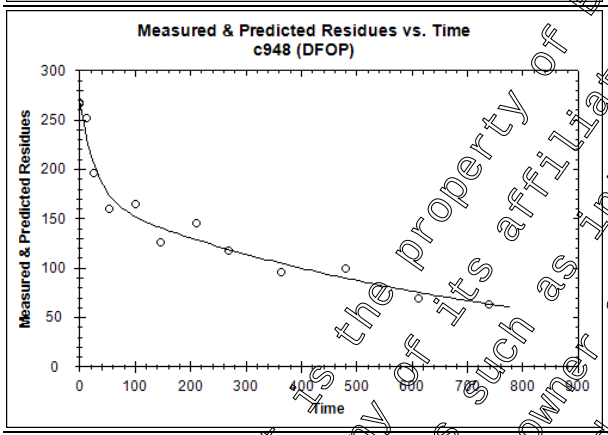
Kinetic model	DT_{50} actual	DT_{90} actual	VA	χ^2err / SWARC	k_1 / α	k_2 / β	g / t_b	t-test k_1 / k_2	95th CI of k_1	95th CI of k_2
	(d)	(d)		(% / -)	(1/d / -)	(1/d / d)	(- / d)	(-)	(1/d)	(1/d)
SFO	291.7	969		13.4 / 92.7	0.00238		- / -	<0.001	0.00162 to 0.003	-
DFOP	**172.2**	**>1000**	+	6.87 / 2.40	0.03402	0.00134	0.3720 / 61.1	0.013 / <0.001	0.00903 to 0.059	0.00082 to 0.002
FOMC	151.3	>1000	o	8.05 / 6.25	0.3944	31.5522	- / -	- / -	-	-
HS	232.1	1069	o	12.0 / 27.9	0.09756	0.00192	0.2226 / 2.58	0.002 / <0.001	0.04911 to 0.146	0.00128 to 0.003

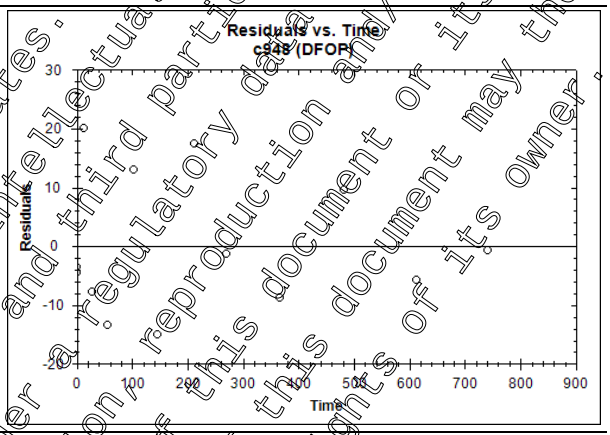
VA = visual assessment, + = good, o = acceptable, - = poor
SWARC = Scaled Weighted Area under Residue Curve
CI = confidence intervall

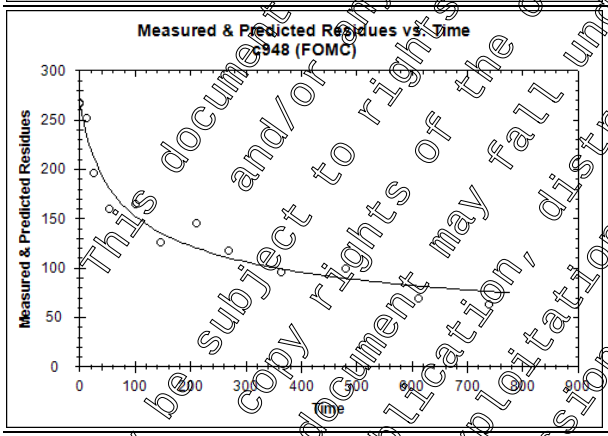
Trigger Endpoints: SFO fit is statistically (χ^2err, t-test) acceptable, but visually poor. DFOP, FOMC and HS fits were alternatively tested. For FOMC, DT_{90} is extrapolated far beyond study end and the fit therefore not suitable, especially for accumulation assessments. DFOP shows lowest χ^2err and SWARC value in combination with a good visual fit and passed t-tests. Consequently, **DFOP** degradation model is appropriate for trigger endpoints.

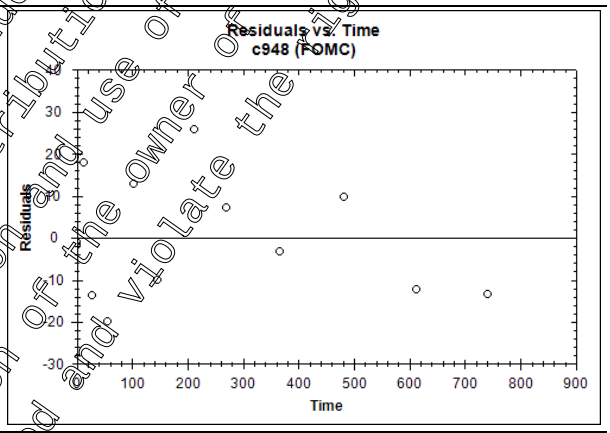


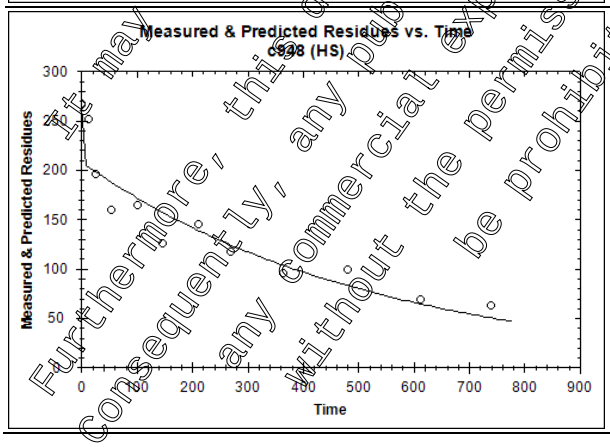












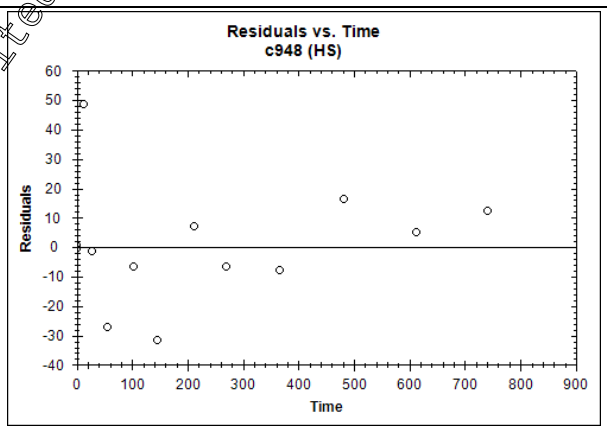
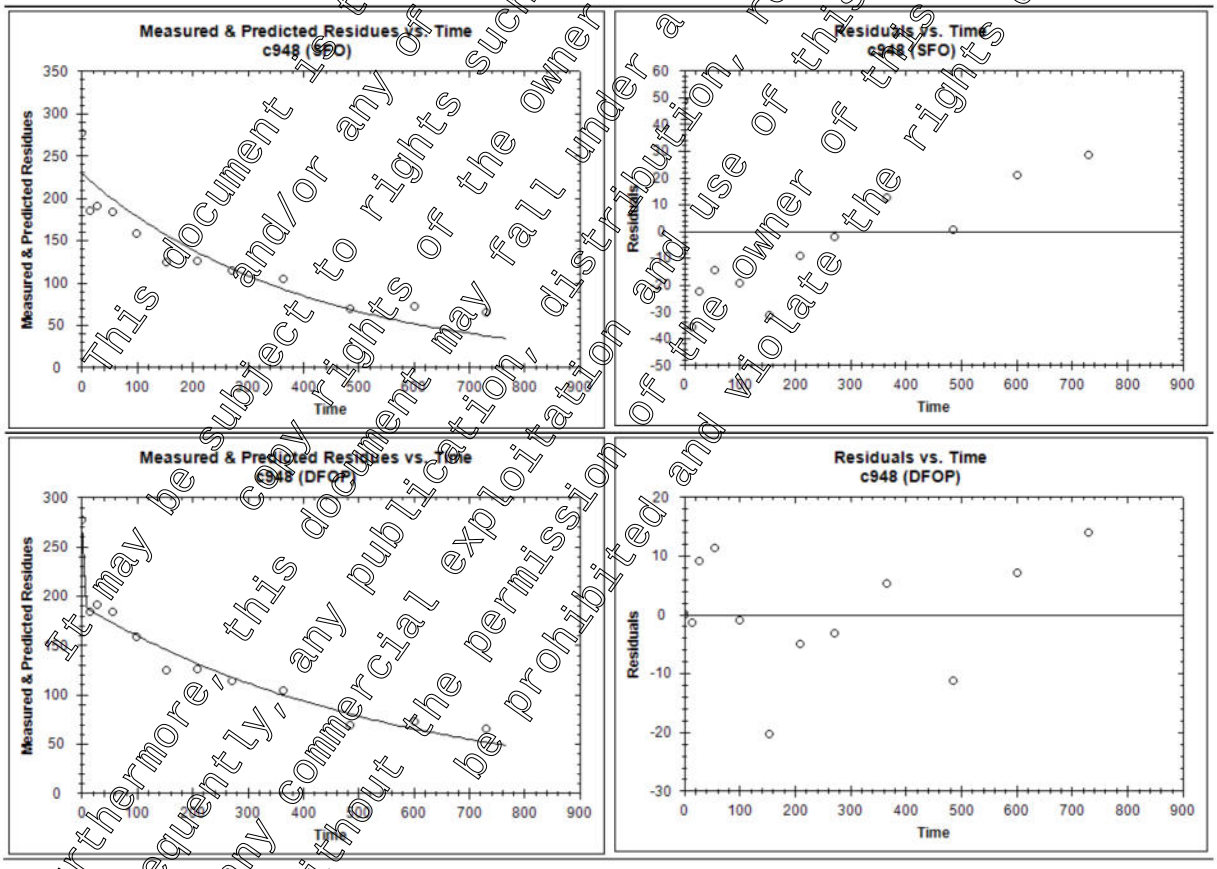


Table 7.1.2.2.1-87: Fluopyram: kinetic and statistical results of dissipation in soil Staffanstorp, Sweden

Kinetic model	DT_{50} actual	DT_{90} actual	VA	χ^2err / SWARC	k_1 / α	k_2 / β	g / t_b	t-test k_1 / k_2	95th CI of k_1	95th CI of k_2
	(d)	(d)		(% / -)	(1/d / -)	(1/d / d)	(- / d)	(-)	(1/d)	(1/d)
SFO	278.0	923.5	-	14.3 / 217	0.00249	-	- / -	<0.001	0.00165 to 0.003	-
DFOP	**178.7**	**1075**	+	5.96 / 15.6	1.5210	0.0018	0.3109 / 7.37	<0.001 / <0.001	1.52100 to 1.521	0.00148 to 0.002
FOMC	114.2	>1000	o	9.11 / 20.3	0.31895	14.6705	- / -	- / -	-	-
HS	178.7	1075	+	5.96 / 15.6	0.1256	0.0018	0.3146 / 7.01	<0.001 / <0.001	0.10436 to 0.147	0.00148 to 0.002

VA = visual assessment, + = good, o = acceptable, - = poor
SWARC = Scaled Weighted Area under Residue Curve
CI = confidence intervall

Trigger Endpoints: SFO fit is statistically (χ^2err and t-test) acceptable, but visually poor. DFOP, FOMC and HS fits were alternatively tested. For FOMC, DT_{90} is extrapolated far beyond study end and the fit therefore not suitable, especially for accumulation assessments. DFOP and HS fits are both statistically (χ^2err and t-test) and visually good. Finally, **DFOP** is considered best appropriate for trigger endpoints, as DFOP is a slighlty more widespread model than HS.



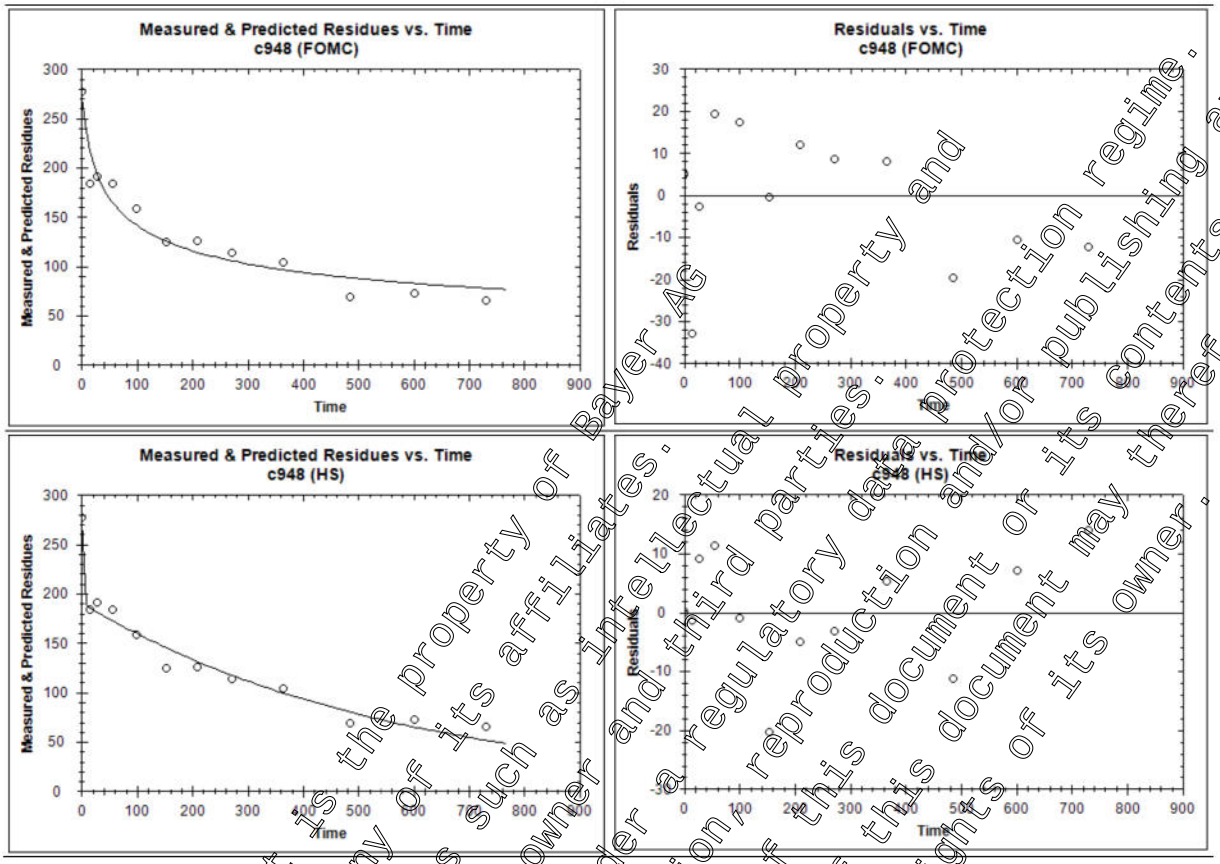
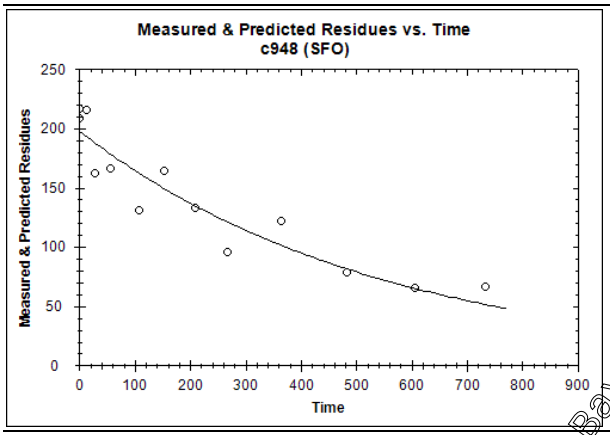


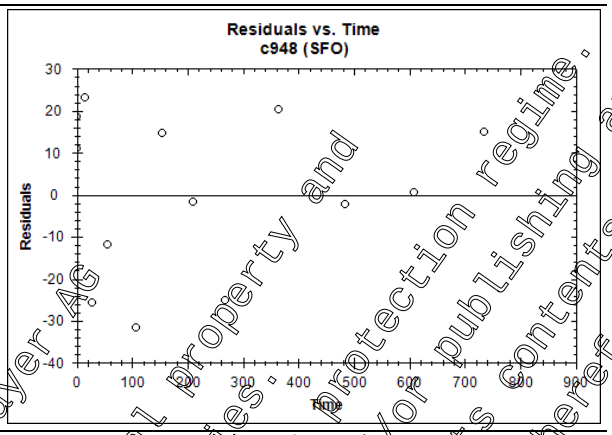
Table 7.1.2.2.1-88: Fluopyram: kinetic and statistical results of dissipation in soil Vatteville, France

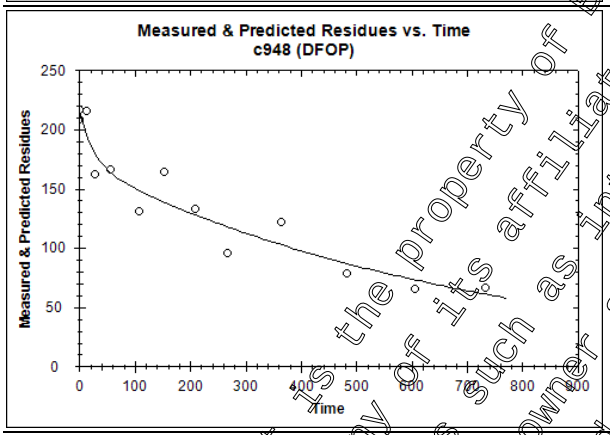
Kinetic model	DT_{50} actual	DT_{90} actual	VA	χ^2err / SWARC	k_1 / α	k_2 / β	g / t_b	t-test k_1 / k_2	95th CI of k_1	95th CI of k_2
	(d)	(d)		(% / -)	(1/d / -)	(1/d / d)	(- / d)	(-)	(1/d)	(1/d)
SFO	**376.9**	**>1000**	o	11.4 / 23.1	0.00184		-	<0.001	0.00133 to 0.002	-
DFOP	3285	>1000	o	9.93 / 4.51	0.03815	0.00141	0.2044 / 54.5	0.197 / 0.001	-0.04547 to 0.122	0.00073 to 0.002
FOMC	309.9	>1000	o	10.4 / 18.5	0.64880	162.186	- / -	- / -	-	-
HS	341.4	>1000	o	14.2 / 9.93	0.11220	0.00166	0.1206 / 1.15	0.030 / <0.001	0.00995 to 0.214	0.00111 to 0.002

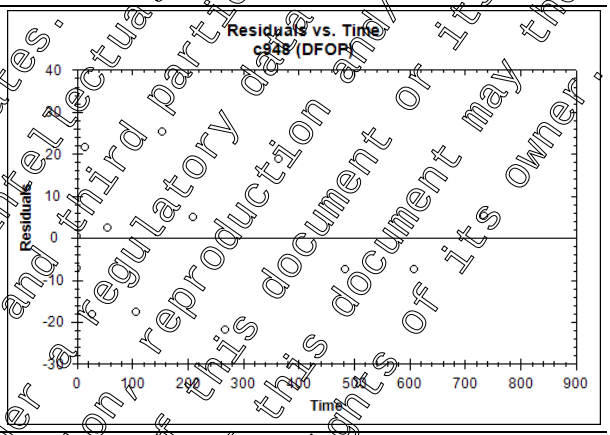
VA = visual assessment, + = good, o = acceptable, - = poor
SWARC = Scaled Weighted Area under Residue Curve
CI = confidence intervall

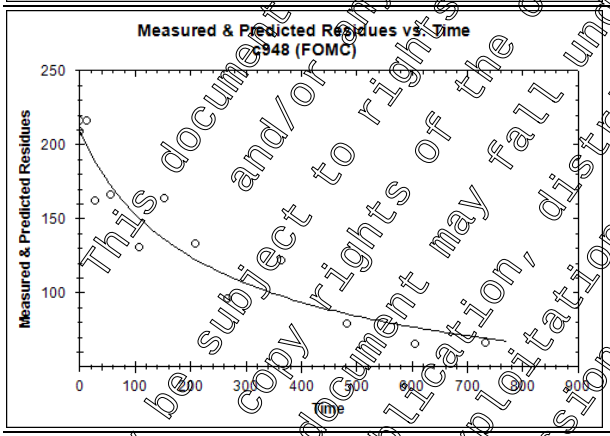
Trigger Endpoints: SFO fit is statistically (χ^2err, t-test) and visually acceptable. SWARC value is < 40, not indicating a biphasic decline. DFOP, FOMC and HS fits were alternatively tested.
For DFOP, t-test of k_{fast} failed in combination with a DT_{90} extrapolated far beyond study end. For FOMC, DT_{90} is also extrapolated far beyond study end. Both fits are therefore not suitable, especially for accumulation assessments. HS fit is acceptable, but not better than SFO. Consequently, **SFO** degradation model is appropriate for trigger endpoints.

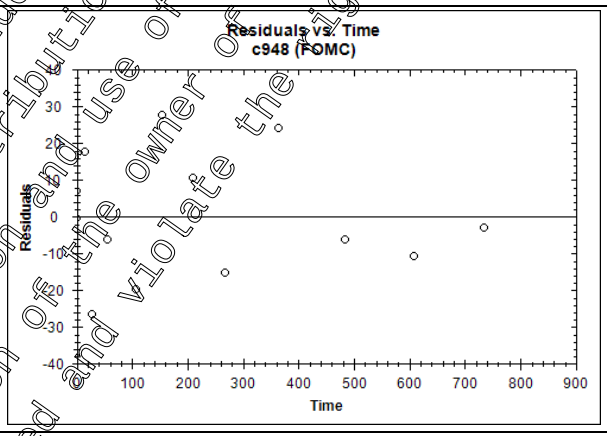


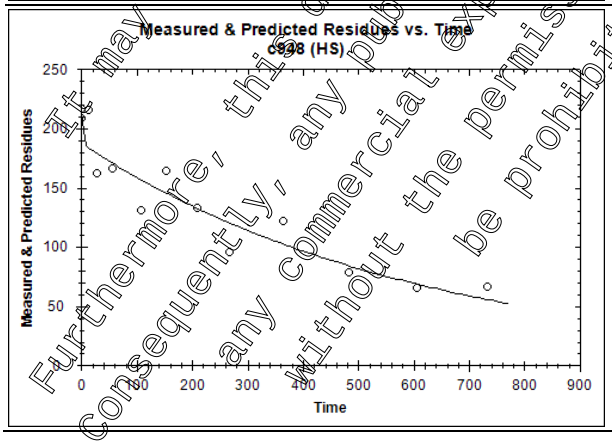












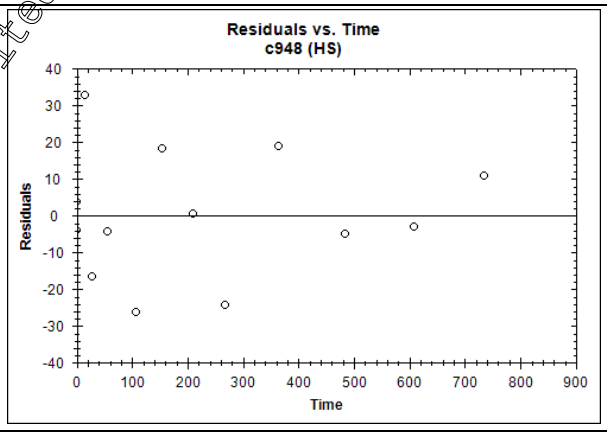
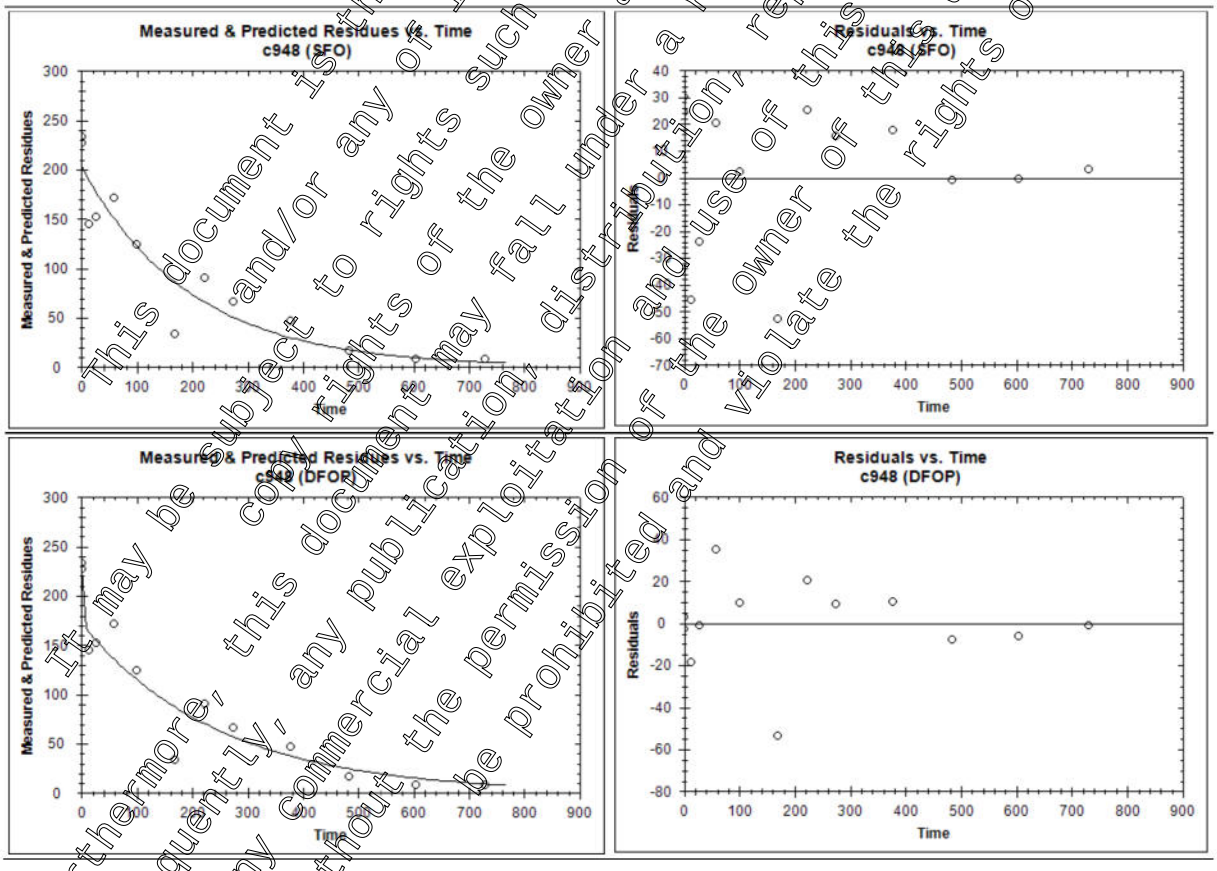


Table 7.1.2.2.1-89: Fluopyram: kinetic and statistical results of dissipation in soil Vilobi d'Onyar, Spain

Kinetic model	DT_{50} actual	DT_{90} actual	VA	χ^2err / SWARC	k_1 / α	k_2 / β	g / t_b	t-test k_1 / k_2	95th CI of k_1	95th CI of k_2
	(d)	(d)		(% / -)	(1/d / -)	(1/d / d)	(- / d)	(-)	(1/d)	(1/d)
SFO	136.1	452.3	o	22.6 / 15.6	0.00509	-	- / -	<0.001	0.00419 to 0.007	-
DFOP	99.32	498.4	o	20.2 / 17.3	101.40	0.00403	0.2567 / 0.021	NA / <0.001	NA	0.00235 to 0.006
FOMC	109.7	583.7	o	23.2 / 26.5	1.9289	253.738	- / -	- / -	-	-
HS	**99.32**	**498.4**	o	20.2 / 17.3	0.3602	0.00402	0.2567 / 0.821	0.003 / <0.001	0.15866 to 0.562	0.00235 to 0.006

VA = visual assessment, + = good, o = acceptable, - = poor
SWARC = Scaled Weighted Area under Residue Curve
CI = confidence intervall

Trigger Endpoints: SFO fit is statistically (χ^2err, t-test) and visually acceptable. SWARC value is < 40, not indicating a biphasic decline. DFOP, FOMC and HS fits were alternatively tested. For DFOP, t-test of k_{fast} failed. Although DFOP DT_{90} is not extrapolated beyond study end, the fit is statistically not reliable. FOMC has no better χ^2err than SFO. HS fit is statistically (χ^2err, t-test) and visually good. Consequently, **HS** model is appropriate for trigger endpoints.



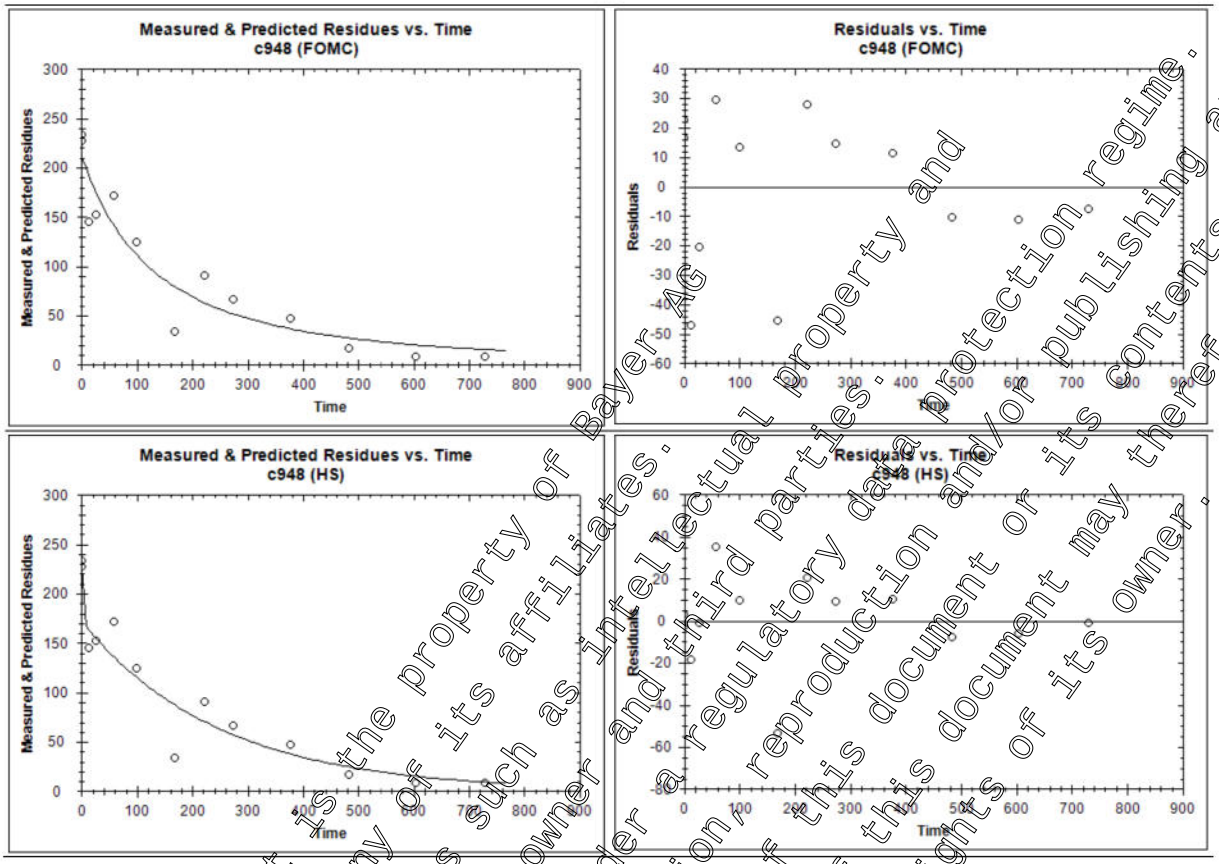
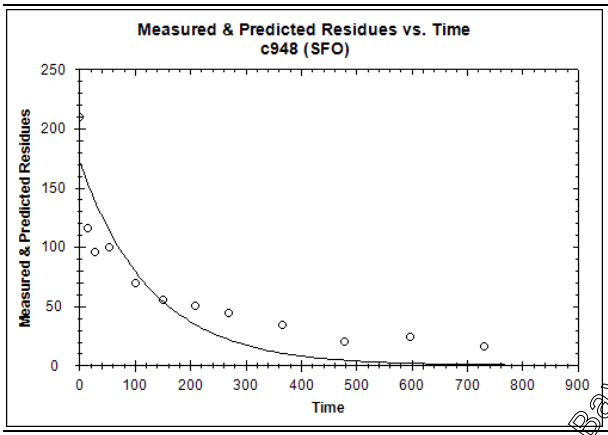


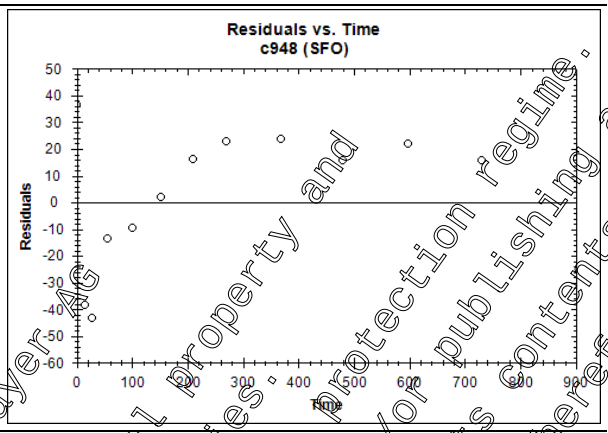
Table 7.1.2.2.1-90: Fluopyram: kinetic and statistical results of dissipation in soil Albaro, Italy

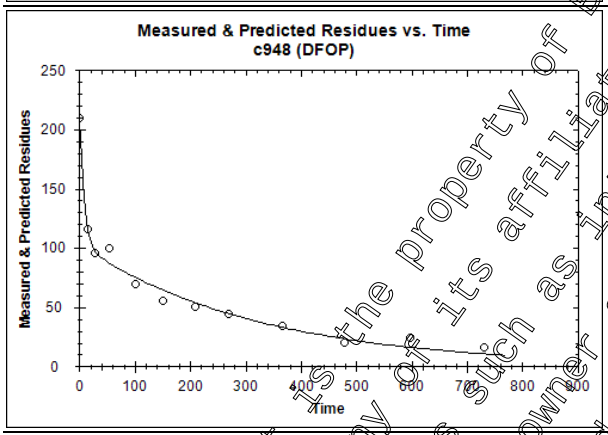
Kinetic model	DT_{50} actual	DT_{90} actual	VA	χ^2err / SWARC	k_1 / α	k_2 / β	g / t_b	t-test k_1 / k_2	95th CI of k_1	95th CI of k_2
	(d)	(d)		(% / -)	(1/d / -)	(1/d / d)	(- / d)	(-)	(1/d)	(1/d)
SFO	89.87	298.5	-	28.7 / 348	0.00771	-	- / -	<0.001	0.00399 to 0.011	-
DFOP	**20.89**	**511.3**	+	7.06 / 6.06	0.12190	0.00311	0.5090 / 17.1	0.002 / <0.001	0.05763 to 0.186	0.00244 to 0.004
FOMC	26.89	>1000	o	10.6 / 36.7	0.14537	7.18582	- / -	- / -	-	-
HS	17.86	480.3	+	8.39 / 7.98	0.19660	0.00348	0.4740 / 3.27	<0.001 / <0.001	0.16880 to 0.224	0.00278 to 0.004

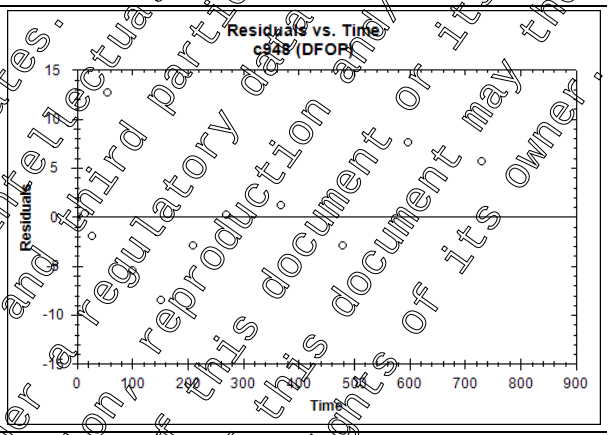
VA = visual assessment, + = good, o = acceptable, - = poor
SWARC = Scaled Weighted Area under Residue Curve
CI = confidence intervall

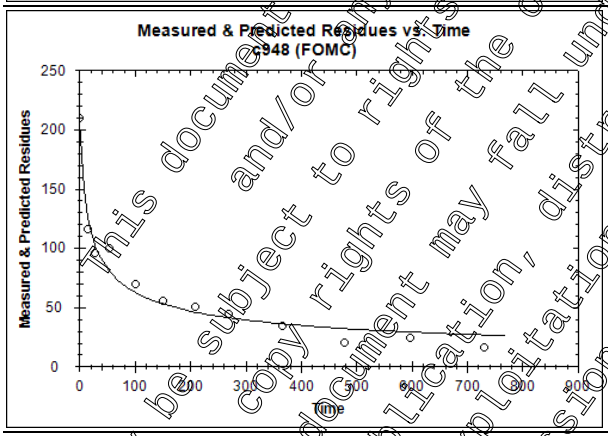
Trigger Endpoints: SFO fit is statistically (χ^2err) and visually poor. DFOP, FOMC and HS fits were alternatively tested. For FOMC, DT_{50} is extrapolated far beyond study end and the fit therefore not suitable, especially for accumulation assessments. DFOP shows lowest χ^2err and SWARC value in combination with a good visual fit and passed t-tests. Consequently, **DFOP** degradation model is appropriate for trigger endpoints.

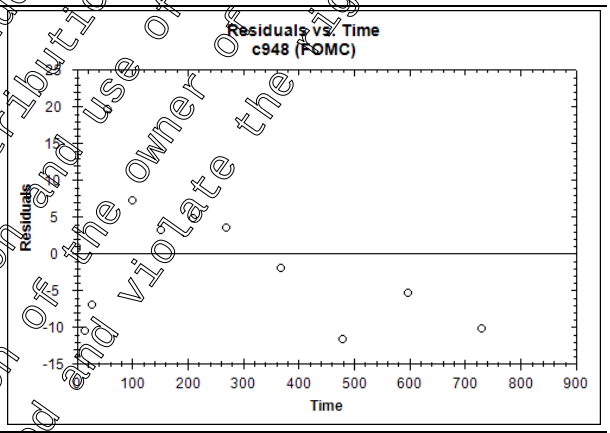


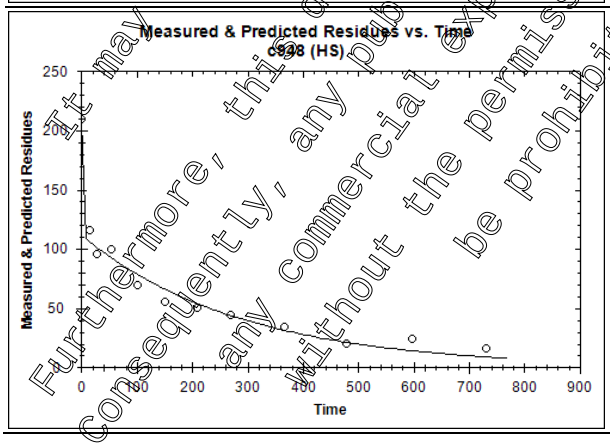


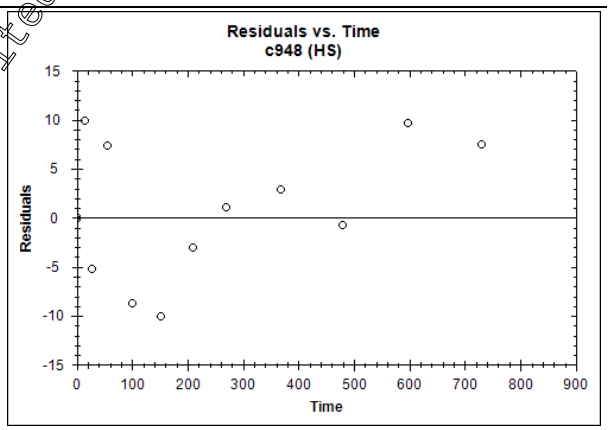












III. CONCLUSIONS

The non-normalised $DisT_{50}$ parameters of fluopyram based on residue data from a field dissipation study in Europe are summarised in the table below.

Table 7.1.2.2.1-91: Fluopyram: Field dissipation endpoints for trigger purpose

Fluopyram	**Field conditions**							
Soil type (USDA) [1], vegetation	**Location**	**pH ($CaCl_2$) [1]**	**Depth (cm)**	**$DisT_{50}$ actual (d)**	**$DisT_{90}$ actual (d)**	**St. (χ^2) (%)**	**$DegT_{50}$ matrix (d) norm. [2]**	**Method of calculation**
Silt loam, grass	Höfchen, Burscheid, D	6.2	20	137.5	1030	7.43	-	DFOP
Sandy loam, grass	Little Shelford, UK	7.3	20	172.2	>1000	6.87	-	DFOP
Loam, grass	Staffanstorp, Sweden	7.3	20	178.7	1075	5.96	-	DFOP
Silt loam, grass	Vatteville, France	6.6	20	376.9	>1000	11.1	-	SFO
Loam, grass	Vilobi d'Onyar, Spain	8.1	20	99.32	498.4	20.2	-	HS
Silt loam, grass	Albaro, Italy	7.4	20	20.89	511.3	7.06	-	DFOP

[1] analysed in topsoil, M-293999-01-1

[2] normalised using a Q10 of 2.58 and Walker equation coefficient of 0.7

3. Assessment and conclusion

Assessment and conclusion by applicant:
The kinetic evaluation followed FOCUS guidances and is considered to be valid and reliable.

Assessment and conclusion by RMS:
Outcome and conclusion of the study: RMS should indicate if they agree to the results and conclusions of the APPL.

1. Information on the study

Data Point:	KCA 7.1.2.2.1/20
Report Author:	[redacted]
Report Year:	2020
Report Title:	Fluopyram (FLU): Kinetic evaluation of field dissipation studies in USA according to FOCUS kinetics for trigger purpose using KinGUI 2.1
Report No:	EnSa-20-0250
Document No:	M-761904-01-1
Guideline(s) followed in study:	not applicable
Deviations from current test guideline:	Current Guideline: not applicable (kinetic evaluation)
Previous evaluation:	No, not previously submitted
GLP/Officially recognised testing facilities:	No, not conducted under GLP/Officially recognised testing facilities
Acceptability/Reliability:	Yes

2. Full summary of KCA 7.1.2.2.1/20

Executive Summary

Non-normalised dissipation $DisT_{50}$ values of fluopyram (FLU) in soil under field conditions were derived for trigger purpose using the software tool KinGUI 2.1 following the recommendations given by FOCUS Kinetics. The trigger analysis is based on residue data of three terrestrial field dissipation studies on US agricultural soils (KCA 7.1.2.2.1/03, M-306817-01-2; KCA 7.1.2.2.1/04, M-306809-01-2 and KCA 7.1.2.2.1/07, M-306820-01-2).

The best fit $DisT_{50}$ values for fluopyram (trigger endpoints) were calculated to be 161, 351 and 194 days for the soils, respectively. $DisT_{90}$ values were >1000 days for all three soils.

I. METHODS

Non-normalised dissipation $DisT_{50}$ values of fluopyram (FLU) in soil under European field conditions were derived for trigger purpose using the software tool KinGUI 2.1. The identification of the appropriate kinetic model followed the recommendations given by FOCUS Kinetics (FOCUS, 2006, 2014) based on a detailed statistical analysis including visual assessment, χ^2 statistic, significance t-test and correlation analysis, using correspondingly pre-processed residue data. Additionally, the Scaled Weighted Area under Residue Curve (SWARC) was used as a further indicator for the visual assessment and to choose the appropriate model.

The trigger analysis is based on residue data from terrestrial field dissipation studies conducted at the field sites located in the US in California, New York and Washington.

In the experimental studies the active substance has been applied to bare soil at 4 subplots per site at a nominal rate of 500 g/ha fluopyram in summer 2006. Throughout the study period, no cultivation activities were carried out. Herbicides other than fluopyram were applied to maintain bare soil conditions. Supplemental irrigation events were conducted.

Concentrations of metabolites of fluopyram remained very low throughout the study, e.g. for fluopyram-7-hydroxy. Therefore, it was assumed for the kinetic evaluation that the parent directly degraded into the sink.

II. RESULTS

Dissipation of fluopyram

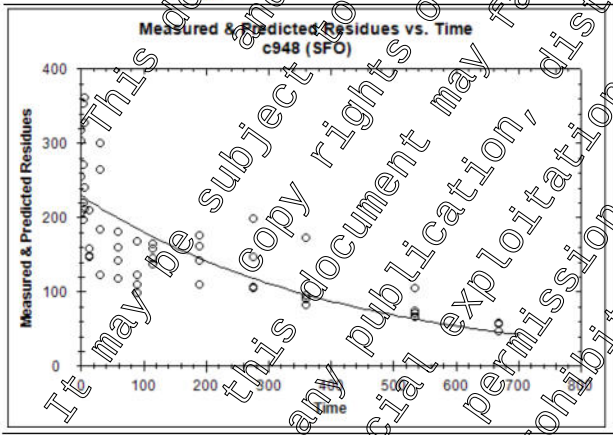
Results of the kinetic evaluation for trigger purpose based on residue data from the terrestrial field dissipation studies on US soils are summarised in the tables below.

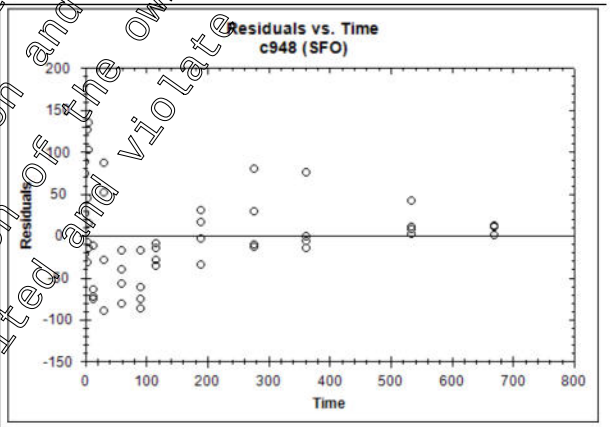
Table 7.1.2.2.1-92: Fluopyram (M-306820-01-2): kinetic and statistical results of dissipation in soil Huron, California

Kinetic model	DT_{50} actual	DT_{90} actual	VA	χ^2err / SWARC	k_1 / α	k_2 / β	g / n	t-test k_1 / k_2	95th CI of k_1	95th CI of k_2
	(d)	(d)		(% / -)	(1/d / -)	(1/d / d)	(- / d)	(-)	(1/d)	(1/d)
SFO	286.5	952	o	17.7 / 69.6	0.002419	-	-	<0.001	0.00160 to 0.003	-
DFOP	149.3	>1000	+	12.4 / 24.6	0.05977	0.001353	0.3881 / 348	0.055 / 0.002	-0.01223 to 0.132	-0.00049 to 0.002
FOMC	113.6	>1000	o	13.3 / 41.1	0.02846	10.9125	- / -	- / -		-
HS	**161.2**	**1160**	+	12.1 / 16.6	0.02051	0.001612	0.3670 / 150	0.002 / <0.001	0.01028 to 0.031	0.00084 to 0.002

VA = visual assessment, + = good, o = acceptable, - = poor
SWARC = Scaled Weighted Area under Residue Curve
CI = confidence intervall

Trigger Endpoints: SFO fit is statistically (χ^2err, t-test) and visually acceptable. SWARC value > 40 indicates that decline may be biphasic. DFOP, FOMC and HS fits were alternatively tested. For DFOP, t-test of k_{fast} failed in combination with a DT_{90} extrapolated beyond study end. For FOMC, DT_{90} is extrapolated far beyond study end. Both fits are therefore not suitable, especially for accumulation assessments. HS fit is statistically (χ^2err, t-test) and visually good. Consequently, **HS** degradation model is appropriate for trigger endpoints, as it shows lowest χ^2err of all suitable models (SFO, HS).





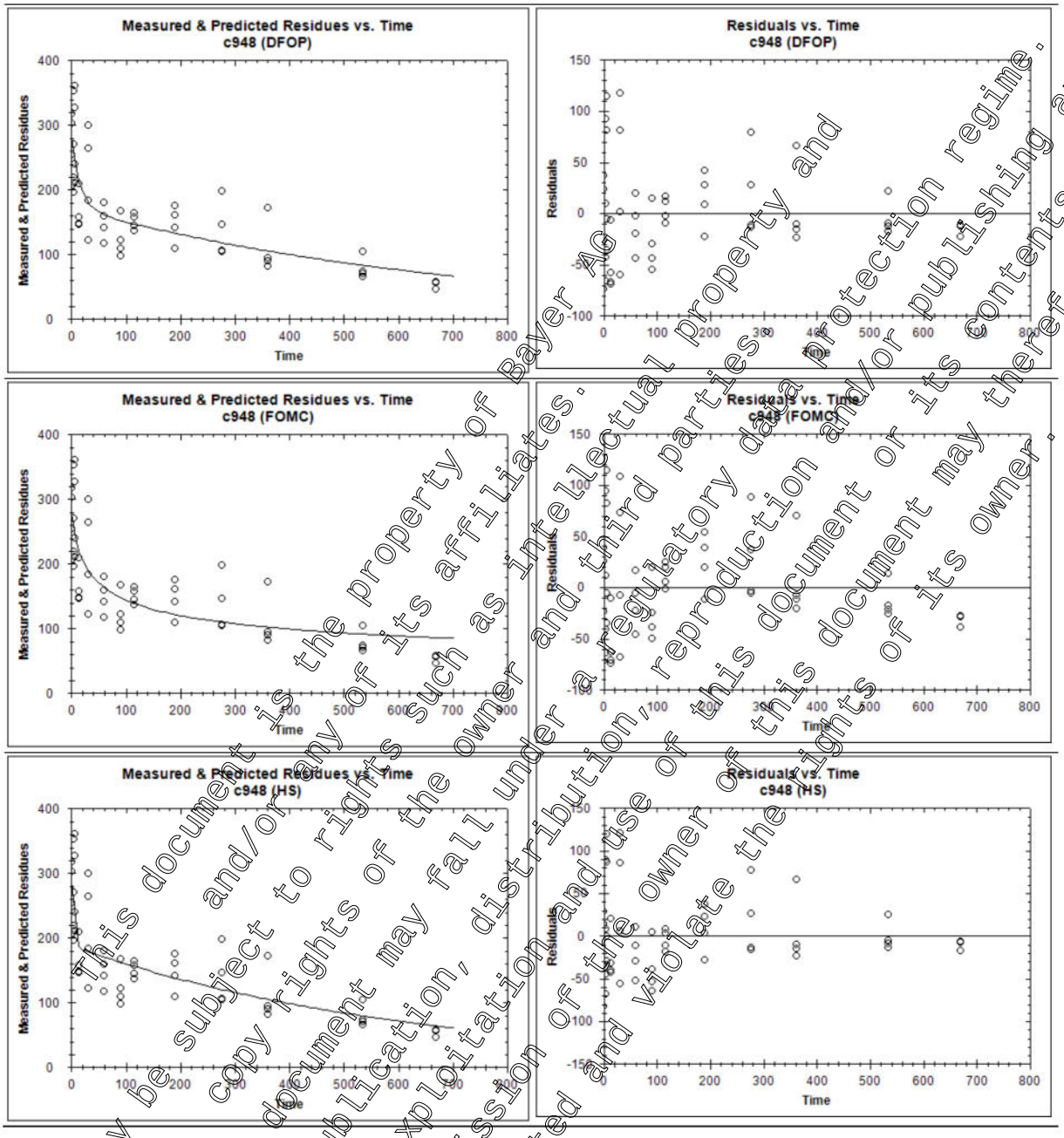


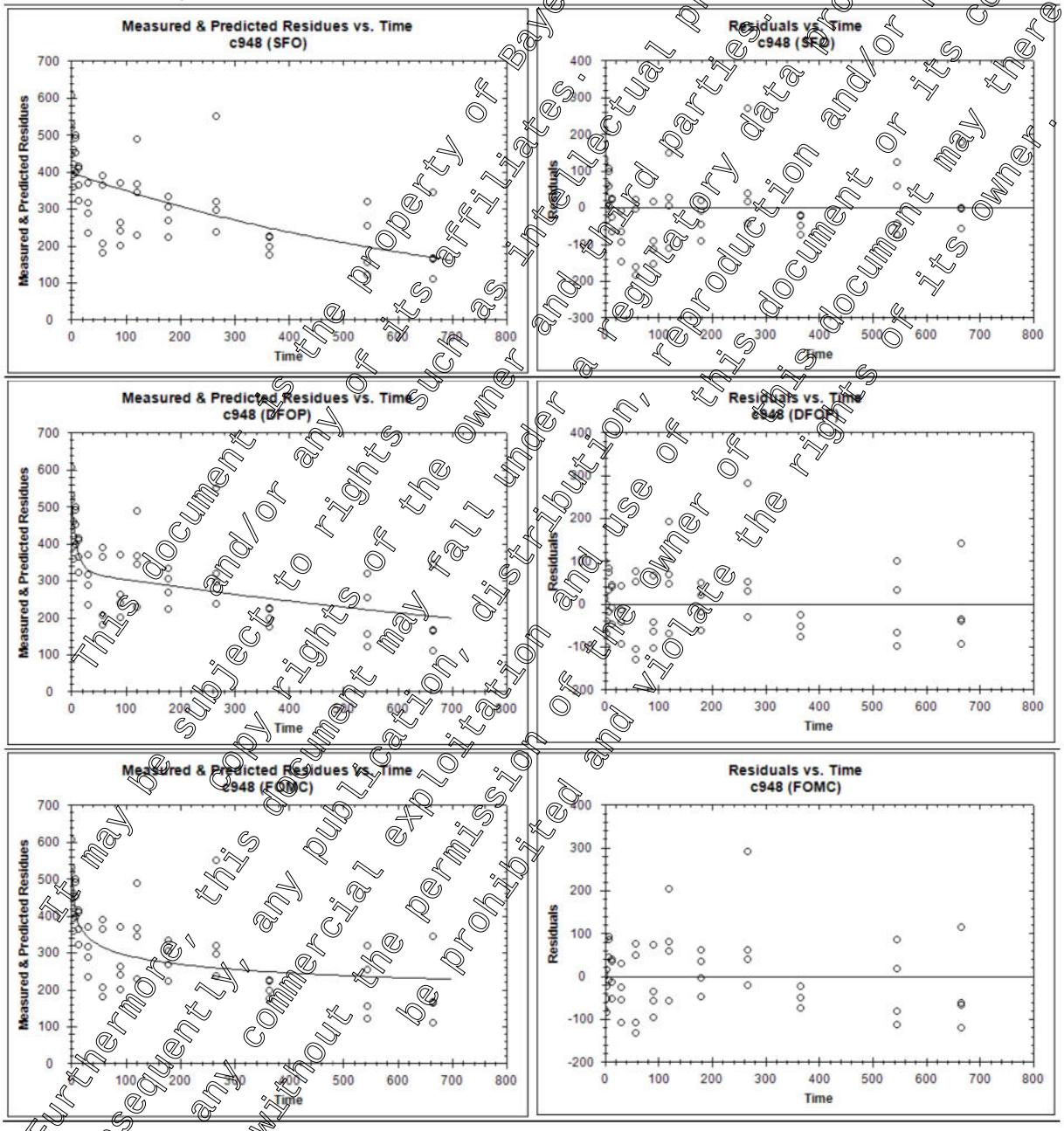
Table 7.1.2.2.1-93: Fluopyram (M-306809-01-2): kinetic and statistical results of dissipation in soil North Rose, New York

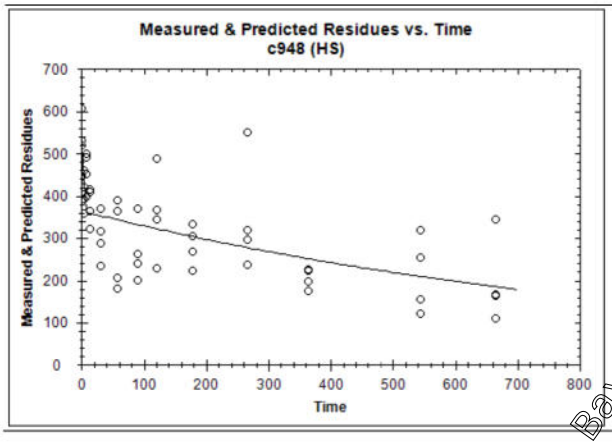
Kinetic model	DT_{50} actual	DT_{90} actual	tVA	χ^2err / SWARC	k_1 / α	k_2 / β	g / t_b	t-test k_1 / k_2	95th CI of k_1	95th CI of k_2
	(d)	(d)		(% / -)	(1/d / -)	(1/d / d)	(- / d)	(-)	(1/d)	(1/d)
SFO	523.3	>1000	o	15.6 / 31.5	0.001295	-	- / -	<0.001	0.00076 to 0.002	-
DFOP	**350.5**	**>1000**	+	10.6 / 17.7	0.09327	0.000709	0.3588 / 22.3	0.047 / 0.008	-0.01394 to 0.200	0.00015 to 0.001
FOMC	248.3	>1000	+	11.3 / 42.0	0.13077	1.24437	- / -	- / -	-	-

HS	320.3	>1000	+	12.8 / 10.3	0.08392	0.00102	0.3098 / 4.42	0.034 / <0.001	-0.00432 to 0.172	0.00051 to 0.002

VA = visual assessment, + = good, o = acceptable, - = poor
SWARC = Scaled Weighted Area under Residue Curve
CI = confidence intervall

Trigger Endpoints: SFO fit is statistically (χ^2err, t-test) and visually acceptable. SWARC is < 40. DFOP, FOMC and HS fits were alternatively tested. For FOMC, DT_{90} is extrapolated far beyond study end. The fit is therefore not suitable, especially for accumulation assessments. DFOP and HS fits are both statistically (χ^2err and t-test) and visually good. Consequently, **DFOP** degradation model is appropriate for trigger endpoints, as it shows lowest χ^2err of all suitable models (SFO, DFOP, HS).





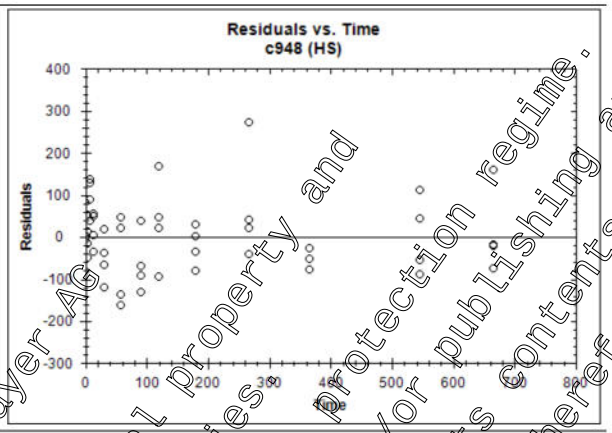
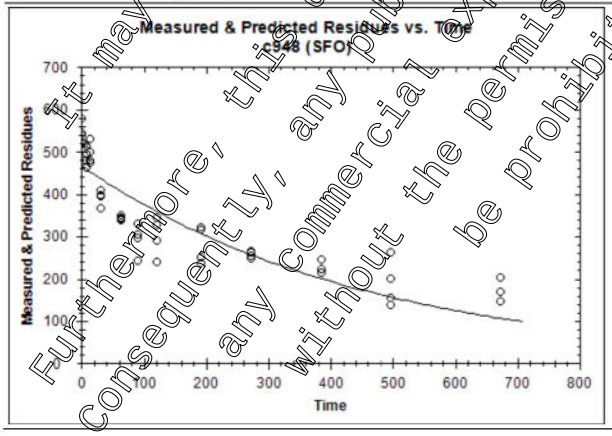


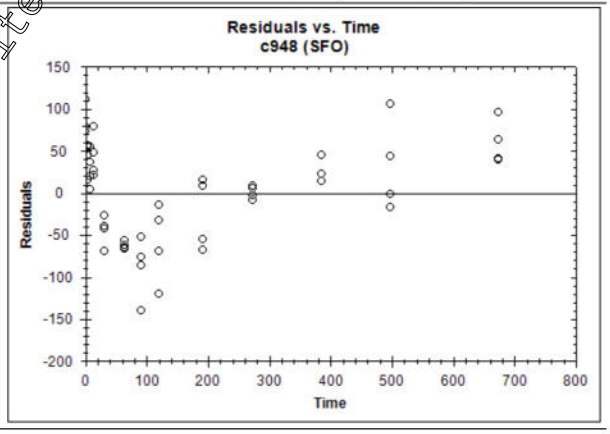
Table 7.1.2.2.1-94: Fluopyram (M-306817-01-2): kinetic and statistical results of dissipation in soil Ephrata, Washington

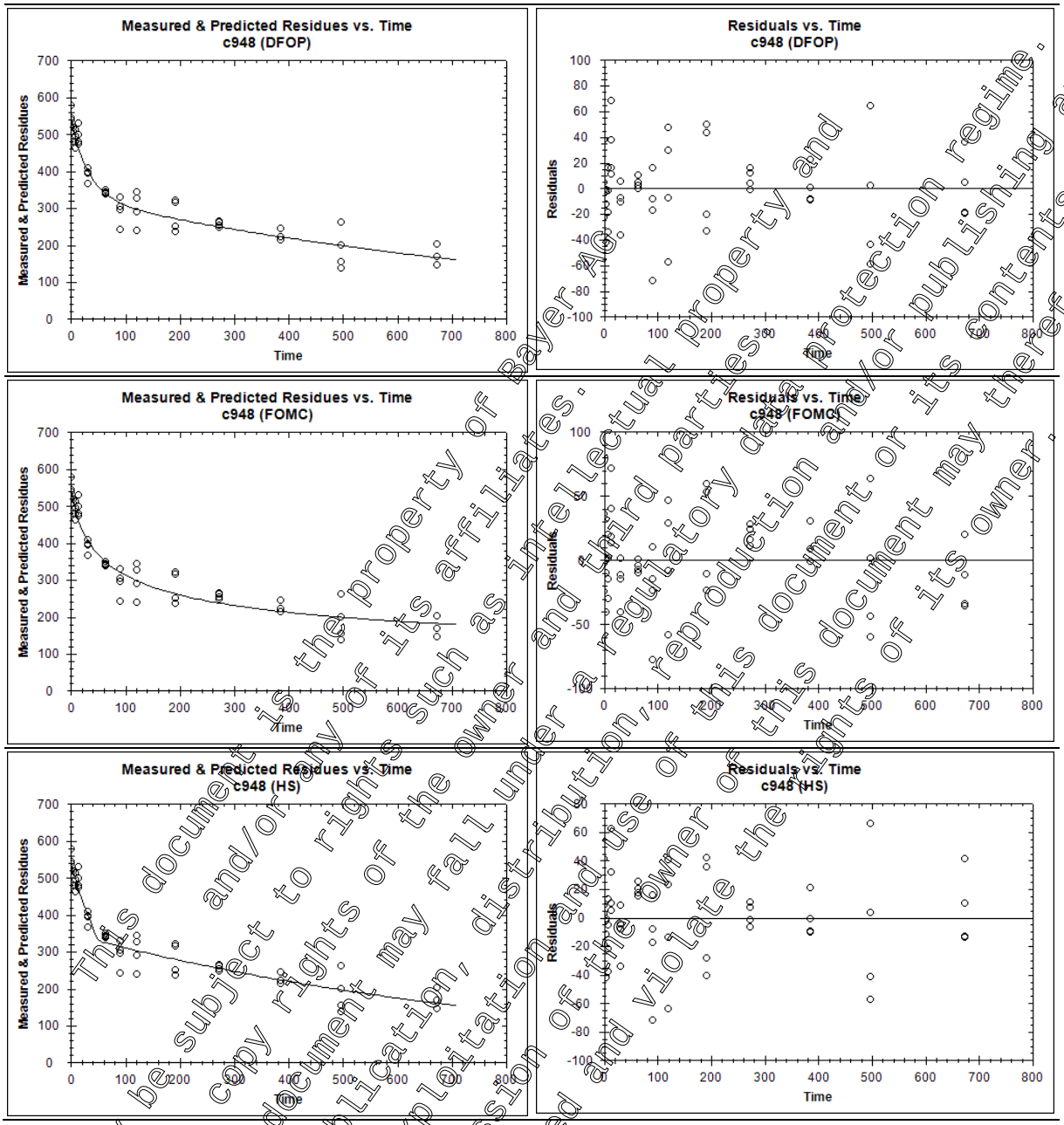
Kinetic model	DT_{50} actual	DT_{90} actual	VA	χ^2err / SWARC	k_1 / α	k_2 / β	g / t_b	t-test k_1 / k_2	95th CI of k_1	95th CI of k_2
	(d)	(d)		(%, -)	(1/d / -)	(1/d / d)	(- / d)	(-)	(1/d)	(1/d)
SFO	314.7	1046	-	12.0 / 230	0.002202	-	- / -	<0.001	0.00181 to 0.003	-
DFOP	**194.4**	**>1000**	+	3.35 / 5.66	0.03015	0.004917	0.3921 / 69.0	<0.001 / <0.001	0.01669 to 0.044	0.00070 to 0.001
FOMC	169	>1000	+	4.31 / 17.3	0.30820	1.993290	- / -	- / -	-	-
HS	226.1	>1000	+	3.32 / 17.3	0.009632	0.001151	0.3884 / 51.1	<0.001 / <0.001	0.00680 to 0.012	0.00091 to 0.001

VA = visual assessment, + = good, o = acceptable, - = poor
SWARC = Scaled Weighted Area under Residue Curve
CI = confidence interval

Trigger Endpoints: SFO fit is statistically (χ^2err, t-test) acceptable, but visually poor. SWARC value > 40 indicates that decline may be biphasic. DFOP, FOMC and HS fits were alternatively tested. For FOMC, DT_{90} is extrapolated far beyond study end. The fit is therefore not suitable, especially for accumulation assessments.
DFOP and HS fits are both statistically good and very similar (χ^2err, t-test) and visually good. Consequently, **DFOP** model is considered appropriate for trigger endpoints, as it shows a low χ^2err, the lowest SWARC and best visual fit of all suitable models (SFO, DFOP, HS).







III. CONCLUSIONS

The non-normalised trigger endpoints of field dissipation studies of fluopyram based on residue data from US agricultural soils are summarised in the table below.

Table 7.1.2.2.1-95: Fluopyram: Field dissipation endpoints for trigger purpose

Fluopyram	Field conditions								
Soil type (USDA) [2]	**Location**		**pH ($CaCl_2$) [2]**	**Depth (cm)**	**$DisT_{50}$ actual (d)**	**$DisT_{90}$ actual (d)**	**St. (χ^2) (%)**	**$DegT_{50}$ matrix (d) norm. [1]**	**Method of calculation**
Sandy loam, bare [3]	Huron / Kerman California		7.3	15	161.2	>1000	12.1		HS
Loamy sand, bare [4]	North Rose New York		5.9	15	350.9	>1000	10.6		DFOP
Sandy loam, bare [5]	Ephrata Washington		7.5 [2]	15	194.4	>1000	3.35		DFOP

[1] normalised using a Q10 of 2.58 and Walker equation coefficient of 0.7, values correspond with $DT_{50,mod}$ of selected kinetic models
[2] analysed in topsoil
[3] M-306820-01-2
[4] M-306809-01-2
[5] M-306817-01-2

3. Assessment and conclusion

Assessment and conclusion by applicant:
The kinetic evaluation followed FOCUS guidances and is considered to be valid and reliable.

Assessment and conclusion by RMS:
Outcome and conclusion of the study: RMS should indicate if they agree to the results and conclusions of the APPI.

1. Information on the study

Data Point:	KCA 7.1.2.2.1/25
Report Author:	[redacted]
Report Year:	2020
Report Title:	Fluopyram (FLU): Interim kinetic evaluation of a field dissipation study in Europe (Doig, 2020) according to FOCUS kinetics for trigger purpose using KinGUI 2.1
Report No:	EnSa-20-0856
Document No:	M-769887-01-1
Guideline(s) followed in study	not applicable
Deviations from current test guideline:	Current Guideline: not applicable (kinetic evaluation)
Previous evaluation:	No, not previously submitted
GLP/Officially recognised testing facilities:	No, not conducted under GLP/Officially recognised testing facilities
Acceptability/Reliability:	Yes

2. Full summary of KCA 7.1.2.2.1/21

Executive Summary

Non-normalised dissipation DT_{50} values of fluopyram in soil under European field conditions were derived for trigger purpose, using the software tool KinGUI 2.1 following the recommendations given by FOCUS Kinetics. The trigger analysis is based on interim residue data from a terrestrial field dissipation study (KCA 7.1.2.2.1/14, M-758583-01-1) conducted at the field sites located in Europe.

No metabolites of fluopyram were analysed throughout the study. Therefore, in the following kinetic evaluation only the dissipation of the parent compound was considered.

The $DisT_{50}$ values for fluopyram (trigger endpoints) were calculated to be between 301.6 and >1000 days and $DisT_{90}$ values were >1000 days for all soils.

I. METHODS

Non-normalised dissipation DT_{50} values of fluopyram (FLU) in soil under European field conditions were derived for trigger purpose, using the software tool KinGUI 2.1. The identification of the appropriate kinetic model followed the recommendations given by FOCUS Kinetics (FOCUS, 2006, 2014) based on a detailed statistical analysis including visual assessment, χ^2 statistic, significance t-test and correlation analysis, using correspondingly pre-processed residue data. Additionally, the Scaled Weighted Area under Residue Curve (SWARC) was used as a further indicator for the visual assessment and to choose the appropriate model.

The trigger analysis is based on interim residue data from a terrestrial field dissipation study conducted at the field sites located in Little Oliver (Malton, UK), Auchy les Mines (France), Urbanowice (Poland), Charles River Farm (Alpicat, Lleida, Spain) and Sindos (Greece).

In the 5 experimental trials, the active substance has been applied to bare soil at 3 subplots per site at a nominal rate of 250 g/ha fluopyram in spring 2019. After application, 3 - 5 mm of sand was applied evenly to the treated plots, to exclude surface processes of the active compound, e.g. photolysis, evaporation. No cultivation activities were carried out throughout the study period. Herbicides other than fluopyram were applied to maintain bare soil conditions. Supplemental irrigation events were conducted.

No metabolites of fluopyram were analysed throughout the study. Therefore, only the parent compound was considered and it was assumed in the kinetic evaluation that the parent directly dissipated into a sink.

II. RESULTS

Dissipation of Fluopyram

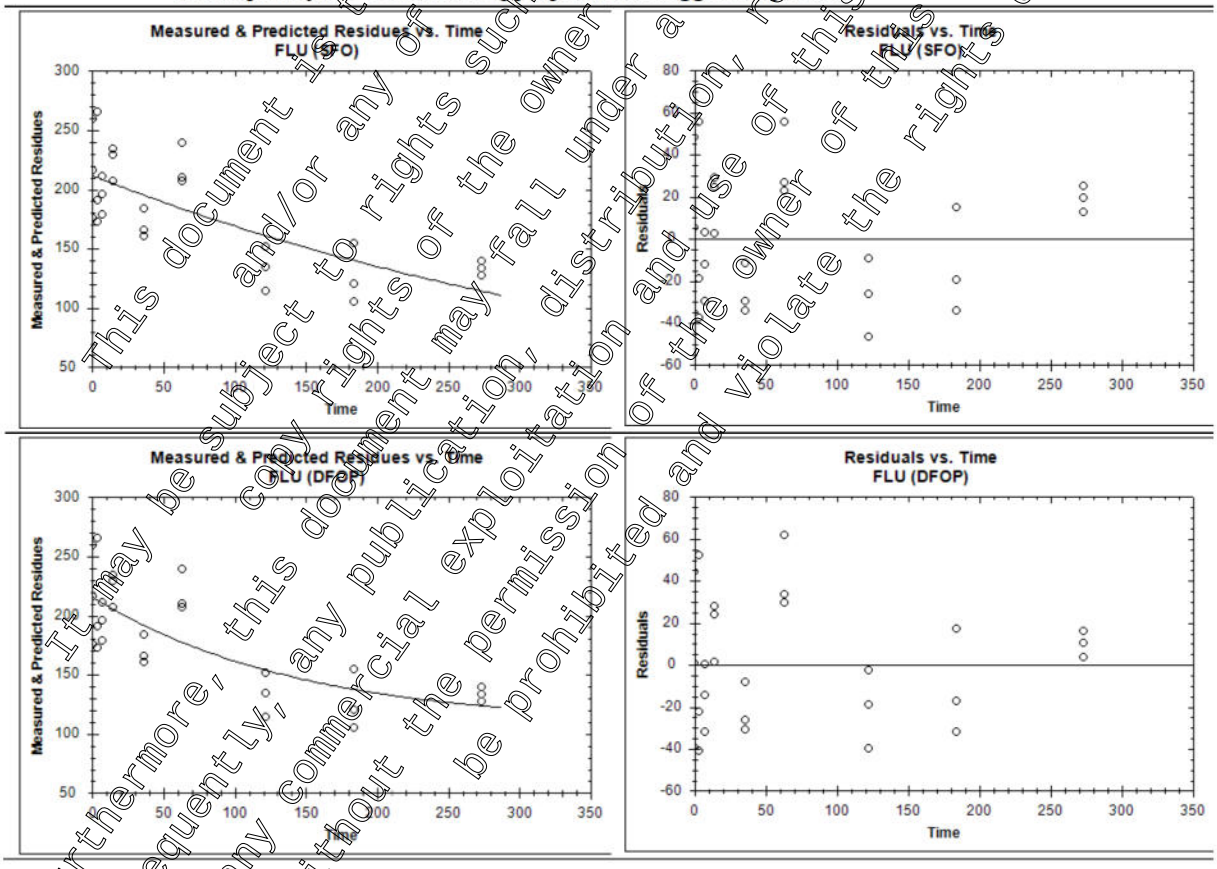
Results of the kinetic evaluation for trigger purpose based on residue data from the terrestrial field dissipation studies on European soils are summarised in the tables below.

Table 7.1.2.2.1-96: Fluopyram: kinetic and statistical results of dissipation in soil Little Oliver, UK

Kinetic model	DT_{50} actual	DT_{90} actual	VA	χ^2err / SWARC	k_1 / α	k_2 / β	g / t_b	t-test k_1 / k_2	95th CI of k_1	95th CI of k_2
	(d)	(d)		(% / -)	(1/d / -)	(1/d / d)	(- / d)	(-)	(1/d)	(1/d)
SFO	**307.6**	**1022**	o	8.96 / 18.0	0.002254	-	- / -	<0.001	0.00136 to 0.003	-
DFOP	778.6	>1000	o	9.67 / 7.34	0.006965	< 5 E-7	0.5022 / 299	0.426 / 0.5	-0.06533 to 0.079	-0.03113 to 0.031
FOMC	368.6	>1000	o	9.19 / 10.0	0.6145	174.960	- / -	- / -	-	-
HS	299.7	1037	o	10.0 / 17.0	0.01246	0.002162	0.0462 / 4.32	0.380 / <0.001	-0.06682 to 0.092	0.001415 to 0.003

VA = visual assessment, + = good, o = acceptable, - = poor
SWARC = Scaled Weighted Area under Residue Curve
CI = confidence intervall

Trigger Endpoints: SFO fit is statistically (χ^2err, t-test) and visually acceptable. SWARC value is < 40, not indicating a biphasic decline. DFOP, FOMC and HS fits were alternatively tested.
For DFOP, t-test of k_{fast} failed in combination with a DT_{90} extrapolated far beyond study end. For FOMC, DT_{90} is also extrapolated far beyond study end. Both fits are therefore not suitable, especially for accumulation assessments. HS fit might be acceptable (k_2), but not better than SFO. Consequently, **SFO** model is appropriate for trigger endpoints.



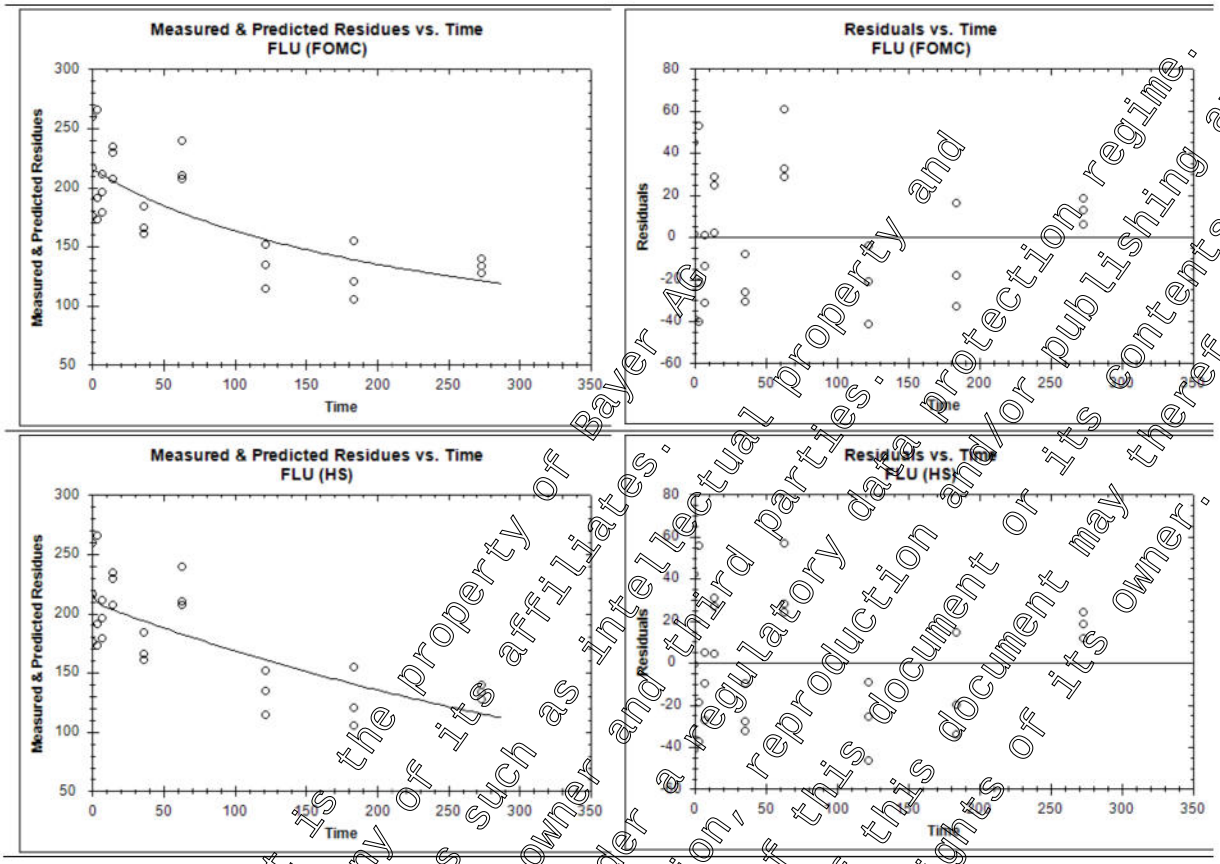
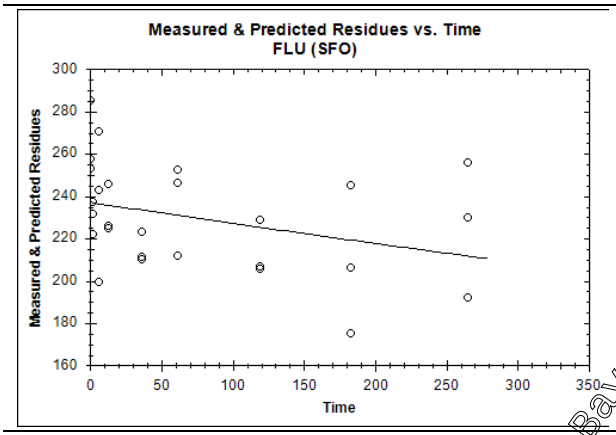


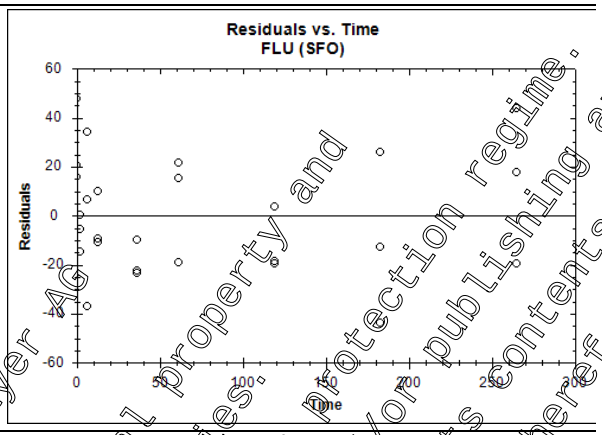
Table 7.1.2.2.1-97: Fluopyram: kinetic and statistical results of dissipation in soil Auchy les Mines, France

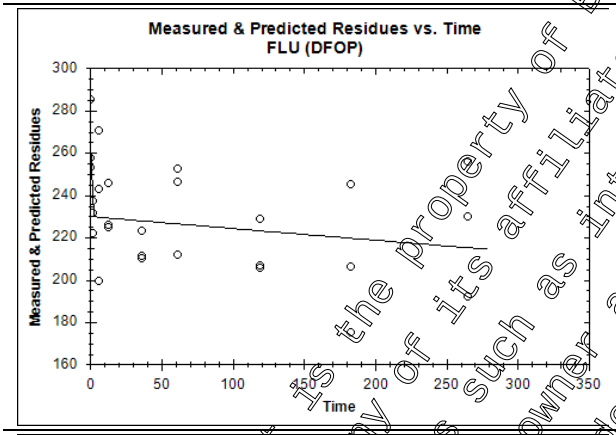
Kinetic model	DT_{50} actual	DT_{90} actual	VA	χ^2err / SWARC	k_1 / α	k_2 / β	g / t_b	t-test k_1 / k_2	95th CI of k_1	95th CI of k_2
	(d)	(d)		(% / -)	(1/d / -)	(1/d / d)	(- / d)	(-)	(1/d)	(1/d)
SFO	**>1000**	**>1000**	o	4.74 / 7.14	0.000427		- / -	0.042	-0.00004 to 0.001	-
DFOP	>1000	>1000	o	3.38 / 3.57	>1.101	0.00025	0.1335 / 0.990	0.441 / 0.160	-25.120 to 29.326	-0.00023 to 0.001
FOMC	>1000	>1000	o	2.95 / 3.25	0.01619	0.001322	- / -	- / -	-	-
HS	>1000	>1000	o	3.38 / 4.64	0.03743	0.000253	0.1335 / 1.85	<0.001 / 0.142	0.04851 to 0.106	-0.00020 to 0.001

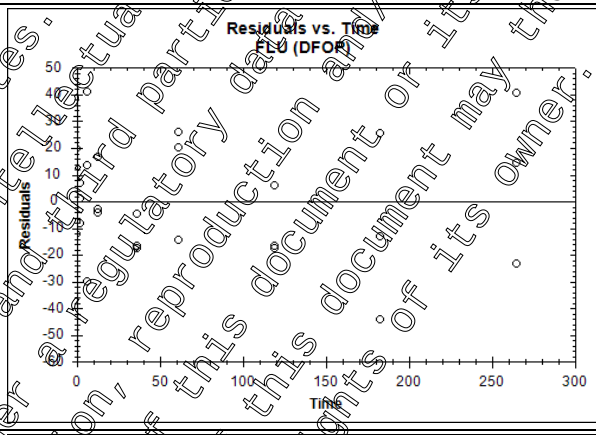
VA = visual assessment, + = good, o = acceptable, - = poor
SWARC = Scaled Weighted Area under Residue Curve
CI = confidence intervall

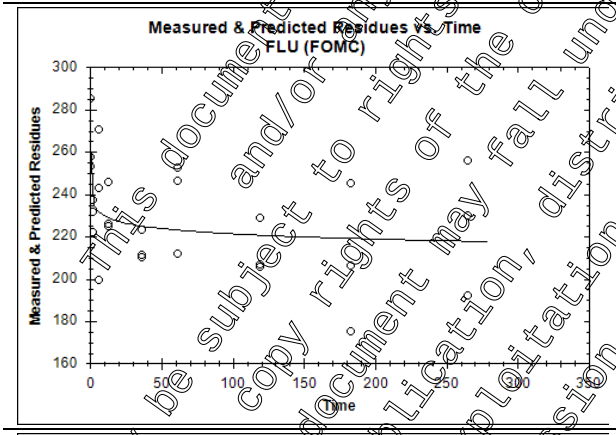
Trigger Endpoints: SFO fit is statistically (χ^2err / t-test) and visually acceptable. SWARC value is < 40, not indicating a biphasic decline. DFOP, FOMC and HS fits were alternatively tested.
For DFOP and HS, t-test of k_{fast} or k_{slow} failed in combination with a DT_{90} extrapolated far beyond study end. For FOMC, DT_{90} is also extrapolated far beyond study end. All 3 fits are therefore not suitable, especially for accumulation assessments. In addition, all 3 biphasic models did not result in a significant improvement of χ^2err, nor a better visual fit, mainly due to scattering data. Consequently, **SFO** model is appropriate for trigger endpoints.

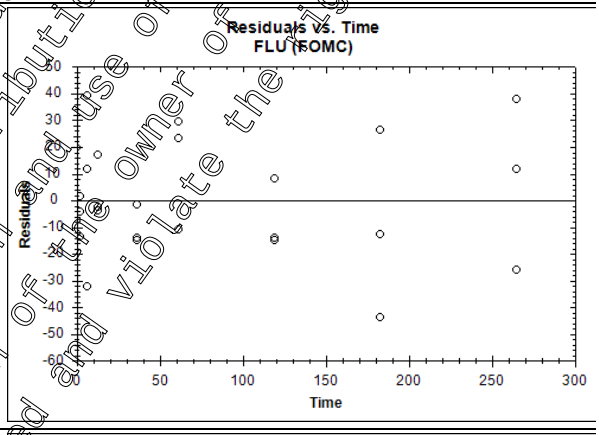


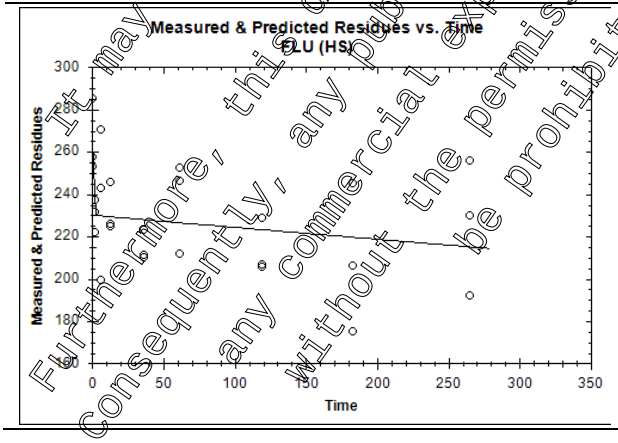












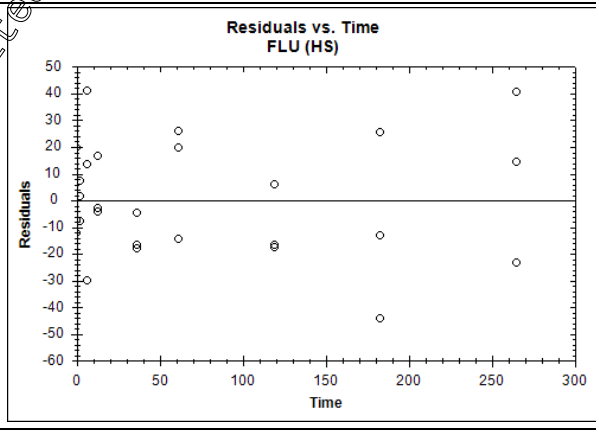
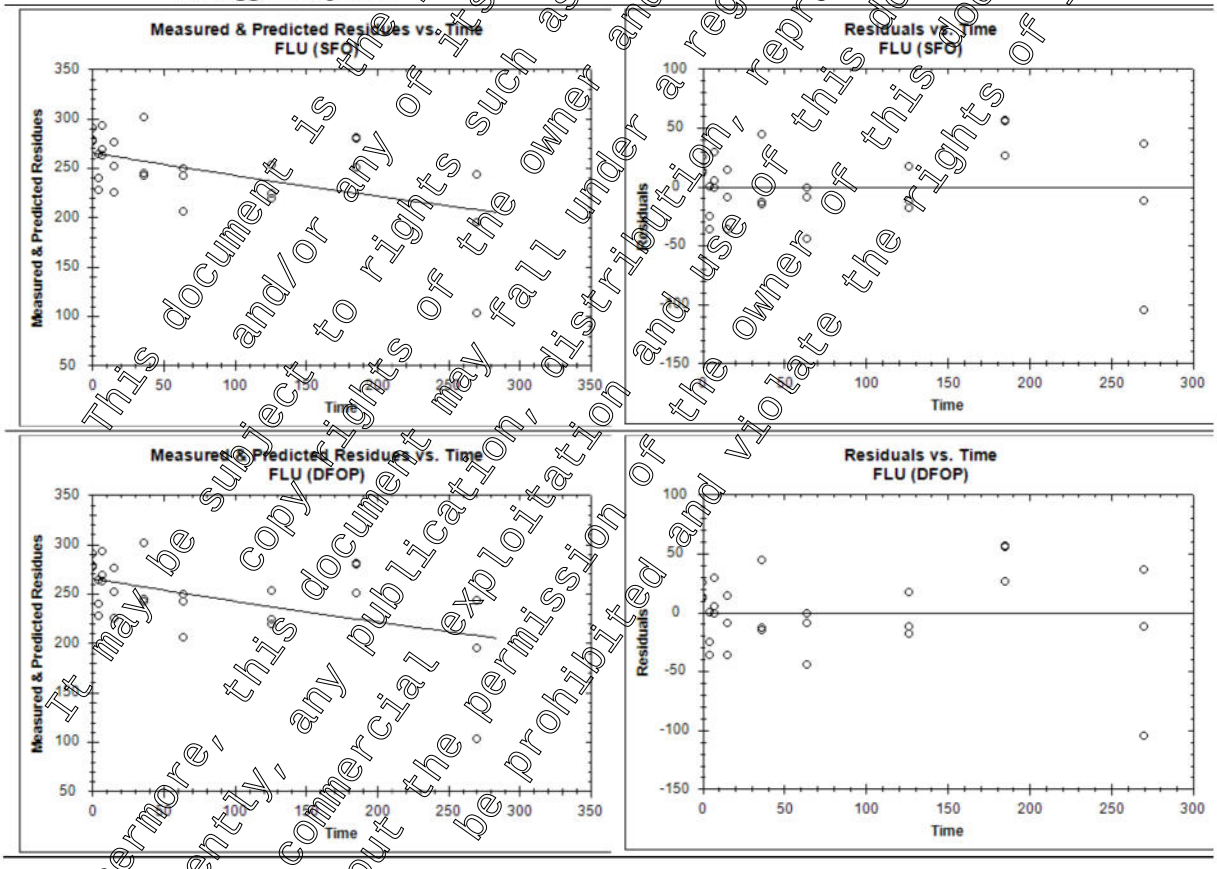


Table 7.1.2.2.1-98: Fluopyram: kinetic and statistical results of dissipation in soil Urbanowice, Poland

Kinetic model	DT_{50} actual	DT_{90} actual	VA	χ^2err / SWARC	k_1 / α	k_2 / β	g / t_b	t-test k_1 / k_2	95th CI of k_1	95th CI of k_2
	(d)	(d)		(% / -)	(1/d / -)	(1/d / d)	(- / d)	(-)	(1/d)	(1/d)
SFO	**765.7**	**>1000**	o	6.97 / 3.64	0.000905	-	- / -	0.005	0.00027 to 0.002	-
DFOP	765.7	>1000	o	7.85 / 3.64	0.000905	0.000905	0.842 / 2297	0.004 / <0.001	0.00031 to 0.002	0.00079 to 0.001
FOMC	765.8	>1000	o	7.36 / 3.64	1538	1.7 E+6	- / -	- / -	-	-
HS	758.9	>1000	o	7.51 / 3.05	31.19	0.00080	0.0752 / 0.003	<0.001 / 0.015	31.19 to 31.186	0.00042 to 0.001

VA = visual assessment, + = good, o = acceptable, - = poor
SWARC = Scaled Weighted Area under Residue Curve
CI = confidence intervall

Trigger Endpoints: SFO fit is statistically (χ^2err, t-test) and visually acceptable. SWARC value is < 40, not indicating a biphasic decline. DFOP, FOMC and HS fits were alternatively tested. No visual nor statistical improvement could be reached with biphasic models. Consequently, **SFO** model is appropriate for trigger endpoints.



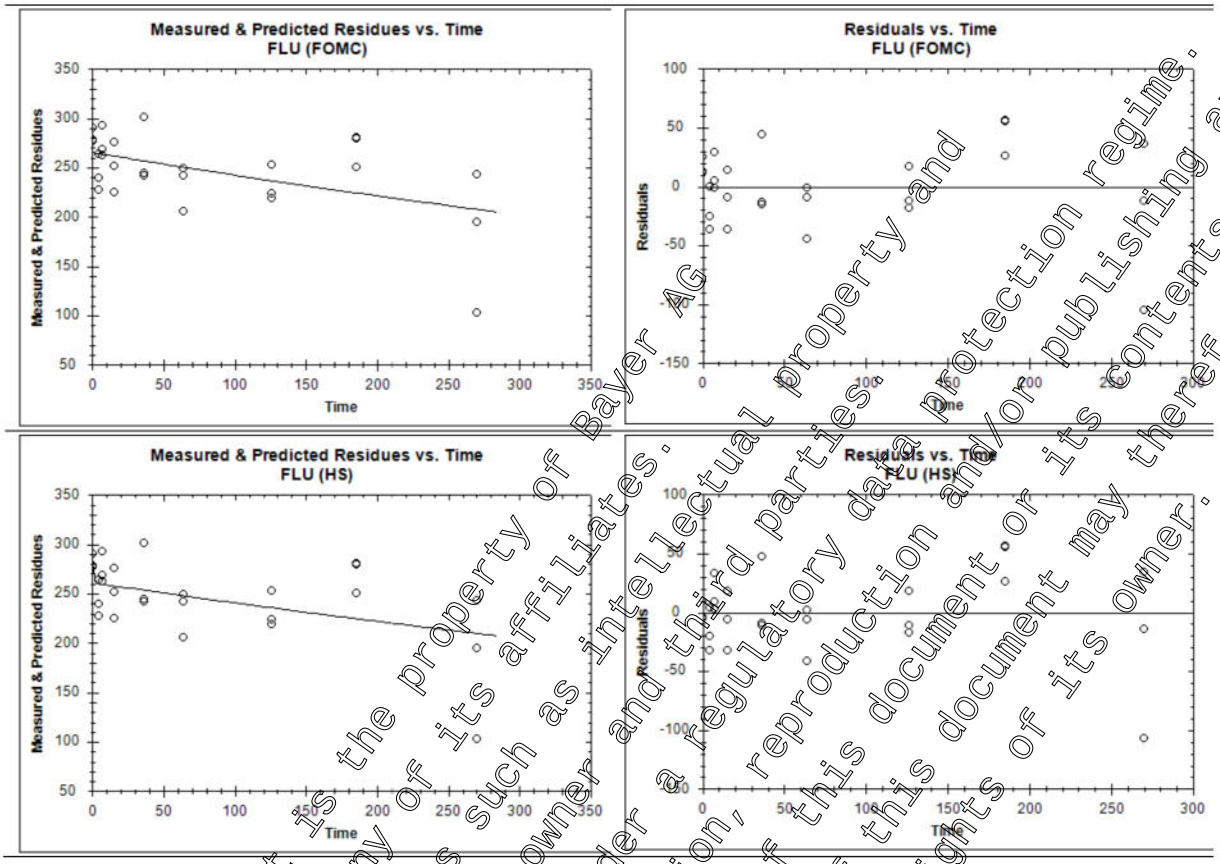
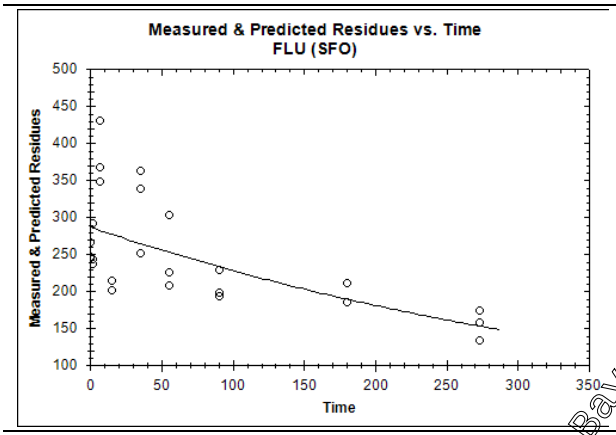


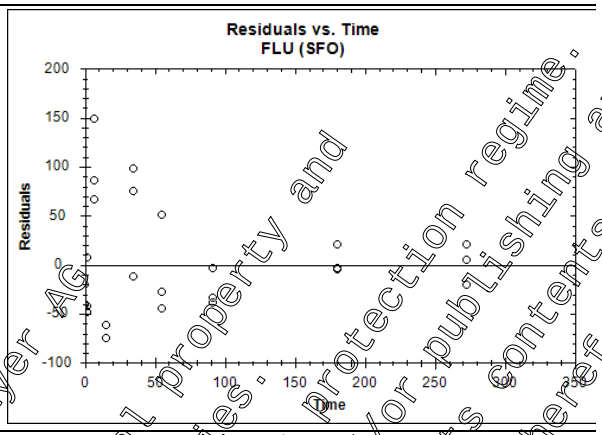
Table 7.1.2.2.1-99: Fluopyram: kinetic and statistical results of dissipation in soil Charles River Farm, Spain

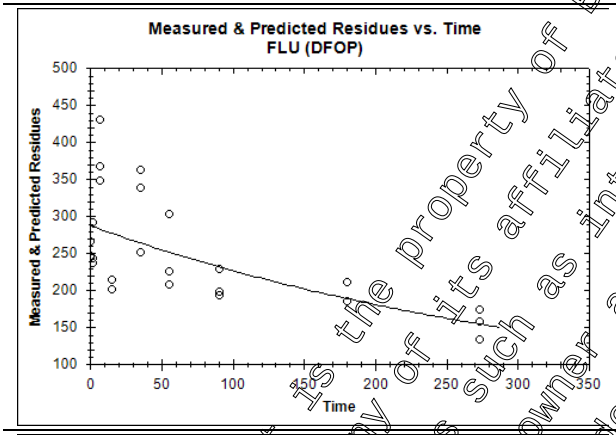
Kinetic model	DT_{50} actual	DT_{90} actual	VA	χ^2err / SWARC	k_1 / α	k_2 / β	g / t_b	t-test k_1 / k_2	95th CI of k_1	95th CI of k_2
	(d)	(d)		(% / -)	(1/d / -)	(1/d / d)	(- / d)	(-)	(1/d)	(1/d)
SFO	**301.6**	**1002**	o	15.2 / 3.59	0.002298		- / -	<0.001	0.00102 to 0.004	-
DFOP	309.2	>1000	o	17.2 / 3.28	0.002866	2.2 E-14	0.8507 / 726	0.490 / 0.5	-0.21000 to 0.216	-0.84550 to 0.846
FOMC	306.2	>1000	o	16.7 / 3.36	5.671	2355.43	- / -	- / -	-	-
HS	290.6	890.7	o	17.0 / 6.20	0.00221	0.002682	- / 35.0	0.488 / 0.009	-0.01357 to 0.014	0.00060 to 0.005

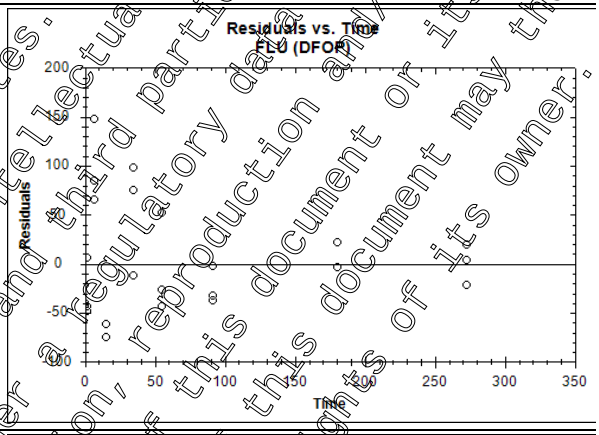
VA = visual assessment, + = good, o = acceptable, - = poor
SWARC = Scaled Weighted Area under Residue Curve
CI = confidence intervall

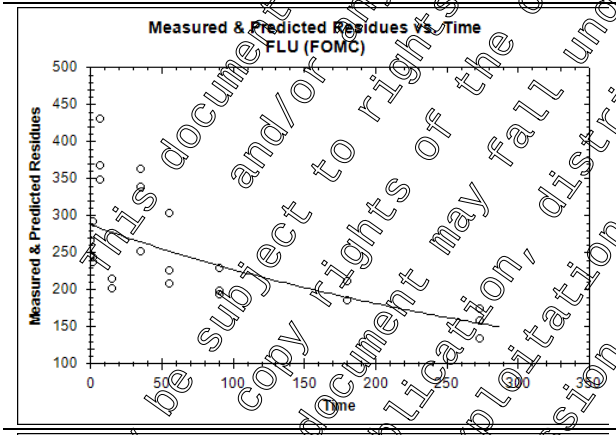
Trigger Endpoints: SFO fit is statistically (χ^2err / t-test) and visually acceptable. SWARC value is < 40, not indicating a biphasic decline. DFOP, FOMC and HS fits were alternatively tested. No visual nor statistical improvement could be reached with biphasic models. Consequently, **SFO** model is appropriate for trigger endpoints.

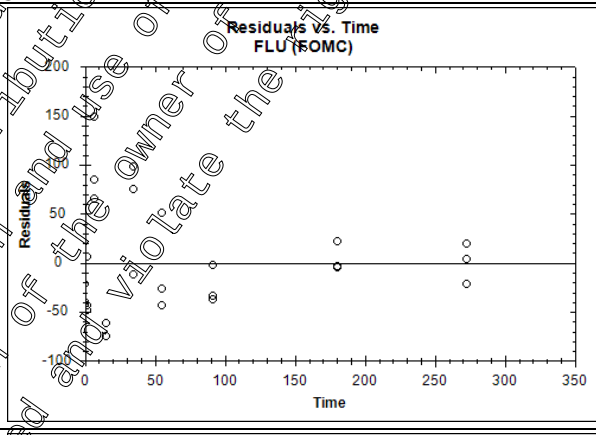


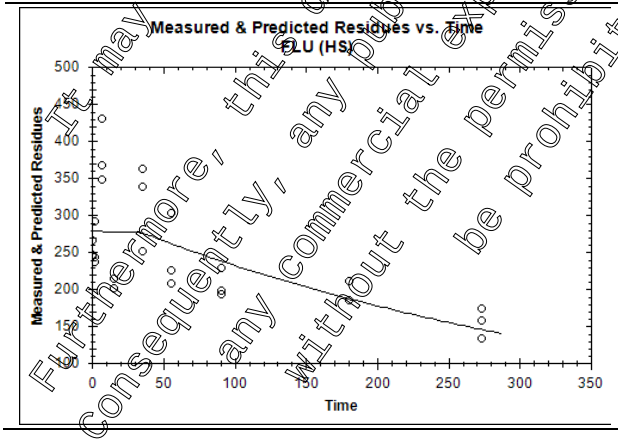












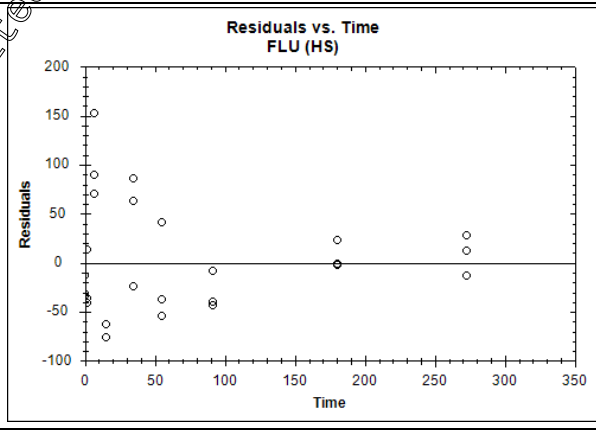
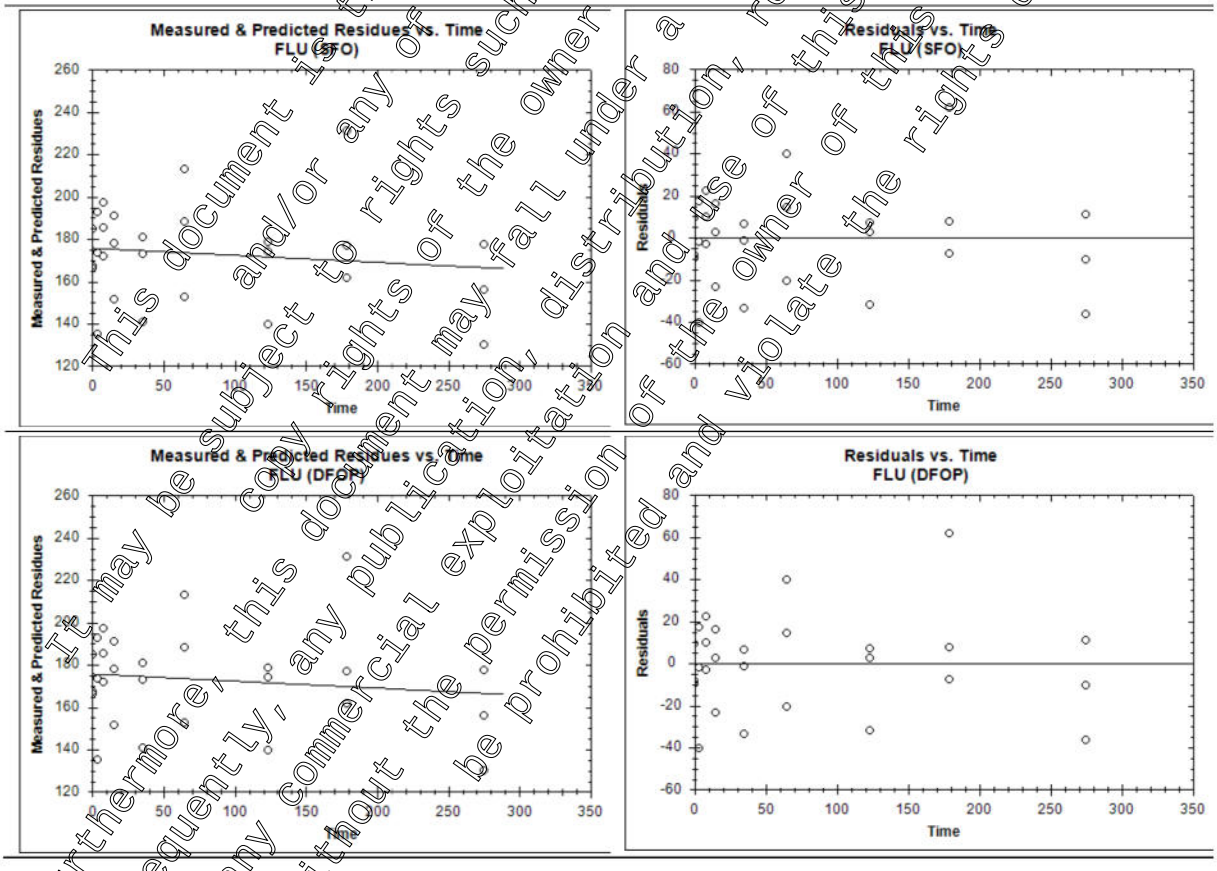


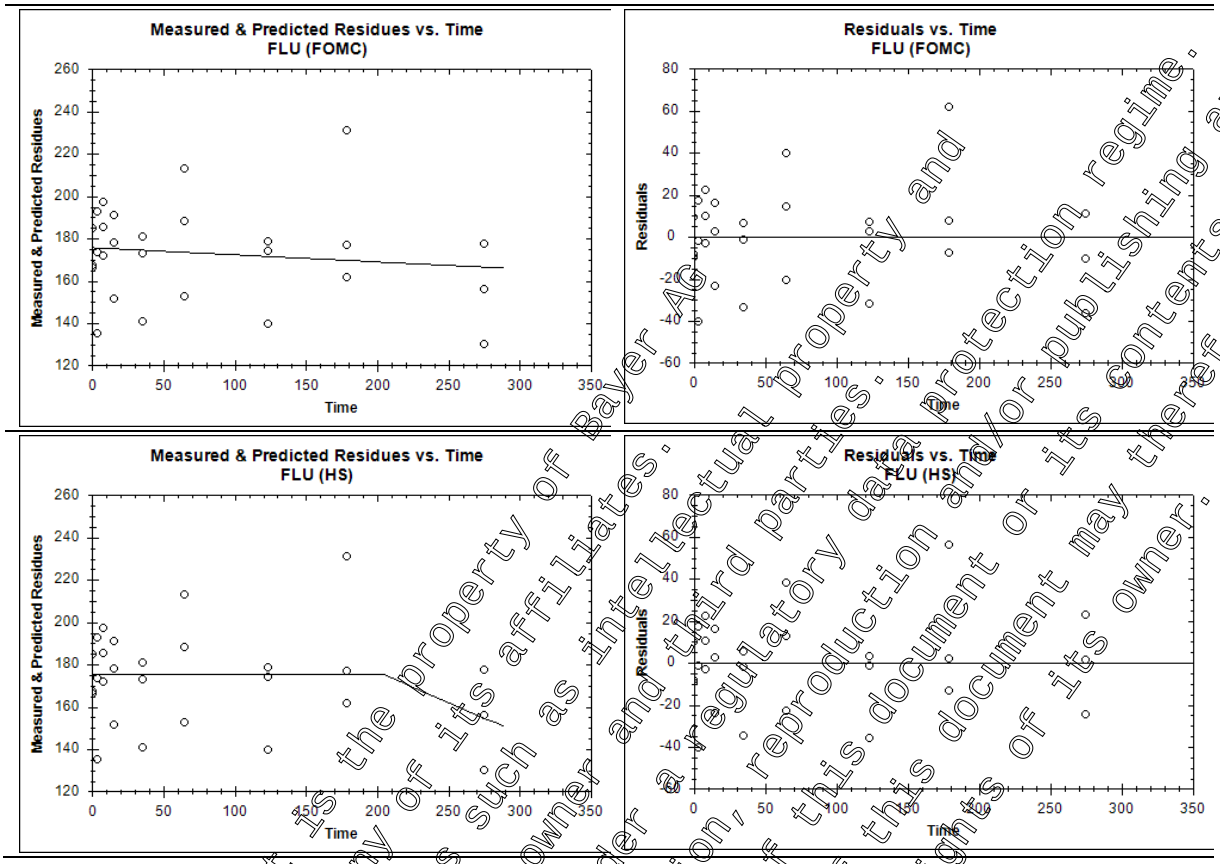
Table 7.1.2.2.1-100: Fluopyram: kinetic and statistical results of dissipation in soil Sindos, Greece

Kinetic model	DT_{50} actual	DT_{90} actual	VA	χ^2err / SWARC	k_1 / α	k_2 / β	g / t_b	t-test k_1 / k_2	95th CI of k_1	95th CI of k_2
	(d)	(d)		(% / -)	(1/d / -)	(1/d / d)	(- / d)	(-)	(1/d)	(1/d)
SFO	**>1000**	**>1000**	o	4.89 / 0.972	0.000195	-	- / -	0.255	-0.00038 to 0.001	-
DFOP	>1000	>1000	o	5.51 / 0.972	0.000195	2.2 E-14	10 / 10653	0.205 / <0.001	-0.00036 to 0.001	<0.00001 to <0.00002
FOMC	>1000	>1000	o	5.16 / 0.973	20800	1.10E+09	- / -	-	-	
HS	>1000	>1000	o	4.62 / 6.49	< 5.E-7	0.001805	- / 205	0.5 0.136	-0.00066 to 0.001	-0.00134 to 0.005

VA = visual assessment, + = good, o = acceptable, - = poor
SWARC = Scaled Weighted Area under Residue Curve
CI = confidence intervall

Trigger Endpoints: SFO fit is visually acceptable, χ^2err is acceptable, but t-test failed. SWARC value is < 40, not indicating a biphasic decline. DFOP, FOMC and HS fits were alternatively tested. No visual nor statistical improvement could be reached with biphasic models. Consequently, **SFO** model can be accepted for trigger endpoints, leading to a default DT_{50} of 1000 d anyway.





III. CONCLUSIONS

The non-normalised trigger endpoints of field dissipation studies of fluopyram based on residue data from European soils are summarised in the table below.

Table 7.1.2.2.1-101: Fluopyram: Field dissipation endpoints for trigger purpose

Fluopyram	**Field conditions**								
Soil type (USDA) [2]	**Location**		**pH ($CaCl_2$)** [2]	**Depth (cm)**	**$DisT_{50}$ actual (d)**	**$DisT_{90}$ actual (d)**	**St. (χ^2) (%)**	**$DegT_{50}$ matrix (d) norm.** [1]	**Method of calculation**
Sandy clay loam	Little Oliver, UK		5.3	20	307.6	1022	8.96	-	SFO
Loam	Auchy les Mines, N-France		7.3	20	>1000	>1000	4.74	-	SFO
Silt loam	Urbanowice, Poland		5.2	20	765.7	>1000	6.97	-	SFO
Clay	Charles River Farm, Lleida, ES		7.8	20	301.6	1002	15.2	-	SFO
Loam	Sindos, GR		6.6	20	>1000	>1000	4.89	-	SFO

[1] normalised using a Q10 of 2.58 and Walker equation coefficient of 0.7, values correspond with $DT_{50\ mod}$ of selected kinetic models

[2] analysed in topsoil, M-758583-01-1

3. Assessment and conclusion

Assessment and conclusion by applicant:
The kinetic evaluation followed FOCUS guidances and is considered to be valid and reliable.

Assessment and conclusion by RMS:
Outcome and conclusion of the study: RMS should indicate if they agree to the results and conclusions of the APPL.

A final kinetic evaluation will be conducted when the final study report M-758583-01-1 is available and will be provided at the latest by end of February 2022.

1. Information on the study

Data Point:	KCA 7.1.2.2.1/22
Report Author:	[redacted]
Report Year:	2021
Report Title:	Fluopyram (FLU) Interim kinetic evaluation of a field dissipation study in Europe (Gut, 2021) according to FOCUS kinetics for trigger purpose using KinGUI 2.1
Report No:	EnSa-20-0801
Document No:	M-761915-01-1
Guideline(s) followed in study:	not applicable
Deviations from current test guideline:	Current Guideline: not applicable (kinetic evaluation)
Previous evaluation:	No, not previously submitted
GLP/Officially recognised testing facilities:	No, not conducted under GLP/Officially recognised testing facilities
Acceptability/Reliability:	Yes

2. Full summary of KCA 7.1.2.2.1/22

Executive Summary
Non-normalised dissipation DT_{50} values of fluopyram in soil under European field conditions were derived for trigger purpose, using the software tool KinGUI 2.1. The identification of the appropriate kinetic model following the recommendations given by FOCUS Kinetics. The trigger analysis is based on interim residue data from a terrestrial field dissipation study (KCA 7.1.2.2.1/15, M-758589-01-1) conducted at the field sites located in Europe.

No metabolites of fluopyram were analysed throughout the study. Therefore, in the following kinetic evaluation only the dissipation of the parent compound was considered.

The $DisT_{50}$ values for fluopyram (trigger endpoints) were calculated to be between 150.1 and >608.0 days and $DisT_{90}$ values were between 498.6 and >1000 days for all soils.

I. METHODS

Non-normalised dissipation DT_{50} values of fluopyram (FLU) in soil under European field conditions were derived for trigger purpose, using the software tool KinGUI 2.1. The identification of the appropriate kinetic model followed the recommendations given by FOCUS Kinetics (FOCUS, 2006,

2014) based on a detailed statistical analysis including visual assessment, χ^2 statistic, significance t-test and correlation analysis, using correspondingly pre-processed residue data. Additionally, the Scaled Weighted Area under Residue Curve (SWARC) was used as a further indicator for the visual assessment and to choose the appropriate model.

The trigger analysis is based on interim residue data from a terrestrial field dissipation study conducted at the field sites located in Hoeltinghausen (Emstek, Germany), Hornton (Banbury, UK), Le Thour (N-France), Brannens (S-France), Balbiano (Italy), and Almayate East (Spain).

In the 6 experimental trials, the active substance has been applied to bare soil at 3 subplots per site at a nominal rate of 250 g/ha fluopyram in spring 2019. After application, 6 – 10 mm of sand was applied evenly to the treated plots, to exclude surface processes of the active compound, e.g. photo-degradation, volatilisation. No cultivation activities were carried out throughout the study period. Herbicides other than fluopyram were applied to maintain bare soil conditions. Supplemental irrigation events were conducted.

No metabolites of fluopyram were analysed throughout the study. Therefore only the parent compound was considered and it was assumed in the kinetic evaluation that the parent directly dissipated into a sink.

II. RESULTS

Dissipation of Fluopyram

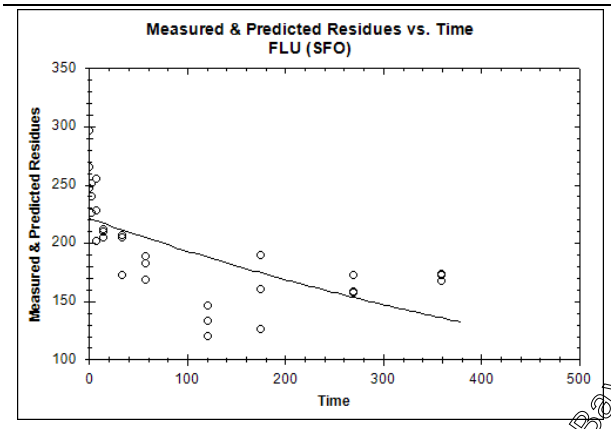
Results of the kinetic evaluation for trigger purpose based on residue data from the terrestrial field dissipation studies on European soils are summarised in the tables below.

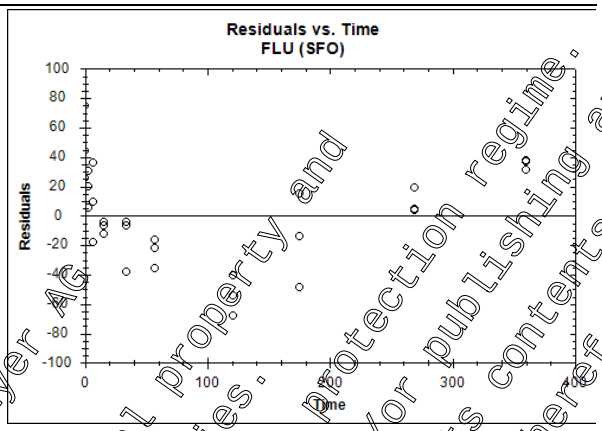
Table 7.1.2.2.1-102: Fluopyram: kinetic and statistical results of dissipation in soil Hoeltinghausen, Germany

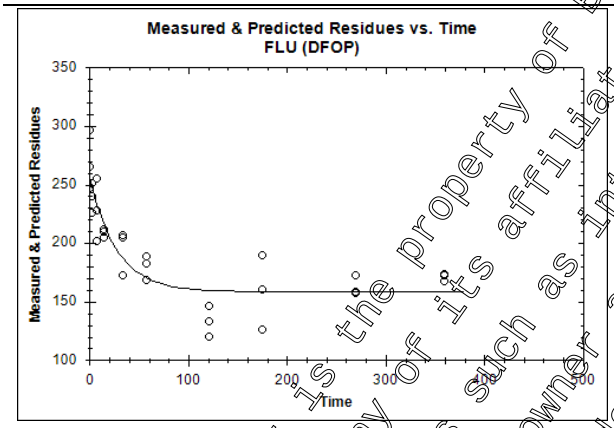
Kinetic model	DT_{50} actual	DT_{90} actual	VA	χ^2err / SWARC	k_1 / α	k_2 / β	g / t_b	t-test k_1 / k_2	95th CI of k_1	95th CI of k_2
	(d)	(d)		(%) / (-)	(1/d / -)	(1/d / d)	(- / d)	(-)	(1/d)	(1/d)
SFO	510.3	>1000	-	11.9 / 210	0.001358	-	- / -	<0.001	0.000741 to 0.002	-
DFOP	>1000	>1000	o	5.26 / 8.86	0.03688	2.5 E-12	0.3836 / 56.4	0.009 / 0.5	0.00849 to 0.065	-0.00080 to 0.001
FOMC	985.3	>1000	o	5.78 / 48.0	0.001427	1.2797	- / -	- / -	-	-
HS	**608.0**	**>1000**	o	7.85 / 52.1	0.02375	0.000570	0.2990 / 15.0	0.027 / 0.022	0.00075 to 0.047	0.00004 to 0.001

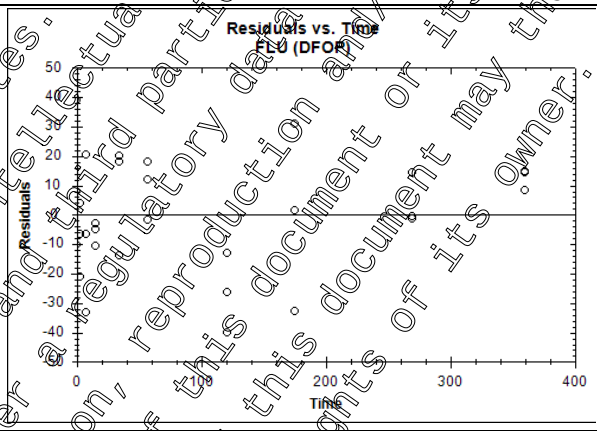
VA = visual assessment, + = good, o = acceptable, - = poor
SWARC = Scaled Weighted Area under Residue Curve
CI = confidence intervall

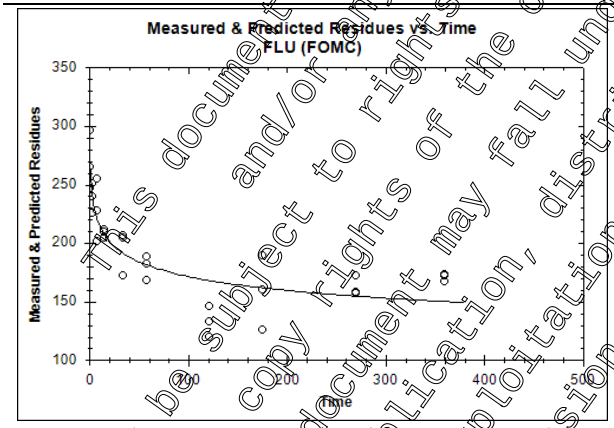
Trigger Endpoints: SFO fit is statistically (χ^2err, t-test) acceptable, but visually poor. DFOP, FOMC and HS fits were alternatively tested. For DFOP, t-test of k_{slow} failed in combination with DT_{50} and DT_{90} extrapolated beyond study duration. For FOMC, DT_{50} and DT_{90} is also extrapolated far beyond study end. Both fits are therefore not suitable, especially for accumulation assessments. HS fit is statistically (χ^2err, t-test) and visually acceptable. Consequently, **HS** model is appropriate for trigger endpoints.

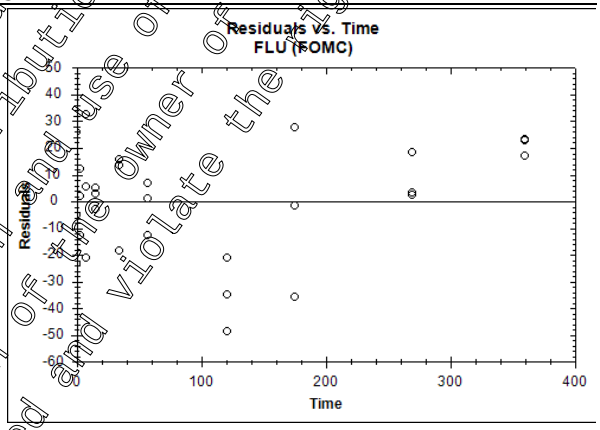


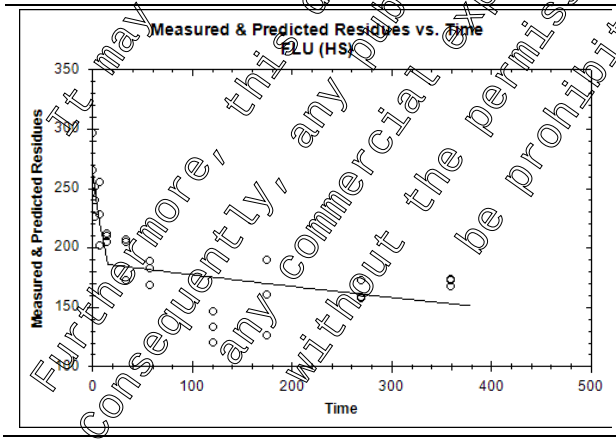












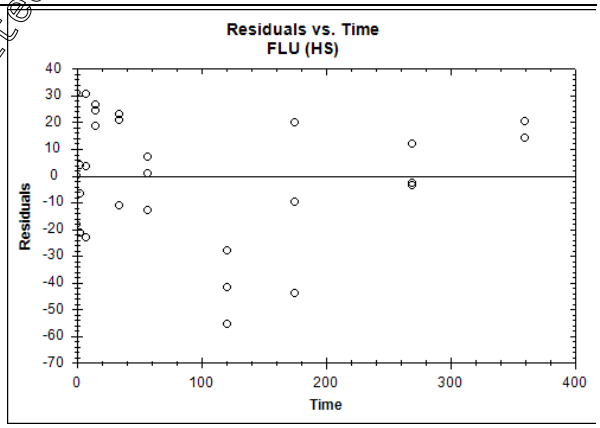
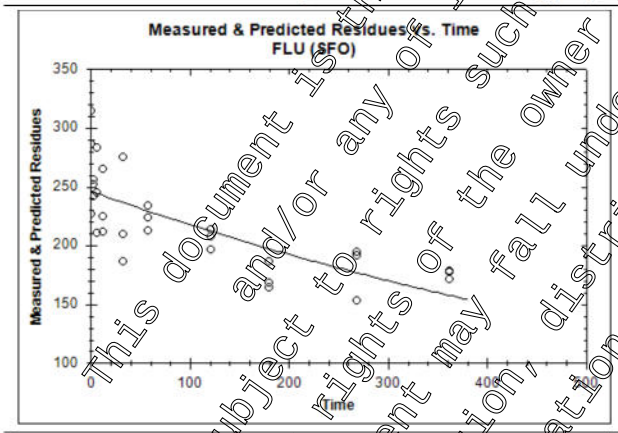


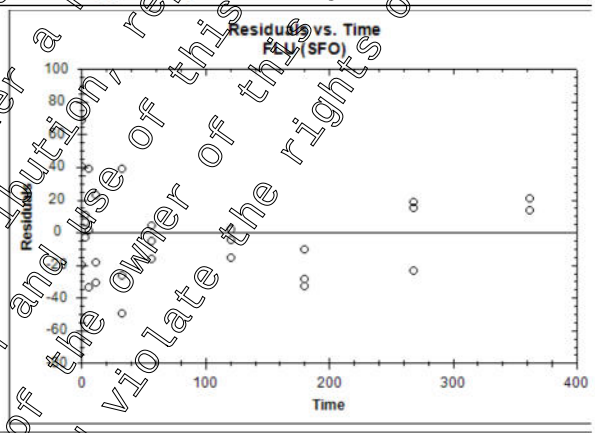
Table 7.1.2.2.1-103: Fluopyram: kinetic and statistical results of dissipation in soil Hornton, UK

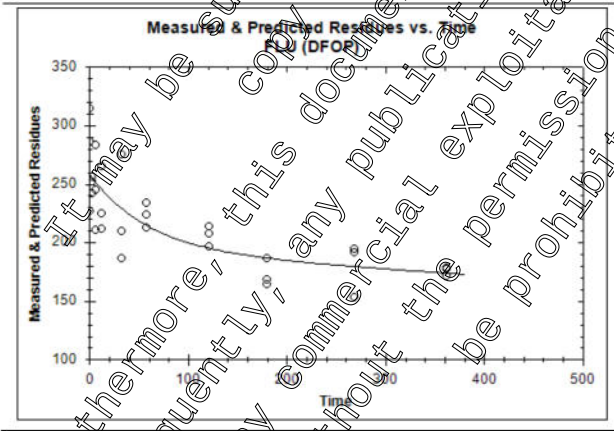
Kinetic model	DT_{50} actual	DT_{90} actual	VA	χ^2err / SWARC	k_1 / α	k_2 / β	g / t_b	t-test k_1 / k_2	95th CI of k_1	95th CI of k_2
	(d)	(d)		(% / -)	(1/d / -)	(1/d / d)	(- / d)	(-)	(1/d)	(1/d)
SFO	561.9	>1000	o	5.37 / 53.3	0.001234	-	- / -	<0.001	0.00080 to 0.002	-
DFOP	>1000	>1000	+	3.88 / 5.91	0.01726	0.000313	0.2474 / 120	0.202 / 0.356	-0.02263 to 0.055	-0.00153 to 0.002
FOMC	>1000	>1000	+	3.14 / 15.2	0.09626	4.35244	- / -	- / -	-	-
HS	**520.6**	**>1000**	o	3.79 / 7.77	0.03316	0.001028	0.1506 / 4.92	0.111 / <0.001	-0.01887 to 0.085	0.00038 to 0.001

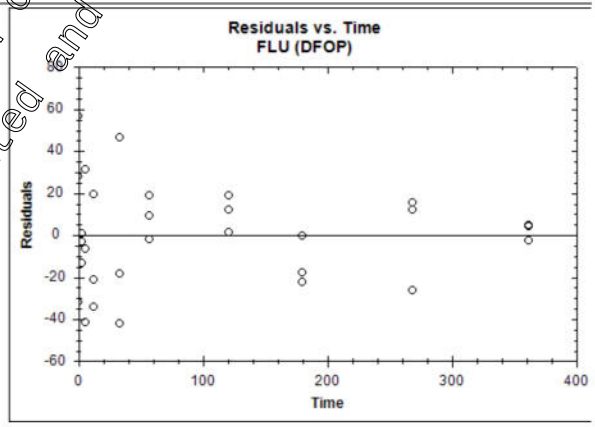
VA = visual assessment, + = good, o = acceptable, - = poor
SWARC = Scaled Weighted Area under Residue Curve
CI = confidence intervall

Trigger Endpoints: SFO fit is statistically (χ^2-err, t-test) and visually acceptable. DFOP, FOMC and HS fits were alternatively tested. For DFOP, t-test of k_{fast} and k_{slow} failed in combination with DT_{50} and DT_{90} extrapolated far beyond study end. For FOMC, DT_{50} and DT_{90} is also extrapolated far beyond study end. Both fits are therefore not suitable, especially for accumulation assessments. HS fit might be acceptable, at least k_{slow}, with a lower χ^2-err than SFO. Consequently, **HS** model is appropriate for trigger endpoints.









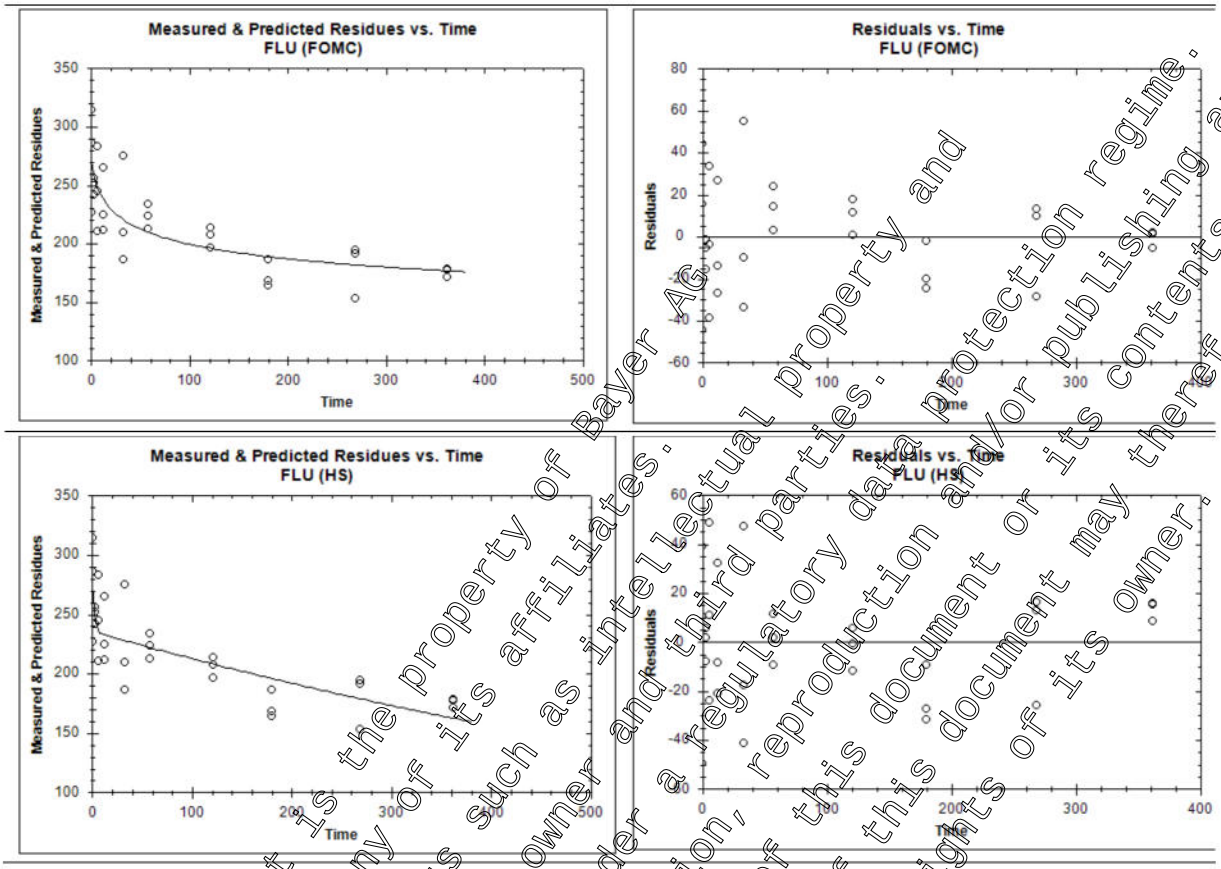
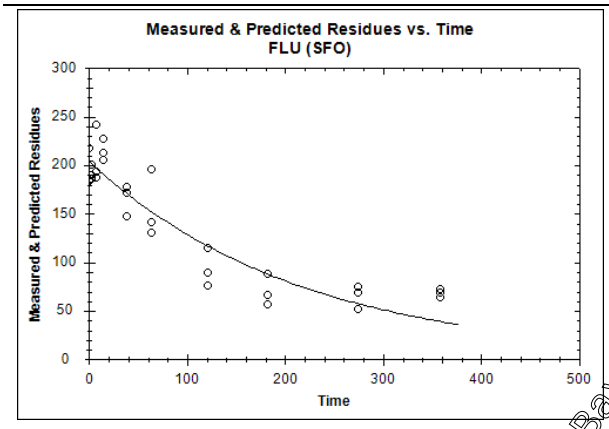


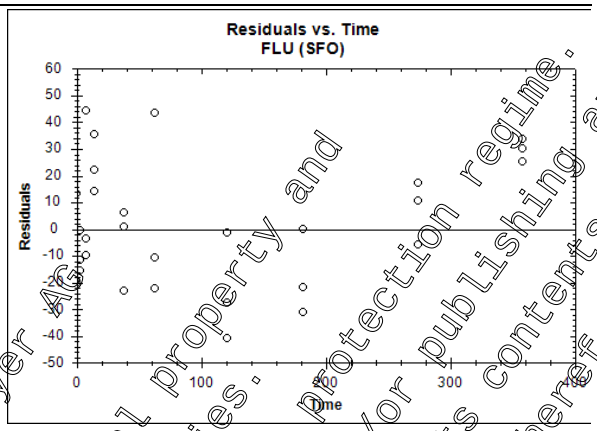
Table 7.1.2.2.1-104: Fluopyram: kinetic and statistical results of dissipation in soil Le Thour, France

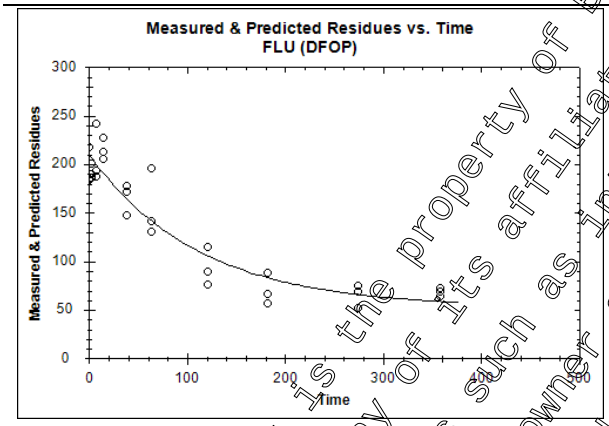
Kinetic model	DT_{50} actual	DT_{90} actual	VA	χ^2err / SWARC	k_1 / α	k_2 / β	g / t_b	t-test k_1 / k_2	95th CI of k_1	95th CI of k_2
	(d)	(d)		(% / -)	(1/d / -)	(1/d / d)	(- / d)	(-)	(1/d)	(1/d)
SFO	**150.1**	**498.6**		9.19 / 53.3	0.004618		- / -	<0.001	0.00366 to 0.006	-
DFOP	132.7	>1000	+	7.99 / 28.2	0.008992	2.3 E-14	0.7516 / 231	0.140 / 0.5	-0.00700 to 0.025	-0.01291 to 0.013
FOMC	131.6	906.8		8.35 / 35.2	1.308	188.361	- / -	- / -	-	-
HS	154.0	483.9	o	9.86 / 59.8	2.3 E-14	0.004878	- / 11.9	0.5 / <0.001	-0.02752 to 0.028	0.00369 to 0.006

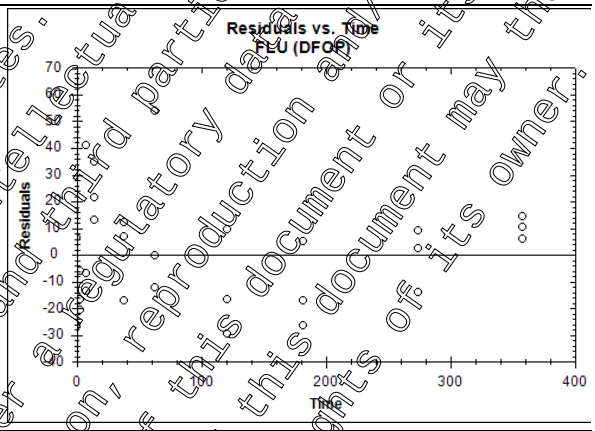
VA = visual assessment, + = good, o = acceptable, - = poor
SWARC = Scaled Weighted Area under Residue Curve
CI = confidence interval

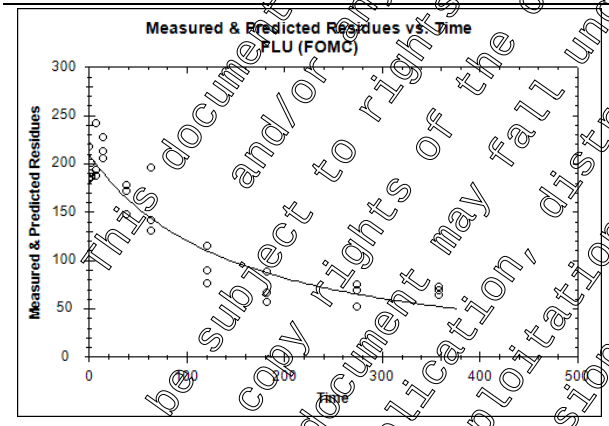
Trigger Endpoints: SFO fit is statistically (χ²-err, t-test) and visually acceptable. DFOP, FOMC and HS fits were alternatively tested.
For DFOP t-test of k_{fast} and k_{slow} failed in combination with DT_{90} extrapolated far beyond study end. For FOMC, DT_{90} is also extrapolated far beyond study end. Both fits are therefore not suitable, especially for accumulation assessments. HS fit might be acceptable (k_2), but not better than SFO. Consequently, **SFO** model is appropriate for trigger endpoints.

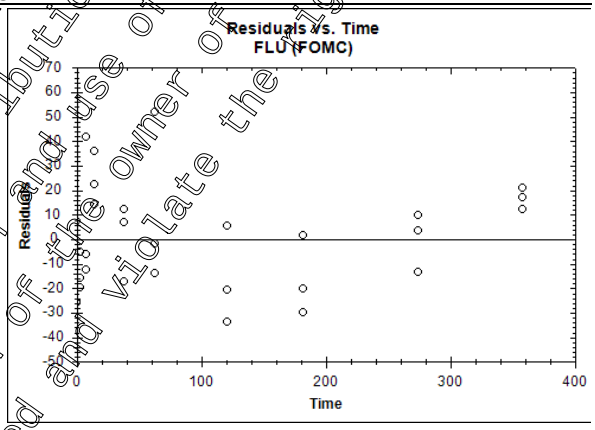


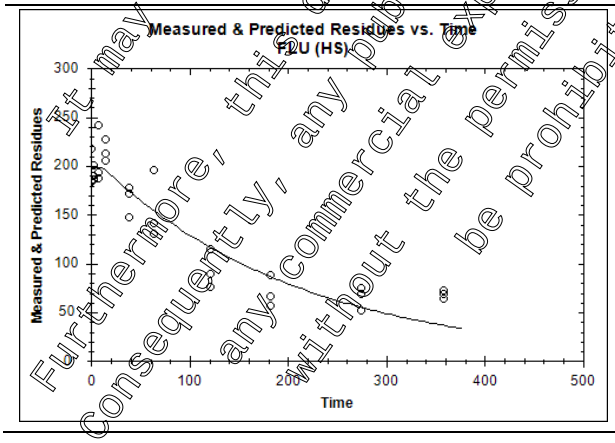












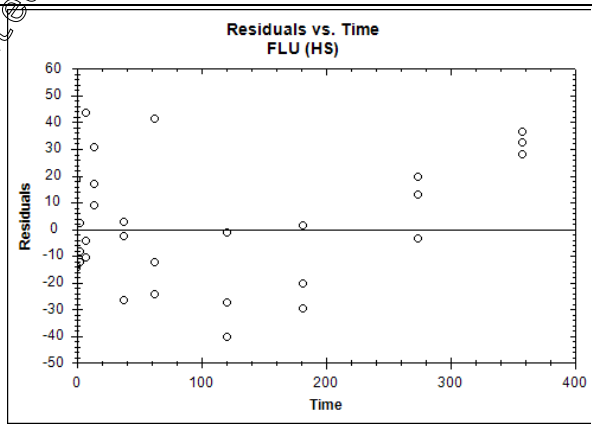
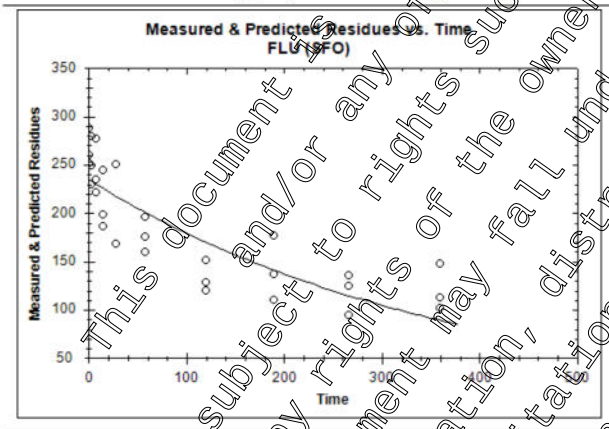


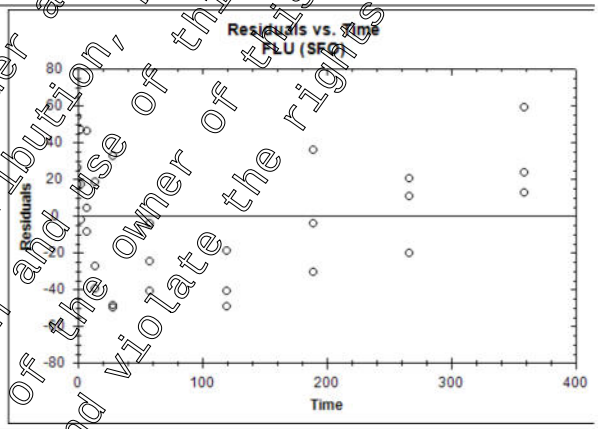
Table 7.1.2.2.1-105: Fluopyram: kinetic and statistical results of dissipation in soil Brannens, France

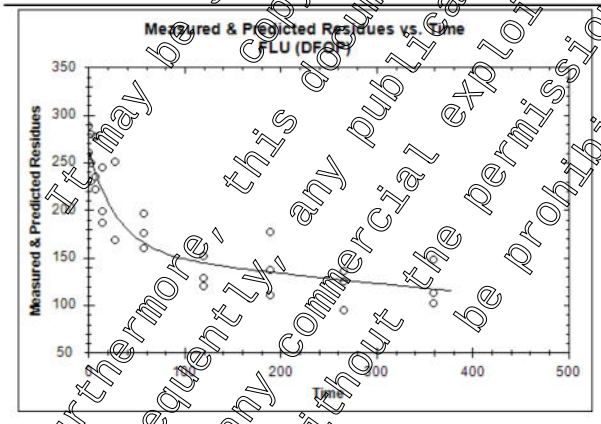
Kinetic model	DT_{50} actual	DT_{90} actual	VA	χ^2err / SWARC	k_1 / α	k_2 / β	g / t_b	t-test k_1 / k_2	95th CI of k_1	95th CI of k_2
	(d)	(d)		(% / -)	(1/d / -)	(1/d / d)	(- / d)	(-)	(1/d)	(1/d)
SFO	257.8	856.4	o	9.93 / 153	0.002689	-	- / -	<0.001	0.00191 to 0.003	-
DFOP	212.5	>1000	+	3.63 / 0.92	0.03362	0.000825	0.404 / 61.9	0.030 / 0.123	0.00015 to 0.007	-0.00054 to 0.002
FOMC	181.1	>1000	+	3.16 / 0.52	0.22815	9.11494	- / -	- / -	-	-
HS	**220.0**	**>1000**	+	4.87 / 1.38	0.01665	0.001663	0.3125 / 22.5	0.007 / 0.001	0.00421 to 0.029	0.00082 to 0.002

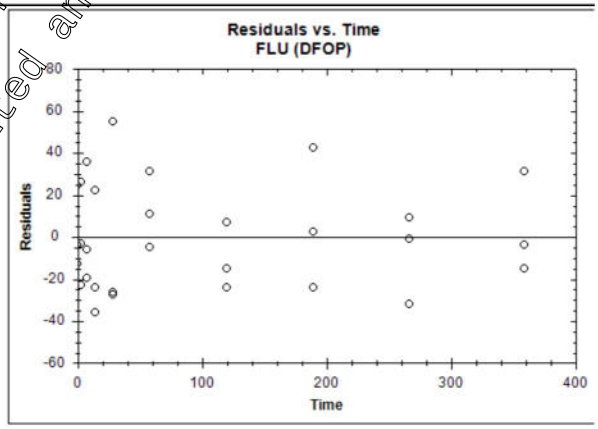
VA = visual assessment, + = good, o = acceptable, - = poor
SWARC = Scaled Weighted Area under Residue Curve
CI = confidence intervall

Trigger Endpoints: SFO fit is statistically (χ^2err, t-test) acceptable, but visually rather poor. DFOP, FOMC and HS fits were alternatively tested. For DFOP, t-test of k_{slow} failed in combination with DT_{90} extrapolated far beyond study end. For FOMC, DT_{90} is also extrapolated far beyond study end. Both fits are therefore not suitable, especially for accumulation assessments. HS fit is statistically (χ^2err, t-test) and visually good. Consequently, **HS** degradation model is appropriate for trigger endpoints.









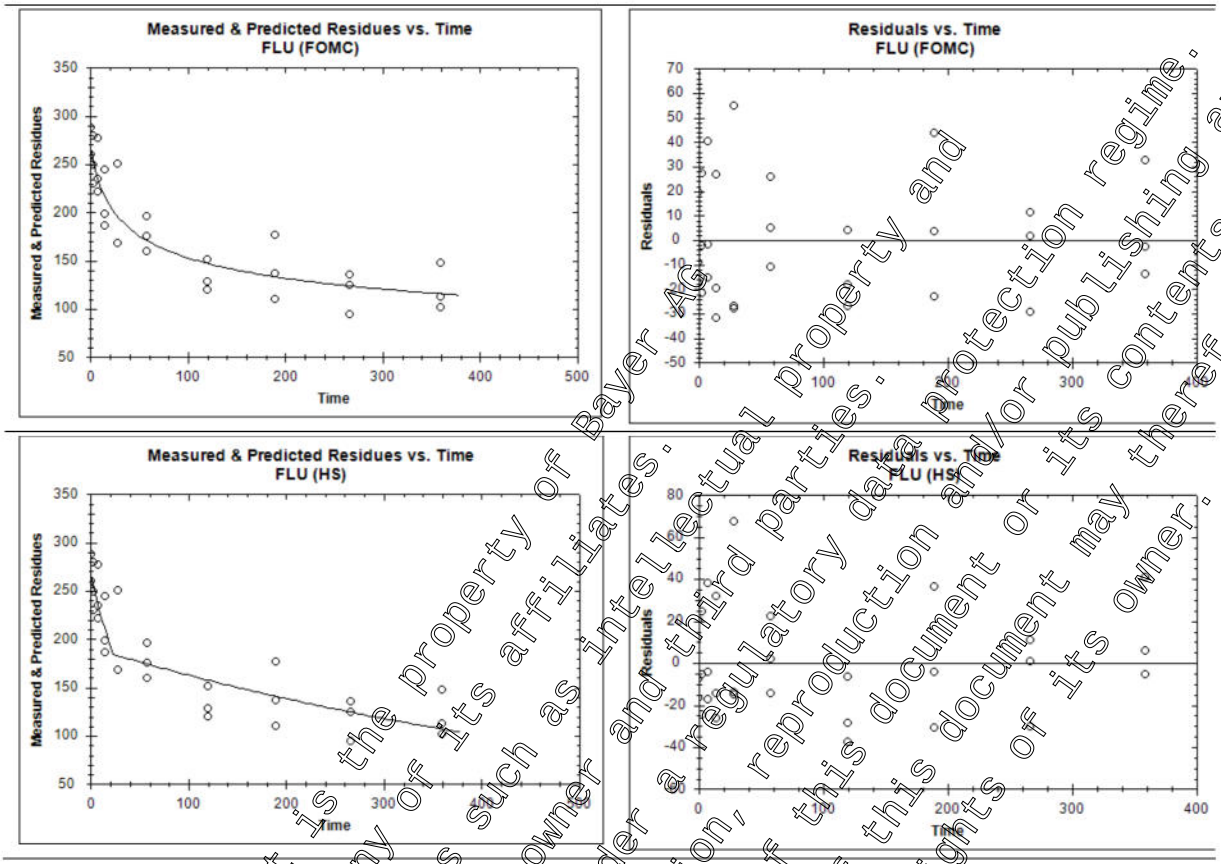


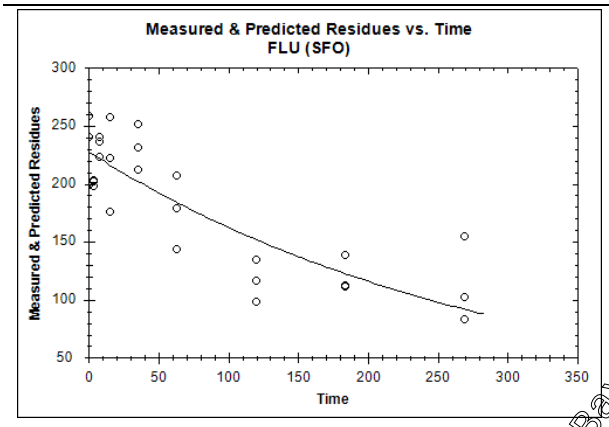
Table 7.1.2.2.1-106: Fluopyram: kinetic and statistical results of dissipation in soil Balbiano, Italy

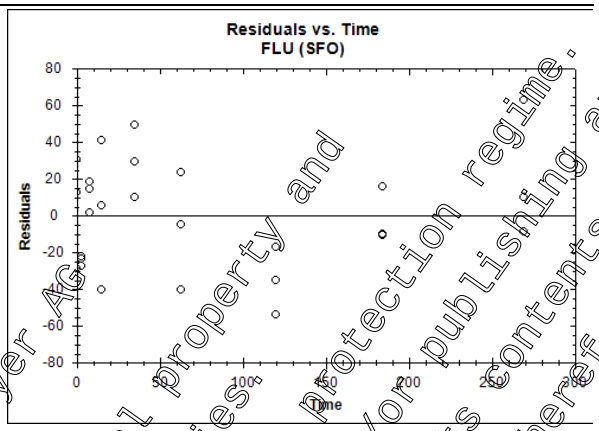
Kinetic model	DT_{50} actual	DT_{90} actual	VA	χ^2err / SWARC	k_1 / α	k_2 / β	g / t_b	t-test k_1 / k_2	95th CI of k_1	95th CI of k_2
	(d)	(d)		(%) / -)	(1/d / -)	(1/d / d)	(- / d)	(-)	(1/d)	(1/d)
SFO	**205.5**	**682.7**	o	8.52 / 21.4	0.003373	-	- / -	<0.001 / -	0.00238 to 0.004	-
DFOP	203.0	>1000	o	8.04 / 23.1	0.007981	<0.0001	0.6234 / 261	0.369 / 0.5	-0.03810 to 0.054	-0.02957 to 0.03
FOMC	205.9	>1000	o	8.55 / 21.1	0.022	212.017	- / -	- / -	-	-
HS	200.2	665.2	o	9.55 / 79.6	0.3977	0.003319	0.0286 / 0.073	<0.001 / <0.001	0.35850 to 0.436	0.00224 to 0.004

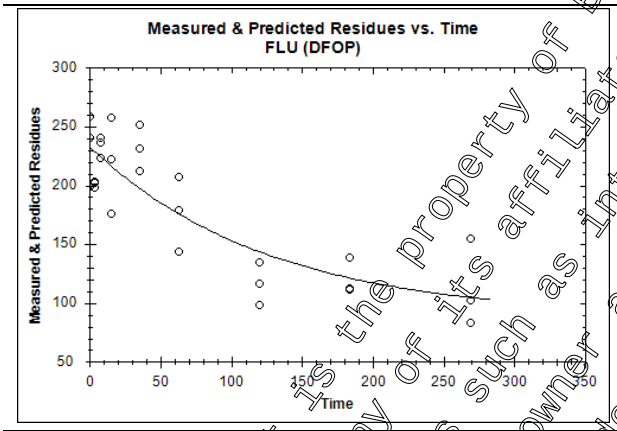
VA = visual assessment, + = good, o = acceptable, - = poor
SWARC = Scaled Weighted Area under Residue Curve
CI = confidence interval

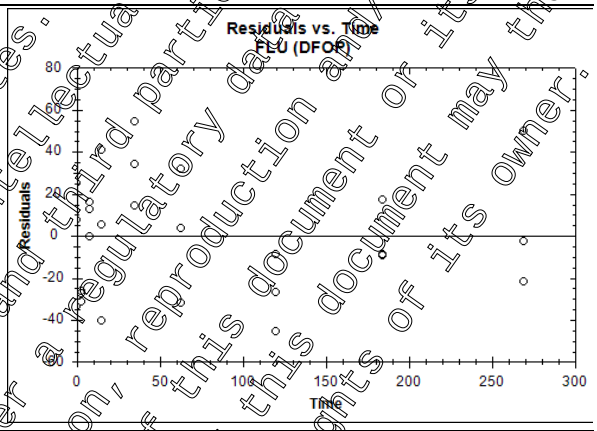
Trigger Endpoints: SFO fit is statistically (χ^2err, t-test) and visually moderately acceptable. DFOP, FOMC and HS fits were alternatively tested.

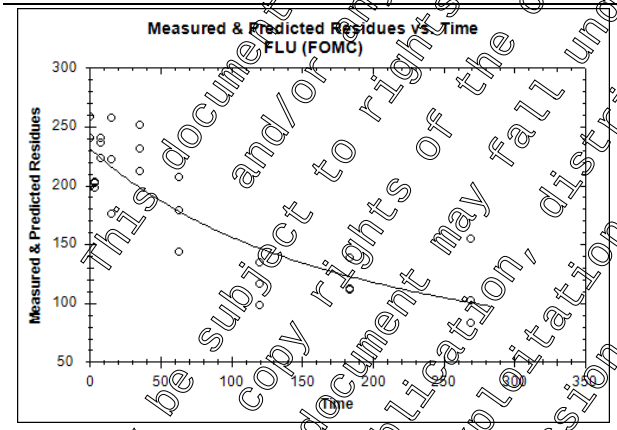
For DFOP, t-test of k_{fast} and k_{slow} failed in combination with DT_{90} extrapolated far beyond study end. For FOMC, DT_{90} is also extrapolated far beyond study end. Both fits are therefore not suitable, especially for accumulation assessments. HS fit might be acceptable (t-test), but not better than SFO (χ^2err). Consequently, **SFO** model is appropriate for trigger endpoints.

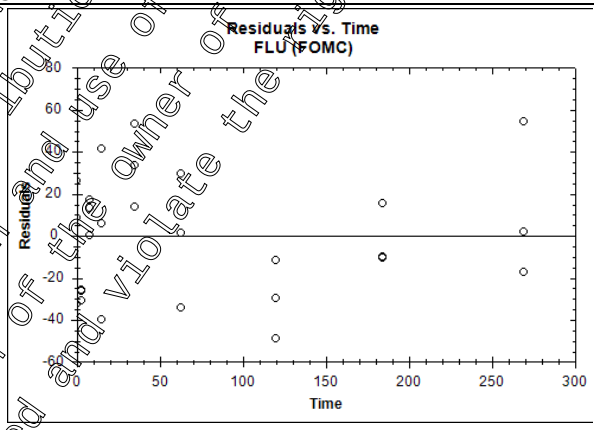


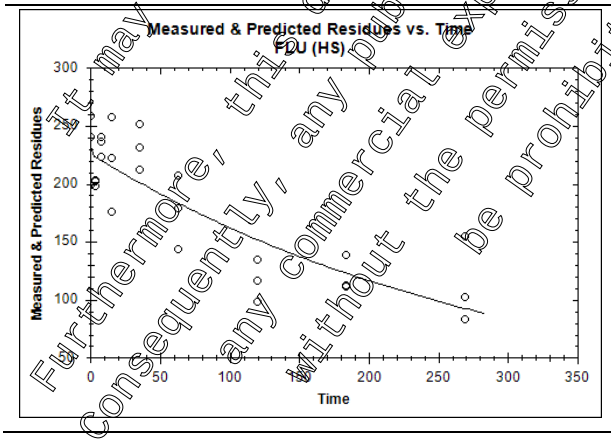












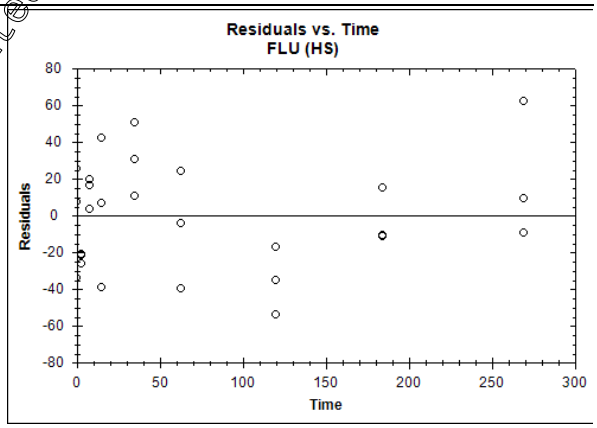
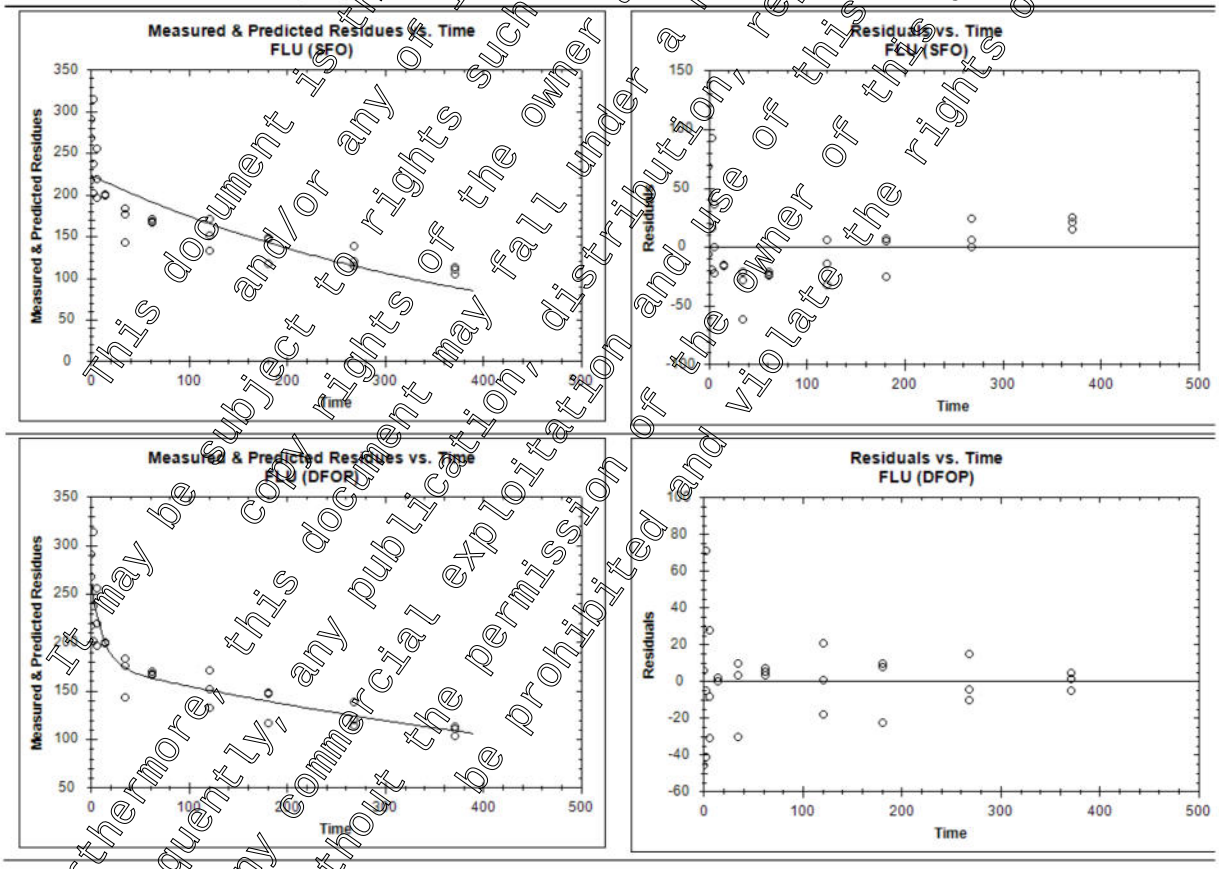


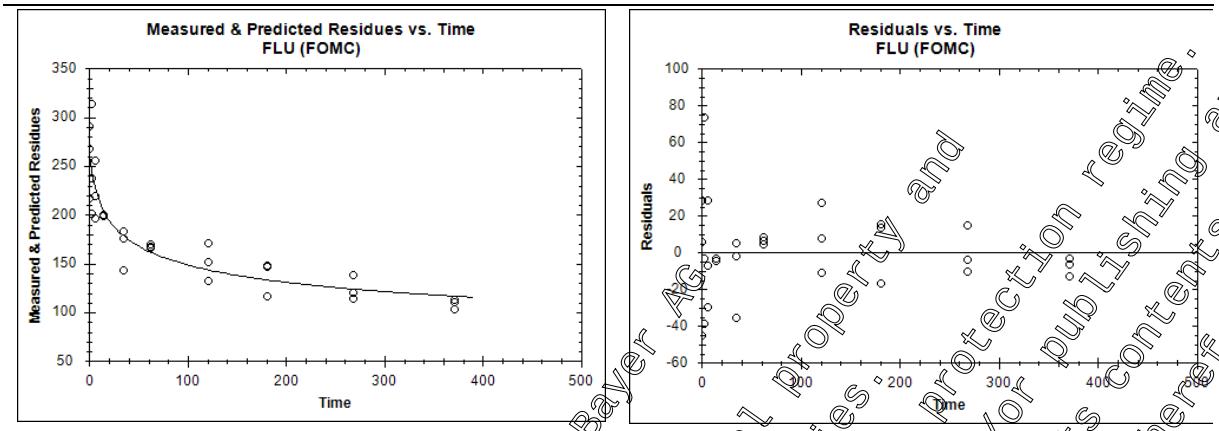
Table 7.1.2.2.1-107: Fluopyram: kinetic and statistical results of dissipation in soil Almayate East, Spain

Kinetic model	DT_{50} actual	DT_{90} actual	VA	χ^2err / SWARC	k_1 / α	k_2 / β	g / t_b	t-test k_1 / k_2	95th CI of k_1	95th CI of k_2
	(d)	(d)		(% / -)	(1/d / -)	(1/d / d)	(- / d)	(-)	(1/d)	(1/d)
SFO	278.3	924.5	o	10.1 / 113	0.002491	-	- / -	<0.001 / -	0.00173 / 0.003	-
DFOP	**225.0**	**>1000**	+	2.00 / 1.11	0.08158	0.001301	0.3300 / 2.55	0.026 / 0.002	0.003093 to 0.16	0.00050 to 0.002
FOMC	197.2	>1000	+	3.14 / 13.4	0.18921	5.18948	- / -	- / -	-	-
HS	224.3	944.8	o	9.23 / 68.1	0.09972	0.002234	0.1755 / 1.97	<0.001 / <0.001	0.05855 to 0.141	0.00150 to 0.003

VA = visual assessment, + = good, o = acceptable, - = poor
SWARC = Scaled Weighted Area under Residue Curve
CI = confidence intervall

Trigger Endpoints: SFO fit is statistically (χ^2err / t-test) and visually acceptable. DFOP, FOMC and HS fits were alternatively tested. For FOMC, DT_{90} is extrapolated beyond last sampling time. This fit is therefore not suitable, especially for accumulation assessments. Consequently, **DFOP** model is appropriate for trigger endpoints, as it shows lowest χ^2err of all suitable models (SFO, DFOP, HS).





III. CONCLUSIONS

The non-normalised trigger endpoints of field dissipation studies of fluopyram based on residue data from European soils are summarised in the table below.

Table 7.1.2.2.1-108: Fluopyram: Field dissipation endpoints for trigger purpose

Fluopyram	**Field conditions**								
Soil type (USDA) [2]	**Location**		**pH ($CaCl_2$)** [2]	**Depth (cm)**	**DT_{50} actual (d)**	**DT_{90} actual (d)**	**St. (χ^2) (%)**	**$DegT_{50}$ matrix (d) norm.** [1]	**Method of calculation**
Loamy fine sand	Hoeltinghausen, Emstek, Germany		5.56	20	608.0	>1000	7.89		HS
Silt loam	Hornton, Banbury, UK		6.11	20	520.6	>1000	3.79		HS
Silt loam	Le Theur, Ne, France		7.50	20	150.1	498.6	9.19		SFO
Sandy loam	Brannens, S-France		4.44	50	220.0	>1000	4.87		HS
Loam	Balbiano, Italy		7.20	40	205.5	682.7	8.52		SFO
Silt loam	Almayate East, Es		7.74	20	225.0	>1000	2.00		DFOP

[1] normalised using a Q10 of 2.58 and Walker equation coefficient of 0.7, values correspond with $DT_{50\ mod}$ of selected kinetic models

[2] analysed in topsoil, M-758589-01-1

3. Assessment and conclusion

Assessment and conclusion by applicant:
The kinetic evaluation followed FOCUS guidances and is considered to be valid and reliable.

Assessment and conclusion by RMS:
Outcome and conclusion of the study: RMS should indicate if they agree to the results and conclusions of the APPL.

A final kinetic evaluation will be conducted when the final report of study M-758589-01-1 is available and will be provided at the latest by end of February 2022.

Soil dissipation of TFA

For simple PECsoil calculations, with an Excel spread sheet, typically worst-case non-normalised trigger DT_{50} values are used, which should describe conservatively the dissipation of a compound in the ecotoxicological relevant layer.
For Trifluoroacetic acid (TFA), assuming a microbial default DT_{50} in soil of 1000 d would not describe adequately the very mobile TFA compound in an ecotoxicological assessment. It is expected that leaching into deeper soil layers is a significant process for dissipation in the topsoil of a field and accumulation of TFA is very unlikely.

EFSA PECsoil guidance (2017, Appendix B, equation A13) describes a leaching rate k_{leach} (1/d) which accounts for leaching processes in the soil risk assessment:

$$k_{leach} = \frac{q}{z_{eco}(\theta + \rho \cdot f_{OM} \cdot K_{OM})}$$

with
- q — mean annual downward water flow, dm/d
- z_{eco} — ecotoxicological averaging depth, e.g. 1 - 20 cm
- θ — volumetric water content at field capacity, m3/m3
- ρ — dry soil bulk density, kg/L
- f_{OM} — mass fraction of organic matter, kg/kg
- K_{OM} — Freundlich sorption coefficient on organic matter, L/kg

The mean annual downward water flow q can be estimated as follows:

$$q = f_q \cdot (p + Irr)$$

with
- f_q — ratio annual downward water flow / (precipitation + irrigation)
- p — annual mean precipitation, e.g. in mm/a
- Irr — annual mean irrigation, e.g. in mm/a

The microbial trigger degradation rate k_{deg} (TFA: default DT_{50} 1000 d) is than summed up with k_{leach} to result in an overall dissipation rate. This dissipation rate will be transformed into a dissipation $DisT_{50\ deg + leach}$ which can finally be used for simple PECsoil calculations.

EFSA PECsoil guidance predefined 3 Tier1 soil scenarios (North, Centre and South zone) for concentration in total soil (EFSA, 2017, p.14, Tab. 1). Most of the needed parameters for the equations above were used from these predefined scenarios.

Further on, EFSA defined mean values for f_q, the ratio of mean annual downward flow and precipitation, for different crops and depths of 1, 2.5, 5 and 20 cm (EFSA, 2017, Appendix B.4., Tab. B.12 - 15). In this evaluation, a mean f_q in 20 cm depth for all crops of 0.50 was found to result in a worst-case rate k_{leach} (EFSA, 2017, p. 71, Tab. B.15). The irrigation amount was conservatively assumed to be 0.

Finally, the worst case of all 3 scenarios (see table below), a **maximum $DisT_{50}$ of 50.29 d** (SEO) is considered appropriate for simple **PECsoil** simulations of TFA.

Table 7.1.2.2.1-109: Soil dissipation of TFA, for PEC soil modelling purpose (based on EFSA PECsoil guidance, 2017)

Trifluoroacetic acid (TFA)	**Soil dissipation, including degradation and leaching**			
	Unit	**North zone**	**Centre zone**	**South zone**
p, annual mean preciptiation	mm/a	639	617	667
Irr, annual mean irrigation	mm/a	0	0	0
f_q, ratio annual downward water flow / precipitation		0.5	0.5	0.5
q, mean annual downward water flow	dm/d	0.009	0.008	0.009
Z_{eco}, ecological averaging depth	cm	20	20	20
θ, volumetric water content at field capacity	m3/m3	0.244	0.244	0.349
ρ, dry soil bulk density	kg/L	0.707	0.934	1.117
f_{OM}, organic matter	kg/kg	0.22	0.122	0.07
K_{OM}, Freundlich sorption coefficient on OM, of TFA	L/kg	0	0	0
k_{leach}, rate accounting for leaching	**1/d**	0.01794	0.01732	0.01309
$DisT_{50\ deg + leach}$, DT_{50} accounting for degradation and leaching	**d**	37.20	38.48	**50.29**

CA 7.1.2.2.2 Soil accumulation studies

Data Point:	KCA 7.1.2.2.2/01
Report Author:	[redacted]
Report Year:	2007
Report Title:	1. Interim report - Determination of the residues of AE C656948 in/on soil after spraying of AE C656948 (250 SC) in Germany and France
Report No:	MEF-07/288
Document No:	M-293946-01-1
Guideline(s) followed in study:	Commission Directive 95/36/EC amending Council Directive 91/414/EEC (Annexes I and II, Fate and Behaviour in the Environment), 1995-07-14; IVA Guidance Document on Field Soil Studies (1993); SETAC Procedures for Assessing the Environmental Fate and Ecotoxicity of Pesticides (1995); BBA guideline, part IV, 4-1, Fate and Behavior of Plant Protection Compounds in Soil (1986)
Deviations from current test guideline:	Current Guideline not applicable (see justification)
Previous evaluation:	yes, evaluated and accepted DAR (2011)
GLP/Officially recognised testing facilities:	No, not conducted under GLP/Officially recognised testing facilities
Acceptability/Reliability:	No

This study was previously submitted as interim report and is superseded by the final report below (KCA 7.1.2.2.2/02, M-452925-01-1).

1. Information on the study

Data Point:	KCA 7.1.2.2.2/02
Report Author:	[redacted]
Report Year:	2013
Report Title:	Determination of the residues of AE C656948 in/on soil after spraying of AE C656948 (250 SC) and fluopyram (500 SC) in the field in Germany and France
Report No:	09-2802
Document No:	M-452925-01-1
Guideline(s) followed in study:	Commission Directive 95/36/EC amending Council Directive 91/414/EEC (Annexes II and III, Fate and Behaviour in the Environment), 1995; IVA Guidance Document on Field Soil Studies (1993); SETAC Procedures for Assessing the Environmental Fate and Ecotoxicity of Pesticides (1995); BBA guideline, part IV, 4-1, Fate and Behaviour of Plant Protection Compounds in Soil (1986); US EPA OCSPP Guideline # SUPP
Deviations from current test guideline:	Current Guideline: Guidance Document for Conducting Pesticide Terrestrial Field Dissipation Studies (2016) None
Previous evaluation:	No, not previously submitted
GLP/Officially recognised testing facilities:	Yes, conducted under GLP/Officially recognised testing facilities
Acceptability/Reliability:	Yes

2. Full summary of KCA 7.1.2.2.2/02

Executive Summary

Soil accumulation of fluopyram under European field conditions was investigated in two sites, in Monheim (Germany) and Tarascon (France).

AE C656948 250 SC or Fluopyram 500 SC were sprayed once per year with nominal application rates of 1.0 L or 0.5 L product/ha (annual application rate) and nominal water rates of 300 L/ha, corresponding to 250 g fluopyram/ha per year, over a period of 8 and 6 years for the test site in Germany and France, respectively.

Soil cores were taken 0 days before, immediately after application and at several dates up to 2702 days post-application to a maximum depth of 75 cm.

The soil cores were cut into 10 - cm soil layers and bulked soil layers were homogenized prior to analysis of fluopyram.

Soil samples of 20 g were extracted in a microwave extractor with 40 mL of a mixture of water/acetonitrile (1/4, v/v). After extraction, subsamples of the extracts were centrifuged to remove fine particles of the soil. Identification and quantitation of the analyte was done by high performance liquid chromatography (HPLC) using MS/MS detection in the Multiple Reaction Monitoring mode. Possible matrix effects were eliminated by using an internal standard solution of isotopically labelled reference item. This solution was added to the sample solutions after extraction. The limit of quantitation (LOQ) was 5.0 µg/kg and the limit of detection (LOD) was 1.5 µg/kg.

The maximum concentration of fluopyram in the 0 – 10 cm layer was 276 µg/kg (Monheim, Germany) and 237 µg/kg (Tarascon, France), respectively. The maximum concentration in the 10 – 20 cm layer was 34.6 µg/kg at the test site in Germany and 22.2 µg/kg in France, respectively. In the 20 – 30 cm layer, up to 6.4 µg/kg and 7.3 µg/kg fluopyram were determined at the Monheim and Tarascon test site, respectively. The concentrations of fluopyram in all soil samples of deeper soil layers remained below the LOQ of 5 µg/kg.

A plateau concentration of fluopyram residues was reached in soil at both sites after eight (site Monheim, Germany) or six annual applications (site Tarascon, France) at a nominal rate of 250 g/ha.

I. MATERIALS AND METHODS

A. MATERIALS

1. Test Item

Chemical Code	AE C656948 / Fluopyram
Type of Formulation	SC (Suspension Concentrate)
Content of active substance	250 g/L (2005 - 2010) / 500 g/L (2011 - 2012)
Bayer Product/Development No.	0359427
Batch number	OP250119 / 2009-002566 / 2010-008479

2. Test Sites

The study comprises two supervised field soil residue trials with grass in Monheim (Germany) and Tarascon (France). A treated and an untreated plot were used for each test site. The sites were subjected to neither erosion, flooding nor run-off. The test plots were nearly flat and not very stony. The identification, its locations and site details are presented in the following table.

Table 7.1.2.2.2- 1: Properties of the field soils

Details	09-2802-01 D-40789 Monheim, Germany			09-2802-02 F-13103 St. Etienne du Gres (Tarascon), France		
Designation	Plot 712/718			Les Cayades		
Country	Germany			France		
Ecoregion	Northern EU			Southern EU		
Plot Size (qm²)	255			360		
Site History	2002 – 2004 grass sown, no application of chemicals			2001 KH 2023 (400SC) – 48.8 mL/ha Nemacur (CS240) – 25 L/ha grass sown 2002 – 2004 grass sown, no application of chemicals		
Distance from weather station used for climatic measurements	Test location			9.5 km (temperature/rainfall) 54 km (radiation)		
Meteorological conditions compared to long-term average within normal levels (Yes/No)	Yes Temperature and rainfall: Temperatures were in part higher than the average, a high amount of precipitation was observed in 2010			Yes Temperature and rainfall: Some extreme months compared to the long-term average; especially dry summers 2005 to 2007, high amounts of precipitation observed in 2008 and 2010		
Other details, if any						
Depth compartment (cm)	0 - 30	30 - 50	50 - 75	0 - 30	30 - 50	50 - 75
Surface soil texture (USDA)	sandy loam	sandy loam	loamy sand	silt loam	silt loam	silt loam
Sand (%) [0.05 – 2.00 mm]	72.1	76.6	77	17.9	19.7	15.7
Silt (%) [0.002 – 0.05 mm]	18.0	16.1	17	62.9	59.0	64.4
Clay (%) [< 0.002 mm]	9.9	7.3	6	19.2	21.3	19.9
pH (water)	6.9	7.1	6.7	8.3	8.4	8.5
pH ($CaCl_2$)	6.3	6.3	6.4	7.5	7.6	7.7
CEC (meq/100g)	5.8	3.3	6.0	13.1	9.9	11.5
$CaCO_3$ (%)	0.1	0.1	0.2	39.4	40.2	42.2
Organic carbon (%)	0.89	0.28	0.3	0.67	0.57	0.41
WHC max (g/100 g)	38.4	33.6	n.d.	41.6	43.8	39.9
WHC pF 2 (vol%)	22.0	18.6	12.2	32.6	33.0	41.8

B. STUDY DESIGN

1. Experimental Conditions

AE C656948 250 SC or Fluopyram 500 SC were sprayed once per year with nominal application rates of 1.0 L or 0.5 L product/ha (annual application rate) and nominal water rates of 300 L/ha, corresponding to 250 g fluopyram/ha per year. The product was applied according to the local application practice on harrowed and levelled bare soil with grass sown prior to application.

Considering the application rate of 250 g/ha fluopyram and assuming a soil density of 1.5 kg/L, the fluopyram concentration in the upper soil layer (0 – 10 cm) would be 167 µg/kg soil after a single application in one year. Without any degradation this would lead to a concentration of 1336 µg/kg after

8 consecutive annual applications (site Monheim) or 1002 µg/kg after 6 consecutive annual applications (site Tarascon).

Air temperature, precipitation including irrigation, and sunshine data were recorded from weather stations located at or nearby each test site. The soil cultivation and the agronomic and maintenance activities on the trial plots were conducted according to the usual local agricultural practice and had no influence on the conduct or results of these trials. Before application the soil was prepared to have a fine crumb structure and grass was sown as a model crop.

Soil accumulation of fluopyram was studied for up to 2702 days.

The plots received no rainfall within 24 h after the application, with exception of application six (1 mm rainfall at Monheim, 14 mm rainfall at Tarascon).

Table 7.1.2.2.2- 2: Data on the Application Equipment

Trial No.	Device	Nozzle Type	Working Width (m)	No. of Nozzles	Pressure (bar)
Monheim 09-2808-01, VG08	Knapsack-sprayer Spraying boom	Lurmark 03	1.5	3	2
		Teejet 03	1.5	3	2
Tarascon 09-2802-02, FR08	Knapsack-sprayer Spraying boom	Teejet XR 800 15 VS	2	8	2.6

2. Sampling

All samplings were performed with a "Wacker Hammer" (Ø 48 to 50 mm). Samples were taken to a maximum depth of 50 cm until 2009 and up to a depth of 75 cm staring with samplings in 2010. At each occasion 20 cores from treated and 10 cores from the control plots were taken randomly over the area to obtain representative samples. Soil samples were taken three times per year according the following intervals: before application (end of winter), after application and before winter dormancy. Sampling at the Germany plot was performed on 0 (before and after application), 194, 353, 354, 565, 710, 711, 914, 1082 (before and after application), 1284, 1460 (before and after application), 1665, 1797, 1804, 2021, 2161, 2176, 2390, 2524, 2526 and 2702 days after the 1st application. Sampling at the French plot was performed on 0 (before and after application), 215, 334, 335, 570, 697, 698, 913, 1062, 1063, 1293, 1426, 1427, 1665, 1795, 1797, 2015 and 2153 days after 1st application.

Samples from the untreated control were taken at days 0, 353, 710, 1082, 1460, 1797, 2161 and 2524 at the German plot and at days 0, 334, 697, 1062, 1426, 1795 and 2153 at the French plot.

In addition, samples for soil characterisation were taken on day 0 before and day 3 after 1st application from the treated plots to a depth of 50 cm.

The samples from both trials were deep-frozen within 24 hours and stored at – 18 °C or below until dispatch with deep-freeze lorry to the Laboratory for Sampling, Preparation Technique and Sample Logistics (PVTL), Bayer CropScience AG, in Monheim, Germany. The cores from the frozen field samples were cut into 10 cm segments. The control samples or the treated samples of each horizon separately (laboratory samples) were milled in a hammer mill and carefully homogenised. A portion of each of the homogenised laboratory samples was transferred into polystyrene boxes (analytical samples) and stored at or below – 18 °C, either in the cold storage depot or in a freezer at the analytical laboratory until analysis.

A storage stability study was performed to determine the effect of frozen storage on residues of fluopyram in two representative soil types (KCA 7.1.2.2.1/12, M-348402-01-1). According to the results of this study fluopyram is stable for at least 864 days of storage under frozen conditions. The maximum period between soil sampling and analysis was 594 days, therefore the storage stability was covered.

3. Analytical Procedures

The moisture of the soil samples was measured using a moisture analyser Sartorius MA50. Soil samples of 20 g were extracted in a microwave extractor with 40 mL of a mixture of water/acetonitrile (1/4, v/v). After extraction, subsamples of the extracts were centrifuged to remove fine particles of the soil. Identification and quantitation of the analyte was done by high performance liquid chromatography (HPLC) using MS/MS detection in the Multiple Reaction Monitoring mode. Possible matrix effects were eliminated by using an internal standard solution of isotopically labelled reference item. This solution was added to the sample solutions after extraction.

The analytical method used for fluopyram is BCS Method No. 00973 (M-265498-01-1). The method was validated with a silt loam soil (Hoefchen) and a sandy loam soil (Laacher Hof). The mass spectrometric detector showed linear correlation between concentration and peak area ratio in the range of about 1.0 to 120 µg/L with a correlation coefficient of 0.99985 (1/x weighted). The overall mean recovery of the method was 101 % for fluopyram with a relative standard deviation (RSD) of 2.2 %. The LOQ of the method is 5.0 µg/kg for fluopyram. The LOD of the method is 1.5 µg/kg for fluopyram. The blank values in all control samples were below 1.5 µg/kg (<1/3 x LOQ).

Full details and acceptable validation data to support the analytical method are presented within document M-CA 4, which comply with the EU regulatory requirements outlined within SANTE/2020/12830, Rev.1.

II. RESULTS AND DISCUSSION

A. DATA

The measured initial mean concentration for fluopyram were 135 µg/kg (Monheim) and 143 µg/kg (Tarascon), representing 81 and 86 % of the intended concentration (167 µg/kg considering distribution in top 10 cm of soils and assuming soil density of 1.5 kg/L). These deviations are considered to be acceptable since soil concentrations can vary considerably due to several uncertainties related to the first samplings after application.

Table 7.1.2.2.2- 3: Analytical results of fluopyram, values in entire soil profiles at Monheim (0 - 75 cm) [µg/kg]

09-2808-01		Fluopyram (µg/kg)							
Layer (cm)	Replicate	DAT (d)							
		0[1]	0	194	353	354	565	710	714
0 – 10	A	0.00	137	39.8	37.9	142	70.2	81.2	228
	B	0.00	133	40.1	38.2	150	68.2	80.6	228
	Mean	0.00	135	39.9	38.0	146	69.2	80.9	228
10 -20	A	0.00	2.73[2]	0.75[3]	0.75[3]	3.88[2]	2.40[2]	4.19[2]	5.01
	B	0.00	2.34[2]	0.75[3]	0.75[3]	2.72[2]	2.37[2]	3.96[2]	4.63[2]
	Mean	0.00	2.53[2]	0.75[3]	0.75[3]	3.30[2]	2.38[2]	4.08[2]	4.82[2]
20 -30	A	0.00	0.00	0.00	0.00	0.75[3]	0.75[3]	0.75[3]	0.75[3]
	B	0.00	0.00	0.00	0.00	0.75[3]	0.75[3]	0.75[3]	0.75[3]
	Mean	0.00	0.00	0.00	0.00	0.75[3]	0.75[3]	0.75[3]	0.75[3]
30 -40	A	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	B	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	Mean	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
40 - 50	A	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	B	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	Mean	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
50 - 60	A	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	B	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	Mean	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
60 - 75	A	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	B	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	Mean	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Layer (cm)	Replicate	DAT (d)							
		914	1082	1082.1	1284	1460	1460.1	1665	1797
0 – 10	A	109	91.7	243	121	117	251	130	163
	B	106	91.1	242	118	117	255	132	159
	Mean	108	91.4	243	120	117	253	131	161
10 -20	A	10.4	14.3	18.4	12.1	27.2	23.0	18.9	34.6
	B	10.7	14.2	18.8	11.9	25.2	22.1	18.5	34.7
	Mean	10.5	14.2	18.6	12.0	26.2	22.5	18.7	34.6
20 -30	A	0.75[3]	0.75[3]	2.88[2]	0.75[3]	2.99[2]	2.64[2]	2.62[2]	4.02[2]
	B	0.75[3]	0.75[3]	2.90[2]	0.75[3]	3.19[2]	2.56[2]	2.63[2]	4.23[2]
	Mean	0.75[3]	0.75[3]	2.89[2]	0.75[3]	3.09[2]	2.60[2]	2.62[2]	4.13[2]
30 -40	A	0.00	0.00	0.75[3]	0.00	0.75[3]	0.75[3]	0.75[3]	0.75[3]
	B	0.00	2.02[2]	0.75[3]	0.00	0.75[3]	0.75[3]	1.69[2]	0.75[3]
	Mean	0.00	1.01[2]	0.75[3]	0.00	0.75[3]	0.75[3]	1.22[2]	0.75[3]
40 - 50	A	0.00	0.00	0.00	0.00	0.00	2.94[2]	2.41[2]	0.00
	B	0.00	0.00	0.00	0.00	0.00	3.13[2]	2.32[2]	0.00
	Mean	0.00	0.00	0.00	0.00	0.00	3.04[2]	2.36[2]	0.00
50 - 60	A	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	1.85[2]	0.00
	B	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	1.87[2]	0.00
	Mean	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	1.86[2]	0.00

Layer (cm)	Replicate	DAT (d)							
		914	1082	1082.1	1284	1460	1460.1	1665	1797
60 - 75	A	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.75[3]	0.00
	B	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.75[3]	0.00
	Mean	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.75[3]	0.00
Layer (cm)	**Replicate**	**DAT (d)**							
		1804	**2021**	**2161**	**2176**	**2390**	**2524**	**2526**	**2702**
0 – 10	A	281	162	142	241	137	128	244	142
	B	271	165	141	230	137	128	268	143
	Mean	276	163	141	235	137	128	256	143
10 -20	A	33.7	23.6	27.6	28.5	29.7	31.6	28.2	29.0
	B	34.2	23.9	27.7	31.3	31.7	32.0	28.2	28.3
	Mean	33.9	23.8	27.6	29.9	30.7	31.8	28.2	28.6
20 -30	A	6.22	2.74[2]	3.93[2]	4.81[2]	6.50	4.58[2]	3.77[2]	5.68
	B	6.50	2.66[2]	3.94[2]	4.64[2]	6.09	4.58[2]	3.68[2]	5.75
	Mean	6.36	2.70[2]	3.94[2]	4.72[2]	6.29	4.58[2]	3.73[2]	5.70
30 -40	A	2.07[2]	0.75[3]	0.75[3]	0.75[3]	1.80[2]	0.75[3]	1.95[2]	2.35[2]
	B	2.16[2]	0.75[3]	0.75[3]	0.75[3]	0.75[3]	0.75[3]	1.83[2]	2.28[2]
	Mean	2.11[2]	0.75[3]	0.75[3]	0.75[3]	1.28[2]	0.75[3]	1.89[2]	2.32[2]
40 - 50	A	2.01[2]	0.00	0.00	0.00	0.75[3]	0.00	0.75[3]	0.75[2]
	B	2.03[2]	0.00	0.00	0.00	0.75[3]	0.00	0.75[3]	0.75[3]
	Mean	2.02[2]	0.00	0.00	0.00	0.75[3]	0.00	0.75[3]	0.75[3]
50 - 60	A	0.75[3]	0.00	0.00	0.00	1.93[2]	0.00	0.75[3]	0.00
	B	0.75[3]	0.00	0.00	0.00	1.68[2]	0.00	0.75[3]	0.00
	Mean	0.75[3]	0.00	0.00	0.00	1.80[2]	0.00	0.75[3]	0.00
60 - 75	A	0.00	0.00	0.00	0.00	0.75[3]	0.00	2.04[2]	0.00
	B	0.00	0.00	0.00	0.00	0.75[3]	0.00	1.95[2]	0.00
	Mean	0.00	0.00	0.00	0.00	0.75[3]	0.00	2.00[2]	0.00

[1] Before treatment
[2] Values < LOQ (5.0 µg/kg)
[3] Values of 0.75 µg/kg have been added in case of values < LOD, based on 0.5 LOD (1.5 µg/kg), according to requirements of FOCUS kinetics

Table 7.1.2.2.2- 4: Analytical results of fluopyram, values in entire soil profiles at Tarascon (0-75 cm) [µg/kg]

09-2802-02		Fluopyram (µg/kg)							
Layer (cm) /	Replicate	DAT (d)							
		0[1]	0	215	334	335	570	697	698
0 – 10	A	0.00	142	72.6	69.7	177	99.1	98.2	233
	B	0.00	144	70.4	71.0	181	101	93.2	241
	Mean	0.00	143	71.5	70.3	179	99.8	95.7	237
10 -20	A	0.00	0.00	2.42[2]	5.91	5.06	6.72	13.1	9.35
	B	0.00	0.00	5.18	6.02	4.75[2]	6.83	13.6	9.89
	Mean	0.00	0.00	3.80[2]	5.96	4.90[2]	6.78	13.4	9.62
20 -30	A	0.00	0.00	0.75[3]	0.75[3]	2.26[2]	0.75[3]	0.75[3]	2.75[2]
	B	0.00	0.00	0.75[3]	0.75[3]	2.23[2]	0.75[3]	0.75[3]	2.76[2]
	Mean	0.00	0.00	0.75[3]	0.75[3]	2.24[2]	0.75[3]	0.75[3]	2.76[2]
30 -40	A	0.00	0.00	0.00	0.00	0.75[2]	0.00	0.00	0.75[2]
	B	0.00	0.00	0.00	0.00	0.75[2]	0.00	0.00	0.75[2]
	Mean	0.00	0.00	0.00	0.00	0.75[2]	0.00	0.00	0.75[2]
40 - 50	A	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	B	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	Mean	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
50 - 60	A	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	B	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	Mean	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
60 - 75	A	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	B	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	Mean	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Layer (cm)	Replicate	DAT (d)							
		913	1062	1063	1293	1426	1427	1655	1795
0 – 10	A	131	142	223	119	105	191	82.3	95.0
	B	130	136	238	116	101	191	82.7	96.2
	Mean	131	139	230	118	103	191	82.5	95.6
10 -20	A	2.36[2]	7.64	9.52	11.0	15.4	14.3	9.80	14.8
	B	2.47[2]	8.00	10.2	11.1	14.6	12.3	10.4	14.9
	Mean	2.40[2]	7.82	9.88	11.0	15.0	13.3	10.1	14.9
20 -30	A	0.75[3]	2.64[2]	3.31[2]	3.12[2]	4.67[2]	5.42	3.23[2]	4.16[2]
	B	0.75[3]	2.61[2]	3.61[2]	3.15[2]	4.45[2]	6.15	3.04[2]	3.96[2]
	Mean	0.75[3]	2.62[2]	3.46[2]	3.13[2]	4.56[2]	5.78	3.14[2]	4.06[2]
30 -40	A	0.00	0.75[3]	1.94[2]	0.75[3]	0.75[3]	3.46[2]	0.75[3]	0.75[3]
	B	0.00	0.75[3]	2.05[2]	0.75[3]	0.75[3]	3.30[2]	0.75[3]	0.75[3]
	Mean	0.00	0.75[3]	2.00[2]	0.75[3]	0.75[3]	3.38[2]	0.75[3]	0.75[3]
40 - 50	A	0.00	0.00	2.14[2]	0.00	0.00	2.52[2]	0.00	0.00
	B	0.00	0.00	1.99[2]	0.00	0.00	2.31[2]	0.00	0.00
	Mean	0.00	0.00	2.06[2]	0.00	0.00	2.41[2]	0.00	0.00
50 - 60	A	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.00	0.00
	B	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.00	0.00
	Mean	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.00	0.00

Layer (cm)	Replicate	DAT (d)							
		913	1062	1063	1293	1426	1427	1655	1795
60 - 75	A	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.00	0.00
	B	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.00	0.00
	Mean	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.00	0.00

Layer (cm)	Replicate	DAT (d)		
		1797	2015	2153
0 – 10	A	206	103	72.9
	B	233	107	72.8
	Mean	220	105	72.8
10 -20	A	21.1	21.5	17.3
	B	23.2	21.0	16.9
	Mean	22.2	21.2	17.1
20 -30	A	6.42	7.18	6.72
	B	6.19	7.38	6.42
	Mean	6.30	7.28	6.57
30 -40	A	2.21[2]	0.75[3]	0.75[3]
	B	1.98[2]	1.81[2]	0.75[3]
	Mean	2.09[2]	1.28[2]	0.75[3]
40 - 50	A	0.75[3]	0.00	0.00
	B	0.75[3]	0.00	0.00
	Mean	0.75[3]	0.00	0.00
50 - 60	A	0.00	0.00	0.00
	B	0.00	0.00	0.00
	Mean	0.00	0.00	0.00
60 - 75	A	0.00	0.00	0.00
	B	0.00	0.00	0.00
	Mean	0.00	0.00	0.00

[1] Before treatment
[2] Values < LOQ (5.0 µg/kg)
[3] Values of 0.75 µg/kg have been added in case of values < LOD, based on 0.5 LOD (1.5 µg/kg), according to requirements of FOCUS kinetics

B. METEOROLOGICAL DATA

The temperature throughout the study represent typical conditions for the trial sites for the years 2005 to 2011/2012 compared to the long-term average. In Germany the temperatures were in part higher than the average, whilst the overall precipitation was normal in Germany. In southern France, the years 2005 to 2007 were dry compared to the long-term average while precipitation was higher than values for the long-term average in 2008 and 2010.

C. RESIDUES

The results (in µg/kg) obtained for treated soil samples are summarised in Table 7.1.2.2.2- 3 and Table 7.1.2.2.2- 4. The results are based on the dry weight of the sample material and are not corrected with respect to the recovery rates.

The maximum concentration of fluopyram in the 0 – 10 cm layer was 276 µg/kg (Monheim, Germany) after 1804 days and 237 µg/kg after 698 days (Tarascon, France), respectively. The maximum concentration in the 10 – 20 cm layer was 34.6 µg/kg at the test site in Germany and 22.2 µg/kg in France, respectively. In the 20 – 30 cm layer, up to 6.4 µg/kg and 7.3 µg/kg fluopyram were determined at the Monheim and Tarascon test site, respectively. The concentrations of fluopyram in all soil samples of deeper soil layers remained below the LOQ of 5 µg/kg.

III. CONCLUSIONS

The total residue of fluopyram in soil following annual treatment for eight or six years, was degraded to 13.5 % at the Monheim site in Germany, and to 13.4 % at the Tarascon site in France when being compared to the nominal applied amount of 1336 and 1002 µg/kg, respectively.

A plateau concentration was reached for fluopyram residues in soil at both sites after eight (site Monheim, Germany) or six annual applications (site Tarascon, France) at a nominal rate of 250 g/ha.

3. Assessment and conclusion

Assessment and conclusion by applicant: The study is considered to be valid and reliable.

Assessment and conclusion by RMS: Outcome and conclusion of the study: RMS should indicate if they agree to the results and conclusions of the APPL.

CA 7.1.3 Adsorption and desorption in soil

CA 7.1.3.1 Adsorption and desorption

Overall summary of adsorption data for the active substance

The Freundlich adsorption coefficients of fluopyram derived from the batch equilibrium adsorption studies ranged from 1.45 mL/g to 6.83 mL/g (geometric mean: 3.33 mL/g). The respective $K_{oc(ads)}$ values were in the range of 156 mL/g to 400 mL/g (geometric mean: 232 mL/g) and respective Freundlich exponents 1/n ranged from 0.73 to 0.92 (arithmetic mean: 0.84). There was no significant correlation between pH and adsorption properties for the investigated soils.

Table 7.1.3.1- 1: Soil adsorption parameters of fluopyram

Parent							
Soil Type	**OC %**	**Soil pH[1]**	**K_d (mL/g)**	**K_{doc} (mL/g)**	**K_F (mL/g)**	**K_{Foc} (mL/g)**	**1/n**
Laacherhof AXXa, sandy loam	1.3	6.0	-	-	3.031	233.2	0.7645
Laacherhof Wurmwiese, loam	2.1	5.4	-	-	4.839	233.8	0.8492
Hoefchen a. Hohenseh, silt loam	2.6	6.1	-	-	6.825	260.5	0.8376
Pikeville Pik, loamy sand	1.1	5.0	-	-	2.941	267.4	0.8463
Stanley, Stilwell SSC, clay loam	1.1	5.4	-	-	4.396	399.6	0.8367
Little Oliver, sandy loam	1.5	5.5	-	-	3.991	266.1	0.8793
Auchy-les-Mines, silt loam	2.0	7.5	-	-	3.702	185.1	0.7321
Urbanowice, silt loam	1.1	4.9	-	-	2.522	229.3	0.8578
Charles River Farm, clay	1.6	7.7	-	-	2.519	157.4	0.8363
Sindos, loam	1.3	7.2	-	-	2.474	190.3	0.8548
Paradiso San Zenone, sandy loam	1.2	5.4	-	-	1.872	156.0	0.8260
Hoeltinghausen, sand	0.9	4.5	-	-	2.881	320.1	0.9179
Hornton, loam	2.1	5.9	-	-	5.126	244.1	0.8673
Le Thour, silt loam	2.8	7.4	-	-	5.109	182.5	0.8868
Brannens, sandy loam	0.6	4.7	-	-	1.452	242.0	0.8944
Balbiano, sandy loam	1.7	7.1	-	-	3.639	214.1	0.8392
Almayate, loam	1.2	7.7	-	-	3.340	278.3	0.8083
Geometric mean (if not pH dependent)					3.327	232.1	
Arithmetic mean (if not pH dependent)							0.8432
pH dependence			No				

[1] Measured in calcium chloride solution

Overall summary of adsorption data for degradation product fluopyram-7-hydroxy

Batch equilibrium tests with the degradation product fluopyram-7-hydroxy indicated soil adsorption coefficients of 0.99 mL/g to 2.39 mL/g (geometric mean: 1.44 mL/g). The respective $K_{oc(ads)}$ values were in the range of 85 mL/g and 149 mL/g (geometric mean: 100 mL/g). The Freundlich exponents 1/n were in the range of 0.91 to 0.94 (arithmetic mean: 0.93), indicating that the concentration of fluopyram-7-hydroxy affected the adsorption behaviour. The desorption constants $K_{F(des)}$ were approximately 3 times higher than the respective adsorption constants, demonstrating a strengthened binding of fluopyram-7-hydroxy once adsorbed to the soil. For fluopyram-7-hydroxy there was no significant correlation between pH and adsorption properties for the investigated soils as well.

Table 7.1.3.1- 2: Soil adsorption parameters of fluopyram-7-hydroxy

Fluopyram-7-hydroxy							
Soil Type	**OC %**	**Soil pH[1]**	**K_d (mL/g)**	**K_{doc} (mL/g)**	**K_F (mL/g)**	**K_{Foc} (mL/g)**	**1/n**
Laacherhof AIIIa, loam	1.1	6.4			0.991	90.1	0.9241
Laacherhof AXXa, sandy loam	1.5	6.1			1.321	88.1	0.9391
Hoefchen a. Hohenseh, silt loam	1.6	6.6			2.390	149.4	0.9104
Laacherhof Wurmwiese, sandy loam	1.6	5.1			1.362	85.1	0.9432
Geometric mean (if not pH dependent)*					1.437	100.2	
Arithmetic mean (if not pH dependent)							0.9292
pH dependence			No				

[1] Measured in calcium chloride solution

Overall adsorption data for degradation product TFA

For the degradation product TFA batch equilibrium and column leaching experiments were conducted. However, due to very low adsorption of TFA to soils no adsorption coefficients could be determined by both different testing methods. In conclusion, default values are proposed to be used for TFA: a $K_{oc(ads)}$ value of 0 and a Freundlich exponent 1/n of 1.

Asssment of pH dependency

Based on the available adsorption data, it was investigated if the adsorption of fluopyram and its soil degradation product fluopyram-7-hydroxy are pH-dependent using the Kendall tau test. The Input Decision tool v3.3 of Federal Environment Agency (UBA) was used. The K_f and K_{foc} values of the soils and the corresponding pH values, measured in water, were tested.

Table 7.1.3.1- 3: Correlation parameters for K_f and K_{foc} values and pH_{H2O} values

Compound		**Kendall tau (stringency of the correlation)**	**p (level of significance)**
Fluopyram	K_f	0.155	0.410
	K_{foc}	-0.258	0.161
Fluopyram-7-hydroxy	K_f	0.000	1.000
	K_{foc}	1.000	0.089

In case p values are < 0.05, a correlation between the data points of the investigated factors exists

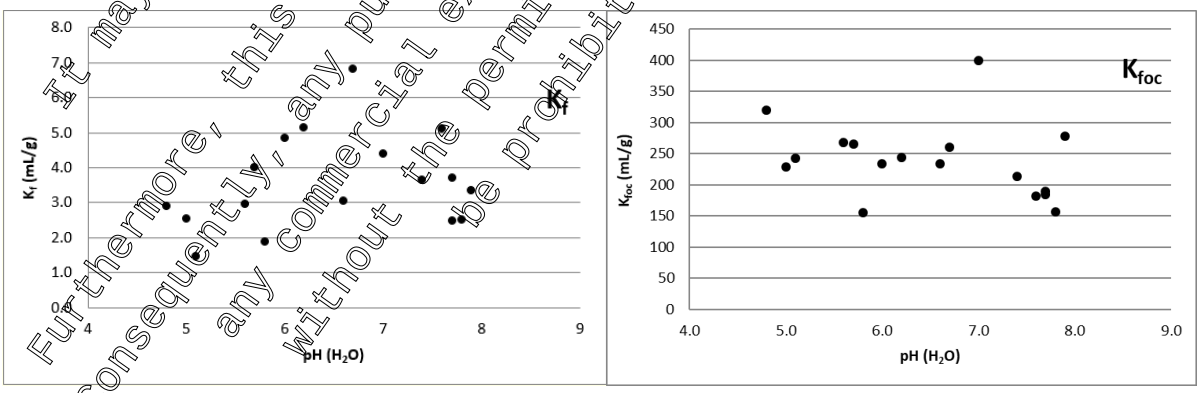


Figure 7.1.3.1- 1: Fluopyram: Correlation between K_f values and pH_{H2O} as well as K_{foc} and pH_{H2O}

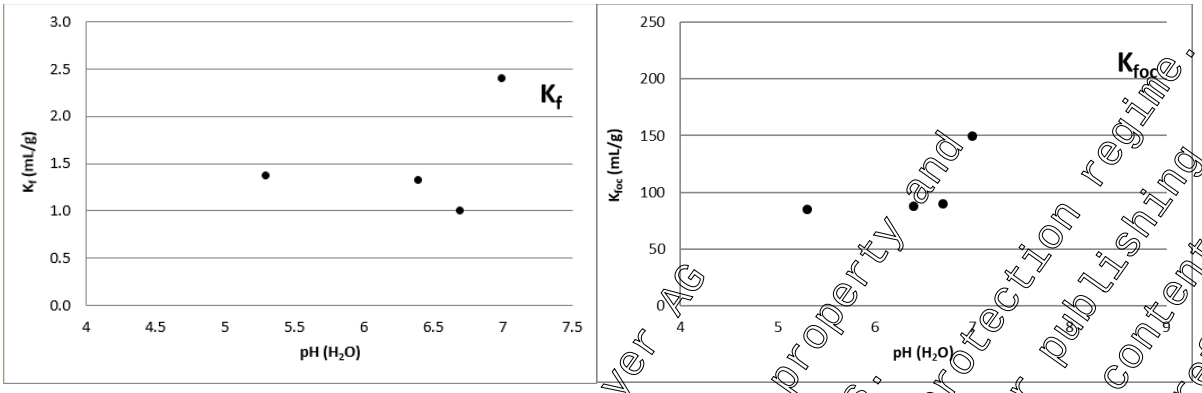


Figure 7.1.3.1- 2: Fluopyram-7-hydroxy: Correlation between K_f values and pH_{H2O} as well as K_{foc} and pH_{H2O}

For fluopyram and fluopyram-7-hydroxy, there is no significant correlation between the pH-value and the adsorption coefficients K_f and K_{foc}. Therefore, it is concluded that the adsorption behaviour of fluopyram and its soil metabolite fluopyram-7-hydroxy is not pH-dependent. For TFA sorption was very low and no adsorption coefficients could be derived. Consequently, the pH dependency of adsorption coefficients cannot be assessed.

CA 7.1.3.1.1 Adsorption and desorption of the active substance

1. Information on the study

Data Point:	KCA 7.1.3.1.1/01
Report Author:	[redacted]
Report Year:	2005
Report Title:	AE C656948: Adsorption/desorption on five soils
Report No:	MEF-04/499
Document No:	M-248464-01-1
Guideline(s) followed in study:	Commission Directive 95/36/EC amending Council Directive 91/414/EEC (Annexes II, Fate and Behaviour in Environment) July 14, 1995; EPA Pesticide Assessment Guidelines, Subdivision N, Chemistry Environmental Fate, 163-1 Leaching and Adsorption/Desorption Studies (1982); Equivalent to US EPA OPPTS Guideline No. 835.1240; Environmental Chemistry and Fate Guidelines for Registration of Pesticides in Canada. PMRA DACO Number 8.2.4.2 Adsorption-Desorption Measurements (1987); Japanese MAFF New Test Guidelines for Supporting Registration of Chemical Pesticides; OECD Guideline for Testing of Chemicals No. 106, Adsorption/Desorption (2000)
Deviations from current test guideline:	Current Guideline: OECD 106 (2000) For a single concentration of the soil SSC, the overall material balance was <90 %. Slight adsorption to the test vessels was observed in control samples without soil but was assumed negligible in presence of soil.
Previous evaluation:	Yes, evaluated and accepted DAR (2011)
GLP/Officially recognised testing facilities:	Yes, conducted under GLP/Officially recognised testing facilities
Acceptability/Reliability:	Yes

2. Full summary of KCA 7.1.3.1.1/01

Executive Summary

The adsorption/desorption behaviour of fluopyram was studied in five soils in batch equilibrium experiments in the dark in the laboratory at 20 ± 1 °C.

Soil	Soil ID	Source	Texture (USDA)	pH [1]	OC [%]
Laacherhof AXXa	AXXa	Monheim, Germany	Sandy loam	6.4	1.30
Hoefchen am Hohenseh	HaH	Burscheid, Germany	Silt loam	6.6	2.62
Laacherhof Wurmwiese	WuW	Monheim, Germany	Loam	5.8	2.07
Pikeville	Pik	Pikeville, USA	Loamy sand	5.6	1.10
Stanley	SSC	Stilwell, USA	Clay loam	6.2	1.10

[1] pH values were measured in supernatant in adsorption test (0.01 M $CaCl_2$ suspensions).

The adsorption phase was carried out using air-dried soils equilibrated in aqueous 0.01 M $CaCl_2$ solution with a soil-to-solution ratio of 1/4. Fluopyram was applied at five different test concentrations in a range of 0.01 to 1.0 mg/L in aqueous 0.01 M $CaCl_2$ solution. The desorption phase was performed by supplying pre-adsorbed soil samples with fresh aqueous 0.01 M $CaCl_2$ solution for one desorption cycle. A second and third desorption cycle was performed for the highest concentration only. The adsorption step was carried out for 48 hours and the desorption steps for 24 hours, both under continuous agitation.

Fluopyram was stable during the test for the duration of the adsorption and desorption phase. The parental mass balance was ≥ 90.9% AR. No degradation products were observed.

The overall mass balance for all soils were in the range of 93.2 to 94.9% AR (mean: 94.2% AR).

$K_{F(ads)}$ values ranged from 2.9 mL/g to 6.8 mL/g. The respective $K_{Foc(ads)}$ values were in the range of 233.2 mL/g and 399.7 mL/g (arithmetic mean: 278.9 mL/g; geometric mean: 273.0 mL/g). There was no significant correlation between pH and adsorption for the investigated soils. The complete material balance found at all sampling intervals demonstrated that no significant amount of test item dissipated from the test vessels or was lost during processing.

In the adsorption test 43.6 to 82.7% of the applied test material was adsorbed. After the desorption phase, between 11.6-67.2% of the initially adsorbed radioactivity was desorbed from the respective soils. The desorption constants K_{Foc} were in a range of 367.9-to 688.2 mL/g (arithmetic mean 468.8 mL/g; geometric mean: 456.5 mL/g). 1/n values were calculated to be in the range of 0.765 to 0.849 and of 0.784 to 0.870 for adsorption and desorption, respectively.

There is no significant correlation between pH and adsorption for the investigated soils.

I. MATERIALS AND METHODS

A. MATERIALS

1. Test Item

[phenyl-UL-^{14}C]AE C656948 (fluopyram)

Sample ID	BECH 1609
Specific activity	3.85 MBq/mg
Radiochemical purity	> 98%

2. Test Soils

The soils were sampled before study start (upper horizon of 0 to 20 cm), air dried, sieved to a particle size of ≤ 2 mm and stored at < 4 °C for approximately 3 months. The soils were taken from agricultural

areas representing different geographical origins and different soil properties as required by the guidelines. Soil characteristics are summarised in the table below.

Table 7.1.3.1.1-1: Test soil characteristics

Soil	Laacherhof AXXa	Hoefchen am Hohenseh HaH	Laacherhof Wurmwiese WuW	Pikeville Pik	Stilwell SSC
Geographic Location (City/State/Country)	Monheim / NRW / Germany	Burscheid / NRW / Germany	Monheim/ NRW/ Germany	Pikeville, N.Carolina, USA	Stilwell, Kansas, USA
Pesticide use history	No pesticide use for the previous 5 years				
Collection procedures	Field sampled with shovel into plastic bag (bucket)				
Sampling depth	0–20 cm			0-8 inches	0-6 inches
Storage conditions	4°C, stored moist in aerated plastic bag and air-dried at ambient temperature prior to use				
Storage length	87 d			163 d	31 d
Soil preparation	Sieved (2 mm) ca. 3 months after collection				
Soil Taxonomic Classification (USDA)	Sandy, mixed, mesic Typic Cambudolls	Loamy, mixed, mesic Typic Argudalfs	Loamy, mixed, mesic Typic Argudalfs	Fine-loamy, siliceous, subactive thermic Aquic Paleudults	Fine montmorillonitic, mesic, typic argiudolls/ Aquic Argiudolls
Soil Series	n.d.	n.d.	n.d.	Goldsboro	Oska-Martin
Texture Class (USDA)	sandy loam	silt loam	loam	loamy sand	clay loam
Sand (%)[1]	73	13	49	78	37
Silt (%)[1]	18	73	32	16	32
Clay (%) [1]	9	15	19	6	31
pH 0.01 M $CaCl_2$	6.0	6.1	5.4	5.0	5.4
pH in Water	6.6	6.7	6.0	5.6	7.0
pH in 1 M KCl	6.3	6.4	5.5	5.0	n.a.
Org. Matter [2] (%)	2.2	4.5	3.6	1.9	1.9
Org. Carbon (%)	1.3	2.6	2.1	1.1	1.1
CEC (meq/100 g)	6.4	16.6	11.3	5.0	27.1
MWHC (g/100 g)	38.2	72.7	59.9	34.1	46.1
WHC 0.33 bar (g/100g)	19.5	31.3	15.7	13.3	36.1

CEC: Cation exchange capacity; 1/3 bar WHC: Water Holding Capacity at 0.33 bar; MWHC: Maximum Water Holding Capacity; n.d.: not determined
[1] acc. USDA classification
[2]% organic matter =% organic carbon x 1.724

B. STUDY DESIGN

1. Experimental Conditions

The test system for adsorption and desorption in batch equilibrium experiments consisted of Teflon® centrifuge tubes (volume 42 mL) closed with screw caps. The experiments were performed in duplicate.

In preliminary tests, the adsorption of the test item to the test system surface, the optimal soil-to-solution ratio, the appropriate adsorption and desorption equilibration times and the stability of the test item were determined. Samples without soil were used as control in the stability and adsorption and desorption equilibration times tests.

The adsorption phase was carried out using air-dried soils equilibrated for three days in aqueous 0.01 M $CaCl_2$ solution with a soil-to-solution ratio of 1/4 (5 g soil (dry weight equivalents)/ 20 mL solution). The test item [phenyl-UL-^{14}C]fluopyram was applied at nominal concentrations in a range of 0.01 to 1.0 mg/L in 0.01 M aqueous $CaCl_2$ solution, covering two orders of magnitude. The desorption phase was performed by supplying pre-adsorbed soil samples with fresh aqueous 0.01 M $CaCl_2$ solution. The adsorption step was carried out for 48 hours and the desorption steps for 24 hours, both under continuous agitation. The adsorption parameters were calculated using the Freundlich adsorption isotherm

2. Analytical Procedures

After each adsorption and desorption step the aqueous supernatant was separated from the soil by centrifugation and the amount of [phenyl-UL-^{14}C]fluopyram in the supernatants was analysed by liquid scintillation counting (LSC).

In the preliminary parental mass balance test, the supernatant and extract of soil samples were analysed by LSC and HPLC in order to confirm the stability of the test item. The limit of detection (LOD) for HPLC analysis was <0.01% AR.

The partition of the test item in the adsorption and desorption batch equilibrium experiment was determined based on the radioactivity content in the supernatant only due to the stability of the test item demonstrated by the parental mass balance. After adsorption and 1 to 3 desorption steps, the soils (highest test concentration) were extracted with acetonitrile for 3 hours at ambient temperature, followed by LSC to establish the material balance.

Adsorption and desorption constants (K_F) were calculated from the concentration of the test item in solution at equilibrium and the adsorbed amount of the test item at equilibrium.

II. RESULTS AND DISCUSSION

A. MATERIAL BALANCE

Mean material balances were 94.9% AR (range from 90.9 to 97.1% AR) for soil Laacherhof AXXa, 93.9% AR (range from 91.9 to 95.9% AR) for soil Hoefchen am Hohenseh, 94.6% AR (range from 91.8 to 97.0% AR) for soil Laacherhof Wurmwiese, 94.2% AR (range from 92.4 to 97.1% AR) for soil Pikeville and 93.2% AR (range from 87.0 to 95.4% AR) for soil Stilwell. The complete material balances found for all soils and concentrations demonstrated that there was no significant loss of radioactivity dissipated from the test systems or during sample processing, with exception of samples at the lowest test concentration of Stilwell where mass balance is slightly below 90%.

B. STABILITY OF TEST ITEM

Fluopyram was sufficiently stable throughout the study. Mean parental mass balances of the test item were 103.0, 91.5, 95.0, 99.2, and 90.9% AR for soil Laacherhof AXXa, Hoefchen am Hohenseh, Laacherhof Wurmwiese, Pikeville and soil Stilwell, respectively. The stability was adequate to determine the test item distribution based on LSC measurements of the supernatant only in the adsorption and desorption experiments of the definitive test. Results of the parental mass balance test are sumamrised in the table below.

Table 7.1.3.1.1-2: Recovery of [phenyl-UL-^{14}C]fluopyram in soil at the end of the adsorption phase (after 96 hours) , expressed as percentage of applied radioactivity

Matrices	Laacherhof AXXa	Hoefchen a. Hohenseh	Laacherhof Wurmwiese	Pikeville	Stilwell
Supernatant solution	44.9	28.7	37.9	51.6	37.3
Solid phase (ACN extract)[1]	58.2	62.8	57.1	47.6	53.7
Non-extractable residues	N/A	N/A	N/A	N/A	N/A
Total recovery	103.0	91.5	95.0	99.2	90.9

[1] test item is stable, HPLC = 100% (comparison: purity of application solution > 99%)

C. FINDINGS

At the end of the adsorption phase 48.2-76.1% AR, 67.4-82.7% AR, 57.9-74.2% AR, 43.6-62.1% AR and 55.3-74.0% AR were adsorbed in soil Laacherhof AXXa, Hoefchen am Hohenseh, Laacherhof Wurmwiese, Pikeville and soil Stilwell, respectively (Table 7.1.3.1.1-3). For the five test soils the calculated adsorption constants $K_{F(ads)}$ ranged from 2.9 mL/g to 6.8 mL/g. The respective $K_{oc(ads)}$ values were in the range of 233.2 mL/g and 399.7 mL/g (arithmetic mean 278.9 mL/g; geometric mean: 273.0 mL/g, see Table 7.1.3.1.1-4). 1/n values ranged from 0.7645 to 0.8492 and from 0.7838 to 0.8697 form adsorption and desorption, respectively.

At the end of the desorption phase, 14.6-59.1, 11.6-49.0, 17.4-58.4, 25.4-67.2 and 18.1-60.9% of the initially adsorbed amount were desorbed in soil Laacherhof AXXa, Hoefchen am Hohenseh, Laacherhof Wurmwiese, Pikeville and soil Stilwell respectively (Table 7.1.3.1.1-3). The calculated desorption constants for the five soils raged from 5.3 to 10.2 mL/g (mean 7.2 mL/g) and the K_{doc} values ranged from 367.9 to 688.2 mL/g (mean 468.8 mL/g, see Table 7.1.3.1.1-4).

Table 7.1.3.1.1-3: Percentage of adsorbed and desorbed fluopyram in soils (mean values of two replicates and standard deviation)

Concentration (mg a.i./L)	Adsorption [1]	Desorption [2]
Soil ID	**Laacherhof AXXa**	
0.011	76.1 ± 8.88	14.6 ± 5.42
0.034	66.9 ± 0.04	20.3 ± 0.45
0.11	61.0 ± 0.24	20.2 ± 0.56
0.32	53.7 ± 0.15	30.1 ± 0.08
1.06	48.2 ± 0.21	59.1 ± 0.37
Soil ID	**Hoefchen a. Hohenseh**	
0.011	82.7 ± 0.47	11.6 ± 0.81
0.034	79.1 ± 1.61	14.0 ± 0.73
0.11	75.5 ± 0.10	13.9 ± 0.02
0.32	71.0 ± 0.42	20.0 ± 0.18
1.06	67.4 ± 0.14	49.0 ± 0.42
Soil ID	**Laacherhof Wurmwiese**	
0.011	74.2 ± 0.51	17.4 ± 0.84
0.034	71.4 ± 0.20	19.9 ± 0.51
0.11	67.0 ± 0.34	19.6 ± 0.22
0.32	61.7 ± 0.17	26.8 ± 0.04
1.06	57.9 ± 0.05	58.4 ± 0.21
Soil ID	**Pikeville**	
0.011	62.1 ± 0.30	25.4 ± 0.05
0.034	59.6 ± 0.13	27.3 ± 0.22
0.11	54.5 ± 0.54	25.7 ± 0.40
0.32	49.4 ± 0.16	36.0 ± 0.33

Concentration (mg a.i./L)	Adsorption [1]	Desorption [2]
1.06	43.6 ± 0.66	67.2 ± 1.14
Soil ID	**Stilwell**	
0.011	74.0 ± 0.30	18.1 ± 0.16
0.034	70.4 ± 0.24	20.1 ± 0.06
0.11	64.6 ± 0.10	20.6 ± 0.34
0.32	61.0 ± 0.51	26.6 ± 0.56
1.06	55.3 ± 0.55	60.9 ± 0.73

[1] end of adsorption phase, mean values expressed as percentage of applied radioactivity
[2] end of desorption phase, mean values expressed as percentage of the initially adsorbed amount
Desorption steps: One desorption for conc. 0.01-0.32 mg/L
Three desorption steps for conc. 1.06 mg/L

Table 7.1.3.1.1-4: Adsorption and desorption constants of fluopyram in the test soils

Soil	Adsorption			Desorption		
	$K_{F(ads)}$ [mL/g]	1/n	$K_{Foc(ads)}$ [mL/g]	$K_{F(des)}$ [mL/g]	1/n	$K_{Foc(des)}$ [mL/g]
Laacherhof AXXa	3.031	0.7645	233.2	5.455	0.7837	419.6
Hoefchen a. Hohenseh	6.825	0.8376	260.5	10.216	0.8357	389.9
Laacherhof Wurmwiese	4.839	0.8492	233.7	7.616	0.8548	367.9
Pikeville	2.941	0.8463	267.3	5.264	0.8620	478.5
Stilwell	4.396	0.8367	399.7	7.570	0.8697	688.2
Mean	**4.406**	**0.8268**	**278.9**	**7.224**	**0.8392**	**468.8**

III. CONCLUSIONS

In the adsorption test, 43.6 to-82.7% of the applied test material was adsorbed. After the desorption phase, between 11.6 and-67.2% of the initially adsorbed radioactivity was desorbed from the respective soils.

The adsorption constants $K_{F(ads)}$ of fluopyram ranged from 2.9 mL/g to 6.8 mL/g. The respective $K_{oc(ads)}$ values were in the range of 233.2 mL/g and 399.7 mL/g (mean 278.9 mL/g). The desorption constants K_{FOC} were in a range of 367.9-688.2 mL/g (arithmetic mean 468.8 mL/g; geometric mean: 456.5). Adsorption and desorption constants do not depend on the pH of the soil.

1/n values ranged from 0.765 to 0.849 and from 0.784 to 0.870 for adsorption and desorption, respectively.

[phenyl-UL-^{14}C]fluopyram was sufficiently stable throughout the study. Mean parental mass balances of the test item were 103.0, 91.5, 95.0, 99.2, and 90.9% AR for soil Hoefchen am Hohenseh, Laacherhof Wurmwiese, Pikeville and Stilwell, respectively.

3. Assessment and conclusion

Assessment and conclusion by applicant:
The study and its data are considered to be valid and reliable for use in risk assessment.

Assessment and conclusion by RMS:
Outcome and conclusion of the study: RMS should indicate if they agree to the results and conclusions of the APPL.

EVALUATION ACCORDING TO EFSA CHECKLIST

The above study M-248464-01-1 was performed according to the OECD 106 guideline, dating from 2000, for the determination of the Freundlich isotherm. The indirect method was used for all soils. All relevant quality checks were performed as part of confirming the acceptability of the data and endpoints reported. The parental mass balance of 90.9 to 103% and adsorption in terms of percentage adsorbed to soil was from 43.15 to 81.65% for all soils (see Table 7.1.3.1.1-5). The graphical fits of the Freundlich equation are presented below based on the standard linear regression form using log-log transformed data alongside the associated residual plots (see Figure 7.1.3.1.1-1 to Figure 7.1.3.1.1-5). The R^2 of the standard linear regressions was ≥0.993 for all soils. Systematic errors were shown to be low by maximum K_{fE}/K_f values of ≤1.2 for all soils.

Table 7.1.3.1.1-5: Results of evaluation according to EFSA OECD 106 Evaluators Checklist for fluopyram

Soil	Units	Laacherhof AXXa	Hoefchen am Hohenseh	Laacherhof Wurmwiese	Pikeville	Stilwell
Adsorption method	-	indirect	indirect	indirect	indirect	indirect
Soil:solution ratio	g dw/mL	1:4	1:4	1:4	1:4	1:4
Mean parental mass balance (at highest test conc.)	%	103	91.5	95.0	99.2	90.9
Adsorbed percentage	%	48.04 – 81.65	67.24 – 81.65	57.93 – 72.48	43.15 – 63.30	54.91 – 72.48
K_d × (soil:solution ratio)	-	0.92 – 4.50	2.05 – 4.50	1.38 – 2.67	0.76 – 1.69	1.22 – 2.67
$^{ads}K_F$ (95% confidence interval)	L/kg dw	3.037 (2.493 – 3.700)	6.940 (6.733 – 7.154)	4.967 (4.732 – 5.213)	2.925 (2.814 – 3.040)	4.473 (4.269 – 4.686)
$^{ads}1/n$ (95% confidence interval)	-	0.763 (0.711 – 0.816)	0.845 (0.838 – 0.852)	0.863 (0.850 – 0.876)	0.844 (0.833 – 0.855)	0.846 (0.833 – 0.858)
$^{ads}R^2$	-	0.993	1.000	1.000	1.000	1.000
$^{ads}K_{F,OC}$	L/kg OC	234	265	240	266	407
K_{fE} / K_f	-	1.000 / 1.000	1.144 / 1.145	1.094 / 1.094	1.018 / 1.019	1.195 / 1.199

Note: Values derived from the EFSA evaluators checklist may vary from those in the study reports due to rounding errors.

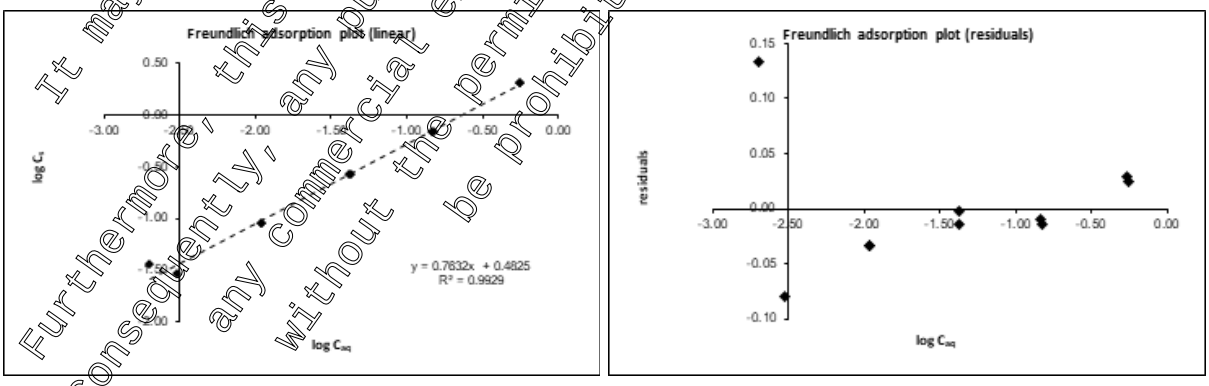


Figure 7.1.3.1.1-1: Graphical presentation of Freundlich adsorption isotherm analysis (linear regression, left) and the corresponding plot of the residuals (right) for soil Laacherhof AXXa

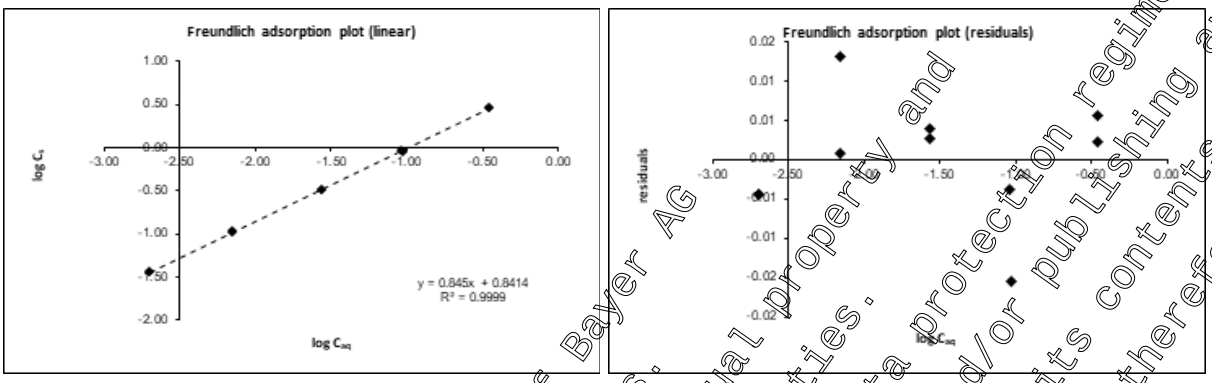


Figure 7.1.3.1.1-2: Graphical presentation of Freundlich adsorption isotherm analysis (linear regression, left) and the corresponding plot of the residuals (right) for soil Hoefchen am Hohenseh

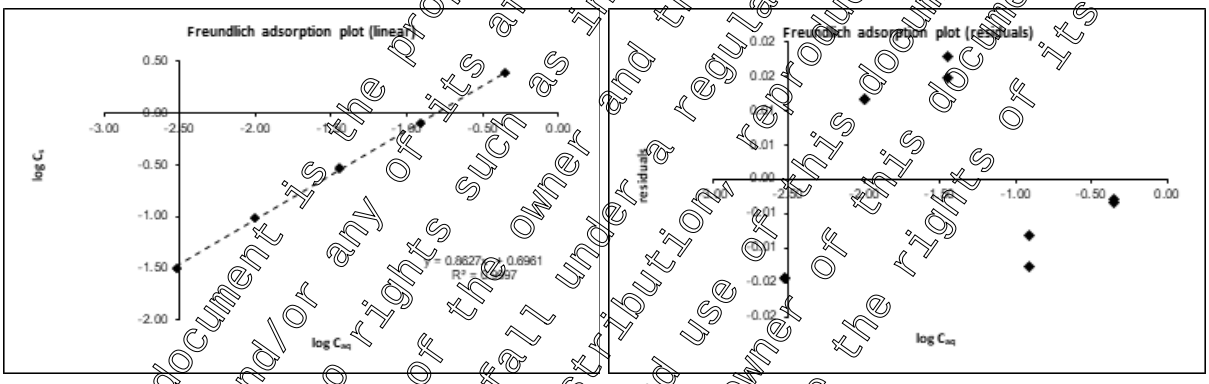


Figure 7.1.3.1.1-3: Graphical presentation of Freundlich adsorption isotherm analysis (linear regression, left) and the corresponding plot of the residuals (right) for soil Laacherhof Wurmwiese

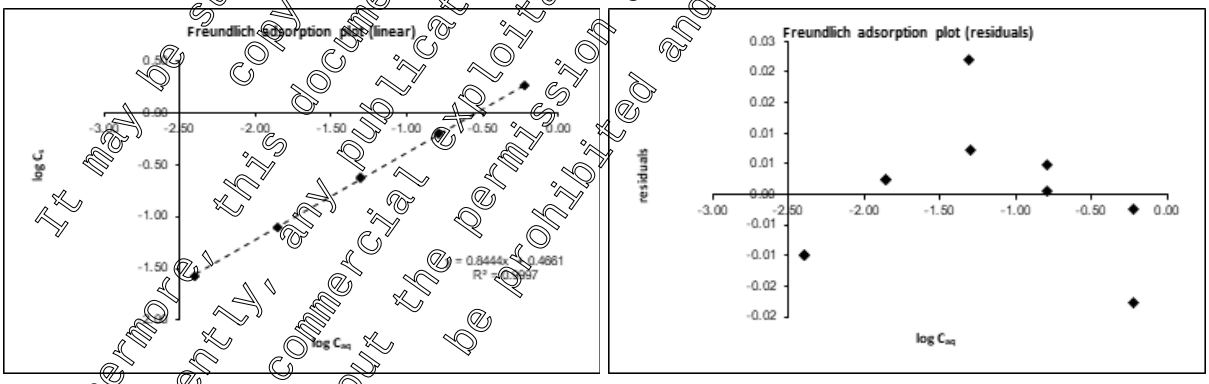


Figure 7.1.3.1.1-4: Graphical presentation of Freundlich adsorption isotherm analysis (linear regression, left) and the corresponding plot of the residuals (right) for soil Pikeville

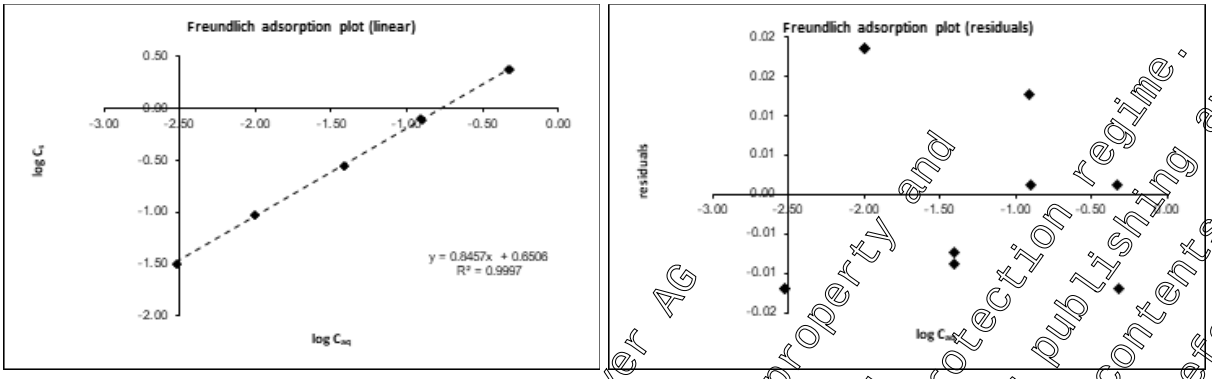


Figure 7.1.3.1.1-5: Graphical presentation of Freundlich adsorption isotherm analysis (linear regression, left) and the corresponding plot of the residuals (right) for soil Stilwell

1. Information on the study

Data Point:	KCA 7.1.3.1.1/02
Report Author:	[redacted]
Report Year:	2020
Report Title:	Fluopyram: Adsorption on twelve soils
Report No:	M13105405-9
Document No:	M-753424-01-1
Guideline(s) followed in study:	OECD Test Guideline No. 106 (2000); Commission Regulation (EU) No 283/2013 in accordance with Regulation (EC) No 1107/2009; US EPA OCSPP Test Guideline No. 835.1230 (2008); EFSA Technical report on the outcome of the pesticides peer review meeting on the OECD 106 evaluators checklist (2017)
Deviations from current test guideline:	Current Guideline: OECD 106 (2000) None
Previous evaluation:	No, not previously submitted
GLP/Officially recognised testing facilities:	Yes, conducted under GLP/Officially recognised testing facilities
Acceptability/Reliability:	Yes

2. Full summary of KCA 7.1.3.1.1/02

Executive Summary

The adsorption behaviour of fluopyram was studied in twelve soils in batch equilibrium experiments in the dark in the laboratory at 19.1 °C.

Soil	Soil ID	Source	Texture (USDA)	pH [1]	OC [%]
Little Oliver	LO	Malton, UK	sandy loam	5.5	1.5
Auchy les Mines	AM	Armancourt, France	silt loam	7.5	2.0
Urbanowice	UW	Urbanowice, Poland	silt loam	4.9	1.1
Charles River Farm	FA	Lleida, Spain	clay	7.7	1.6
Sindos	SD	Thessaloniki, Greece	loam	7.2	1.3
Paradiso San Zenone	PZ	Lodi, Italy	sandy loam	5.4	1.2
Hoeltinghausen	HS	Emstek, Germany	sand	4.5	0.9
Hornton	HT	Banbury, UK	loam	5.9	2.1
Le Thour	LT	Pontgivart-Auménancourt, France	silt loam	7.4	2.8
Brannens	BS	Tonneins, France	sandy loam	4.7	0.6
Balbiano	BB	Caleppio di Settala, Italy	sandy loam	7.1	1.7
Almayate East	AE	Malaga-Velez, Andalusia, Spain	loam	7.7	1.2

[1] pH values were derived from aqueous 0.01 M $CaCl_2$ suspensions

The adsorption phase of the study was carried out using air-dried soils equilibrated in aqueous 0.01 M $CaCl_2$ solution with soil-to-solution ratios of 1/4 for all soils. Test concentrations of 1.0, 0.3, 0.1, 0.03 and 0.01 mg/L of fluopyram were applied in aqueous 0.01 M $CaCl_2$ solution. Adsorption took place for 48 hours. The test was performed in centrifuge tubes with screw caps.

Fluopyram was sufficiently stable throughout the study. Mean parental mass balances at the lowest test concentration (0.01 mg/L) were 98.3% AR for soil LO, 102.2% AR for soil AM, 100.1% AR for soil UW, 99.5% AR for soil FA, 97.8% AR for soil SD, 91.4% AR for soil PZ, 94.5% AR for soil HS, 104.0% AR for soil HT, 103.8% AR for soil LT, 99.0% AR for soil BS, 101.6% AR for soil BB and 104.2% AR for soil AE. Mean parental mass balances at the highest test concentration (1.0 mg/L) were104.1% AR for soil LO, 104.4% AR for soil AM, 105.0% AR for soil UW, 106.1% AR for soil FA, 107.0% AR for soil SD, 107.4% AR for soil PZ, 102.8% AR for soil HS, 103.5% AR for soil HT, 99.3% AR for soil LT, 102.5% AR for soil BS, 103.2% AR for soil BB and 103.2% AR for soil AE.

In the definitive adsorption test the adsorbed amounts of fluopyram were 50.0 – 67.0% AR in soil LO, 56.6 – 86.8% AR in soil AM, 41.0 – 56.5% AR in soil UW, 41.6 – 56.0% AR in soil FA, 40.4 – 55.5% AR in soil SD, 34.5 – 53.7% AR in soil PZ, 43.5 – 53.9% AR in soil HS, 58.4 – 73.6% AR in soil HT, 57.3 – 70.2% AR in soil LT, 27.8 – 40.0% AR in soil BS, 49.5 – 69.3% AR in soil BB and 47.6 – 71.4% AR in soil AE.

The calculated adsorption constants K_F of the Freundlich isotherms ranged from 1.452 to 5.126 mL/g (arithmetic mean: 3.219 mL/g) for the tested soils. The Freundlich exponents 1/n ranged from 0.7321 to 0.9179 (arithmetic mean: 0.8500), indicating that the concentration of the test item affected the adsorption behaviour in the examined concentration range.

In general, the organic matter in soil, determined as organic carbon content, is the most important component responsible for binding organic chemicals. Therefore, the adsorption coefficients K_F were correlated with the organic carbon content of the soil to get a comparability of the adsorption behaviour in different soils. For fluopyram the $K_{F,oc}$ values ranged from 156 to 320 mL/g (arithmetic mean: 222 mL/g).

I. MATERIALS AND METHODS

A. MATERIALS

1. Test Item

[phenyl-UL-^{14}C]fluopyram

Sample ID	KML 10699
Specific activity	5.15 MBq/mg
Radiochemical purity	> 98% (HPLC with radioactivity detector)
Chemical purity	> 98% (HPLC with UV-detector, 210 nm)

2. Test Soils

The study was carried out using twelve different soils. The soils were taken from agricultural use areas representing different geographical origins and different soil properties. These soils are used for terrestrial field dissipation (TFD) studies as well and are thus well characterised. Details such as pesticide use history is reported in the respective field dissipation study (KCA 7.1.1.1/06, M-753426-01-1; KCA 7.1.1.1/05, M-681092-01-1, amended report M-681092-02-1, KCA 7.1.2.2.1/14, M-758583-01-1 and KCA 7.1.2.2.1/15, M-758589-01-1). The physico-chemical characteristics of the test soils are summarized in the tables below.

Table 7.1.3.1.1-6: Physico-chemical properties of test soils LO, AM, UW, FA, SD and PZ

Soil	Little Oliver	Auchy-les Mines	Urbanowice	Charles River Farm	Sindos	Paradiso San Zenone
Geographic Location (City/State/Country)	Malton / North Yorkshire / UK	Armancourt / Hauts de France / France	Urbanowice / Opole / Poland	Lleida / Catalunya / Spain	Thessaloniki / Central Macedonia / Greece	Lodi / Lombardia / Italy
Sampling depth	0 - 10 cm					
Storage conditions	Stored after sieving at < 6 °C prior to use					
Storage length after sieving	22 days	24 days	29 days	29 days	38 weeks	37 weeks
Soil preparation	Sieved (2 mm) within 5 days after sampling					
Soil Taxonomic Classification	Not reported					
Soil Series	Not reported					
Texture Class (USDA)	sandy loam	silt loam	silt loam	clay	loam	sandy loam
Sand (%)[1]	55	23	35	19	35	45
Silt (%)[1]	26	58	62	38	38	50
Clay (%)[1]	19	19	3	43	27	5
pH 0.01 M $CaCl_2$	5.5	7.5	4.9	7.7	7.2	5.4
pH in Water	5.7	7.7	5.0	7.8	7.7	5.8
pH in 1 M KCl	5.3	7.1	4.5	7.5	6.7	4.7
Org. Matter [2] (%)	2.6	3.4	1.9	2.8	2.2	2.1
Org. Carbon (%)	1.5	2.0	1.1	1.6	1.3	1.2
CEC (meq/100 g)	13.6	15.0	9.0	18.2	16.8	11.8
MWHC (g/100 g)	49.3	53.2	43.9	55.4	55.0	51.1
WHC 0.1 bar (g/100g)	17.0	27.2	32.7	29.5	24.7	21.6

CEC: Cation exchange capacity; WHC: Water Holding Capacity; MWHC: Maximum Water Holding Capacity; USDA: United States Department of Agriculture

[1] acc. USDA classification

[2] % organic matter =% organic carbon x 1.724

Table 7.1.3.1.1-7: Physico-chemical properties of test soils HS, HT, LT, BS, BB and AE

Soil	Hoeltinghausen	Hornton	Le Thour	Brannens	Balbiano	Almayate East
Geographic Location (City/State/Country)	Emstek / Lower Saxony / Germany	Banbury / South East / UK	Pontgivart-Aumenancourt / Grand Est / France	Tonneins / Nouvelle-Aquitaine / France	Caleppio di Settala / Lombardy / Italy	Malaga-Velez / Andalusia / Spain
Sampling depth	0–10 cm					
Storage conditions	Stored after sieving at ≤ 6 °C prior to use					
Storage length	36 weeks	36 weeks	37 weeks	33 weeks	37 weeks	36 weeks
Soil preparation	Sieved (2 mm)					
Soil Taxonomic Classification (USDA)	Not reported					
Soil Series	Not reported					
Texture Class (USDA)	sand	loam	silt loam	sandy loam	sandy loam	loam
Sand (%)[1]	87	35	25	65	57	33
Silt (%)[1]	10	40	66	28	26	42
Clay (%) [1]	3	25	9	7	17	25
pH 0.01 M $CaCl_2$	4.5	5.9	7.4	4.7	7.1	7.7
pH in Water	4.8	6.2	7.6	5.1	7.4	7.9
pH in 1 M KCl	4.0	5.5	7.1	4.3	6.8	7.3
Org. Matter [2] **(%)**	1.6	3.6	4.8	1.0	2.9	2.1
Org. Carbon (%)	0.9	2.1	2.8	0.6	1.7	1.2
CEC (meq/100 g)	5.3	16.5	15.6	4.6	13.8	18.2
MWHC (g/100 g)	29.0	54.3	62.5	39.4	48.7	46.6
WHC 0.1 bar (g/100g)	7.5	30.9	31.2	12.4	18.7	27.7

CEC: Cation exchange capacity; WHC: Water Holding Capacity; MWHC: Maximum Water Holding Capacity; USDA: United States Department of Agriculture
[1] acc. USDA classification
[2] % organic matter =% organic carbon x 1.724

B. STUDY DESIGN

1. Experimental Conditions

The test system for batch equilibrium experiments (preliminary and definitive tests) consisted of Teflon® centrifuge tubes (volume 42 mL) closed with screw caps. The experiments were performed in duplicate.

In preliminary tests, the adsorption of the test item to the test system surface, the optimal soil-to-solution ratio, the appropriate adsorption equilibration time and the stability of the test item were determined. Samples without soil were used as control in the stability and adsorption equilibration time tests.

The adsorption phase was carried out using air-dried soils equilibrated for two days in aqueous 0.01 M $CaCl_2$ solution with a soil-to-solution ratio of 1/4 (5 g soil (dry weight equivalents)/ 20 mL solution). The test item [phenyl-UL-^{14}C]fluopyram was applied at nominal concentrations in a range of 0.01 to 1.0 mg/L in 0.01 M aqueous $CaCl_2$ solution, covering two orders of magnitude. The adsorption step was carried out for 48 hours under continuous agitation at 19.1 °C. The adsorption parameters were calculated using the Freundlich adsorption isotherm. No desorption was performed.

2. Analytical Procedures

After the adsorption step the aqueous supernatant was separated from the soil by centrifugation and the amount of [phenyl-UL-^{14}C]fluopyram in the supernatants was analysed by liquid scintillation counting (LSC).

The parental mass balances were determined with a soil-to-solution ratio of 1/4 for all soils. The parental mass balance test for the highest test concentration (1 mg/L) and the lowest test concentration (0.01 mg/L) was performed following 48 hours of adsorption. Following the adsorption step and separation of soil and supernatant, the soil was extracted four times at ambient temperature by shaking for 30 minutes each, followed by one extraction using a microwave at 70 °C with a magnetic stirrer. The extraction solvents were acetonitrile/water (1/1, *v/v*), acetonitrile/water (4/1, *v/v*) and 2x acetonitrile for the ambient extraction and acetonitrile/water (4/1, *v/v*) for the microwave extraction. After each extraction step, extract and soil were separated by centrifugation and decantation. The ambient soil extracts were combined and the volumes of the combined ambient and microwave extracts were determined. The radioactivity contents in supernatant and soil extracts were determined by LSC. For the highest test concentration, the stability of the test item was determined by HPLC/radiodetection of aqueous supernatants and of the combined (ambient and microwave extracts) soil extracts. Samples of supernatants and combined soil extracts of preliminary tests at the lowest test concentration of 0.01 mg/L were characterized by normal-phase (NP) TLC/radiodetection. The maximum total limits of detection LOD for TLC and HPLC were determined to be 1.2 and 0.8% AR, respectively. The corresponding limits of quantification (LOQ) were set to three times LOD corresponding to 3.6 and 2.4% AR, respectively.

The partition of the test item in the adsorption batch equilibrium experiment was determined based on the radioactivity content in the supernatant only due to the stability of the test item demonstrated by the parental mass balance.

Adsorption and desorption constants (K_F) were calculated from the concentration of the test item in solution at equilibrium and the adsorbed amount of the test item at equilibrium.

II. RESULTS AND DISCUSSION

A. MATERIAL BALANCE

Mean overall material balances were 96.4% AR for soil LO (range from 87.9 to 102.3% AR), 99.7% AR for soil AM (range from 96.7 to 109.8% AR), 99.8% AR for soil UW (range from 94.3 to 109.2% AR), 97.8% AR for soil FA (range from 94.7 to 104.2% AR), 99.1% AR for soil SD (range from 95.3 to 106.4% AR), 97.9% AR for soil PZ (range from 90.9 to 99.8% AR), 98.7% AR for soil HS (range from 94.7 to 101.8% AR), 100.9% AR for soil HT (range from 94.9 to 109.6% AR), 100.4% AR for soil LT (range from 98.0 to 107.9% AR), 99.9% AR for soil BS (range from 95.2 to 108.6% AR), 101.1% AR for soil BB (range from 96.9 to 109.6% AR) and 101.5% AR for soil AE (range from 97.2 to 119.4% AR).

The complete material balances found for all samples and for all soils demonstrated that there was no significant loss of radioactivity from the test systems or during sample processing. Material balances of two samples (soil LO 0.3 mg/L replicate 4 and soil AE 0.01 mg/L replicate 2) were outside of the range of 90 to 110% AR. However, these values are considered as outliers and have no effect on the validity of the results of the study.

B. STABILITY OF TEST ITEM

Fluopyram was sufficiently stable throughout the study. Mean parental mass balances of the test item at the highest test concentration (0.01 mg/L) were 104.1% AR for soil LO, 104.4% AR for soil AM, 105.0% AR for soil UW, 106.1% AR for soil FA, 107.0% AR for soil SD, 107.4% AR for soil PZ,

102.8% AR for soil HS, 103.5% AR for soil HT, 99.3% AR for soil LT, 102.5% AR for soil BS, 103.2% AR for soil BB and 103.2% AR for soil AE.

Mean parental mass balances of the test item at the lowest test concentration (0.01 mg/L) were 98.3% AR for soil LO, 102.2% AR for soil AM, 101.1% AR for soil UW, 99.5% AR for soil FA, 97.8% AR for soil SD, 91.4% AR for soil PZ, 94.5% AR for soil HS, 104.0% AR for soil HT, 103.8% AR for soil LT, 99.0% AR for soil BS, 101.6% AR for soil BB and 104.2% AR for soil AE.

Table 7.1.3.1.1-8: Preliminary parental mass balance test: Recovery of [phenyl-UL-^{14}C]fluopyram in soil at a test concentration of 1.0 mg/L (mean)

Compartment	Soil ID											
	LO	AM	UW	FA	SD	PZ	HS	HT	LT	BS	BB	AE
Radioactivity in supernatant [% AR]	33.0	26.0	40.0	41.8	45.1	43.9	39.8	30.4	26.8	37.5	38.6	38.9
Test item in supernatant [% ROI] [1]	97.6	94.9	97.5	96.8	96.9	97.4	96.1	96.3	95.3	98.1	97.0	95.8
Test item in supernatant [% AR]	**32.2**	**24.7**	**38.9**	**40.4**	**43.7**	**42.8**	38.3	29.3	25.5	36.4	37.5	37.3
Radioactivity in soil extracts [% AR]	71.9	79.6	66.1	65.7	63.2	64.6	64.5	74.2	73.8	46.1	65.8	65.9
Test item in soil extracts [% ROI] [1]	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0
Test item in soil extracts [% AR]	**71.9**	**79.6**	**66.1**	**65.7**	**63.2**	**64.6**	**64.5**	**74.2**	**73.8**	**46.1**	**65.8**	**65.9**
Total recovery of radioactivity [% AR]	104.9	105.7	106.0	107.5	108.4	108.5	104.4	104.6	100.5	103.6	104.4	104.8
Total recovery of test item [% AR]	**104.1**	**104.4**	**105.0**	**106.1**	**107.0**	**107.4**	**102.8**	**103.5**	**99.3**	**102.5**	**103.2**	**103.2**

[1] percentage of regions of interest [% ROI] from primary chromatographic method

Table 7.1.3.1.1-9: Preliminary parental mass balance test: Recovery of [phenyl-UL-^{14}C]fluopyram in soil at a test concentration of 0.01 mg/L (mean)

Compartment	Soil ID											
	LO	AM	UW	FA	SD	PZ	HS	HT	LT	BS	BB	AE
Radioactivity in supernatant [% AR]	27.5	10.9	35.2	29.0	33.8	36.8	41.4	21.4	23.2	53.5	25.7	23.5
Test item in supernatant [% ROI] [1]	100.0	100.0	95.2	89.0	94.2	94.7	97.9	89.6	89.5	95.6	92.2	90.8
Test item in supernatant [% AR]	**27.5**	**10.9**	**33.5**	**25.9**	**31.8**	**34.9**	**40.5**	**19.2**	**20.8**	**50.9**	**23.7**	**21.3**
Radioactivity in soil extracts [% AR]	70.8	91.3	67.7	73.6	66.0	56.5	54.0	84.9	83.0	48.1	77.9	82.9
Test item in soil extracts [% ROI] [1]	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0
Test item in soil extracts [% AR]	**70.8**	**91.3**	**67.7**	**73.6**	**66.0**	**56.5**	**54.0**	**84.9**	**83.0**	**48.1**	**77.9**	**82.9**
Total recovery of radioactivity [% AR]	98.3	102.2	102.8	102.6	99.8	93.4	95.4	106.2	106.2	101.3	103.6	106.4
Total recovery of test item [% AR]	**98.3**	**102.2**	**101.1**	**99.5**	**97.8**	**91.4**	**94.5**	**104.0**	**103.8**	**99.0**	**101.6**	**104.2**

[1] percentage of regions of interest [% ROI] from primary chromatographic method

C. FINDINGS

In the definitive adsorption test the adsorbed amounts of fluopyram were 50.0 – 67.0% AR in soil LO, 56.6 – 86.8% AR in soil AM, 41.0 – 56.5% AR in soil UW, 41.6 – 56.0% AR in soil FA, 40.4 – 55.5% AR in soil SD, 34.5 – 53.7% AR in soil PZ, 43.5 – 53.9% AR in soil HS, 58.4 – 73.6% AR in soil HT, 57.3 – 70.2% AR in soil LT, 27.8 – 40.0% AR in soil BS, 49.5 – 69.3% AR in soil BB and 47.6 – 71.4% AR in soil AE.

The calculated adsorption constants K_d of the Freundlich isotherms ranged from 1.452 to 5.126 mL/g (arithmetic mean: 3.219 mL/g) for the tested soils. The Freundlich exponents 1/n ranged from 0.7321 to 0.9179 (arithmetic mean: 0.8500), indicating that the concentration of the test item affected the adsorption behaviour in the examined concentration range.

In general the organic matter in soil, determined as organic carbon content, is the most important component responsible for binding organic chemicals. Therefore, the adsorption coefficients K_F were correlated with the organic carbon content of the soil to get a comparability of the adsorption behaviour in different soils. For fluopyram the K_{Foc} values ranged from 156 to 320 mL/g (arithmetic mean: 222 mL/g). The results of the adsorption isotherm test (i.e. adsorbed percentage and Freundlich adsorption coefficients) are summarised in the tables below.

Table 7.1.3.1.1-10: Percentage of adsorbed fluopyram in soils (mean values and standard deviation)

Concentration of Test Item	Soil [mg/kg]	Solution [mg/L]	Percentage Adsorbed [% AR]	
Soil	**Little Oliver (Soil ID: LO)**			
Control	N/A	N/A		
0.010 mg/L	0.027	0.003	67.0	± 0.2
0.034 mg/L	0.082	0.013	60.5	± 0.1
0.11 mg/L	0.250	0.045	58.1	± 0.2

Concentration of Test Item	Soil [mg/kg]	Solution [mg/L]	Percentage Adsorbed [% AR]	
0.28 mg/L	0.676	0.107	61.3	± 6.0
1.02 mg/L	2.038	0.510	50.0	± 0.0
Soil	**Auchy les Mines (Soil ID: AM)**			
Control	N/A	N/A		
0.010 mg/L	0.035	0.001	86.8	± 2.1
0.034 mg/L	0.096	0.010	71.4	± 0.3
0.11 mg/L	0.291	0.035	67.5	± 0.3
0.28 mg/L	0.702	0.100	63.6	± 0.1
1.02 mg/L	2.309	0.442	56.6	± 0.1
Soil	**Urbanowice (Soil ID: UW)**			
Control	N/A	N/A		
0.010 mg/L	0.023	0.004	56.5	± 1.0
0.034 mg/L	0.069	0.016	51.3	± 0.1
0.11 mg/L	0.210	0.055	48.8	± 0.3
0.28 mg/L	0.497	0.151	45.1	± 0.5
1.02 mg/L	1.671	0.602	41.0	± 0.1
Soil	**Charles River Farm (Soil ID: FA)**			
Control	N/A	N/A		
0.010 mg/L	0.023	0.003	56.0	± 1.2
0.034 mg/L	0.073	0.016	53.8	± 0.1
0.11 mg/L	0.214	0.054	49.7	± 0.6
0.28 mg/L	0.508	0.149	46.1	± 0.0
1.02 mg/L	1.696	0.595	41.6	± 0.4
Soil	**Sindos (Soil ID: SD)**			
Control	N/A	N/A		
0.010 mg/L	0.022	0.004	55.5	± 0.6
0.034 mg/L	0.070	0.016	52.0	± 0.3
0.11 mg/L	0.207	0.056	48.1	± 0.5
0.28 mg/L	0.494	0.152	44.8	± 0.4
1.02 mg/L	1.648	0.607	40.4	± 0.2
Soil	**Paradiso San Zenone (Soil ID: PZ)**			
Control	N/A	N/A		
0.010 mg/L	0.022	0.004	53.7	± 0.2
0.034 mg/L	0.062	0.018	46.3	± 0.1
0.11 mg/L	0.183	0.062	42.6	± 0.0
0.28 mg/L	0.426	0.169	38.7	± 0.3
1.02 mg/L	1.406	0.668	34.5	± 0.2
Soil	**Hoeltinghausen (Soil ID: HS)**			
Control	N/A	N/A		
0.010 mg/L	0.022	0.005	53.9	± 0.7
0.034 mg/L	0.066	0.017	48.9	± 0.5
0.11 mg/L	0.204	0.057	47.4	± 0.0
0.28 mg/L	0.503	0.150	45.7	± 0.4
1.02 mg/L	1.774	0.576	43.5	± 0.0

Concentration of Test Item	Soil [mg/kg]	Solution [mg/L]	Percentage Adsorbed [% AR]	
Soil	**Hornton (Soil ID: HT)**			
Control	N/A	N/A		
0.010 mg/L	0.029	0.003	73.6	± 0.1
0.034 mg/L	0.095	0.010	70.1	± 0.9
0.11 mg/L	0.288	0.036	66.9	± 0.1
0.28 mg/L	0.707	0.099	64.1	± 0.0
1.02 mg/L	2.381	0.424	58.4	± 0.2
Soil	**Le Thour (Soil ID: LT)**			
Control	N/A	N/A		
0.010 mg/L	0.028	0.003	70.2	± 0.5
0.034 mg/L	0.093	0.011	68.7	± 0.0
0.11 mg/L	0.284	0.037	66.0	± 0.2
0.28 mg/L	0.692	0.103	62.8	± 0.0
1.02 mg/L	2.338	0.425	57.5	± 0.1
Soil	**Brannens (Soil ID: BS)**			
Control	N/A	N/A		
0.010 mg/L	0.016	0.006	40.0	± 1.4
0.034 mg/L	0.045	0.023	33.1	± 0.8
0.11 mg/L	0.139	0.073	32.3	± 0.3
0.28 mg/L	0.333	0.192	30.2	± 0.7
1.02 mg/L	1.133	0.736	27.8	± 0.6
Soil	**Balbiano (Soil ID: BB)**			
Control	N/A	N/A		
0.010 mg/L	0.028	0.003	69.3	± 0.8
0.034 mg/L	0.088	0.012	65.2	± 0.0
0.11 mg/L	0.260	0.042	60.4	± 0.0
0.28 mg/L	0.650	0.118	57.1	± 0.2
1.02 mg/L	2.016	0.515	49.5	± 0.1
Soil	**Almayate East (Soil ID: AE)**			
Control	N/A	N/A		
0.010 mg/L	0.029	0.003	71.4	± 2.1
0.034 mg/L	0.089	0.011	66.3	± 0.5
0.11 mg/L	0.265	0.041	61.6	± 0.5
0.28 mg/L	0.619	0.121	56.1	± 0.1
1.02 mg/L	1.942	0.534	47.6	± 0.1

Table 7.1.3.1.1-11: Adsorption constants of fluopyram in the test soils

Soil ID	Adsorption			
	K_F [mL/g]	1/n	R^2	K_{Foc} [mL/g]
LO	3.991	0.8793	0.9903	266
AM	3.702	0.7321	0.9864	185
UW	2.522	0.8578	0.9989	229
FA	2.519	0.8363	0.9990	157
SD	2.474	0.8548	0.9995	190
PZ	1.872	0.8260	0.9983	156
HS	2.881	0.9179	0.9995	320
HT	5.126	0.8673	0.9998	244
LT	5.109	0.8868	0.9993	183
BS	1.452	0.8944	0.9982	242
BB	3.639	0.8392	0.9996	214
AE	3.340	0.8083	0.9988	278
Arithmetic mean	**3.219**	**0.8500**	**0.9973**	**222**

III. CONCLUSIONS

In the adsorption test, 27.8-86.8% of the applied test material was adsorbed.

The adsorption constants K_F of fluopyram for the tested soils calculated based on the Freundlich isotherms ranged from 1.452 to 5.126 mL/g (arithmetic mean: 3.219 mL/g). The respective K_{Foc} values ranged from 156 to 320 mL/g (arithmetic mean: 222 mL/g). 1/n values ranged from 0.7321 to 0.9179.

Fluopyram was stable during the test. At the lowest test concentration the parental mass balance was ≥ 91.4% AR, at the highest test concentration it was ≥ 99.3% AR. No degradation product was observed.

EVALUATION ACCORDING TO EFSA CHECKLIST

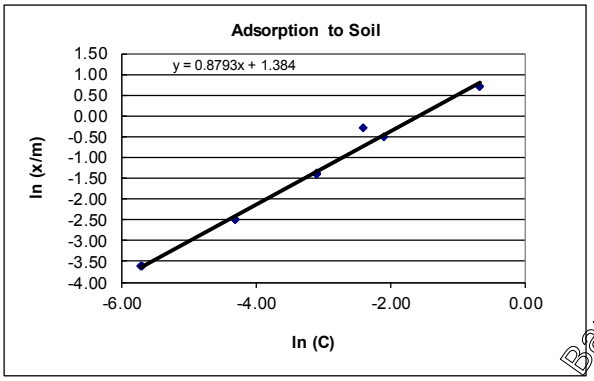
All relevant quality checks were performed as part of confirming the acceptability of the reported data and endpoints of the above study M-753424-01-1. The indirect method was used for all soils. The parental mass balance ranged from 91.4 to 107.4%, the mean material balance from 96.4 to 101.5% (overall mean 99.4%) and adsorption from 28.3 to 88.8% (adsorption values derived from the EFSA evaluators checklist may vary from those calculated in this study due to rounding errors) and are presented in Table 7.1.3.1.1-12. Systematic errors estimated via K_{fe}/K_f were shown to be low (i.e. ≤ 1.2). Over the entire range of concentrations the applied amount was approx. 37 times higher than LOQ. The graphical fits of the Freundlich equation are presented below based on the standard linear regression form using log-log transformed data, including the corresponding plot of the residuals from the standard linear regression (see Figure 7.1.3.1.1-6 to Figure 7.1.3.1.1-17). The R^2 of the standard linear regressions ranged from 0.986 to 1.000 for the tested soils.

Table 7.1.3.1.1-12: Results of evaluation according to EFSA OECD 106 Evaluators Checklist for fluopyram

Soil	Units	LO	AM	UW	FA	SD	PZ
Adsorption method	-	indirect	indirect	indirect	indirect	indirect	indirect
Soil:solution ratio	(g dw/mL)	1:4	1:4	1:4	1:4	1:4	1:4
Parental mass balance (at highest test conc.)	%	104.1	104.4	105.0	106.1	107.0	107.4
Adsorbed percentage	%	50.0-67.4	56.5-88.8	40.8-62.9	31.2-68.4	40.2-61.9	34.3-60.7
Kd x (soil:solution ratio)		1.0-2.1	1.3-8.0	0.7-1.6	0.7-1.8	0.7-1.5	0.5-1.4
$^{ads}K_F$ (95% confidence interval)	L/kg dw	3.991 (3.080-5.171)	3.702 (2.785-4.923)	2.522 (2.326-2.734)	2.519 (2.337-2.716)	2.474 (2.353-2.604)	1.872 (2.337-2.716)
^{ads}"1/n" (95% confidence interval)	-	0.879 (0.808-0.950)	0.732 (0.662-0.802)	0.858 (0.834-0.881)	0.836 (0.815-0.858)	0.855 (0.840-0.870)	0.826 (0.798-0.854)
$^{ads}R^2$	-	0.990	0.986	0.999	0.999	1.000	0.998
$^{ads}K_{F,OC}$	L/kg OC	266	185	229	158	190	156
K_{fE} / K_f	-	1.00	1.00	1.00	1.00	1.00	1.00

Soil	Units	HS	HT	LT	BS	BB	AE
Adsorption method	-	indirect	indirect	indirect	indirect	indirect	indirect
Soil:solution ratio	(g dw/mL)	1:4	1:4	1:4	1:4	1:4	1:4
Parental mass balance (at highest test conc.)	%	102.8	103.5	99.3	102.5	103.2	103.2
Adsorbed percentage	%	43.5-54.5	58.2-73.7	57.2-70.6	28.3-41.3	49.3-70.1	47.5-73.4
Kd x (soil:solution ratio)		0.8-1.2	1.4-2.8	1.3-2.4	0.4-0.7	1.0-2.3	0.9-2.8
^{ads}KF (95% confidence interval)	L/kg dw	2.881 (2.719-3.053)	5.126 (4.914-5.347)	5.109 (4.559-8.346)	1.452 (1.504-1.737)	3.639 (3.594-4.426)	3.340 (3.296-4.575)
^{ads}"1/n" (95% confidence interval)		0.918 (0.901-0.935)	0.867 (0.856-0.878)	0.887 (0.897-1.032)	0.894 (0.940-0.977)	0.839 (0.855-0.902)	0.808 (0.838-0.911)
$^{ads}R^2$	-	0.999	1.000	0.999	0.998	1.000	0.999
$^{ads}K_{F,OC}$	L/kg OC	320	244	183	242	214	278
K_{fE} / K_f	-	1.00	1.00	1.01	1.00	1.00	1.00

Note: Values derived from the EFSA evaluators checklist may vary from those calculated in this study due to rounding errors.



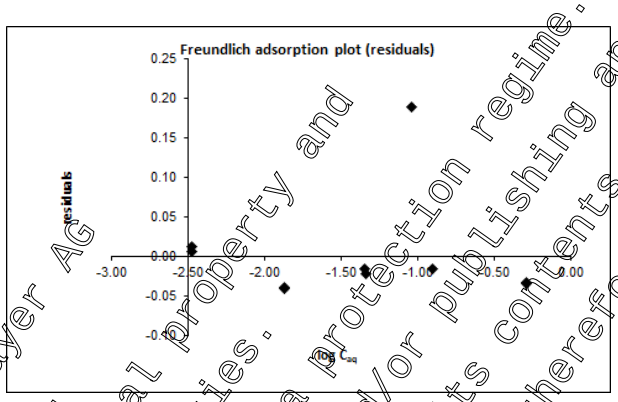
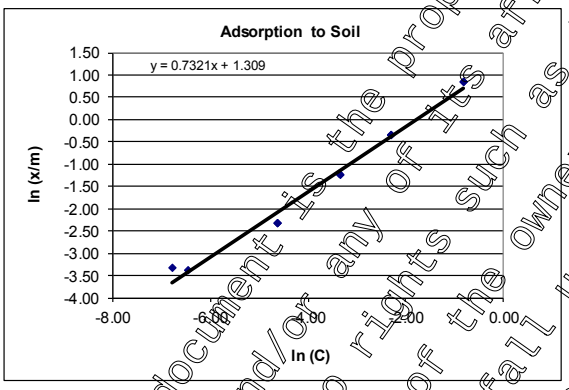


Figure 7.1.3.1.1-6: Graphical presentation of Freundlich adsorption isotherm analysis (linear regression, left) and the corresponding plot of the residuals (right) for soil Little Oliver



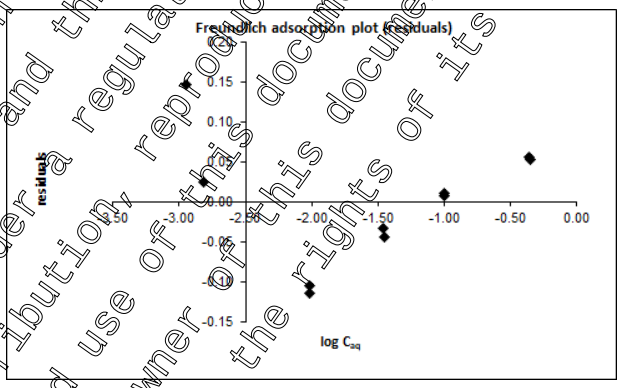
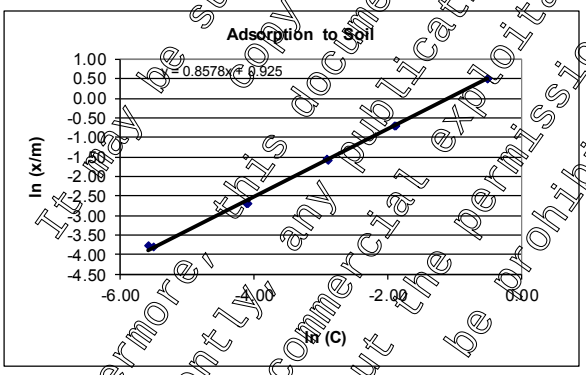


Figure 7.1.3.1.1-7: Graphical presentation of Freundlich adsorption isotherm analysis (linear regression, left) and the corresponding plot of the residuals (right) for soil Auchy les Mines



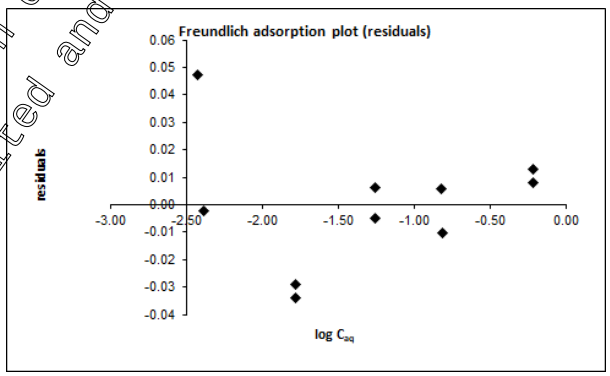
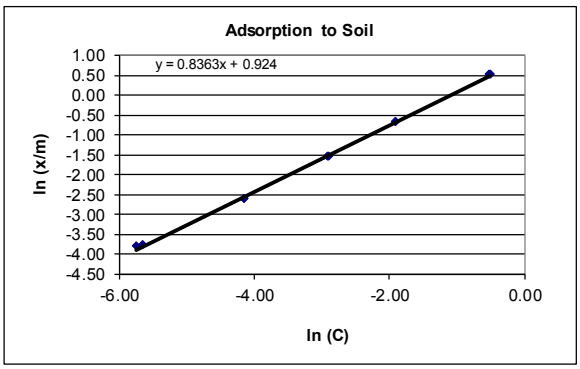


Figure 7.1.3.1.1-8: Graphical presentation of Freundlich adsorption isotherm analysis (linear regression, left) and the corresponding plot of the residuals (right) for soil Urbanowice



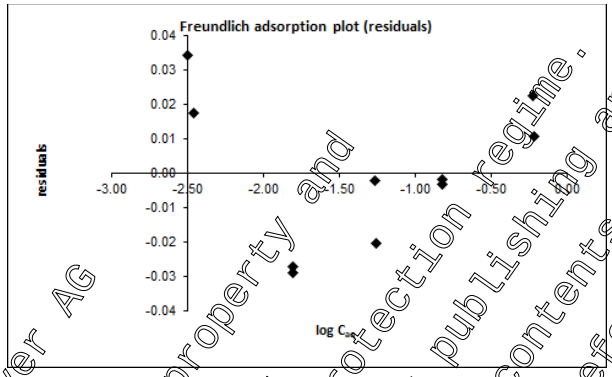
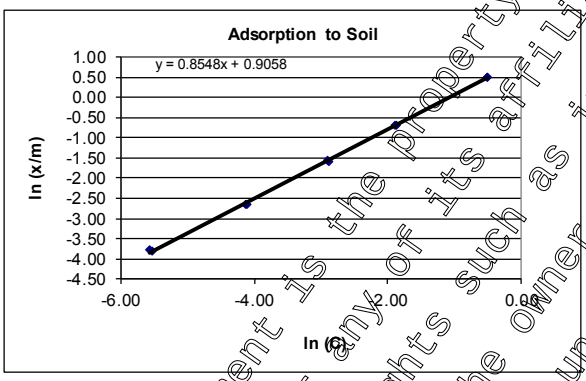


Figure 7.1.3.1.1-9: Graphical presentation of Freundlich adsorption isotherm analysis (linear regression, left) and the corresponding plot of the residuals (right) for soil Charles River Farm



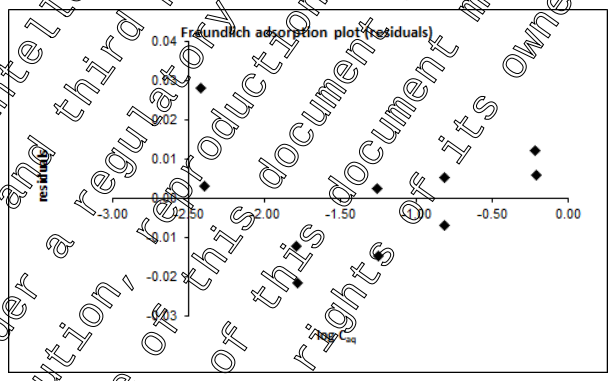
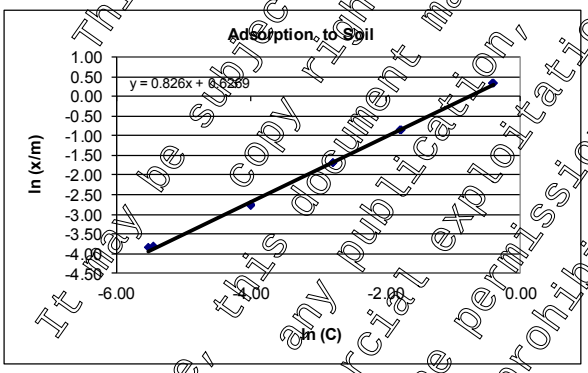


Figure 7.1.3.1.1-10: Graphical presentation of Freundlich adsorption isotherm analysis (linear regression, left) and the corresponding plot of the residuals (right) for soil Sindos



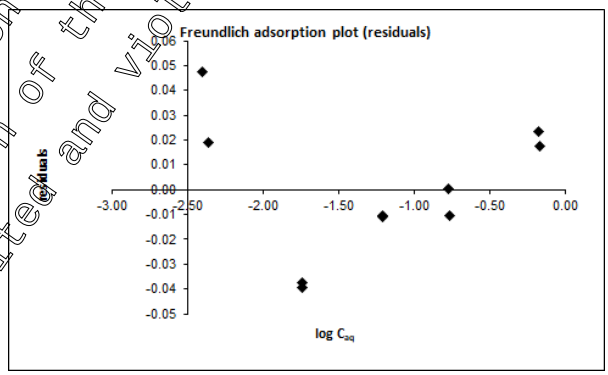
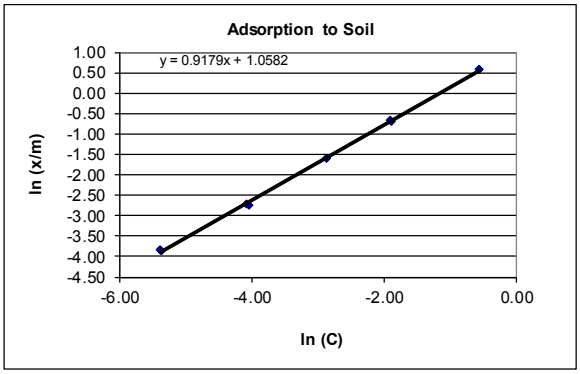


Figure 7.1.3.1.1-11: Graphical presentation of Freundlich adsorption isotherm analysis (linear regression, left) and the corresponding plot of the residuals (right) for soil Paradiso San Zenone



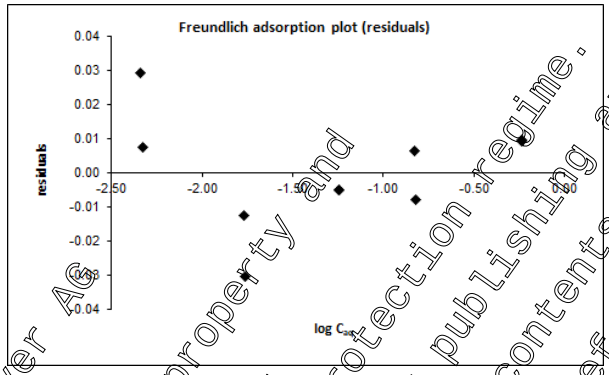
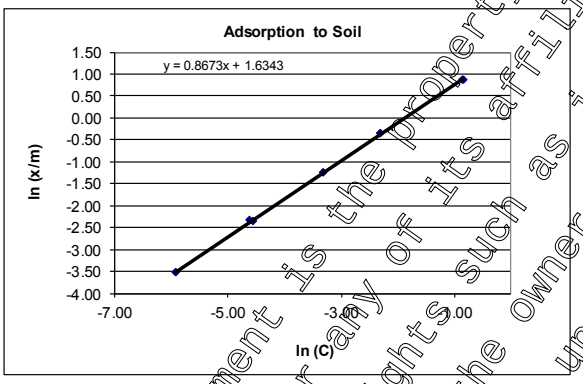


Figure 7.1.3.1.1-12: Graphical presentation of Freundlich adsorption isotherm analysis (linear regression, left) and the corresponding plot of the residuals (right) for soil Hoeltinghausen



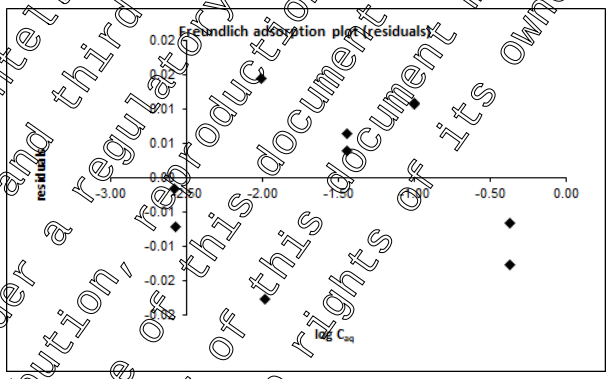
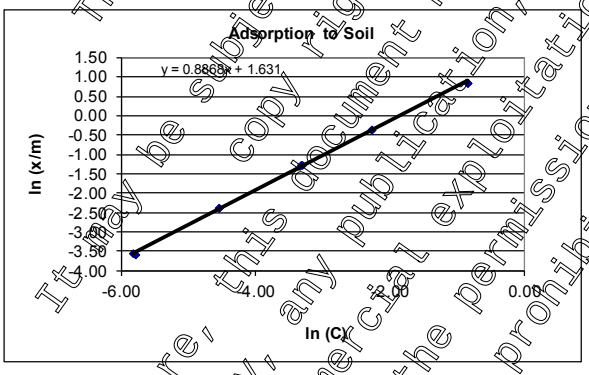


Figure 7.1.3.1.1-13: Graphical presentation of Freundlich adsorption isotherm analysis (linear regression, left) and the corresponding plot of the residuals (right) for soil Hornton



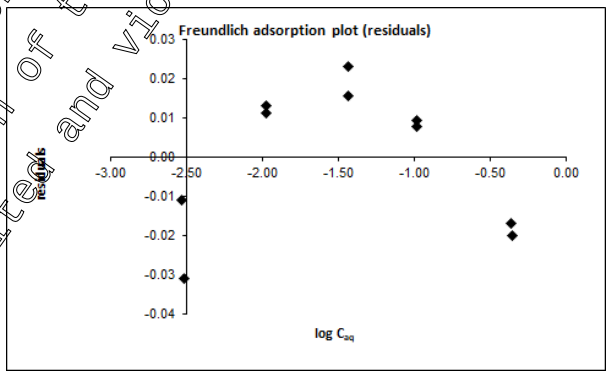
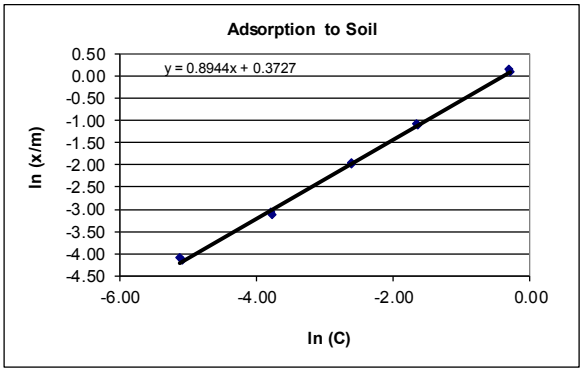


Figure 7.1.3.1.1-14: Graphical presentation of Freundlich adsorption isotherm analysis (linear regression, left) and the corresponding plot of the residuals (right) for soil Le Thour



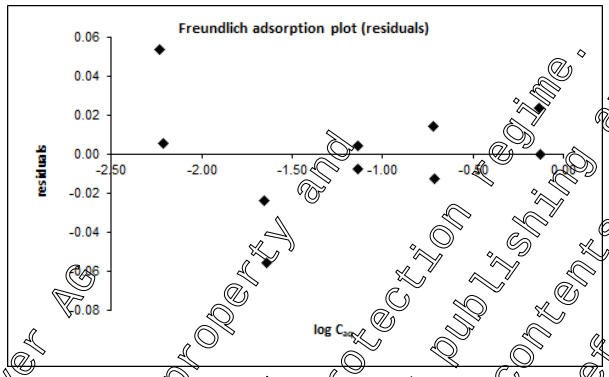
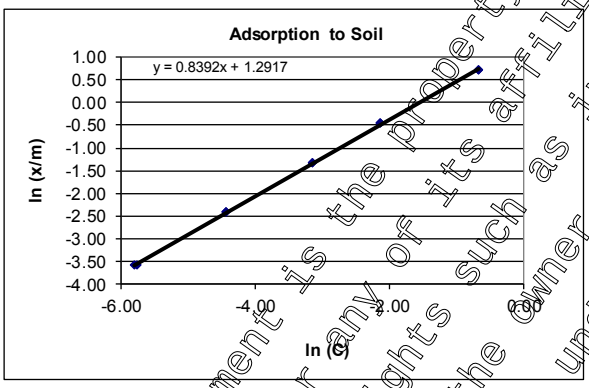


Figure 7.1.3.1.1-15: Graphical presentation of Freundlich adsorption isotherm analysis (linear regression, left) and the corresponding plot of the residuals (right) for soil Brannens



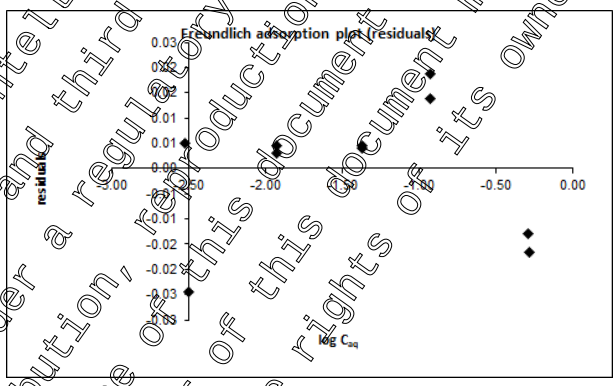
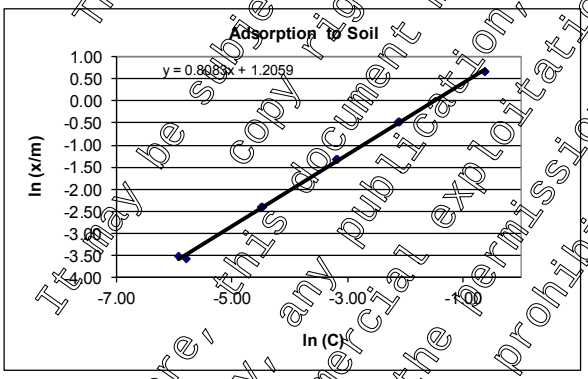


Figure 7.1.3.1.1-16: Graphical presentation of Freundlich adsorption isotherm analysis (linear regression, left) and the corresponding plot of the residuals (right) for soil Balbiano



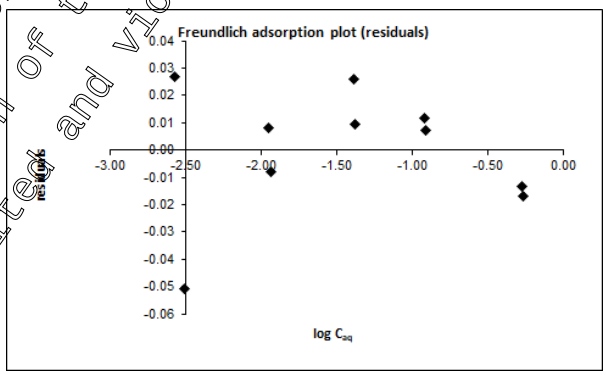


Figure 7.1.3.1.1-17: Graphical presentation of Freundlich adsorption isotherm analysis (linear regression, left) and the corresponding plot of the residuals (right) for soil Almayate East

3. Assessment and conclusion

Assessment and conclusion by applicant:

The study and its data are considered to be valid and reliable for use in risk assessment.

Assessment and conclusion by RMS:

Outcome and conclusion of the study: RMS should indicate if they agree to the results and conclusions of the APPL.

CA 7.1.3.1.2 Adsorption and desorption of metabolites, breakdown and reaction products

1. Information on the study

Data Point:	KCA 7.1.3.1.2/01
Report Author:	[redacted]
Report Year:	2007
Report Title:	[Pyridine-2,6-14C]AE C656948-7-hydroxy: Adsorption/desorption on four EU soils
Report No:	MEF-07/149
Document No:	M-289570-01-2
Guideline(s) followed in study:	OECD 106, U.S. EPA OPPTS Guideline No. 835.1240
Deviations from current test guideline:	Current Guideline: OECD 106 (2000) None
Previous evaluation:	yes, evaluated and accepted DAR (2011)
GLP/Officially recognised testing facilities:	Yes, conducted under GLP/Officially recognised testing facilities
Acceptability/Reliability:	Yes

2. Full summary of KCA 7.1.3.1.2/01

Executive Summary

The adsorption desorption behaviour of [pyridine-2,6-^{14}C]fluopyram-7-hydroxy was studied in four soils in batch equilibrium experiments in the dark in the laboratory at 20 ± 1 °C:

Soil	Soil ID	Source	Texture (USDA)	pH [1]	OC [%]
Laacher Hof AIIIa	AIIIa	Monheim, Germany	Loam	6.4	1.1
Laacher Hof AXXa	AXXa	Monheim, Germany	Sandy loam	6.1	1.5
Hoefchen am Hohenseh 4a	HaH	Burscheid, Germany	Silt loam	6.6	1.6
Laacher Hof Wurmwiese	WuW	Monheim, Germany	Sandy loam	5.1	1.6

[1] pH values were derived from aqueous 0.01 M $CaCl_2$ suspensions

The adsorption phase of the study was carried out using air-dried soils equilibrated in aqueous 0.01 M $CaCl_2$ solution with a soil-to-solution ration of 1/2 (soils Laacher Hof, AIIIa, Laacher Hof, AXXa, Hoefchen am Hohenseh 4a, HaH and Laacher Hof Wurmwiese, WuW). $HgCl_2$ (50 mg/L) was added to

the 0.01 M $CaCl_2$ solution to inhibit microbial activity. [Pyridine-2,6-^{14}C]fluopyram-7-hydroxy was applied at test concentrations in a range of 0.01 to 1.0 mg/L in aqueous 0.01 M $CaCl_2$ solution. The desorption phase was performed by supplying pre-adsorbed soil samples with fresh aqueous 0.01 M $CaCl_2$ solution for the first desorption step. For the highest concentration two additional desorption steps were performed. The adsorption and desorption steps were carried out each for 24 hours under continuous agitation.

[Pyridine-2,6-^{14}C]fluopyram-7-hydroxy was stable during the test for the duration of the adsorption and the desorption phase. The parental mass balance was ≥ 93.1 % AR for an equilibration time of 96 h. No degradation product was observed.

The overall mass balances for all soils were in the range of 91.8-98.1 %AR (mean: 94.5% AR).

The Freundlich adsorption constants ($K_{F(ads)}$) of [pyridine-2,6-^{14}C]fluopyram-7-hydroxy were determined. $K_{F(ads)}$ values ranged from 0.991 mL/g to 2.4 mL/g. The respective $K_{oc(ads)}$ values were in the range of 85.1 mL/g and 149.4 mL/g (arithmetic mean: 103.2 mL/g; geometric mean: 100.2 mL/g).

In the adsorption test, 33.9-66.3 % of the applied test material was adsorbed. After the desorption phase, 18.3-37.5 %of the initially adsorbed radioactivity was desorbed from the respective soils. The desorption constants $K_{dOC(des)}$ ranged from 236.8 to 372.8 mL/g (arithmetic mean: 291.2 mL/g; geometric mean: 286.4 mL/g).
1/n values ranged from 0.91 to 0.94 and from 0.95 to 0.99 for adsorption and desorption, respectively. There is no significant correlation between pH and adsorption for the investigated soils.

I. MATERIALS AND METHODS

A. MATERIALS

1. Test Item

[Pyridyl-2,6-^{14}C]AE C656928-7-hydroxy (fluopyram)
Sample ID BECH 2141
Specific activity 3.16 MBq/mg
Radiochemical purity > 99 %
Chemical Purity > 99%

2. Test Soils

The soils were sampled before study start (upper horizon of 0 to 20 cm), sieved to a particle size of ≤ 2 mm and stored at 5 °C for up to 3 month. The soils were air-dried before use. The soils were taken from agricultural areas representing different geographical origins and different soil properties as required by the guidelines. Soil characteristics are summarised in the table below.

Table 7.1.3.1.2-1: Soil characteristics

Soil	Laacherhof AIIIa	Laacherhof AXXa	Hoefchen am Hohenseh	Laacherhof, Wurmwiese
Geographic Location (City/State/Country)	Monheim / NRW / Germany	Monheim / NRW / Germany	Burscheid / NRW / Germany	Monheim / NRW / Germany
Pesticide use history	No pesticide use for the previous 5 years			
Collection procedures	Field sampled with shovel into plastic bag (bucket)			
Sampling depth	0–20 cm			
Storage conditions	Ambient, after sieving ca. 5°C (stored in plastic container)			
Storage length	28 d after sieving	90 d after sieving	60 d after sieving	28 d after sieving
Soil preparation	Sieved (2 mm) ca. 3 months after collection			
Texture Class (USDA)	loam	sandy loam	silt loam	Sandy loam
Sand (%)[1]	47	73	23	55
Silt (%)[1]	32	18	59	30
Clay (%) [1]	21	9	18	15
pH 0.01 M $CaCl_2$	6.4	6.1	6.6	5.1
pH in Water	6.7	6.4	7.0	5.3
pH in 1 M KCl	6.1	5.8	6.4	4.7
Org. Matter [2] (%)	1.7	2.6	3.4	3.0
Org. Carbon (%)	1.1	1.5	1.6	1.6
CEC (meq/100 g)	10.1	7.5	12.4	10.4
MWHC (g/100 g)	46.7	43.1	53.6	52.1
WHC 0.33 bar (g/100g)	15.2	9.5	21.5	16.8

[1] acc. USDA classification [2]% organic matter = % organic carbon x 1.724
CEC: Cation exchange capacity; 1/3 bar MWHC: Water Holding Capacity at 0.33 bar; MWHC: Maximum Water Holding Capacity

B. STUDY DESIGN

1. Experimental Conditions

The test system for adsorption and desorption in batch equilibrium experiments consisted of Teflon® centrifuge tubes (volume 42 mL) closed with screw caps. The experiments were performed in duplicate.

In preliminary tests, the adsorption of the test item to the test system surface, the optimal soil-to-solution ratio, the appropriate adsorption and desorption equilibration times and the stability of the test item were determined.

10 g dry soil (corrected for soil humidity) were weighed into centrifuge tubes and aqueous 0.01 M $CaCl_2$ solution was added to reach a final volume of 20 mL. Mercury (II) chloride was added to the 0.01 M $CaCl_2$ solution to inhibit microbial activity (concentration $HgCl_2$ = 50 mg/L). Control samples without soil were prepared in the same way. After pre-equilibration for three days, the adsorption phase of the study was carried out adding 20 µL of fluopyram-7-hydroxy solutions corresponding to test item concentrations covering two orders of magnitude. Individual concentrations were 1.0, 0.3, 0.1, 0.03, and 0.01 mg/L in the supernatant water phase. Acetonitrile (≤ 0.1 %) was used as co-solvent. Each test was performed in duplicate. In preliminary tests for all soils the plateau concentration was established after 24 hours. The aqueous supernatant was decanted and separated by centrifugation (5 min at 9000 rpm) and the fluopyram-7-hydroxy residues were analyzed by liquid scintillation counting (LSC). Additionally, the remaining soil was extracted to establish the mass balance. The desorption phase of the study was carried out by replacing the aqueous supernatant removed from each soil sample with fresh 0.01 M $CaCl_2$ solution for one desorption cycle, except for the highest concentration, where three desorption cycles were performed. A total volume of 20 mL 0.01 M $CaCl_2$ was used as equilibrium

solution (soil/solution ratio of 1:2). The vessels were sealed, shaken (overhead shaker 30 ± 2 rpm) for 24 hours in the dark (20 ± 1 °C) and processed as described in the adsorption experiment above. After the desorption step, the soil was extracted and analyzed by LSC. The adsorption parameters were calculated using the Freundlich adsorption isotherm.

2. Analytical Procedures

After each adsorption and desorption step the aqueous supernatant was separated from the soil by centrifugation and the amount of fluopyram-7-hydroxy in the supernatants was analysed by liquid scintillation counting (LSC).

In the preliminary parental mass balance test, the soil was additionally extracted four times using acetonitrile.

Fluopyram-7-hydroxy in solutions was determined as radioactive residue by liquid scintillation counting (LSC). The limit of detection (LOD) was 0.5 Bq/aliquot and the limit of quantification (LOQ) was 2 Bq (0.63 ng)/500 µL. Radio-HPLC was used to demonstrate the stability of the test item.

The HPLC LOD in the aqueous phase was determined to be at least 304 Bq absolute, corresponding to 0.45% applied radioactivity (AR) and for organic extracts, the LOD was 608 Bq absolute, corresponding to 0.89 % of AR. LOQ was set to three time LOD, which is 1.35 % of AR for the aqueous phase and 2.67 % of AR for the organic extracts.

The partition of the test item in the adsorption and desorption batch equilibrium experiment was determined based on the radioactivity content in the supernatant only due to the stability of the test item demonstrated by the parental mass balance. After the desorption step, the soils were extracted with acetonitrile followed by combustion/LSC to establish the material balance.

Adsorption and desorption constants (K_d) were calculated from the concentration of the test item in solution at equilibrium and the adsorbed amount of the test item at equilibrium.

II. RESULTS AND DISCUSSION

A. MATERIAL BALANCE

The overall material balance for all concentrations was in the range of 91.8 to 98.1 % of the applied radioactivity (mean: 94.5 % of the AR). No degradation of fluopyram-7-hydroxy in the test solutions was detected by HPLC. The test item was absolutely stable in control samples. The complete material balance found at all sampling intervals demonstrated that no significant amount of radioactivity dissipated from the test containers or was lost upon processing.

B. STABILITY OF TEST ITEM

In preliminary tests the parental mass balance was found to be 93.1 % to 95.5 % of the AR (mean values) for all soils. The stability of the test item in the solution was proven by the parental mass balance (above 90 % of the AR). Thus, subsequent measurements were performed by LSC analysis of the supernatant only in both adsorption and desorption experiments. Results of the parental mass balance test are summarised in the table below.

Table 7.1.3.1.2-2: Recovery of fluopyram-7-hydroxy in soil after 96 hours, expressed as percentage of applied radioactivity (% AR, mean)

Soil	Lacherhof AIIIa	Laacherhof AXXa	Hoefchen	Wurmwiese
Supernatant solution	50.5	43.8	28.7	40.8
Solid phase (ACN) extract [1]	44.0	50.5	64.4	54
Non-extractable residues in soil, if measured	N/A	N/A	N/A	N/A
Total recovery	94.5	94.4	93.1	95.5

[1] test item is stable, HPLC = 100% (comparison: purity of application solution > 99%)

C. FINDINGS

At the end of the adsorption phase 33.9-43.6, 40.3-49.3, 55.6-66.3 and 40.6-48.0% AR were adsorbed in soil Laacher Hof AIIIa, AXXa, Hoefchen am Hohenseh 4a and Laacher Hof Wurmwiese, respectively (see Table 7.1.3.1.2-3). The adsorption behaviour of [pyridyl-2,6-^{14}C]fluopyram-7-hydroxy in the concentration range of two orders of magnitude (i.e. from projected 1.0 mg/L to 0.01 mg/L) was accurately described for all soils by the Freundlich equation. The correlation coefficient (R^2) of measured data and the respective calculated adsorption isotherms ranged from 0.9977 to 0.9998. The adsorption constants $K_{F(ads)}$ of the Freundlich isotherms ranged from 0.991 to 2.4 mL/g (see Table 7.1.3.1.2-4). The Freundlich exponents 1/n were below 1.0 for all soils (0.91 to 0.94), indicating that the concentration of the test item affected the adsorption behaviour. The adsorption coefficients $K_{F(ads)}$ were normalized for the organic carbon content of the soils, in order to obtain K_{OC} values. $K_{OC(ads)}$ varied between 85.1 mL/g and 149.4 mL/g (arithmetic mean: 103.2 mL/g; geometric mean: 100.2 mL/g).

At the end of the desorption phase, 32.3-37.5, 31.5-34.6, 18.3-24.2 and 30.2-34.8% of the initially adsorbed amount were desorbed in soil Laacher Hof AIIIa, AXXa, Hoefchen am Hohenseh 4a and Laacher Hof Wurmwiese, respectively. The calculated desorption constant $K_{F(des)}$ of the Freundlich isotherms ranged from 3.4 mL/g to 6.0 mL/g. Desorption $K_{OC(des)}$ values ranged from 236.8 mL/g to 372.8 mL/g (mean: 291.2 mL/g).

Table 7.1.3.1.2-3: Percentage of adsorbed and desorbed fluopyram-7-hydroxy in soils (mean values and standard deviation)

Concentration (mg a.i./L)	Adsorption [1]	Desorption [2]
Soil ID	**AIIIa**	
0.011	43.6±0.51	32.3±0.67
0.030	37.5±2.72	37.5±1.88
0.10	39.6±0.71	33.8±0.98
0.31	35.3±0.54	35.7±1.59
1.10	33.9±0.10	36.0±0.02
Soil ID	**AXXa**	
0.011	49.3±0.00	31.5±0.00
0.030	44.6±0.56	34.6±0.48
0.10	44.0±1.18	33.7±1.46
0.31	42.9±0.18	33.2±0.35
1.10	40.3±0.23	34.6±0.77
Soil ID	**Hoefchen a. Hohenseh**	
0.011	66.3±0.34	18.3±0.33
0.030	63.4±0.00	20.7±0.00
0.10	62.3±0.18	21.2±0.36
0.31	59.2±0.36	24.2±1.59
1.10	55.6±0.66	21.4±3.05

Concentration (mg a.i./L)	Adsorption [1]	Desorption [2]
Soil ID	Wurmwiese	
0.011	48.0±0.97	30.2±1.89
0.030	45.4±0.28	34.8±0.13
0.10	44.8±1.01	31.2±2.20
0.31	43.8±1.44	32.6±0.57
1.10	40.6±2.02	33.9±2.50

[1] end of adsorption phase, mean values expressed as percentage of applied radioactivity
[2] end of desorption phase, mean values expressed as percentage of the initially adsorbed amount
Desorption steps: One desorption for conc. 0.01-0.31 mg/L
Three desorption steps for conc. 1.10 mg/L

Table 7.1.3.1.2-4: Adsorption and desorption constants of fluopyram-7-hydroxy in the test soils

Soil	Adsorption			Desorption		
	$K_{F(ads)}$ [mL/g]	1/n	$K_{OC(ads)}$ [mL/g]	$K_{F(des)}$ [mL/g]	1/n	$K_{OC(des)}$ [mL/g]
AIIIa	0.991	0.9241	90.1	3.375	0.9781	306.8
AXXa	1.321	0.9391	88.1	3.728	0.9869	248.5
Hoefchen	2.390	0.9104	149.4	5.965	0.9464	372.8
Wurmwiese	1.362	0.9432	85.1	3.789	0.9784	236.8
Mean	**1.516**	**0.9292**	**103.2**	**4.214**	**0.9725**	**291.2**

III. CONCLUSIONS

The adsorption constants ($K_{F(ads)}$) of [pyridine-2,6-^{14}C]fluopyram-7-hydroxy for the four test soils calculated ranged from 0.991 mL/g to 2.4 mL/g. The respective $K_{oc(ads)}$ values were in the range of 85.1 mL/g and 149.4 mL/g (arithmetic mean: 103.2 mL/g; geometric mean: 100.2 mL/g).

Desorption $K_{OC(des)}$ values ranged from 236.8 mL/g to 372.8 mL/g (mean: 291.2 mL/g). 1/n values ranged from 0.91 to 0.94 and from 0.95 to 0.99 for adsorption and desorption, respectively.

Adsorption and desorption constants do not depend on the pH of the soil.

[Pyridine-2,6-^{14}C]fluopyram-7-hydroxy was stable during the test for the duration of the adsorption and the desorption phase. The parental mass balance was ≥ 93.1 % AR for an equilibration time of 96 h. No degradation product was observed.

3. Assessment and conclusion

Assessment and conclusion by applicant:
The study and its data are considered to be valid and reliable for use in risk assessment..

Assessment and conclusion by RMS:
Outcome and conclusion of the study: RMS should indicate if they agree to the results and conclusions of the APPL.

EVALUATION ACCORDING TO EFSA CHECKLIST

The above study M-289570-01-2 was performed according to the OECD 106 guideline dating from 2000 for the determination of the Freundlich isotherm. The indirect method was used for all soils. All relevant quality checks were performed as part of confirming the acceptability of the reported data and

endpoints. The parental mass balance ranged from 93.1 to-95.5%, and % adsorption from 33.73 to 96.36% for all soils (see Table 7.1.3.1.2-5). The LOD and LOQ for the HPLC method were reported as 0.89 and 2.67% AR, respectively. The graphical fits of the Freundlich equation are presented below based on the standard linear regression form using log-log transformed data alongside the associated residual plots (see Figure 7.1.3.1.2-1 to Figure 7.1.3.1.2-4). The R^2 of the standard linear regressions was >0.998 for all soil. Systematic errors estimated via K_{fE}/K_f were shown to be low (i.e. ≤1.2) for all soils.

Table 7.1.3.1.2-5: Results of evaluation according to EFSA OECD 106 Evaluators Checklist

Soil	Units	AIIIa	AXXa	HaH	WuW
Adsorption method	-	indirect	indirect	indirect	indirect
Soil:solution ratio	(g dw/mL)	1:2	1:2	1:2	1:2
Mean parental mass balance (at highest test conc.)	%	94.5	94.4	93.1	95.5
Adsorbed percentage	%	33.73 – 94.53	40.09 – 95.45	55.0 – 96.36	39.09 – 95.45
K_d × (soil:solution ratio)	-	0.51– 0.75	0.67 – 1.00	1.23 – 1.75	0.64 – 1.00
$^{ads}K_F$ (95% confidence interval)	L/kg dw	0.999 (0.894 – 1.116)	1.315 (1.214 – 1.425)	2.474 (2.290 – 2.673)	1.363 (1.239 – 1.500)
$^{ads}1/n$ (95% confidence interval)	-	0.928 (0.894 – 0.962)	0.937 (0.911 – 0.964)	0.930 (0.908 – 0.951)	0.946 (0.917 – 0.975)
$^{ads}R^2$	-	0.998	1.000	1.000	0.999
$^{ads}K_{F,OC}$	L/kg OC	90.8	87.7	154.6	85.2
K_{fE} / K_f	-	1.194 / 1.195	1.161 / 1.162	1.141 / 1.143	1.120 / 1.130

Note: Values derived from the EFSA evaluators checklist may vary from those in the study reports due to rounding errors.

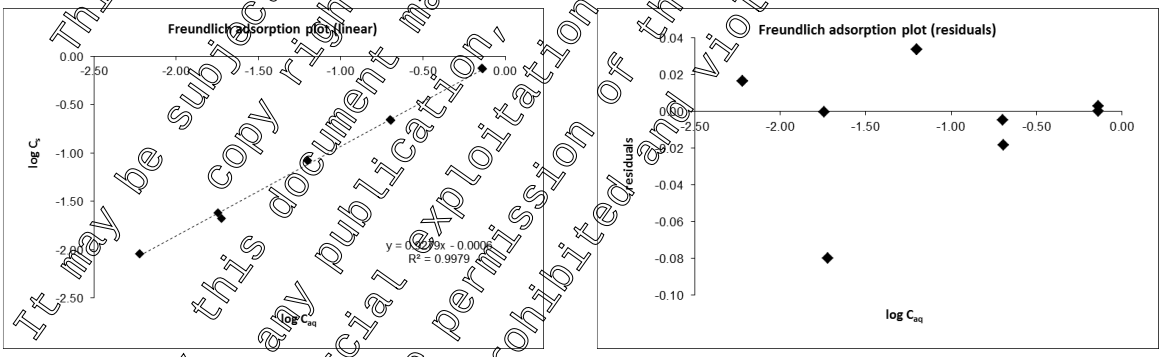
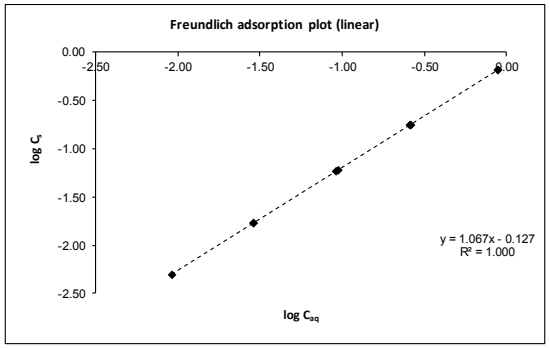


Figure 7.1.3.1.2-1: Graphical presentation of Freundlich adsorption isotherm analysis (linear regression, left) and the corresponding plot of the residuals (right) for soil Laacher Hof AIIIa (AIIIa)



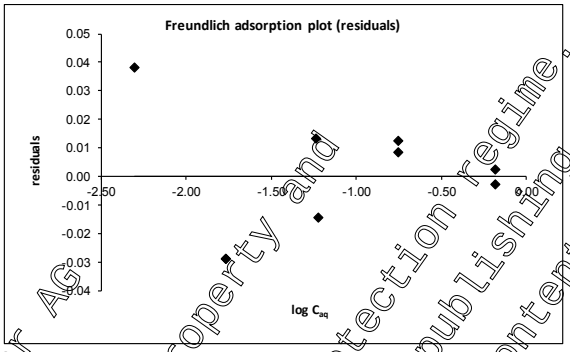
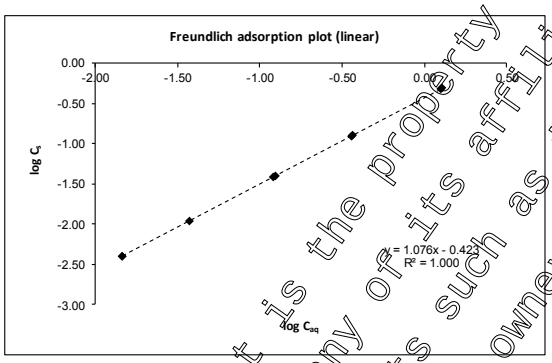


Figure 7.1.3.1.2-2: Graphical presentation of Freundlich adsorption isotherm analysis (linear regression, left) and the corresponding plot of the residuals (right) for soil Laacher Hof AXXa (AXXa)



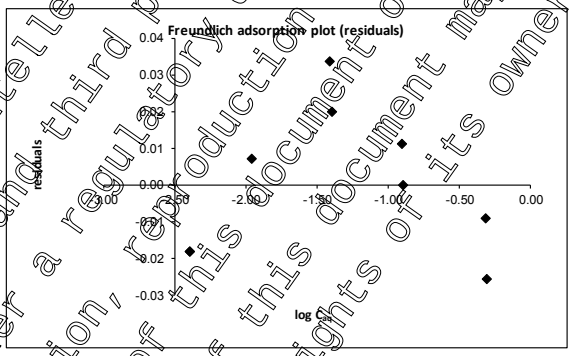
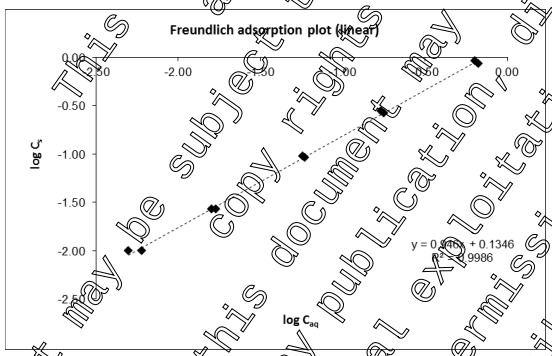


Figure 7.1.3.1.2-3: Graphical presentation of Freundlich adsorption isotherm analysis (linear regression, left) and the corresponding plot of the residuals (right) for soil Hoefchen am Hohensch 4a (HaH)



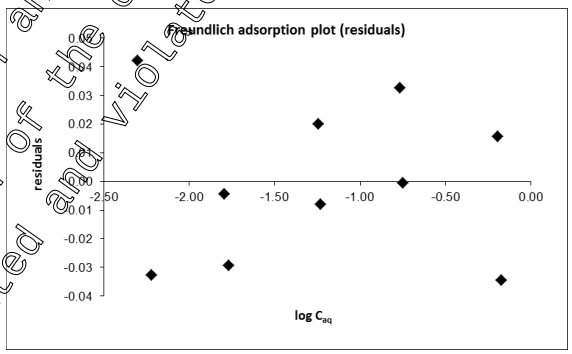


Figure 7.1.3.1.2-4: Graphical presentation of Freundlich adsorption isotherm analysis (linear regression, left) and the corresponding plot of the residuals (right) for soil Wurmwiese (WuW)

1. Information on the study

Data Point:	KCA 7.1.3.1.2/02
Report Author:	[redacted]
Report Year:	2011
Report Title:	[1-14C] BCS-AZ56567: Adsorption/desorption in five different soils
Report No:	AS155
Document No:	M-406740-01-1
Guideline(s) followed in study:	EU 95/36/EC amending 91/414/EEC; OECD 106; US EPA OPPTS 835.1220; Canada PMRA, 1987
Deviations from current test guideline:	Current Guideline: OECD 106 (2000) None
Previous evaluation:	yes, evaluated and accepted RAR flurtamone (2016)
GLP/Officially recognised testing facilities:	Yes, conducted under GLP/Officially recognised testing facilities
Acceptability/Reliability:	Yes

2. Full summary of KCA 7.1.3.1.2/02

Executive Summary

The adsorption/desorption characteristics of [1-^{14}C]trifluoroacetate (TFA) were studied in five soils in batch equilibrium experiments in the dark at 20.4 °C.

Soil ID	Source	Texture (USDA)	pH [2]	OC [%]
WW/ WuW[1]	Monheim, Germany	Loam	5.3	1.8
HH/ HaH[1]	Burscheid, Germany	Silt loam	6.6	2.4
DD/ DoII[1]	Blankenheim, Germany	Clay loam	7.3	4.7
GL	Guadalupe, California, USA	Sandy loam	6.7	0.7
SF	Springfield, Nebraska, USA	Silt loam	6.6	1.7

[1] differing abbreviation used in study report
[2] pH values were derived from aqueous 0.01 M $CaCl_2$ suspensions

The adsorption phase of the study (definitive test) was carried out using air-dried soils equilibrated with 0.01 M $CaCl_2$ solution with a soil/solution ratio of approx. 1:1 for at least 16 hours. Then, TFA was applied at nominal concentrations of 1.0, 0.3, 0.1, 0.03, and 0.01 mg/L. Resulting samples were shaken for an equilibration period of 24 hours with a soil/solution ratio of 1:1. The desorption phase was performed by supplying pre-adsorbed soil samples with fresh aqueous 0.01 M $CaCl_2$ solution for one desorption cycle for 24 hours.

After adsorption and desorption, the aqueous supernatant was separated by 10 min centrifugation at approx. 4200 g. The TFA residues in the supernatant were analysed by liquid scintillation counting (LSC). The adsorption parameters were calculated using the Freundlich adsorption isotherm. Samples without soil were used as control in preliminary test and did not show adsorption to the vessels or degradation. The test item was found to be stable under test conditions.

For all soils the parental mass balance after 96 h showed that 90.2-94.6% of applied TFA could be recovered (preliminary test). The mass balance of the soils (definitive test) was determined by LSC of the supernatants after adsorption and desorption and by combustion of the remaining soils. The overall material balance for all concentrations for individual specimens was in the range of 89.9-98.7%, 96.2-98.2%, 97.4-103.1%, 97.8-100.5%, and 96.1-98.9% of the applied radioactivity in soils WW, HH, DD, GL and SF, respectively.

Adsorption of TFA to soil was not measurable, therefore no adsorption isotherms could be calculated. It can be assumed from the results with [1-^{14}C]trifluoroacetate that TFA has a very high mobility in soil (i.e. K_{FOC} = 0).

I. MATERIALS AND METHODS

A. MATERIALS

1. Test Item

[1-^{14}C]BCS-AZ56567/ sodium trifluoroacetate (sodium salt of trifluoroacetic acid, TFA)

Sample ID	KML 9027
Specific activity	3.48 MBq/mg (94.04 µCi/mg)
Radiochemical purity	> 98% by HPLC

2. Test Soils

Five different soils from Europe and the USA were chosen for this study, representing a range of different physico-chemical soil properties. After sampling, soils were air-dried, sieved to a particle size of ≤ 2 mm and stored at 0-10°C for up to 587 days. The soil characteristics are listed below.

Table 7.1.3.1.2-6: Soil characteristics

Soil ID	WW	HH	DD	GL	SF
Geographic Location	Monheim am Rhein, North Rhine-Westphalia, Germany	Burscheid, North Rhine-Westphalia, Germany	Blankenheim, North Rhine-Westphalia, Germany	Guadalupe, California USA	Springfield Nebraska USA
Textural Class (USDA)	Loam	Silt loam	Clay Loam	Sandy Loam	Silt Loam
Sand (%)	51	27	31	56	13
Silt (%)	28	54	38	33	61
Clay (%)	21	19	31	11	27
pH in $CaCl_2$	5.3	6.6	7.3	6.7	6.6
pH in water	5.5	6.8	7.4	6.8	7.2
Organic Matter (%)	3.0[1]	4.2[1]	8.1[1]	1.1	2.9
Organic Carbon (%)	1.8	2.4	4.7	0.7	1.7
Cation Exchange Capacity (meq/100g)	10.8	13.9	21.9	16.1	16.1

[1] organic matter = organic carbon * 1.724

B. STUDY DESIGN

1. Experimental Conditions

Preliminary tests were conducted in order to confirm the stability of the test item in calcium chloride solution and to determine appropriate soil/solution ratios and equilibration periods. The solubility and stability of test item in 0.01 M $CaCl_2$ was tested using the highest proposed concentration for the definitive study experiments (1.0 mg/L). After shaking periods of 24, 48, 72 and 96 hours, centrifuged aliquots from each solution were taken and analysed.

To determine the appropriate soils/solution ratios 20, 10 and 2 g soil aliquots were weighted into centrifuge tubes and 18 mL of calcium chloride solution were added. After a pre-equilibration period, 2 mL of the application solution was applied to the test vessels to achieve a concentration of 1.00 mg/L. The centrifuge tubes were capped and shaken for 24 hours.

To decide on the most appropriate equilibration time for the adsorption/desorption measurements samples were prepared with a soil/solution ratio of 1:1 and at a concentration of 1.0 mg/L. Before adding

the test item, samples were pre-equilibrated with $CaCl_2$ solution. Samples were taken after 2, 4, 6, 24, 30, 48, 72, 96 and 120 hours of agitation, respectively. Additionally, mass balance was determined of all test systems.

For the definitive experiments, parameters determined in the preliminary tests were used. Air-dried soils were equilibrated in $CaCl_2$ solution for at least 16 hours. The adsorption measurements were carried out in duplicate at five different concentrations in a range of 0.01 mg/L to 1.0 mg/L. Soil/solution ratios of 1:1 (20 g soil (dry weight equivalents)/ 20 mL 0.01 M $CaCl_2$ solution) was chosen and samples were agitated for 24 hours after application. Following the equilibration period, the test vessels were centrifuged for 10 minutes at approx. 4200 g, then the supernatant was completely decanted. The volumes were measured gravimetrically (density of the solution was set equivalent to 1 g/mL) and recorded, and two aliquots of 1 mL from all soils were taken for LSC.

For all soils, one single point desorption was performed on all concentrations. The volume of solution removed was replaced by an equal volume of calcium chloride solution. The test vessels were shaken for 24 hours, equal to the adsorption equilibration time, and handled as described in the previous section. Aliquots of the supernatants from all soils were taken for LSC. After the desorption step, all soil residues were mixed with approximately 0.4 g cellulose/g soil air-dried, homogenised and aliquots of 300 mg were combusted. Mass balance was established on all specimens from the definitive tests. No chromatographic analysis was carried out since the stability of the test item was already proved in the preliminary tests.

2. Analytical Procedures

For preliminary and definitive test, the aqueous supernatant was separated from the soil by centrifugation at the end of the equilibration time and the amount of ^{14}C-labeled test item was analysed by liquid scintillation counting (LSC). Samples to determine the stability of the test item in calcium chloride solution and parental mass balance samples were additionally subjected to HPLC.

To determine the parental mass balance, the test item was further extracted from the soils, up to five times, using 40 mL distilled water for 30 min (15 min using an ultrasonic bath) after separation of soil and supernatant. The amount of radioactivity of the combined extraction solvents was determined by LSC (aliquots of 1.0 mL). Additionally, the amount of the test item in the combined and concentrated extracts and in the supernatants was investigated by means of HPLC. Radioactivity remaining in the soil was quantified after combustion in a sample oxidiser.

High performance liquid chromatography was carried out on a system that comprised a Sequant ZIC®-HILIC, 5 µm, 150 x 4.6 mm column connected to a radio detector fitted with a 500 µL scintillation cell and to a conductivity detector. Three radio-HPLC runs without injection of radioactive compounds were conducted. The whole radioactive signal of the runs was marked (cpm was chosen as signal unit). The background was calculated as the cpm-mean value (e.g. 8.3 cpm) of these HPLC-runs. For all following HPLC-runs the two-fold of the determined background (e.g.17 cpm) was subtracted from each run. All signals higher than 50 cpm and with a minimum area of 100 area units were integrated.

The amount of test item adsorbed to the soil was calculated by subtracting the concentration at adsorption equilibrium in the supernatant solution from the initially applied concentration (indirect method). The calculation of the distribution of the test item after desorption was based on the radio-concentration measured in the supernatant in the desorption step. All calculations were carried out considering the radioactivity carried over from the adsorption step within the sedimented soil interstitial water.

The equilibrium partitioning in adsorption and desorption measured for five concentration dilution series per soil was used to calculate Freundlich isotherms for adsorption and desorption.

II. RESULTS AND DISCUSSION

A. PRELIMINARY TESTS INCUDING MASS BALANCE

Solubility and stability of test item were regarded acceptable. Radioactive recoveries in $CaCl_2$ solution without soil was between 93.0 and 97.9 % of applied radioactivity (AR). The purity of the test item determined via HPLC showed that the radiochemical purity was determined to be higher than 99.0% after the 96 hrs testing period.

The test item did not show significant adsorption to the inner surfaces of the test vessels. There was virtually no adsorption of the test item on the tested soils at any of the tested soil/solution ratios. Based on the very low adsorption of test item in this test a soil/solution ratio of 1:1 was used for all soils.

Furthermore, the time for the establishment of the equilibrium between the test item concentration in the solution and the amount adsorbed to soil was examined. In addition, the parental mass balance was determined to demonstrate the stability of the test item during testing adsorption and desorption. The test item was found to be stable under test conditions for up to 120 hrs. The parental mass balances were ≥ 90.2% for all soils after an equilibration time of 96 hrs, calculated as recovery of the test item in supernatants and soil extracts. The tests showed that equilibrium was established after 24 hrs of agitation for all soils.

B. DEFINITIVE TESTS

The adsorption behaviour of TFA was investigated in soil/water slurries based on five different nominal concentrations ranging from approximately 0.01 mg/L to 1.00 mg/L (two orders of magnitude).

For these experiments, the applied radioactivity (AR) was defined as the total amount of radioactivity contained in the dosed 2 mL aliquots of the respective application solutions for each concentration. The radioactive material balance in the test soils was calculated as sum of the radioactivity detected within the decanted supernatant solutions after the adsorption and desorption steps and the radioactivity found in the air-dried and combusted soil residues.

The total radioactivity recovery with respect to the individual vessel ranged from 89.9% to 103.1% of the applied radioactivity (see table below). The complete material balance observed for all test systems therefore demonstrated that no significant amount of radioactivity dissipated from the test vessels or was lost upon processing.

Table 7.1.3.1.2-7: Recovery after definitive adsorption test

Soil WW Conc.	Rep.	Supernatant adsorption	Supernatant desorption	Soil residue	Total recovery
		%AR	%AR	%AR	%AR
1.04 mg/L	a	61.4	21.8	14.5	97.7
	b	61.2	21.8	14.2	97.2
0.31 mg/L	a	59.2	22.0	8.7	89.9
	b	60.2	21.5	16.2	97.9
0.10 mg/L	a	58.4	21.5	17.5	97.4
	b	58.1	22.0	17.9	98.0
0.03 mg/L	a	57.9	21.3	17.5	96.7
	b	58.1	21.0	19.4	98.5
0.01 mg/L	a	57.5	22.2	18.3	98.0
	b	59.3	20.7	18.7	98.7

Soil HH Conc.	Rep.	Supernatant adsorption	Supernatant desorption	Soil residue	Total recovery
		%AR	%AR	%AR	%AR
1.04 mg/L	a	55.4	22.9	18.9	97.2
	b	55.7	23.4	18.4	97.5
0.31 mg/L	a	56.1	22.6	19.5	98.2
	b	55.5	23.0	19.2	97.7
0.10 mg/L	a	54.2	22.9	19.5	96.6
	b	55.0	22.9	19.3	97.2
0.03 mg/L	a	56.2	22.8	17.6	96.6
	b	57.2	22.3	16.7	96.2
0.01 mg/L	a	56.9	22.5	18.0	97.4
	b	56.2	23.1	18.6	97.9

Soil DD Conc.	Rep.	Supernatant adsorption	Supernatant desorption	Soil residue	Total recovery
		%AR	%AR	%AR	%AR
1.04 mg/L	a	53.3	24.6	20.8	98.7
	b	52.7	24.3	20.5	97.5
0.31 mg/L	a	52.7	23.0	22.4	98.1
	b	53.6	24.0	20.6	98.2
0.10 mg/L	a	52.6	23.7	21.1	97.4
	b	51.9	23.4	22.3	97.6
0.03 mg/L	a	52.5	23.8	22.3	98.6
	b	52.8	23.7	22.0	98.5
0.01 mg/L	a	52.5	24.6	23.3	100.4
	b	53.5	24.1	25.5	103.1

Soil GL Conc.	Rep.	Supernatant adsorption	Supernatant desorption	Soil residue	Total recovery
		%AR	%AR	%AR	%AR
1.04 mg/L	a	64.5	22.1	11.8	98.4
	b	63.7	22.3	12.1	98.1
0.31 mg/L	a	67.0	21.2	10.5	98.7
	b	66.6	21.5	10.8	98.9
0.10 mg/L	a	66.5	21.1	10.4	98.0
	b	66.2	21.3	10.9	98.4
0.03 mg/L	a	66.1	20.4	11.4	97.9
	b	66.3	20.7	10.8	97.8
0.01 mg/L	a	67.4	21.3	11.8	100.5
	b	66.5	21.8	11.5	99.8

Soil SF Conc.	Rep.	Supernatant adsorption	Supernatant desorption	Soil residue	Total recovery
		%AR	%AR	%AR	%AR
1.04 mg/L	a	63.6	19.8	14.3	97.7
	b	63.8	20.1	14.3	98.2
0.31 mg/L	a	60.0	21.6	16.2	97.8
	b	59.6	21.8	16.0	97.4
0.10 mg/L	a	60.4	21.3	15.7	97.4
	b	59.3	21.8	15.4	96.5
0.03 mg/L	a	59.3	21.6	15.7	96.6
	b	58.7	21.2	16.2	96.1
0.01 mg/L	a	58.9	22.6	17.2	98.7
	b	59.7	21.6	17.6	98.9

C. FINDINGS

Virtually no adsorption for TFA was measured. Using the data generated it was not possible to calculate any reasonable Freundlich isotherm and therefore, no data describing the Freundlich isotherm (K_F-value and 1/n) were determined. Despite these results experiments were continued, and desorption cycles were performed. The results were in the same range as determined for the adsorption cycle. Details of the concentration of TFA at the end of the adsorption period are shown in the table below. Since no meaningful results were measured, Freundlich adsorption isotherms could not be calculated.

Table 7.1.3.1.2-8: TFA in the solid and liquid phase at the end of the adsorption period and percentage adsorbed (mean ± s.d.)

Test concentration	Soil (mg/kg)	Solution (mg/L)	Percentage adsorbed
Soil WW			
0.010 mg/L	-	0.010	-1.1 ± 0.2
0.031 mg/L	-	0.030	0.9 ± 0.3
0.102 mg/L	-	0.102	0.5 ± 0.8
0.306 mg/L	-	0.309	-0.8 ± 0.7
1.025 mg/L	-	1.042	-1.7 ± 1.0
Soil HH			
0.010 mg/L	-	0.010	-3.9 ± 1.2
0.031 mg/L	-	0.031	-2.8 ± 0.5
0.102 mg/L	-	0.105	-2.8 ± 0.3
0.305 mg/L	-	0.318	-4.3 ± 1.0
1.020 mg/L	-	1.055	-3.4 ± 0.4
Soil DD			
0.010 mg/L	-	0.011	-9.6 ± 0.6
0.030 mg/L	-	0.033	-8.9 ± 1.1
0.101 mg/L	-	0.109	-8.5 ± 0.1
0.302 mg/L	-	0.328	-8.5 ± 0.3
1.009 mg/L	-	1.093	-8.2 ± 0.2
Soil GL			
0.010 mg/L	-	0.010	-3.2 ± 1.2
0.031 mg/L	-	0.031	-1.4 ± 0.1
0.102 mg/L	-	0.104	-1.3 ± 0.7
0.306 mg/L	-	0.312	-2.0 ± 0.6
1.024 mg/L	-	1.038	-1.4 ± 0.7
Soil SF			
0.010 mg/L	-	0.010	-5.5 ± 0.3
0.030 mg/L	-	0.031	-5.1 ± 0.1
0.100 mg/L	-	0.104	-4.7 ± 0.3
0.298 mg/L	-	0.316	-6.0 ± 0.3
0.997 mg/L	-	1.061	-6.3 ± 0.4

III. CONCLUSIONS

For all soils and test concnetrations, percentages of TFA adsorbed to soil varied to result in no evaluable values. Consequently, adsorption of TFA to soil was not measurable, therefore no adsorption isotherms could be calculated. The results indicatevery low adsorption (i.e. K_{FOC} = 0) and thus very high potential for mobility of TFA in soil.

3. Assessment and conclusion

Assessment and conclusion by applicant:
The study and its data are considered to be valid and reliable for use in risk assessment.

Assessment and conclusion by RMS:
Outcome and conclusion of the study: RMS should indicate if they agree to the results and conclusions of the APPL.

EVALUATION ACCORDING TO EFSA CHECKLIST
Quality checks according to the EFSA checklist were performed as part of confirming the acceptability of the data and endpoints reported of the above study M-406740-01-1 as far as possible. These checks confirmed that degradation was minor and parental mass balance was therefore evaluated only in the preliminary test, while only the total mass balance was given in the definitive test. Parental mass balance was ≥ 90.2% for all soils after 96 hrs and the total mass balance was between 89.9% to 103.1% AR after the desorption phase. Overall, the parental mass balance falls somewhat short to the expectations of a low adsorbing substance, especially since the indirect method was used. However, since no adsorption was detected, the results represent the worst case and potential errors introduced by using the indirect method or a low parental mass balance will not affect the results. Freundlich adsorption isotherms (described with K_F and 1/n) could not be calculated. Further quality checks such as error estimation via K_{fe}/K_f are therefore not relevant.

1. Information on the published literature article

Data Point:	KCA 7.1.3.1.2/03
Report Author:	Richey, D. G.; Driscoll, C. T.; Likens, G. E.
Report Year:	1997
Report Title:	Soil retention of trifluoroacetate
Report No:	M-263649-01-1
Document No:	M-263649-01-1
Guideline(s) followed in study:	--
Deviations from current test guideline:	Current Guideline: OECD 106 (2000) Publication
Previous evaluation:	yes, evaluated, not accepted RAR flurtamone (2016), not be used for the risk assessment
GLP/Officially recognised testing facilities:	not applicable
Acceptability/Reliability:	Yes

2. Full summary of KCA 7.1.3.1.2/03

Executive Summary
An adsorption-desorption batch-equilibrium study with fifty-four soils (topsoil and sub-soils) was performed with sodium trifluoroacetate (TFA) as part of a terrestrial ecosystem project. Thirty-five soil samples were obtained from 15 terrestrial sites of the National Science Foundation Long-Term Ecological Research Program. Soil samples were air-dried and passed through a 2 mm sieve prior to analysis and characterised.

Batch equilibrium soil sorption experiments were conducted on each of the soils. A 1:5 soil/solution ratio was used for organic soil and 1:20 for mineral soils. The range of concentrations used was: 0, 2, 4, 7, 10, 20, 30 and 40 µmol sodium trifluoroacetate.

The soil/solution suspensions were equilibrated on a reciprocating shaker for 24 hours at 25°C. The samples were then centrifuged and filtered through 0.45 µm polypropylene fibre membrane filters. The TFA concentration of the filtrate was measured using ion chromatography. The possible pH dependence of TFA adsorption was examined using 20 samples of each soil. After the initial equilibration period, acid or base was added to adjust the pH to 2 or 10, which was then followed by an additional period of equilibration.

Thirty-four of the soils tested showed sorption of TFA. At all sites where TFA was evaluated for organic and mineral soils, the organic horizon exhibited greater adsorption. Soils with high organic content were found to retain the highest concentrations of TFA, adsorbing between 20 and 60% of added TFA. The reported soil properties and sorption contents for fine soils with OC <5%, considered to be most representative of agricultural soils, are shown in the table below. K_{OC} values are derived from the reported Freundlich constants and the organic carbon contents (organic matter/1.724). The results are summarised below.

Name (texture)	OC (%)	Clay (%)	pH (-)	CEC (meq/100 g)	K_F (mL/g)	K_{OC} (mL/g)
AB Horizon (mesic)	3.6	9	4.2	17.4	0.68	18.9
E Horizon	1.7	2	3.1	4.0	0.30	17.8
Bs1 Horizon	4.6	6	3.3	11.6	0.54	11.8
Bs2 Horizon	4.1	7	3.8	17.3	0.53	12.9
Wetland	2.3	1	4.1	3.7	0.60	25.9
E Horizon	0.8	2	3.2	1.0	0.34	41.9
Bs1 Horizon	4.7	6	4.0	23	0.42	8.9
Bs2 Horizon	0.3	3	4.7	0.05	0.17	58.6
Mineral Horizon	3.5	11	4.7	10.4	0.32	9.0

Mean K_{OC} (9 soils) = 22.9 mL/g, K_F calculated for 1/n fixed to 1

I. MATERIALS AND METHODS

A. MATERIALS

1. Test Item

Na-Trifluoroacetate (sodium salt of trifluoroacetic acid, TFA)
Batch No: Not given
Chemical purity: Not given

2. Test soils

A non-GLP adsorption-desorption batch-equilibrium study with fifty-four soils (top-soils and sub-soils) was performed with TFA as part of a terrestrial ecosystem project. Thirty-five soil samples were obtained from 13 terrestrial sites of the National Science Foundation Long-Term Ecological Research Program. These sites encompassed a wide range of soil and ecological conditions. Soils were also obtained from Lake Agassa Peatlands, Minnesota, near Found Lake, Wisconsin, from two sites in the Czech Republic and three sites in Brazil. At most sites a surface and subsurface soil were collected, but for some sites only a surface soil was obtained. At three sites, the two sites in the Czech Republic and a New Hampshire site, samples were obtained from each of the major soil horizons.

Soil samples were air-dried and passed through a 2 mm sieve prior to analysis. They were characterised for pH, organic matter, soil texture (% clay, % silt, %sand) exchangeable cations (Ca^{+}, $Mg^{2+,}$ K^{+}, Na^{+}, Fe^{3+}, Al^{3+}), cation exchange capacity, water-extractable anions (Cl^{-}, NO_3^{-}, SO_4^{2-}), total soil carbon and total soil nitrogen. Acid-oxalate, pyrophosphate, and citrate-dithionite extractable Fe^{3+} and Al^{3+} were also determined.

B. STUDY DESIGN

1. Experimental Conditions

Batch equilibrium soil sorption experiments were conducted on each of the soils (and several well characterised soil minerals, such as sodium montmorillinite. A 1:5 soil/solution ratio was used for organic soil and 1:20 for mineral soils. A range of sorbate concentrations (0, 2.4, 7, 10, 20, 30 and 40 µmol sodium trifluoroacetate) was used for each soil to develop sorption isotherms at ambient temperature. Each soil sample was weighed into a 50 mL polypropylene centrifuge tube, the adsorbate was added, and the suspension was equilibrated on a reciprocating shaker for 24 hours at 25°C.

2. Sampling

The samples were then centrifuged and filtered through 0.45 m polypropylene fibre membrane filters. The TFA concentration of the filtrate was measured using ion chromatography. The adsorption to the tubes was also investigated. The difference between the amount of TFA initially in the adsorbate solution and the amount remaining after equilibration was determined to be the amount of TFA retained by the soil (indirect method).

3. Analytical Procedures

Langmuir and Freundlich adsorption isotherms were plotted and fitted to evaluate the extent of retention of TFA on all soils. The sorption distribution coefficient (K_F) was determined for the special case of the Freundlich model where the Freundlich coefficient (n) =1. When the sorption data showed better fit with the Langmuir model, the linear portion of the isotherm was used to determine K_F. This procedure may introduce some error into the use of K_F when evaluating the sorption of TFA, but the distribution constant was determined for being able to compare TFA retention to that of other compounds. Distribution constant (K_F) was reproducible within 0.09 L/kg for soils with low organic matter content (<17%).

Two soils with contrasting physical and chemical characteristics that had relatively high TFA retention were used to examine the factors that influence the compound's adsorption. The possible pH dependence of TFA adsorption was examined using 20 samples of each soil. After the initial equilibration period, acid or base was added to adjust the pH to 2 or 10, which was then followed by an additional period of equilibration.

Comparative adsorption of other inorganic anions was determined by batch adsorption experiments on fluoride, chloride, bromide, nitrate and sulphate (using a salt of each anion). Competitive sorption of TFA with other anions was also measured.

II. RESULTS AND DISCUSSION

A. EXTRACTION AND QUANTITATION OF RADIOACTIVITY IN SOIL SAMPLES

No detectable adsorption of TFA to the polypropylene tubes was detected.

Thirty-four of the soils tested showed sorption of TFA. At all sites where TFA was evaluated for organic and mineral soils, the organic horizon exhibited greater adsorption. Soils with high organic content were found to retain the highest concentrations of TFA, adsorbing between 20 and 60% of added TFA, whilst mineral soils retained 0-15%. The lower effect of adsorption by mineral surfaces was dependent on pH and the presence of other anions in solution. The reported soil properties and sorption contents for nine soils with OC <5%, considered to be most representative of agricultural soils, are shown in the table

below. K_{OC} values are derived from the reported Freundlich constants and the organic carbon contents (organic matter/1.724).

Table 7.1.3.1.2-9: Soil properties and sorption coefficients of the batch-equilibrium study with TFA in 9 soils with OC <5%

Name (texture)	OC (%)	Clay (%)	pH (-)	CEC (meq/100 g)	K_F (mL/g)	K_{OC} (mL/g)
AB Horizon (mesic)	3.6	9	4.2	1.4	0.68	18.9
E Horizon	1.7	2	3.1	4.0	0.30	17.8
Bs1 Horizon	4.6	6	3.3	11.6	0.54	11.8
Bs2 Horizon	4.1	7	3.8	7.3	0.53	12.9
Wetland	2.3	1	4.1	3.7	0.60	25.9
E Horizon	0.8	2	3.2	1.0	0.34	41.9
Bs1 Horizon	4.7	6	4.0	2.3	0.42	8.9
Bs2 Horizon	0.3	3	4.7	0.05	0.17	58.6
Mineral Horizon	3.5	11	4.7	10.4	0.35	9.9

Mean K_{OC} (9 soils) = 22.9 mL/g

III. CONCLUSIONS

Trifluoroacetate (TFA) exhibited a range of adsorption constants showing mobility in some of the 54 soils tested and immobility in others. The organic matter content was shown to strongly influence the adsorption. In soils representative of agricultural soils TFA was shown to be potentially mobile with K_{OC} values of 8.9 to 58.6 mL/g (mean of 22.9 mL/g).

3. Assessment and conclusion

Assessment and conclusion by applicant:
The study and its data are considered as supportive information with no use in risk assessment.

Assessment and conclusion by RMS:
Outcome and conclusion of the study: RMS should indicate if they agree to the results and conclusions of the APPL.

CA 7.1.3.2 Aged sorption

The effect of ageing on the potential mobility (aged sorption) of fluopyram was studied in 20 European soils. The degradation of fluopyram was shown to be influenced by a kinetically controlled sorption. The kinetic sorption model distinguished between dissolved, equilibrium sorbed and non-equilibrium sorbed concentrations of the compound. It is assumed that the sorption behaviour of a compound in soil can be described by two processes: instantaneous (equilibrium sorption) and long-term sorption (or non-equilibrium sorption) which proceeds only gradually. The compound present in the water phase is readily available for microbial transformation and for hydrolysis. Compound sorbed to the equilibrium-sorption sites is rapidly released, and thus also readily available for degradation. However, the release of compound from the slowly sorbing phase only proceeds gradually and consequently, it is assumed transformation does not occur in the non-equilibrium domain. Degradation rates that take this process into account ($DT_{50\ equilibrium}$) were derived using the desorption rate constant (k_{des}) and a factor describing the ratio between non-equilibrium and equilibrium Freundlich coefficients (f_{NE}). Data of aerobic

degradation and time-dependent sorption (TDS) studies was evaluated according to the guidance document on aged sorption (European Commission, 2021) and EFSA PPR Panel Opinion (EFSA, 2018).

Following aging of fluopyram residues for 118 to 121 days, dependence of sorption with time increased by a factor of 1.3 to 3.4. Comparison of the fits for non-equilibrium and equilibrium K_{d_app} compartments demonstrated that strong aged-sorption effects occurred for all soils. This is also evidenced by the equilibrium fit not being able to adequately describe the increase in K_d observed with time. Parameter estimations of f_{NE} and k_{des} were robust for all 20 soils and were suitable for use in exposure modelling. Resulting mean aged-sorption parameters for fluopyram are: f_{ne} 0.525; k_{des} 0.0285 1/d.

Table 7.1.3.2-1: Results of TDS evaluation of fluopyram

#	Soil	f_{NE} (-)	k_{des} (1/d)	$DT_{50,eq}$ (d)	$DT_{50,equilibrium}$ 20°C pF2 (d)	Evidence of aged sorption	Robust parameters
1	Hoefchen	0.540	0.02516	156.7	156.7	Yes	Yes
2	Laacher Hof AXXa	0.551	0.02450	158.0	158.0	Yes	Yes
3	Wurmwiese	0.540	0.07196	171.5	171.5	Yes	Yes
4	Laacher Hof AIIIa	0.583	0.02088	112.8	112.8	Yes	Yes
5	Hoefchen[1]	0.482	0.03358	145.3	145.3	Yes	Yes
6	Laacher Hof AXXa	0.491	0.09746	304.1	304.1	Yes	Yes
7	Wurmwiese	0.470	0.09800	170.4	170.4	Yes	Yes
8	Dollendorf II	0.350	0.08236	118.3	118.3	Yes	Yes
9	Little Oliver [1]	0.910	0.02283	998.7	943.5	Yes	Yes
10	Auchy les Mines	0.957	0.01028	774.5	731.7	Yes	Yes
11	Urbanowice	0.611	0.01940	959.2	719.7	Yes	Yes
12	Charles River Farm	0.716	0.01215	391.9	370.2	Yes	Yes
13	Sindos	0.430	0.01946	212.5	200.8	Yes	Yes
14	Paradiso San Zenone	0.601	0.02661	256.4	242.2	Yes	Yes
15	Hoeltinghausen	0.550	0.04667	472.6	446.5	Yes	Yes
16	Hornton	0.785	0.01491	366.7	347.4	Yes	Yes
17	Le Thour	0.138	0.13818	150.2	141.9	Yes	Yes
18	Brannens	0.323	0.02876	325.1	305.2	Yes	Yes
19	Balbiano	0.403	0.01932	290.2	274.1	Yes	Yes
20	Almayate East	0.918	0.02180	176.9	157.4	Yes	Yes
	Geometric mean	**0.525**	**0.0285**	265	252	-	-

[1] Excluding outlier

Existing lower-tier degradation study data for fluopyram from laboratory and field studies have been evaluated to derive $DegT_{50eq}$ values, which when combined with the higher-tier aged-sorption values, yield to an overall geometric mean normalised $DegT_{50eq}$. The geometric mean normalised $DegT_{50eq}$ based on laboratory data is 254.4 d, in combination with the mean aged-sorption parameters: f_{ne} 0.525; k_{des} 0.0285 1/d. The geometric mean normalised $DegT_{50eq}$ based on field data is 216.5 d. Detailed $DegT_{50eq}$ for both laboratory and field data are given below.

Table 7.1.3.2-2: Overall $DegT_{50eq}$ evaluation results – laboratory data

#	Soil	$DegT_{50eq}$[2] (days)	Derivation
1	Hoefchen	156.7	TDS - PEARLneq
2	Laacher Hof AXXa	158.0	TDS - PEARLneq
3	Wurmwiese	171.5	TDS - PEARLneq
4	Laacher Hof AIIIa	112.8	TDS - PEARLneq
5	Hoefchen	145.3	TDS - PEARLneq
6	Laacher Hof AXXa	304.1	TDS - PEARLneq
7	Wurmwiese	170.4	TDS - PEARLneq

#	Soil	$DegT_{50eq}$[2] (days)	Derivation
8	Dollendorf II	118.3	TDS - PEARLneq
9	Little Oliver	943.5	TDS - PEARLneq
10	Auchy les Mines	731.7	TDS - PEARLneq
11	Urbanowice	719.7	TDS - PEARLneq
12	Charles River Farm	370.2	TDS - PEARLneq
13	Sindos	200.8	TDS - PEARLneq
14	Paradiso San Zenone	242.2	TDS - PEARLneq
15	Hoeltinghausen	446.5	TDS - PEARLneq
16	Hornton	337.4	TDS - PEARLneq
17	Le Thour	141.9	TDS - PEARLneq
18	Brannens	305.2	TDS - PEARLneq
19	Balbiano	274.1	TDS - PEARLneq
20	Almayate East	157.4	TDS - PEARLneq
21	Springfield	333.8	Lab Tier-1 Refit
22	Porterville	521.5	Lab Tier-1 Refit
23	Argissolo	321.9	$DegT_{50}$ [1]
24	Frankenforst	156.3	Lab Tier-1 Refit
25	Wurmwiese	216.4	Lab Tier-1 Refit
26	Höfchen	200.7	Lab Tier-1 Refit
27	Innerdeich	213.7	Lab Tier-1 Refit
	Geometric mean	**254.4**	

[1] Tier-1 refit not acceptable, standard $DegT_{50}$ × SF1 (0.731) used
[2] normalised to 20°C and pF2

Table 7.1.3.2-3: Overall $DegT_{50eq}$ evaluation results – field data

#	Soil	$DegT_{50eq}$[1] (days)	Derivation
1	Little Oliver	90.9	Field Scaling factor 1
2	Auchy les Mines	505.5	Field Scaling factor 1
3	Urbanowice	429.9	Field Scaling factor 1
4	Charles River Farm	205.3	Field Scaling factor 1
5	Sindos	100.0	Default, not corrected
6	Hoeltinghausen	327.5	Field Scaling factor 1
7	Hornton	166.4	Field Scaling factor 1
8	Le Thour	81.7	Field Scaling factor 1
9	Brannens	153.0	Field Scaling factor 1
10	Balbiano	161.6	Field Scaling factor 1
11	Almayate East	130.2	Field Scaling factor 1
12	North Rose, New York	206.0	Field Scaling factor 1
13	Ephrata, Washington	191.5	Field Scaling factor 1
	Geometric mean	**216.5**	

[1] normalised to 20°C and pF2

Details on the aged sorption studies of fluopyram can be found below.

1. Information on the study

Data Point:	KCA 7.1.3.2/01
Report Author:	[redacted]
Report Year:	2008
Report Title:	[Pyridyl-2,6-14C]AE C656948: Aerobic metabolism/degradation and time-dependent sorption in soils
Report No:	MEF-07/424
Document No:	M-298413-01-1
Guideline(s) followed in study:	OECD: Guideline 307, Aerobic and Anaerobic Transformation in Soil (2002); Commission Directive 95/36/EC amending Council Directive 91/414/EEC (Annexes I and II, Fate and Behavior in the Environment) (1995); SETAC Procedures for Assessing the Environmental Fate and Ecotoxicity of Pesticides (1995); US EPA Subdivision N, Section 162-1, Aerobic soil metabolism (1982); OECD: Guideline 106, Adsorption/Desorption (2001) (only where applicable); Equivalent to US-EPA, OPPTS Guideline No. 835.4100
Deviations from current test guideline:	Current Guideline: OECD 307 (2002), OECD 106 (2000) (Only in parts) None
Previous evaluation:	yes, evaluated and accepted DAR (2021)
GLP/Officially recognised testing facilities:	Yes, conducted under GLP/Officially recognised testing facilities
Acceptability/Reliability:	yes

The experimental study is summarised and discussed under point KCA 7.1.1.1/01 of this document. The kinetic evaluation is summarised under KCA 7.1.2.1.1/09 (M-761966-01-1). The results of the aged sorption part of the study are summarised below.

2. Full summary of KCA 7.1.3.2/01

I. MATERIALS AND METHODS

Time-Dependent Sorption Calculations

The results were used to calculate the ratio for the time-dependent sorption (R_{TDS}) based on the amount of test item adsorbed to soil (sum of recovered fluopyram in ambient soil extracts) in relation to the amount of fluopyam desorbed during the so-called batch equilibrium shaking test by the 0.01 M $CaCl_2$ solution. The respective R_{TDS} ratios were normalized to soil % organic carbon content (K_{OC}).

II. RESULTS AND DISCUSSION

The time-dependent sorption ratios R_{TDS} of fluopyram normalized to soil % organic carbon content (K_{OC}) increased from DAT-0 to DAT-128 from 278 to 656 mL/g in soil Hoefchen, from 366 to 809 mL/g in soil LH AXXa, from 317 to 733 mL/g in soil LH Wurmwiese and from 289 to 531 mL/g in soil Dollendorf II. Until an aging time of 128 days the time-dependent sorption ratios increased by a factor of 1.8 to 2.4 (mean: 2.2).

Table 7.1.3.2-4: Time-dependent sorption ratios R_{TDS} of fluopyram in soil under aerobic conditions normalized to soil organic carbon content (Koc, expressed as mL/g; mean value of duplicates)

DAT	Hoefchen	LH AXXa	LH Wurmwiese	Dollendorf II
0	278	366	317	289
1	306	391	341	284
3	331	413	376	332
7	378	463	423	362
15	423 [1]	536	495	386
30	486	619	537	414
58	539	676	585	475
128	656	809	733	531
Factor DAT-128/DAT-0	**2.4**	**2.2**	**2.3**	**1.8**
Mean factor DAT-128/DAT-0	**2.2**			

DAT: days after treatment

[1] Single value

Table 7.1.3.2-5: Time-dependent sorption evaluation for soil Hoefchen

DAT	Sample- ID JR35-	Desorbed and Sorbed Residues			
		C_{des} [µg/mL]	C_{sed} [µg/g]	$R_{TDS\ Kd}$ [mL/g]	$R_{TDS\ Koc}$ [mL/g]
0	HF1-D0	0.061	0.405	6.64	276.7
	HF2-D0	0.061	0.408	6.70	279.1
1	HF1-D1	0.057	0.414	7.29	303.6
	HF2-D1	0.057	0.420	7.40	308.4
3	HF1-D3	0.053	0.422	7.92	330.0
	HF2-D3	0.054	0.433	7.98	332.4
7	HF1-D7	0.049	0.433	8.92	371.6
	HF2-D7	0.047	0.435	9.22	384.1
15	HF1-D15	0.062 [1]	0.363 [1]	5.82 [1]	242.56 [1]
	HF2-D15	0.044	0.450	10.16	423.3
30	HF1-D30	0.037	0.434	11.64	484.8
	HF2-D30	0.037	0.431	11.68	486.6
58	HF1-D58	0.032	0.407	12.89	537.3
	HF2-D58	0.031	0.397	12.95	539.4
128	HF1-D128	0.021	0.339	16.08	670.2
	HF2-D128	0.022	0.344	15.41	642.1

[1] Outlier due to experimental difficulties, values not valid for calculation

Table 7.1.3.2-6: Time-dependent sorption evaluation for soil LH AXXa

DAT	Sample- ID	Desorbed and Sorbed Residues			
		C_{des}	C_{extr}	$R_{TDS\ Kd}$	$R_{TDS\ Koc}$
	JR35-	[µg/mL]	[µg/g]	[mL/g]	[mL/g]
0	AX1-D0	0.053	0.419	7.98	362.7
	AX2-D0	0.052	0.421	8.11	368.7
1	AX1-D1	0.049	0.423	8.56	388.9
	AX2-D1	0.049	0.426	8.66	393.5
3	AX1-D3	0.048	0.437	9.03	410.4
	AX2-D3	0.048	0.436	9.12	414.6
7	AX1-D7	0.044	0.441	10.13	460.7
	AX2-D7	0.043	0.442	10.24	465.5
15	AX1-D15	0.038	0.458	12.06	548.4
	AX2-D15	0.040	0.456	11.54	524.4
30	AX1-D30	0.032	0.443	13.71	623.2
	AX2-D30	0.034	0.454	13.52	614.4
58	AX1-D58	0.031	0.447	14.67	666.7
	AX2-D58	0.029	0.438	14.88	676.3
128	AX1-D128	0.024	0.421	17.88	812.9
	AX2-D128	0.024	0.433	17.70	804.7

Table 7.1.3.2-7: Time-dependent sorption evaluation for soil LH Wurmwiese

DAT	Sample- ID	Desorbed and Sorbed Residues			
		C_{des}	C_{extr}	$R_{TDS\ Kd}$	$R_{TDS\ Koc}$
	JR35-	[µg/mL]	[µg/g]	[mL/g]	[mL/g]
0	WU1-D0	0.068	0.393	5.81	322.8
	WU2-D0	0.069	0.388	5.60	311.1
1	WU1-D1	0.064	0.392	6.08	337.9
	WU2-D1	0.064	0.399	6.19	343.7
3	WU1-D3	0.064	0.406	6.32	351.1
	WU2-D3	0.057	0.414	7.22	400.9
7	WU1-D7	0.057	0.422	7.42	412.2
	WU2-D7	0.054	0.419	7.81	433.8
15	WU1-D15	0.048	0.432	9.09	505.2
	WU2-D15	0.050	0.436	8.74	485.5
30	WU1-D30	0.045	0.430	9.60	533.4
	WU2-D30	0.043	0.423	9.72	540.3
58	WU1-D58	0.036	0.407	11.31	628.5
	WU2-D58	0.037	0.395	10.54	585.3
128	WU1-D128	0.028	0.364	13.10	727.6
	WU2-D128	0.027	0.352	13.28	737.6

Table 7.1.3.2-8: Time-dependent sorption evaluation for soil Dollendorf II

DAT	Sample- ID	Desorbed and Sorbed Residues			
		C_{des}	C_{extr}	$R_{TDS\ Kd}$	$R_{TDS\ aKoc}$
	JR35-	[µg/mL]	[µg/g]	[mL/g]	[mL/g]
0	DD1-D0	0.034	0.504	15.00	294.0
	DD2-D0	0.035	0.508	14.49	284.2
1	DD1-D1	0.035	0.499	14.34	281.1
	DD2-D1	0.034	0.500	14.63	286.8
3	DD1-D3	0.030	0.505	16.59	325.2
	DD2-D3	0.029	0.505	17.27	338.5
7	DD1-D7	0.026	0.487	18.58	364.3
	DD2-D7	0.027	0.496	18.31	359.1
15	DD1-D15	0.024	0.474	19.55	383.3
	DD2-D15	0.025	0.502	19.80	388.3
30	DD1-D30	0.021	0.449	21.59	423.3
	DD2-D30	0.022	0.463	20.62	404.3
58	DD1-D58	0.019	0.413	21.93	430.4
	DD2-D58	0.016	0.399	24.22	475.0
128	DD1-D128	0.013	0.342	27.30	535.3
	DD2-D128	0.012	0.317	26.87	526.9

Table 7.1.3.2-9: Time-dependent sorption study conditions

Parameter	Hoefchen	LH AXXa	LH Wurmwiese	Dollendorf II
Incubation soil moisture (% of MWHC)	55	55	55	55
Maximum water holding capacity (g ad 100 g soil DW)	59.4	48.4	55.5	84.6
Amount of soil per test system (g DW)	100	100	100	100
Moisture per test system (g (mL))	32.7	26.6	30.5	46.5
Gravimetric moisture per g soil (DW) (g water per g soil DW)	0.241	0.181	0.182	0.347
Total volume of $CaCl_2$ solution added to soil for desorption (mL)	400	400	400	400
Total volume of desorption solution ($V_{employed\ desorption\ solution}$ + moisture per test system) (mL)	432.7	426.6	430.5	446.5
Amount of test item applied to soil (µg/100 g soil DW)	66.8	64.5	68.3	66.9

3. Assessment and conclusion

Assessment and conclusion by applicant:
The study and its data are considered to be valid and reliable for use in risk assessment.

Assessment and conclusion by RMS:
Outcome and conclusion of the study: RMS should indicate if they agree to the results and conclusions of the APPL.

1. Information on the study

Data Point:	KCA 7.1.3.2/02
Report Author:	[redacted]
Report Year:	2008
Report Title:	[Phenyl-UL-14C]AE C656948: Aerobic soil metabolism/degradation and time-dependent sorption in four soils
Report No:	MEF-06/299
Document No:	M-298296-01-1
Guideline(s) followed in study:	OECD: Guideline 307, Aerobic and Anaerobic Transformation in Soil (2002); Commission Directive 95/36/EC amending Council Directive 91/414/EEC (Annexes I and II, Fate and Behavior in the Environment) (1995); SETAC: Procedures for Assessing the Environmental Fate and Ecotoxicity of Pesticides (1995); US EPA Subdivision N, Section 162-1, Aerobic soil metabolism (1982); OECD: Guideline 106, Adsorption/Desorption (2001) (only where applicable); Equivalent to US EPA OPPTS Guideline No. 835.4100
Deviations from current test guideline:	Current Guideline: OECD 307 (2002), OECD 106 (2000) (Only in parts) None
Previous evaluation:	yes, evaluated and accepted DAR (2011)
GLP/Officially recognised testing facilities:	Yes, conducted under GLP/Officially recognised testing facilities
Acceptability/Reliability:	Yes

The experimental study is summarised and discussed under point KCA 7.1.1.1/02 of this document. The kinetic evaluation is summarised under KCA 7.1.2.1.1/09 (M-761966-01-1). The results of the aged sorption part of the study are summarised below.

2. Full summary of KCA 7.1.3.2/02

1. MATERIALS AND METHODS

Time-Dependent Sorption Calculations
The results were used to calculate the ratio for the time-dependent sorption (R_{TDS}) based on the amount of test item adsorbed to soil (sum of recovered fluopyram in ambient soil extracts) in relation to the amount of fluopyam desorbed during the so-called batch equilibrium shaking test by the 0.01 M $CaCl_2$ solution. The respective R_{TDS} ratios were normalised to soil % organic carbon content (K_{OC}).

II. RESULTS AND DISCUSSION

The time-dependent sorption ratios R_{TDS} of fluopyram normalised to soil % organic carbon content (K_{OC}) increased from DAT-0 to DAT-121 from 307 to 748 mL/g in soil Hoefchen, from 430 to 1193 mL/g in soil LH AXXa, from 324 to 829 mL/g in soil LH Wurmwiese and from 252 to 862 mL/g in soil LH AIIIa.
Until an aging time of 121 days the time-dependent sorption ratios increased by a factor of 2.4 to 3.4 (mean: 2.8).

Table 7.1.3.2-10: Time-dependent sorption ratios R_{TDS} of fluopyram in soil under aerobic conditions normalised to soil organic carbon content (Koc expressed as mL/g; mean value of duplicates)

DAT	Hoefchen	LH AXXa	LH Wurmwiese	LH AIIIa
0	307	430	324	252
1	325	470	355	298
2	349	512	392	315
7	412	618	493	404
14	435	698	533	451
30	519	809	614	526
62	604	922	707	658
121	748	1193	829	862
Factor DAT-121/DAT-0	**2.4**	**2.8**	**2.6**	**3.4**
Mean factor DAT-121/DAT-0		**2.8**		

DAT: days after treatment

Table 7.1.3.2-11: Time-dependent sorption evaluation for soil Hoefchen

DAT	Sample- ID	Desorbed and Sorbed Residues			
		C_{des}	C_{extr}	$R_{TDS\ Kd}$	$R_{TDS\ Koc}$
	JR33	[µg/mL]	[µg/g]	[mL/g]	[mL/g]
0	00 A	0.066	0.413	6.3	304.1
	00 B	0.067	0.415	6.2	298.7
1	01 A	0.062	0.419	6.8	327.9
	01 B	0.063	0.409	6.5	313.4
2	02 A	0.058	0.417	7.2	345.8
	02 B	0.059	0.421	7.1	342.6
7	07 A	0.054	0.438	8.1	393.7
	07 B	0.052	0.442	8.5	411.4
14	14 A	0.049	0.426	8.6	416.7
	14 B	0.048	0.443	9.2	444.0
30	30 A	0.042	0.440	10.6	512.1
	30 B	0.041	0.445	10.8	520.5
62	62 A	0.033	0.402	12.1	586.8
	62 B	0.033	0.414	12.7	613.7
121	12 A	0.023	0.366	15.9	766.8
	12 B	0.026	0.383	14.9	722.0

Table 7.1.3.2-12: Time-dependent sorption evaluation for soil LH AXXa

DAT	Sample- ID	Desorbed and Sorbed Residues			
		C_{des}	C_{extr}	$R_{TDS\ Kd}$	$R_{TDS\ Koc}$
	JR33	[µg/mL]	[µg/g]	[mL/g]	[mL/g]
0	00 C	0.064	0.410	6.4	420.9
	00 D	0.064	0.416	6.5	426.6
1	01 C	0.060	0.430	7.1	465.2
	01 D	0.059	0.427	7.2	472.0
2	02 C	0.056	0.427	7.7	502.3
	02 D	0.057	0.447	7.8	511.5
7	07 C	0.050	0.454	9.0	590.6
	07 D	0.050	0.479	9.6	628.6
14	14 C	0.044	0.470	10.6	691.2
	14 D	0.045	0.484	10.8	703.9
30	30 C	0.039	0.494	12.6	823.7
	30 D	0.038	0.463	12.1	790.7
62	62 C	0.030	0.424	14.0	915.0
	62 D	0.030	0.429	14.1	923.6
121	12 C	0.020	0.384	19.0	1240.7
	12 D	0.023	0.397	17.4	1137.4

Table 7.1.3.2-13: Time-dependent sorption evaluation for soil LH Wurmwiese

DAT	Sample- ID	Desorbed and Sorbed Residues			
		C_{des}	C_{extr}	$R_{TDS\ Kd}$	$R_{TDS\ Koc}$
	JR33	[µg/mL]	[µg/g]	[mL/g]	[mL/g]
0	00 E	0.063	0.412	6.5	322.5
	00 F	0.064	0.411	6.4	316.5
1	01 E	0.063	0.437	6.9	343.7
	01 F	0.061	0.440	7.2	357.0
2	02 E	0.054	0.428	8.0	394.8
	02 F	0.057	0.438	7.6	377.8
7	07 E	0.047	0.455	9.7	481.1
	07 F	0.048	0.474	9.9	489.6
14	14 E	0.044	0.462	10.6	523.4
	14 F	0.043	0.464	10.9	540.4
30	30 E	0.038	0.463	12.1	599.8
	30 F	0.038	0.477	12.5	621.1
62	62 E	0.034	0.488	14.3	717.9
	62 F	0.034	0.475	14.0	693.4
121	12 E	0.023	0.390	16.6	822.3
	12 F	0.027	0.448	16.7	828.7

Table 7.1.3.2-14: Time-dependent sorption evaluation for soil LH AHIIa

DAT	Sample- ID	Desorbed and Sorbed Residues			
		C_{des}	C_{extr}	$R_{TDS\ Kd}$	$R_{TDS\ Koc}$
	JR33	[µg/mL]	[µg/g]	[mL/g]	[mL/g]
0	00 G	0.093	0.294	3.2	252.4
	00 H	0.098	0.305	3.1	249.7
1	01 G	0.083	0.323	3.9	309.7
	01 H	0.090	0.319	3.6	284.4
2	02 G	0.083	0.323	3.9	311.4
	02 H	0.084	0.334	4.0	317.7
7	07 G	0.071	0.359	5.1	404.6
	07 H	0.072	0.357	5.0	397.3
14	14 G	0.063	0.364	5.8	461.6
	14 H	0.066	0.365	5.5	439.6
30	30 G	0.056	0.368	6.6	525.2
	30 H	0.057	0.376	6.6	531.9
62	62 G	0.043	0.350	8.2	657.8
	62 H	0.044	0.361	8.2	656.9
121	12 G	0.028	0.304	11.0	878.8
	12 H	0.027	0.284	10.6	846.1

Table 7.1.3.2-15: Time-dependent sorption study conditions

Parameter	Hoefchen	LH AXXa	LH Wurmwiese	LH Alla
Incubation soil moisture (% of MWHC)	55	55	55	55
Maximum water holding capacity (g ad 100 g soil DW)	63.3	48.5	68.5	51.6
Amount of soil per test system (g DW)	100	100	100	100
Moisture per test system (g (mL))	34.8	26.7	37.5	28.4
Gravimetric moisture per g soil (DW) (g water per g soil DW)	0.157	0.56	0.147	0.89
Total volume of $CaCl_2$ solution added to soil for desorption (mL)	400	400	400	400
Total volume of desorption solution ($V_{employed\ desorption\ solution}$ + moisture per test system) (mL)	434.8	426.7	437.5	428.4
Amount of test item applied to soil (µg/100 g soil DW)	71.35	72.48	69.81	71.73

3. Assessment and conclusion

Assessment and conclusion by applicant:
The study and its data are considered to be valid and reliable for use in risk assessment.

Assessment and conclusion by RMS:
Outcome and conclusion of the study; RMS should indicate if they agree to the results and conclusions of the APPL.

Data Point:	KCA 7.1.3.2/03
Report Author:	[redacted]
Report Year:	2009
Report Title:	Evaluation of the time-dependent sorption of fluopyram (AE C656948) based on laboratory batch equilibrium experiments in 8 soils
Report No:	MEF-07/32
Document No:	M-296742-01-1
Guideline(s) followed in study:	not applicable
Deviations from current test guideline:	Current Guideline not applicable (see justification)
Previous evaluation:	yes, evaluated and accepted Addendum 1 to the DAR (2012)
GLP/Officially recognised testing facilities:	No, not conducted under GLP/Officially recognised testing facilities
Acceptability/Reliability:	No

Time-dependent sorption was re-assessed according to current guideline and with the additional soils investigated. Therefore, this evaluation is not state-of-the-art and is not considered in the current dossier. See KCA 7.1.3.2/06 (M-762175-01-1) and KCA 7.1.3.2/07 (M-762930-01-1) for the new time-dependent sorption evaluations.

1. Information on the study

Data Point:	KCA 7.1.3.2/04
Report Author:	[redacted]
Report Year:	2020
Report Title:	Amendment no. 01: Fluopyram: Aerobic metabolism / Degradation and time-Dependent sorption in 6 soils
Report No:	EnSa-20-0072
Document No:	M-681092-02-1
Guideline(s) followed in study:	OECD Test Guideline No. 307 (2002). OECD Test Guideline No. 106 (2000, only in parts). Guidance on how aged sorption studies for pesticides should be conducted, analyzed and used in the regulatory process (2012, revised draft 2016); Current revision dates Sep 2016 [this draft guidance was updated based on the PPR statement on aged sorption, EFSA Journal 2015;13(7):4175].
Deviations from current test guideline:	Current Guideline: OECD 307 (2002), OECD 106 (2000) (Only in parts) None
Previous evaluation:	No, not previously submitted
GLP/Officially recognised testing facilities:	Yes, conducted under GLP/Officially recognised testing facilities
Acceptability/Reliability:	Yes

The experimental study is summarised and discussed under point KCA 7.1.1.1/05 of this document. A kinetic evaluation of trigger endpoints following current FOCUS guidance was conducted in the course of the study and is summarised under KCA 7.1.2.1.1/06. Evaluation of modelling endpoints can be found in KCA 7.1.2.1.1/12 (M-761882-01-1). The results of the aged sorption part of the study are summarised below.

2. Full summary of KCA 7.1.3.2/04

I. MATERIALS AND METHODS

Time-Dependent Sorption Calculations

The results were used to calculate the ratio for the time-dependent sorption (R_{TDS}) based on the amount of test item adsorbed to soil (sum of recovered fluopyram in ambient soil extracts) in relation to the amount of fluopyam desorbed during the so-called batch equilibrium shaking test by the 0.01 M $CaCl_2$ solution. The respective R_{TDS} ratios were normalized to soil % organic carbon content (K_{OC}).

II. RESULTS AND DISCUSSION

The time-dependent sorption ratios R_{TDS} of fluopyram increased from DAT-0 to DAT-118 from 6.39 to 18.85 mL/g in soil LO from 12.31 to 27.68 mL/g in soil AM, from 4.44 to 10.65 mL/g in soil UW, from 4.70 to 11.08 mL/g in soil FA, from 4.06 to 8.07 mL/g in soil SD and from 4.55 to 11.05 mL/g in soil PZ. The respective R_{TDS} ratios normalized to soil % organic carbon content (K_{OC}) increased from DAT-0 to DAT-118 from 425.9 to 1256.9 mL/g in soil LO, from 615.3 to 1383.9 mL/g in soil AM, from 403.9 to 968.1 mL/g in soil UW, from 293.4 to 692.4 mL/g in soil FA, from 312.2 to 621.0 mL/g in soil SD and from 379.1 to 921.2 mL/g in soil PZ.

Until an aging time of 118 days the time-dependent sorption ratios increased by a factor of 1.99 to 2.95 (mean: 2.40). The respective R_{TDS} ratios normalized to soil % organic carbon content (K_{OC}) increased for the six soils until DAT-118 to a range of 621 to 1384 mL/g.

Table 7.1.3.2-16: Amounts of Fluopyram in desorption solution and soil extracts under aerobic conditions (expressed as % AR)

Soil	Compartment	Replicate No.	DAT 0	3	7	14	27	48	83	118
LO	$CaCl_2$-solution	1	33.3	30.2	21.1	23.8	22.2	18.0	16.9	14.9
		2	35.7	30.0	21.4	24.8	22.2	18.4	17.2	15.3
		Mean	**34.5**	**30.1**	**21.3**	**24.3**	**22.2**	**18.2**	**17.0**	**15.1**
	Soil extract	1	60.5	63.9	71.6	69.1	70.0	71.6	74.5	75.9
		2	57.7	64.2	72.4	67.6	71.0	70.7	74.6	75.2
		Mean	**59.1**	**64.1**	**72.0**	**68.3**	**70.5**	**71.1**	**74.6**	**75.6**
	Total	1	93.8	94.1	92.8	92.9	92.2	89.6	91.4	90.8
		2	93.4	94.2	93.8	92.4	93.2	89.0	91.7	90.6
		Mean	**93.6**	**94.1**	**93.3**	**92.7**	**92.7**	**89.3**	**91.6**	**90.7**
AM	$CaCl_2$-solution	1	22.1	24.4	26.2	20.2	17.1	14.2	13.1	11.0
		2	21.9	25.4	26.2	20.7	18.2	14.9	12.6	9.9
		Mean	**22.0**	**24.9**	**26.2**	**20.5**	**17.6**	**14.4**	**12.9**	**10.5**
	Soil extract	1	71.4	68.8	66.2	72.9	73.3	73.6	75.0	77.9
		2	71.1	68.7	67.9	73.1	72.5	74.3	75.5	77.5
		Mean	**71.2**	**68.8**	**67.0**	**73.0**	**72.9**	**74.0**	**75.3**	**77.7**
	Total	1	93.5	93.2	92.5	93.1	90.4	87.9	88.1	88.9
		2	93.0	94.1	94.0	93.8	90.7	88.8	88.1	87.4
		Mean	**93.3**	**93.6**	**93.3**	**93.5**	**90.6**	**88.3**	**88.1**	**88.2**
UW	$CaCl_2$-solution	1	42.8	41.0	36.2	34.5	31.5	28.2	27.3	23.0
		2	42.4	41.0	34.6	36.8	31.8	28.9	25.4	23.0
		Mean	**42.6**	**41.0**	**35.4**	**35.5**	**31.7**	**28.1**	**26.3**	**23.0**
	Soil extract	1	50.4	53.8	57.1	57.4	61.4	61.2	64.6	67.2
		2	51.3	52.4	57.6	59.4	60.9	60.5	65.0	64.1
		Mean	**50.8**	**53.1**	**57.4**	**58.4**	**61.1**	**60.8**	**64.8**	**65.6**
	Total	1	93.1	94.8	93.3	91.9	92.9	88.4	91.9	90.2
		2	93.7	93.3	92.2	96.0	92.7	89.4	90.4	87.0
		Mean	**93.4**	**94.1**	**92.8**	**93.9**	**92.8**	**88.9**	**91.1**	**88.6**
FA	$CaCl_2$-solution	1	41.3	40.3	35.0	35.0	32.3	27.4	23.5	20.4
		2	40.2	42.4	35.5	35.0	31.9	26.7	22.4	19.9
		Mean	**40.7**	**41.4**	**35.3**	**35.0**	**32.1**	**27.0**	**23.0**	**20.1**
	Soil extract	1	51.6	52.3	55.4	56.7	59.5	59.3	60.2	60.2
		2	50.9	56.1	55.0	58.1	58.9	60.9	60.7	59.3
		Mean	**51.2**	**54.2**	**55.2**	**57.4**	**59.2**	**60.1**	**60.5**	**59.8**
	Total	1	92.9	92.7	90.4	91.6	91.7	86.6	83.7	80.6
		2	91.0	98.5	90.5	93.1	90.8	87.6	83.2	79.2
		Mean	**92.0**	**95.6**	**90.5**	**92.4**	**91.3**	**87.1**	**83.4**	**79.9**
SD	$CaCl_2$-solution	1	44.1	43.7	38.5	38.2	34.4	28.1	25.3	20.8
		2	43.9	42.9	40.1	38.0	35.2	30.2	25.1	22.4
		Mean	**44.0**	**43.3**	**39.3**	**38.1**	**34.8**	**29.1**	**25.2**	**21.6**
	Soil extract	1	48.0	50.5	51.3	54.3	52.7	49.8	50.3	47.1
		2	48.2	50.3	51.5	51.7	51.5	52.6	50.4	47.8
		Mean	**48.1**	**50.4**	**51.4**	**53.0**	**52.1**	**51.2**	**50.3**	**47.4**
	Total	1	92.2	94.1	89.8	92.4	87.1	77.8	75.6	67.8
		2	92.1	93.2	91.6	89.7	86.7	82.9	75.4	70.2
		Mean	**92.1**	**93.7**	**90.7**	**91.1**	**86.9**	**80.3**	**75.5**	**69.0**
PZ	$CaCl_2$-solution	1	42.8	39.0	34.9	33.7	28.5	23.8	20.6	18.6
		2	41.1	38.4	35.4	32.9	30.4	24.2	21.8	20.1
		Mean	**42.4**	**38.7**	**35.2**	**33.3**	**29.5**	**24.0**	**21.2**	**19.4**
	Soil extract	1	51.9	53.9	56.8	56.7	57.7	55.9	56.5	56.5
		2	51.6	53.9	55.9	56.8	56.9	57.8	57.2	57.1
		Mean	**51.7**	**53.9**	**56.3**	**56.7**	**57.3**	**56.8**	**56.8**	**56.8**
	Total	1	95.6	92.9	91.6	90.3	86.3	79.7	77.1	75.1
		2	92.7	92.2	91.4	89.7	87.3	82.0	78.9	77.2
		Mean	**94.2**	**92.6**	**91.5**	**90.0**	**86.8**	**80.8**	**78.0**	**76.1**

n.d.: not detected, n.a.: not analyzed, DAT: days after treatment

Table 7.1.3.2-17: Time-dependent sorption ratios (R_{TDS}) of fluopyram in soil under aerobic conditions (expressed as mL/g; mean value of duplicates and standard deviation)

DAT	Mean SD	Auchy les Mines	Charles River Farm	Little Oliver	Paradiso San Zenone	Sinalos	Urbanowice
0	Mean	12.31	4.70	6.39	4.55	4.06	4.44
	SD	± 0.00	± 0.01	± 0.05	± 0.03	± 0.00	± 0.01
3	Mean	10.13	4.60	7.82	4.97	4.01	4.67
	SD	± 0.02	± 0.00	± 0.00	± 0.01	± 0.01	± 0.00
7	Mean	9.34	5.75	12.46	5.89	4.77	5.89
	SD	± 0.01	± 0.01	± 0.00	± 0.02	± 0.02	± 0.02
14	Mean	13.37	5.96	10.39	6.35	5.03	5.98
	SD	± 0.01	± 0.00	± 0.02	± 0.02	± 0.01	± 0.02
27	Mean	15.65	6.74	12.06	7.35	5.62	7.21
	SD	± 0.03	± 0.01	± 0.01	± 0.04	± 0.02	± 0.02
48	Mean	19.23	8.25	14.41	8.79	6.48	7.96
	SD	± 0.00	± 0.03	± 0.02	± 0.01	± 0.01	± 0.03
83	Mean	22.39	10.00	16.72	10.18	7.54	9.33
	SD	± 0.02	± 0.03	± 0.01	± 0.02	± 0.01	± 0.04
118	Mean	27.68	11.08	18.85	11.05	8.07	10.65
	SD	± 0.06	± 0.01	± 0.02	± 0.03	± 0.04	± 0.01
Factor: R_{TDS} DAT-118 / R_{TDS} DAT-0		2.25	2.36	2.95	2.43	1.99	2.40
Mean		2.40					

DAT: days after treatment, SD: standard deviation

Table 7.1.3.2-18: Time-dependent sorption ratios (R_{TDS}) of fluopyram in soil under aerobic conditions normalized to soil organic carbon content (Koc, expressed as mL/g; mean value of duplicates and standard deviation)

DAT	Mean SD	Auchy les Mines	Charles River Farm	Little Oliver	Paradiso San Zenone	Sinalos	Urbanowice
0	Mean	615.3	293.4	425.9	379.1	312.2	403.9
	SD	± 0.0	± 0.0	± 0.0	± 0.0	± 0.0	± 0.0
3	Mean	506.4	287.8	521.2	414.5	308.2	424.4
	SD	± 0.0	± 0.0	± 0.0	± 0.0	± 0.0	± 0.0
7	Mean	467.0	359.2	830.5	490.9	367.1	535.5
	SD	± 0.0	± 0.0	± 0.0	± 0.0	± 0.0	± 0.0
14	Mean	668.7	372.5	692.4	528.9	386.7	543.6
	SD	± 0.0	± 0.0	± 0.0	± 0.0	± 0.0	± 0.0
27	Mean	782.3	421.3	804.0	612.3	432.5	655.6
	SD	± 0.0	± 0.0	± 0.0	± 0.0	± 0.0	± 0.0
48	Mean	961.4	515.6	960.7	732.3	498.5	724.0
	SD	± 0.0	± 0.0	± 0.0	± 0.0	± 0.0	± 0.0
83	Mean	1119.3	624.8	1114.4	848.1	580.3	848.5
	SD	± 0.0	± 0.0	± 0.0	± 0.0	± 0.0	± 0.0
118	Mean	1383.9	692.4	1256.9	921.2	621.0	968.1
	SD	± 0.1	± 0.0	± 0.0	± 0.0	± 0.0	± 0.0
Factor: $\frac{R_{TDS}\ DAT\text{-}118}{R_{TDS}\ DAT\text{-}0}$		2.25	2.36	2.95	2.43	1.99	2.40
Mean		2.40					

DAT: days after treatment, SD: standard deviation

Table 7.1.3.2-19: Time-dependent sorption evaluation for soil Auchy les Mines

DAT	Sample- ID	Desorbed and Sorbed Residues							
	JR88-	C_{des} [µg/L]	Mean C_{des} [µg/L]	C_{extr} [µg/g]	Mean C_{extr} [µg/g]	R_{TDS} [mL/g]	Mean R_{TDS} [mL/g]	t.i.total [µg]	Mean t.i.total [µg]
0	AM1-T1	9.528	9.480	0.117	0.117	12.27	12.31	15.50	15.46
	AM2-T1	9.432		0.116		12.35		15.42	
3	AM1-T2	10.771	10.990	0.111	0.111	10.35	10.13	15.45	15.52
	AM2-T2	11.209		0.111		9.91		15.59	
7	AM1-T3	11.596	11.586	0.107	0.108	9.21	9.34	15.32	15.46
	AM2-T3	11.575		0.110		9.47		15.59	
12	AM1-T4	8.814	8.920	0.119	0.119	13.52	13.37	15.44	15.50
	AM2-T4	9.025		0.119		13.23		15.55	
26	AM1-T5	7.461	7.643	0.120	0.120	16.08	15.65	14.98	15.01
	AM2-T5	7.825		0.119		15.22		15.04	
48	AM1-T6	6.286	6.303	0.120	0.121	19.17	19.23	14.56	14.64
	AM2-T6	6.319		0.122		19.29		14.72	
82	AM1-T7	5.632	5.537	0.124	0.124	21.93	22.39	14.60	14.60
	AM2-T7	5.441		0.124		22.84		14.60	
118	AM1-T8	4.918	4.628	0.128	0.128	25.95	27.68	14.73	14.61
	AM2-T8	4.338		0.128		29.40		14.49	

All values for soil weight refer to dry weight equivalents

Table 7.1.3.2-20: Time-dependent sorption evaluation for soil Charles River Farm

DAT	Sample- ID	Desorbed and Sorbed Residues							
	JR88-	C_{des} [µg/L]	Mean C_{des} [µg/L]	C_{extr} [µg/g]	Mean C_{extr} [µg/g]	R_{TDS} [mL/g]	Mean R_{TDS} [mL/g]	t.i.total [µg]	Mean t.i.total [µg]
0	FA1-T1	17.779	17.530	0.083	0.082	4.66	4.70	15.40	15.24
	FA2-T1	17.281		0.082		4.73		15.08	
3	FA1-T2	17.826	18.411	0.082	0.085	4.62	4.60	15.36	15.84
	FA2-T2	18.996		0.087		4.59		16.32	
7	FA1-T3	15.273	15.384	0.089	0.088	5.81	5.75	14.99	14.99
	FA2-T3	15.495		0.088		5.68		15.00	
12	FA1-T4	15.261	15.370	0.091	0.092	5.95	5.96	15.19	15.21
	FA2-T4	15.479		0.092		5.97		15.23	
26	FA1-T5	14.258	14.088	0.095	0.095	6.67	6.74	15.21	15.13
	FA2-T5	13.918		0.095		6.82		15.05	
48	FA1-T6	11.936	11.791	0.096	0.097	8.03	8.25	14.36	14.44
	FA2-T6	11.646		0.099		8.47		14.52	
82	FA1-T7	10.109	9.885	0.098	0.099	9.72	10.00	13.87	13.83
	FA2-T7	9.662		0.099		10.27		13.79	
118	FA1-T8	8.903	8.783	0.098	0.097	11.00	11.08	13.36	13.24
	FA2-T8	8.663		0.097		11.15		13.13	

All values for soil weight refer to dry weight equivalents

Table 7.1.3.2-21: Time-dependent sorption evaluation for soil Little Oliver

DAT	Sample- ID	Desorbed and Sorbed Residues							
	JR88-	C_{des} [µg/L]	Mean C_{des} [µg/L]	C_{extr} [µg/g]	Mean C_{extr} [µg/g]	R_{TDS} [mL/g]	Mean R_{TDS} [mL/g]	t.i.total [µg]	Mean t.i.total [µg]
0	LO1-T1	14.627	14.948	0.097	0.095	6.70	6.39	15.55	15.52
	LO2-T1	15.369		0.093		6.08		15.49	
3	LO1-T2	13.154	13.199	0.103	0.103	7.85	7.82	15.59	15.60
	LO2-T2	13.245		0.103		7.78		15.61	
7	LO1-T3	9.341	9.393	0.116	0.117	12.46	12.46	15.38	15.46
	LO2-T3	9.445		0.118		12.45		15.54	
12	LO1-T4	10.533	10.679	0.112	0.111	10.62	10.39	15.40	15.36
	LO2-T4	10.825		0.110		10.15		15.32	
26	LO1-T5	9.564	9.568	0.115	0.115	11.98	12.06	15.28	15.37
	LO2-T5	9.571		0.116		12.14		15.45	
48	LO1-T6	7.972	8.044	0.117	0.116	14.64	14.41	14.86	14.81
	LO2-T6	8.117		0.115		14.18		14.76	
82	LO1-T7	7.270	7.328	0.122	0.122	16.84	16.72	15.15	15.18
	LO2-T7	7.385		0.123		16.59		15.21	
118	LO1-T8	6.480	6.577	0.125	0.124	19.22	18.85	15.04	15.03
	LO2-T8	6.675		0.123		18.49		15.01	

All values for soil weight refer to dry weight equivalents

Table 7.1.3.2-22: Time-dependent sorption evaluation for soil Paradiso San Zenone

DAT	Sample- ID	Desorbed and Sorbed Residues							
	JR88-	C_{des} [µg/L]	Mean C_{des} [µg/L]	C_{extr} [µg/g]	Mean C_{extr} [µg/g]	R_{TDS} [mL/g]	Mean R_{TDS} [mL/g]	t.i.total [µg]	Mean t.i.total [µg]
0	PZ1-T1	18.846	18.266	0.083	0.083	4.41	4.55	15.85	15.61
	PZ2-T1	17.687		0.083		4.69		15.37	
3	PZ1-T2	17.237	17.097	0.085	0.085	4.93	4.97	15.40	15.34
	PZ2-T2	16.957		0.085		5.01		15.29	
7	PZ1-T3	15.213	15.336	0.091	0.090	5.98	5.89	15.19	15.17
	PZ2-T3	15.460		0.090		5.80		15.14	
12	PZ1-T4	14.680	14.424	0.091	0.092	6.20	6.35	14.97	14.92
	PZ2-T4	14.167		0.092		6.50		14.87	
26	PZ1-T5	12.282	12.685	0.094	0.093	7.64	7.35	14.30	14.38
	PZ2-T5	13.087		0.092		7.05		14.47	
48	PZ1-T6	10.397	10.476	0.091	0.092	8.71	8.59	13.21	13.40
	PZ2-T6	10.556		0.094		8.87		13.58	
82	PZ1-T7	8.885	9.126	0.092	0.093	10.39	10.18	12.79	12.93
	PZ2-T7	9.367		0.093		9.96		13.08	
118	PZ1-T8	8.116	8.387	0.092	0.093	11.33	11.05	12.44	12.62
	PZ2-T8	8.659		0.093		10.78		12.79	

All values for soil weight refer to dry weight equivalents

Table 7.1.3.2-23: Time-dependent sorption evaluation for soil Sindos

DAT	Sample- ID	Desorbed and Sorbed Residues							
	JR88-	C_{des} [µg/L]	Mean C_{des} [µg/L]	C_{extr} [µg/g]	Mean C_{extr} [µg/g]	R_{TDS} [mL/g]	Mean R_{TDS} [mL/g]	t.i.total [µg]	Mean t.i.total [µg]
0	SD1-T1	19.003	18.948	0.077	0.077	4.04	4.06	15.28	15.27
	SD2-T1	18.893		0.077		4.08		15.26	
3	SD1-T2	19.555	19.391	0.078	0.078	3.98	4.01	15.60	15.53
	SD2-T2	19.227		0.078		4.04		15.45	
7	SD1-T3	16.787	17.145	0.082	0.082	4.87	4.77	14.89	15.04
	SD2-T3	17.503		0.082		4.68		15.18	
12	SD1-T4	16.878	16.725	0.086	0.084	5.08	5.03	15.32	15.10
	SD2-T4	16.572		0.082		4.98		14.87	
26	SD1-T5	14.813	14.975	0.085	0.084	5.75	5.62	14.43	14.40
	SD2-T5	15.138		0.083		5.49		14.37	
48	SD1-T6	12.237	12.709	0.080	0.082	6.54	6.48	12.90	13.32
	SD2-T6	13.180		0.085		6.42		13.73	
82	SD1-T7	10.899	10.843	0.082	0.082	7.50	7.54	12.53	12.52
	SD2-T7	10.787		0.082		7.59		12.50	
118	SD1-T8	9.056	9.486	0.076	0.076	8.41	8.07	11.24	11.44
	SD2-T8	9.916		0.077		7.73		11.63	

All values for soil weight refer to dry weight equivalents

Table 7.1.3.2-24: Time-dependent sorption evaluation for soil Urbanowice

DAT	Sample- ID	Desorbed and Sorbed Residues							
	JR88-	C_{des} [µg/L]	Mean C_{des} [µg/L]	C_{extr} [µg/g]	Mean C_{extr} [µg/g]	R_{TDS} [mL/g]	Mean R_{TDS} [mL/g]	t.i.total [µg]	Mean t.i.total [µg]
0	UW1-T1	18.416	18.336	0.081	0.081	4.38	4.44	15.44	15.48
	UW2-T1	18.257		0.082		4.50		15.52	
3	UW1-T2	18.107	17.986	0.085	0.084	4.68	4.67	15.71	15.59
	UW2-T2	17.864		0.083		4.66		15.47	
7	UW1-T3	15.787	15.549	0.092	0.092	5.80	5.89	15.47	15.38
	UW2-T3	15.311		0.092		5.99		15.29	
12	UW1-T4	15.056	15.611	0.092	0.093	6.12	5.98	15.23	15.57
	UW2-T4	16.165		0.094		5.84		15.91	
26	UW1-T5	13.561	13.718	0.100	0.099	7.35	7.21	15.39	15.38
	UW2-T5	13.875		0.098		7.07		15.36	
48	UW1-T6	12.032	12.325	0.098	0.098	8.18	7.96	14.66	14.74
	UW2-T6	12.617		0.098		7.75		14.82	
82	UW1-T7	11.770	11.342	0.105	0.106	8.94	9.33	15.33	15.11
	UW2-T7	10.914		0.106		9.72		14.98	
118	UW1-T8	10.166	10.027	0.109	0.107	10.74	10.65	14.96	14.69
	UW2-T8	9.888		0.105		10.59		14.42	

All values for soil weight refer to dry weight equivalents

Table 7.1.3.2-25: Time-dependent sorption study conditions

Parameter	Auchy les Mines	Charles River Farm	Little Oliver	Paradiso San Zenone	Sindos	Urbanowice
Incubation soil moisture (% of MWHC)	55	55	55	55	55	55
Maximum water holding capacity (g ad 100 g soil DW)	29.3	30	27.1	28.1	30.3	24.1
Amount of soil per test system (g DW)	100	100	100	100	100	100
Moisture per test system (g (mL))	29.3	30.5	27.1	28.1	30.3	24.1
Gravimetric moisture per g soil (DW) (g water per g soil DW)	0.2926	0.3047	0.2712	0.2811	0.3025	0.2415
Total volume of $CaCl_2$ solution added to soil for desorption (mL)	400	400	400	400	400	400
Total volume of desorption solution ($V_{employed\ desorption\ solution}$ + moisture per test system) (mL)	429.3	430.5	427.1	428.1	430.3	424.1
Amount of test item applied to soil (µg/100 g soil DW)	16.6	16.6	16.6	16.6	16.6	16.6

3. Assessment and conclusion

Assessment and conclusion by applicant:
The study and its data are considered to be valid and reliable for use in risk assessment.

Assessment and conclusion by RMS:
Outcome and conclusion of the study: RMS should indicate if they agree to the results and conclusions of the APPL.

1. Information on the study

Data Point:	KCA 7.1.3.2/05
Report Author:	[redacted]
Report Year:	2020
Report Title:	Fluopyram: Aerobic Metabolism / degradation and time - Dependent sorption in 6 soils
Report No:	M12505406-3
Document No:	M-753426-01-1
Guideline(s) followed in study:	OECD Test Guideline No. 307 (2002) OECD Test Guideline No. 106 (2000) (only in parts) Guidance on how aged sorption studies for pesticides should be conducted, analysed and used in the regulatory process (2012, revised draft 2016). Current revision dates Sep 2016 [this draft guidance was updated based on the PPR-statement on aged sorption, EFSA Journal 2015;13(7):4175]
Deviations from current test guideline:	Current Guideline: OECD 307 (2002), OECD 106 (2000) (Only in parts) None
Previous evaluation:	No, not previously submitted
GLP/Officially recognised testing facilities:	Yes, conducted under GLP/Officially recognised testing facilities
Acceptability/Reliability:	Yes

The experimental study is summarised and discussed under point KCA 7.1.1.1/06 of this document. The kinetic evaluation is summarised under KCA 7.1.2.1.1/13 (M-761969-01-1). The results of the aged sorption part of the study are summarised below.

2. Full summary of KCA 7.1.3.2/05

I. MATERIALS AND METHODS

Time-Dependent Sorption Calculations
The results were used to calculate the ratio for the time-dependent sorption (R_{TDS}) based on the amount of test item adsorbed to soil (sum of recovered fluopyram in ambient soil extracts) in relation to the amount of fluopyram desorbed during the so-called batch equilibrium shaking test by the 0.01 M $CaCl_2$ solution. The respective R_{TDS} ratios were normalized to soil % organic carbon content (K_{OC}).

II. RESULTS AND DISCUSSION

The time-dependent sorption ratios R_{TDS} of fluopyram increased from DAT-0 to DAT-118 from 5.43 to 12.70 mL/g in soil HS, from 10.35 to 25.30 mL/g in soil HT, from 10.23 to 12.77 mL/g in soil LT from 2.33 to 4.76 mL/g in soil BS from 6.91 to 13.59 mL/g in soil BB and from 6.06 to 20.35 mL/g in soil AE. The respective R_{TDS} ratios normalized to soil % organic carbon content (K_{OC}) increased from DAT-0 to

DAT-118 from 603.3 to 1411.0 mL/g in soil HS, from 492.8 to 1204.6 mL/g in soil HT, from 365.2 to 456.0 mL/g in soil LT, from 388.4 to 792.8 mL/g in soil BS, from 406.7 to 799.5 mL/g in soil BB and from 504.6 to 1695.9 mL/g in soil AE.

The sorption factor was calculated for each soil by dividing the R_{TDS} value of the last sampling interval by the R_{TDS} value of DAT-0. Until an aging time of 118 days the time-dependent sorption ratios increased by a factor of 1.25 to 3.36 (mean: 2.23). The respective R_{TDS} ratios normalized to soil % organic carbon content (K_{OC}) increased for the six soils until DAT-118 to a range of 456 to 1696 mL/g.

Table 7.1.3.2-26: Amounts of fluopyram in desorption solution and soil extracts under aerobic conditions (expressed as % AR)

Soil	Compartment	Replicate No.	DAT 0	3	7	14	27	48	83	118
HS	$CaCl_2$-solution	1	41.4	36.9	32.3	30.2	27.1	26.4	23.0	21.5
		2	40.7	37.2	32.5	30.0	27.2	25.5	22.6	20.5
		Mean	**41.1**	**37.1**	**32.4**	**30.1**	**27.2**	**26.0**	**22.8**	**21.0**
	Soil extract	1	60.9	62.6	68.4	69.8	72.8	71.6	74.6	73.8
		2	60.7	64.6	67.8	71.3	75.1	73.2	74.2	69.8
		Mean	**60.8**	**63.6**	**68.1**	**70.6**	**74.0**	**72.4**	**74.4**	**71.8**
	Total	1	102.3	99.5	100.8	100.0	99.9	98.0	97.6	95.2
		2	101.4	101.8	100.3	101.4	102.3	98.7	96.9	90.3
		Mean	**101.9**	**100.6**	**100.5**	**100.7**	**101.1**	**98.4**	**97.3**	**92.8**
HT	$CaCl_2$-solution	1	27.1	27.3	22.4	18.7	16.7	16.6	12.5	11.0
		2	24.6	24.0	21.4	21.5	17.9	15.9	13.2	10.6
		Mean	**25.9**	**25.7**	**21.9**	**20.1**	**17.3**	**16.3**	**12.9**	**10.8**
	Soil extract	1	75.2	78.6	75.2	70.8	73.7	73.9	73.9	74.2
		2	73.5	72.4	74.8	72.4	78.4	74.4	75.6	76.0
		Mean	**74.4**	**75.5**	**75.2**	**71.6**	**76.1**	**74.2**	**74.8**	**75.1**
	Total	1	102.3	106.0	97.9	89.5	90.3	90.5	86.4	85.3
		2	98.1	96.3	96.1	93.9	96.2	90.3	88.7	86.6
		Mean	**100.2**	**101.2**	**97.0**	**91.7**	**93.3**	**90.4**	**87.6**	**85.9**
LT	$CaCl_2$-solution	1	26.4	26.5	23.5	22.6	21.5	18.6	15.4	13.9
		2	25.9	25.5	21.4	22.1	20.1	19.8	13.9	14.0
		Mean	**26.2**	**26.0**	**22.4**	**22.4**	**20.8**	**19.2**	**14.7**	**14.0**
	Soil extract	1	74.2	72.7	71.3	72.9	68.4	61.3	55.4	48.9
		2	74.4	71.1	68.6	72.4	71.2	63.2	53.8	49.7
		Mean	**74.3**	**71.9**	**70.0**	**72.7**	**69.8**	**62.3**	**54.6**	**49.3**
	Total	1	100.6	99.2	94.8	95.5	89.8	79.9	70.8	62.8
		2	100.3	96.6	89.9	94.5	91.3	83.1	67.7	63.7
		Mean	**100.4**	**97.9**	**92.4**	**95.0**	**90.6**	**81.5**	**69.2**	**63.3**
BS	$CaCl_2$-solution	1	61.2	57.6	55.2	51.8	50.3	44.4	40.1	36.3
		2	62.9	57.8	55.8	52.6	48.1	43.0	42.4	36.1
		Mean	**62.1**	**57.7**	**55.5**	**52.2**	**49.2**	**43.7**	**41.3**	**36.2**
	Soil extract	1	39.9	41.3	43.8	44.8	49.7	47.4	46.0	45.8
		2	40.1	42.2	43.5	46.0	49.8	46.1	49.6	46.5
		Mean	**40.0**	**41.8**	**43.7**	**45.4**	**49.8**	**46.8**	**47.8**	**46.2**
	Total	1	101.1	99.0	99.0	96.7	100.0	91.7	86.1	82.2
		2	103.0	100.0	99.3	98.6	97.8	89.1	92.0	82.6
		Mean	**102.0**	**99.5**	**99.2**	**97.6**	**98.9**	**90.4**	**89.0**	**82.4**
BB	$CaCl_2$-solution	1	33.4	35.1	30.1	27.8	26.0	24.4	20.1	17.4
		2	35.1	32.5	29.5	27.4	24.9	22.6	21.0	16.9
		Mean	**34.3**	**33.8**	**29.8**	**27.6**	**25.5**	**23.5**	**20.6**	**17.2**
	Soil extract	1	66.2	64.8	68.0	69.7	72.4	69.3	63.7	64.6
		2	64.5	64.7	68.4	69.9	71.3	69.5	64.7	62.0
		Mean	**65.4**	**64.8**	**68.2**	**69.8**	**71.9**	**69.4**	**64.2**	**63.3**
	Total	1	99.6	99.9	98.1	97.5	98.4	93.7	83.8	82.0
		2	99.6	97.2	97.9	97.2	96.2	92.2	85.7	78.9
		Mean	**99.6**	**98.5**	**98.0**	**97.3**	**97.3**	**92.9**	**84.8**	**80.5**
AE	$CaCl_2$-solution	1	36.0	37.9	26.9	24.3	20.8	16.0	12.7	12.3
		2	36.3	34.7	26.3	26.2	22.8	16.4	13.8	11.1
		Mean	**36.2**	**36.3**	**26.6**	**25.3**	**21.8**	**16.2**	**13.3**	**11.7**
	Soil extract	1	64.3	58.4	69.3	72.6	74.9	68.6	65.8	64.7
		2	64.0	61.5	70.1	72.0	77.1	69.8	68.2	65.4
		Mean	**64.2**	**60.0**	**69.7**	**72.3**	**76.0**	**69.2**	**67.0**	**65.1**
	Total	1	100.3	96.4	96.3	96.9	95.7	84.6	78.5	77.1
		2	100.3	96.2	96.4	98.2	99.9	86.3	82.0	76.4
		Mean	**100.3**	**96.3**	**96.3**	**97.5**	**97.8**	**85.4**	**80.2**	**76.7**

n.d.: not detected, n.a.: not analysed, DAT: days after treatment

Table 7.1.3.2-27: Time-dependent sorption ratios (R_{TDS}) of fluopyram in soil under aerobic conditions (expressed as mL/g; mean value of duplicates and standard deviation)

DAT	Mean SD	Hornton	Brannens	Hoeltinghausen	Almayate East	Balbiano	Le Thour
0	Mean	10.35	2.33	5.43	6.06	6.91	10.23
	SD	± 0.04	± 0.01	± 0.01	± 0.03	± 0.04	± 0.01
3	Mean	10.70	2.38	6.26	6.31	6.87	9.75
	SD	± 0.03	± 0.01	± 0.00	± 0.12	± 0.01	± 0.03
7	Mean	12.63	2.97	7.71	9.58	8.33	11.26
	SD	± 0.02	± 0.01	± 0.00	± 0.02	± 0.01	± 0.03
14	Mean	12.81	3.15	8.79	10.51	9.24	11.85
	SD	± 0.07	± 0.01	± 0.01	± 0.04	± 0.01	± 0.02
27	Mean	16.26	3.60	10.05	12.61	10.07	11.91
	SD	± 0.00	± 0.01	± 0.02	± 0.03	± 0.01	± 0.03
48	Mean	16.59	3.86	10.42	15.49	10.63	11.49
	SD	± 0.03	± 0.00	± 0.03	± 0.00	± 0.04	± 0.02
83	Mean	20.70	4.25	11.76	18.40	11.26	13.39
	SD	± 0.02	± 0.02	± 0.01	± 0.02	± 0.00	± 0.02
118	Mean	25.30	4.76	12.70	20.35	13.59	12.77
	SD	± 0.03	± 0.01	± 0.01	± 0.06	± 0.01	± 0.01
Factor: R_{TDS} DAT-118 / R_{TDS} DAT-0		2.44	2.04	2.34	3.36	1.97	1.25
Mean		2.23					

DAT: days after treatment, SD: standard deviation

Table 7.1.3.2-28: Time-dependent sorption ratios (R_{TDS}) of fluopyram in soil under aerobic conditions normalized to soil organic carbon content (Koc, expressed as mL/g; mean value of duplicates and standard deviation)

DAT	Mean SD	Hornton	Brannens	Hoeltinghausen	Almayate East	Balbiano	Le Thour
0	Mean	492.8	388.4	603.3	504.6	406.7	365.2
	SD	± 0.0	± 0.0	± 0.0	± 0.0	± 0.0	± 0.0
3	Mean	509.7	396.5	695.5	525.7	404.1	348.3
	SD	± 0.0	± 0.0	± 0.0	± 0.1	± 0.0	± 0.0
7	Mean	601.2	494.7	856.7	798.6	489.7	402.1
	SD	± 0.0	± 0.0	± 0.0	± 0.0	± 0.0	± 0.0
14	Mean	610.2	525.2	976.2	875.6	543.4	423.3
	SD	± 0.1	± 0.0	± 0.0	± 0.0	± 0.0	± 0.0
27	Mean	774.4	599.4	1117.1	1050.8	592.3	425.3
	SD	± 0.0	± 0.0	± 0.0	± 0.0	± 0.0	± 0.0
48	Mean	790.1	644.1	1157.7	1290.5	625.6	410.5
	SD	± 0.0	± 0.0	± 0.0	± 0.0	± 0.0	± 0.0
83	Mean	985.8	709.0	1307.2	1541.0	662.2	474.6
	SD	± 0.0	± 0.0	± 0.0	± 0.0	± 0.0	± 0.0
118	Mean	1204.6	792.8	1411.0	1695.9	799.5	456.0
	SD	± 0.0	± 0.0	± 0.0	± 0.1	± 0.0	± 0.0
Factor: R_{TDS} DAT-118 / R_{TDS} DAT-0		2.44	2.04	2.34	3.36	1.97	1.25
Mean		2.23					

DAT: days after treatment, SD: standard deviation

Table 7.1.3.2-29: Time-dependent sorption evaluation for soil Hoeltinghausen

DAT	Sample ID YYE014-	Desorbed and Sorbed Residues of Fluopyram							
		C_{des} [µg/L]	Mean C_{des} [µg/L]	C_{extr} [µg/g]	Mean C_{extr} [µg/g]	R_{TDS} [mL/g]	Mean R_{TDS} [mL/g]	t.i.total [µg]	Mean t.i.total [µg]
0	T1-HS1	18.186	18.047	0.098	0.098	5.40	5.43	17.09	17.02
	T1-HS2	17.907		0.098		5.46		16.94	
3	T2-HS1	16.210	16.388	0.101	0.103	6.25	6.26	16.62	16.81
	T2-HS2	16.567		0.104		6.27		17.01	
7	T3-HS1	14.400	14.344	0.111	0.111	7.69	7.71	16.83	16.80
	T3-HS2	14.287		0.110		7.73		16.76	
14	T4-HS1	13.115	13.155	0.115	0.116	8.74	8.79	16.71	16.82
	T4-HS2	13.196		0.117		8.83		16.93	
27	T5-HS1	12.062	12.016	0.119	0.121	9.83	10.05	16.69	16.89
	T5-HS2	11.969		0.123		10.27		17.09	
48	T6-HS1	11.600	11.402	0.117	0.119	10.12	10.42	16.38	16.43
	T6-HS2	11.204		0.120		10.72		16.49	
83	T7-HS1	10.396	10.307	0.122	0.121	11.69	11.76	16.31	16.25
	T7-HS2	10.217		0.121		11.84		16.18	
118	T8-HS1	9.445	9.280	0.121	0.118	12.85	12.70	15.91	15.50
	T8-HS2	9.115		0.114		12.55		15.09	

All values for soil weight refer to dry weight equivalents

Table 7.1.3.2-30: Time-dependent sorption evaluation for soil Horton

DAT	Sample ID YYE014-	Desorbed and Sorbed Residues of Fluopyram							
		C_{des} [µg/L]	Mean C_{des} [µg/L]	C_{extr} [µg/g]	Mean C_{extr} [µg/g]	R_{TDS} [mL/g]	Mean R_{TDS} [mL/g]	t.i.total [µg]	Mean t.i.total [µg]
0	T1-HT1	12.241	11.679	0.122	0.121	9.96	10.35	17.09	16.74
	T1-HT2	11.117		0.119		10.74		16.38	
3	T2-HT1	12.347	11.514	0.128	0.123	10.34	10.70	17.71	16.90
	T2-HT2	10.680		0.118		11.07		16.09	
7	T3-HT1	9.992	9.753	0.124	0.123	12.37	12.63	16.36	16.21
	T3-HT2	9.515		0.123		12.88		16.06	
14	T4-HT1	8.447	9.151	0.116	0.117	13.71	12.81	14.96	15.32
	T4-HT2	9.856		0.118		11.92		15.69	
27	T5-HT1	7.425	7.691	0.121	0.125	16.32	16.26	15.09	15.58
	T5-HT2	7.957		0.129		16.20		16.08	
48	T6-HT1	7.491	7.334	0.121	0.122	16.17	16.59	15.11	15.09
	T6-HT2	7.177		0.122		17.01		15.08	
83	T7-HT1	5.744	5.926	0.121	0.123	21.14	20.70	14.44	14.63
	T7-HT2	6.109		0.124		20.26		14.82	
118	T8-HT1	5.010	4.903	0.122	0.124	24.43	25.30	14.24	14.35
	T8-HT2	4.796		0.125		26.16		14.47	

All values for soil weight refer to dry weight equivalents

Table 7.1.3.2-31: Time-dependent sorption evaluation for soil Le Thour

DAT	Sample ID YYE014-	Desorbed and Sorbed Residues of Fluopyram							
		C_{des} [µg/L]	Mean C_{des} [µg/L]	C_{extr} [µg/g]	Mean C_{extr} [µg/g]	R_{TDS} [mL/g]	Mean R_{TDS} [mL/g]	t.i.total [µg]	Mean t.i.total [µg]
0	T1-LT1	11.911	11.794	0.120	0.121	10.10	10.23	16.80	16.78
	T1-LT2	11.678		0.121		10.35		16.75	
3	T2-LT1	12.295	11.899	0.117	0.116	9.48	9.75	16.57	16.35
	T2-LT2	11.503		0.115		10.03		16.14	
7	T3-LT1	10.621	10.124	0.116	0.114	10.92	11.26	15.84	15.43
	T3-LT2	9.627		0.112		11.60		15.02	
14	T4-LT1	10.183	10.014	0.119	0.119	11.67	11.85	15.95	15.87
	T4-LT2	9.845		0.119		12.04		15.79	
27	T5-LT1	9.685	9.517	0.111	0.113	11.49	11.91	15.00	15.13
	T5-LT2	9.348		0.115		12.32		15.26	
48	T6-LT1	8.492	8.788	0.099	0.101	11.71	11.49	13.34	13.61
	T6-LT2	9.083		0.102		11.28		13.88	
83	T7-LT1	6.955	6.695	0.090	0.089	13.01	13.29	11.83	11.57
	T7-LT2	6.435		0.087		13.57		11.31	
118	T8-LT1	6.283	6.303	0.080	0.080	12.70	12.77	10.49	10.57
	T8-LT2	6.322		0.081		12.84		10.65	

All values for soil weight refer to dry weight equivalents

Table 7.1.3.2-32: Time-dependent sorption evaluation for soil Brannens

DAT	Sample ID YYE014-	Desorbed and Sorbed Residues of Fluopyram							
		C_{des} [µg/L]	Mean C_{des} [µg/L]	C_{extr} [µg/g]	Mean C_{extr} [µg/g]	R_{TDS} [mL/g]	Mean R_{TDS} [mL/g]	t.i.total [µg]	Mean t.i.total [µg]
0	T1-BS1	26.552	26.928	0.063	0.063	2.36	2.33	16.89	17.05
	T1-BS2	27.305		0.063		2.30		17.20	
3	T2-BS1	26.027	26.052	0.061	0.062	2.35	2.38	16.54	16.62
	T2-BS2	26.078		0.063		2.41		16.70	
7	T3-BS1	23.647	23.773	0.071	0.071	3.00	2.97	16.54	16.57
	T3-BS2	23.907		0.070		2.94		16.59	
14	T4-BS1	22.403	22.810	0.072	0.072	3.18	3.15	16.15	16.31
	T4-BS2	23.126		0.072		3.12		16.47	
27	T5-BS1	22.095	21.756	0.079	0.078	3.56	3.60	16.71	16.53
	T5-BS2	21.418		0.078		3.63		16.34	
48	T6-BS1	19.509	19.208	0.075	0.074	3.85	3.86	15.32	15.11
	T6-BS2	18.907		0.073		3.87		14.89	
83	T7-BS1	17.650	18.017	0.073	0.077	4.15	4.25	14.38	14.88
	T7-BS2	18.385		0.080		4.36		15.37	
118	T8-BS1	15.764	15.720	0.074	0.075	4.71	4.76	13.73	13.77
	T8-BS2	15.676		0.075		4.81		13.80	

All values for soil weight refer to dry weight equivalents

Table 7.1.3.2-33: Time-dependent sorption evaluation for soil Balbiano

DAT	Sample ID YYE014-	Desorbed and Sorbed Residues of Fluopyram							
		C_{des} [µg/L]	Mean C_{des} [µg/L]	C_{extr} [µg/g]	Mean C_{extr} [µg/g]	R_{TDS} [mL/g]	Mean R_{TDS} [mL/g]	t.i.total [µg]	Mean t.i.total [µg]
0	T1-BB1	14.876	15.252	0.107	0.105	7.18	6.91	16.63	16.64
	T1-BB2	15.629		0.104		6.65		16.64	
3	T2-BB1	15.429	15.148	0.105	0.104	6.82	6.87	16.69	16.46
	T2-BB2	14.866		0.103		6.92		16.24	
7	T3-BB1	13.429	13.289	0.110	0.111	8.21	8.33	16.39	16.38
	T3-BB2	13.150		0.111		8.44		16.36	
14	T4-BB1	12.381	12.285	0.113	0.113	9.15	9.24	16.28	16.26
	T4-BB2	12.190		0.114		9.32		16.24	
27	T5-BB1	11.728	11.551	0.117	0.116	10.01	10.07	16.43	16.25
	T5-BB2	11.375		0.115		10.13		16.07	
48	T6-BB1	11.017	10.617	0.112	0.113	10.20	10.63	15.65	15.52
	T6-BB2	10.217		0.113		11.07		15.40	
83	T7-BB1	9.204	9.282	0.103	0.104	11.21	11.26	14.00	14.16
	T7-BB2	9.359		0.106		11.31		14.32	
118	T8-BB1	7.759	7.641	0.106	0.104	13.66	13.59	13.71	13.44
	T8-BB2	7.522		0.102		13.52		13.18	

All values for soil weight refer to dry weight equivalents

Table 7.1.3.2-34: Time-dependent sorption evaluation for soil Almayate East

DAT	Sample ID YYE014-	Desorbed and Sorbed Residues of Fluopyram							
		C_{des} [µg/L]	Mean C_{des} [µg/L]	C_{extr} [µg/g]	Mean C_{extr} [µg/g]	R_{TDS} [mL/g]	Mean R_{TDS} [mL/g]	t.i.total [µg]	Mean t.i.total [µg]
0	T1-AE1	16.954	16.671	0.100	0.101	5.89	6.06	16.76	16.76
	T1-AE2	16.388		0.102		6.22		16.75	
3	T2-AE1	16.897	15.697	0.093	0.098	5.53	6.31	16.10	16.09
	T2-AE2	14.497		0.103		7.09		16.08	
7	T3-AE1	11.996	11.849	0.113	0.114	9.41	9.58	16.08	16.09
	T3-AE2	11.701		0.114		9.76		16.10	
14	T4-AE1	10.835	11.245	0.119	0.118	10.94	10.51	16.19	16.29
	T4-AE2	11.654		0.117		10.07		16.40	
27	T5-AE1	9.406	9.849	0.122	0.124	13.01	12.61	15.99	16.34
	T5-AE2	10.291		0.126		12.21		16.69	
48	T6-AE1	7.227	7.324	0.112	0.113	15.56	15.49	14.13	14.27
	T6-AE2	7.421		0.114		15.42		14.41	
83	T7-AE1	5.717	5.965	0.108	0.110	18.94	18.49	13.11	13.41
	T7-AE2	6.214		0.112		18.04		13.70	
118	T8-AE1	5.569	5.280	0.106	0.107	19.12	20.35	12.87	12.82
	T8-AE2	4.990		0.108		21.58		12.77	

All values for soil weight refer to dry weight equivalents

Table 7.1.3.2-35: Time-dependent sorption study conditions

Parameter	Hoeltinghausen	Hornton	Le Thour	Brannens	Balbiano	Almaraz East
Incubation soil moisture (% of MWHC)	55	55	55	55	55	55
Maximum water holding capacity (g ad 100 g soil DW)	29.0	54.3	62.5	39.4	48.7	46.6
Amount of soil per test system (g DW)	100	100	100	100	100	100
Moisture per test system (g (mL))	15.95	29.87	34.38	21.67	26.79	25.63
Gravimetric moisture per g soil (DW) (g water per g soil DW)	0.1595	0.2987	0.3438	0.2167	0.2679	0.2563
Total volume of $CaCl_2$ solution added to soil for desorption (mL)	400	400	400	400	400	400
Total volume of desorption solution ($V_{employed\ desorption\ solution}$ + moisture per test system) (mL)	416.0	429.9	434.4	421.7	426.8	425.6
Amount of test item applied to soil (µg/100 g soil DW)	16.7	16.7	16.7	16.7	16.7	16.7

3. Assessment and conclusion

Assessment and conclusion by applicant:
The study and its data are considered to be valid and reliable for use in risk assessment.

Assessment and conclusion by RMS:
Outcome and conclusion of the study. RMS should indicate if they agree to the results and conclusions of the APPL.

1. Information on the study

Data Point:	KCA 7.1.3.2/06
Report Author:	[redacted]
Report Year:	2021
Report Title:	Fluopyram (FLU) Evaluation of aged-sorption parameters
Report No:	VC/21/001A
Document No:	M-762175-01-1
Guideline(s) followed in study:	none
Deviations from current test guideline:	Current Guideline: not applicable
Previous evaluation:	No, not previously submitted
GLP/Officially recognised testing facilities:	No, not conducted under GLP/Officially recognised testing facilities
Acceptability/Reliability:	Yes

2. Full Summary of KCA 7.1.3.2/06

Executive Summary
Data from four aerobic degradation and time-dependent sorption studies in twenty soils for fluopyram

(KCA 7.1.1.1/02, M-298296-01-1; KCA 7.1.1.1/05, M-681092-01-1 amended report M-681092-02-1; KCA 7.1.1.1/01, M-298413-01-1; KCA 7.1.1.1/06, M-753426-01-1) was evaluated according to current guidance on aged sorption (Morris *et al.*, 2019 and EFSA, 2018).

Optimised parameter results are summarised in the table below. Comparison of the non-equilibrium and equilibrium K_{d_app} fits showed that strong aged-sorption effects occurred for all soils, as shown by equilibrium fits not being able to adequately describe the increased observed in K_d with time. Parameter estimations of f_{NE} and k_{des} are robust for all twenty soils and are suitable for use in exposure modelling.

Table 7.1.3.2-36: Optimised parameter results

#	Soil	f_{NE} (-)	k_{des} (1/d)	$DT_{50,eq}$ (d)	$DT_{50,eq}$ 20°C pF2 (d)	Evidence of aged sorption	Robust parameters
1	Hoefchen	0.540	0.02516	156.7	156.7	Yes	Yes
2	Laacher Hof AXXa	0.551	0.02450	158.0	158.0	Yes	Yes
3	Wurmwiese	0.540	0.01796	171.8	171.5	Yes	Yes
4	Laacher Hof AIIIa	0.583	0.02088	112.8	112.8	Yes	Yes
5	Hoefchen [1]	0.482	0.03378	145.3	145.3	Yes	Yes
6	Laacher Hof AXXa	0.491	0.03746	304.1	304.1	Yes	Yes
7	Wurmwiese	0.470	0.03800	170.4	170.4	Yes	Yes
8	Dollendorf II	0.350	0.08236	118.3	118.3	Yes	Yes
9	Little Oliver [1]	0.910	0.02283	998.7	943.5	Yes	Yes
10	Auchy les Mines	0.957	0.01028	774.5	731.7	Yes	Yes
11	Urbanowice	0.611	0.01940	959.2	719.7	Yes	Yes
12	Charles River Farm	0.716	0.01215	391.9	370.2	Yes	Yes
13	Sindos	0.430	0.01946	212.5	200.8	Yes	Yes
14	Paradiso San Zenone	0.601	0.02661	256.4	242.2	Yes	Yes
15	Hoeltinghausen	0.550	0.04667	472.6	446.5	Yes	Yes
16	Hornton	0.785	0.01491	366.7	337.4	Yes	Yes
17	Le Thour	0.138	0.03818	150.2	141.9	Yes	Yes
18	Brannens	0.323	0.02876	323.1	305.2	Yes	Yes
19	Balbiano	0.403	0.01932	290.2	274.1	Yes	Yes
20	Almayate East	0.918	0.02180	176.9	157.4	Yes	Yes
	Geometric mean	**0.525**	**0.0285**	**265**	**252**		

[1] excluding outlier

The adsorption of fluopyram increased significantly with time under laboratory conditions, with mean aged-sorption parameters of f_{NE} 0.525 and k_{des} 0.0285 1/d.

I METHODS

TDS data

The aerobic degradation and time-dependent sorption of fluopyram has been measured in twenty soils covering a wide range of soil properties. Table 2 summarises the physico-chemical properties of the test soils used.

Table 7.1.3.2-37: Test soils used for the time-dependent sorption testing of fluopyram

#	Soil	Source	Texture (USDA)	pH [1]	OC [%]
1	Hoefchen	Germany	Silt loam	6.6	2.1
2	Laacher Hof AXXa	Germany	Sandy loam	6.6	1.5
3	Wurmwiese	Germany	Loam	5.5	2.0
4	Laacher Hof AIIIa	Germany	Loam	6.6	1.3
5	Hoefchen	Germany	Silt loam	6.2	2.4
6	Laacher Hof AXXa	Germany	Sandy loam	6.2	2.2
7	Wurmwiese	Germany	Sandy loam	5.2	1.8
8	Dollendorf II	Germany	Clay loam	7.3	5.1
9	Little Oliver	UK	sandy loam	5.5	1.5
10	Auchy les Mines	France	silt loam	7.5	2.0
11	Urbanowice	Poland	silt loam	4.9	1.1
12	Charles River Farm	Spain	clay	7.7	1.6
13	Sindos	Greece	loam	7.2	1.3
14	Paradiso San Zenone	Italy	sandy loam	5.4	1.2
15	Hoeltinghausen	Germany	sand	4.5	0.9
16	Hornton	UK	loam	5.9	2.1
17	Le Thour	France	silt loam	7.4	2.8
18	Brannens	France	sandy loam	4.7	0.6
19	Balbiano	Italy	sandy loam	7.1	1.7
20	Almayate East	Spain	loam	7.7	1.2

[1] $CaCl_2$

Soil samples (100g ode) were incubated (20 °C and 55% MWHC) for up to 128 days. At each sampling time point, soils were extracted with 0.01M $CaCl_2$ (400 mL) for 24 hours.

Below important study data for each soil for use in the time-dependent sorption parameter evaluations is summarised.

Table 7.1.3.2-38: Time-dependent sorption study data summary

Parameter	Description	M-298296-01-1			
		Hoefchen	Laacher Hof AXXa	Wurmwiese	Laacher Hof AIIIa
TimStart (d)	Start time	0	0	0	0
TimEnd (d)	End time	121	121	121	121
MasIni (µg)	Initial guess of total mass	71.3	72.5	69.8	71.7
MasSol (g)	Dry mass of soil	100	100	100	100
VolLiqSol (mL)	Vol liq in moist soil	34.8	26.70	37.7	28.4
VolLiqAdd (mL)	Vol liq ($CaCl_2$) added	400.0	400.0	400.0	400.0
CntOm (kg/kg)	Organic Matter	0.036	0.026	0.035	0.022
Temp (°C)	Incubation temperature	20	20	20	20

Parameter	Description	M-298413-01-1			
		Hoefchen	Laacher Hof AXXa	Wurmwiese	Dollendorf II
TimStart (d)	Start time	0	0	0	0
TimEnd (d)	End time	128	128	128	128
MasIni (µg)	Initial guess of total mass	66.8	64.5	68.3	66.9
MasSol (g)	Dry mass of soil	100	100	100	100
VolLiqSol (mL)	Vol liq in moist soil	32.7	26.6	30.5	46.5
VolLiqAdd (mL)	Vol liq ($CaCl_2$) added	367.3	373.4	369.5	353.5
CntOm (kg/kg)	Organic Matter	0.041	0.038	0.031	0.088
Temp (°C)	Incubation temperature	20	20	20	20

Parameter	Description	M-753426-01-1			
		Little Oliver	Auchy les Mines	Urbanowice	Charles River Farm
TimStart (d)	Start time	0	0	0	0
TimEnd (d)	End time	118	118	118	118
MasIni (µg)	Initial guess of total mass	16.6	16.6	16.6	16.6
MasSol (g)	Dry mass of soil	100	100	100	100
VolLiqSol (mL)	Vol liq in moist soil	27.1	29.3	24.1	30.5
VolLiqAdd (mL)	Vol liq ($CaCl_2$) added	400	400	400	400
CntOm (kg/kg)	Organic Matter	0.026	0.034	0.019	0.028
Temp (°C)	Incubation temperature	20	20	20	20

Parameter	Description	M-753426-01-1		M-681092-01-1	
		Sindos	Paradiso San Zenone	Hoeltingha usen	Hornton
TimStart (d)	Start time	0	0	0	0
TimEnd (d)	End time	118	118	118	118
MasIni (µg)	Initial guess of total mass	16.6	16.6	16.7	16.7
MasSol (g)	Dry mass of soil	100	100	100	100
VolLiqSol (mL)	Vol liq in moist soil	30.3	28.1	16	29.9
VolLiqAdd (mL)	Vol liq ($CaCl_2$) added	400	400	400	400
CntOm (kg/kg)	Organic Matter	0.022	0.021	0.016	0.036
Temp (°C)	Incubation temperature	20	20	20	20

Parameter	Description	M-681092-01-1			
		Le Thour	Brannens	Balbiano	Almayate East
TimStart (d)	Start time	0	0	0	0
TimEnd (d)	End time	118	118	118	118
MasIni (µg)	Initial guess of total mass	16.7	16.7	16.7	16.7
MasSol (g)	Dry mass of soil	100	100	100	100
VolLiqSol (mL)	Vol liq in moist soil	34.4	21.7	26.8	25.6
VolLiqAdd (mL)	Vol liq ($CaCl_2$) added	400	400	400	400
CntOm (kg/kg)	Organic Matter	0.048	0.010	0.029	0.021
Temp (°C)	Incubation temperature	20	20	20	20

Adsorption data

Two adsorption-desorption batch-equilibrium studies, (KCA 7.1.3.1.1/01, M-248464-01-1; KCA 7.1.3.1.1/02, M-753424-01-1) with seventeen soils were performed with [^{14}C]fluopyram. The studies were evaluated by fitting the Freundlich equation, $C_{sorb} = K_f C_{aqu}^{1/n}$, to the measured equilibrium concentrations. Soil properties as well as the Freundlich coefficients are given below.

Table 7.1.3.2-39: Soil adsorption data of fluopyram

#	Soil	Texture (USDA)	pH	OC [%]	K_f (mL/g)	$K_{f,oc}$ (mL/g)	1/n (-)
1	Laacher Hof AXXa	Sandy loam	6.0	1.3	3.03	233.2	0.765
2	Wurmwiese	Loam	5.4	2.1	4.84	233.8	0.849
3	Hoefchen	Silt loam	6.1	2.6	6.85	260.5	0.838
4	Pikeville	Loamy sand	5.0	1.1	2.94	267.4	0.846
5	Stanley	Clay loam	5.4	1.1	4.40	399.6	0.837
6	Little Oliver	Sandy loam	5.5	1.5	3.99	266.1	0.879
7	Auchy les Mines	Silt loam	7.5	2.0	3.70	185.1	0.732
8	Urbanowice	Silt loam	4.9	1.1	2.52	229.3	0.858
9	Charles River Farm	Clay	7.7	1.6	2.52	157.4	0.836
10	Sindos	Loam	7.2	1.3	2.47	190.3	0.833
11	Paradiso San Zenone	Sandy loam	5.4	1.2	1.87	156.0	0.826
12	Hoeltinghausen	Sand	4.5	0.9	2.88	320.1	0.918
13	Hornton	Loam	5.9	2.1	5.13	244.1	0.867
14	Le Thour	Silt loam	7.4	2.8	5.11	182.5	0.887
15	Brannens	Sandy loam	4.7	0.6	1.45	242.0	0.894
16	Balbiano	Sandy loam	7.1	1.7	3.64	214.1	0.839
17	Almayate East	Loam	7.7	1.2	3.34	278.3	0.808

Optimisation procedures

The evaluations were conducted according to the guidance document proposed by UK CRD (Morris *et al.*, 2019) in combination with the EFSA PPR Panel Opinion (EFSA, 2018). The guidance document provides details of a number of data requirement and handling checks to be considered:

- The incubation study should follow the guidance given by OECD 307 and the sorption study should follow OECD 106
- The system must be well characterised. The mass and water content of the soil during incubation, the volume of water added during extraction, the duration and intensity of the extraction should be stated. Information on the texture, organic carbon content, pH and water retention or maximum water holding capacity of the sieved soil should also be available.
- Data on total mass and aqueous concentration must be available. Experimental studies must provide sufficient and adequate sampling points to ensure a robust estimation of parameters. The pattern of decline in mass and concentration must be well established
- Incubation studies should be carried out with at least two true, independent replicates. Experimental results often include measurements below the limit of quantification (LOQ). Measurements below the limit of quantification (LOQ) are uncertain and these should be discarded
- A robust optimisation of parameters is only possible if the number of observations is appreciably larger than the number of model parameters. The total number of sampling dates remaining after the elimination of measurements below the limit of quantification or outliers must not be smaller than six

The data was evaluated using PEARLNEQ v5.1 which combines the two-site sorption model with the optimisation software PEST. The two-site kinetic sorption model is illustrated schematically in the figure below. The model is simultaneously fitted against the total mass of the fluopyram in soil (µg) and the concentration of fluopyram in the liquid ($CaCl_2$ extract) phase (µg/mL) which are directly measured experimental data. The datasets used in the evaluations can be found in the respective study summaries.

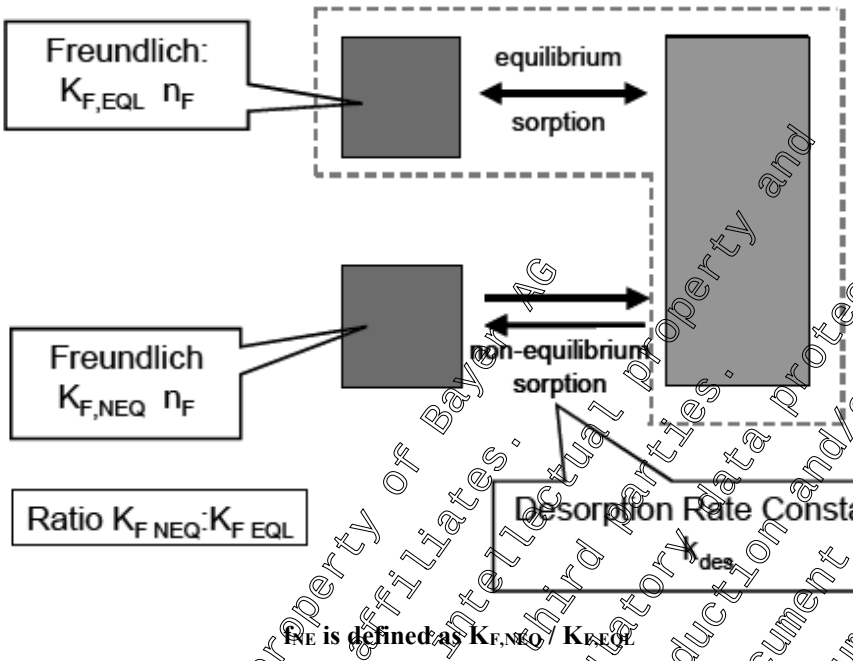


Figure 7.1.3.2-1: Two-site kinetic sorption model description

Five parameters (M_{ini}, DT_{50eq}, $K_{om,eq}$, f_{NE} and k_{des}) were fitted during the optimisations. M_{ini} is the initial mass dosed into the system (µg). DT_{50eq} is the DT_{50} (d) in the equilibrium domain and is only valid in combination with f_{NE} and k_{des}. $K_{om,eq}$ is the sorption coefficient in the equilibrium domain (mL/g). f_{NE} and k_{des} are the aged-sorption parameters, with f_{NE} being the ratio of sorption coefficients in the non-equilibrium and equilibrium domains and k_{des} the desorption rate constant (d^{-1}).

The Freundlich 1/n values were available from OECD 106 studies conducted in the same batches of soils and were used directly. Starting parameters for f_{NE} and k_{des} used in the evaluations are listed below in Table 5. The starting parameter combination that resulted in the lowest objective function value during the PEST optimisation were selected and are provided in this summary. The optimized parameter results for the four sets of starting values are provided in the report.

Table 7.1.3.2-40: Starting values for f_{NE} and k_{des}

f_{NE} (-)	k_{des} (1/d)
0.2	0.004
0.2	0.05
1.5	0.004
1.5	0.05

A fifth evaluation with f_{NE} and k_{des} set to zero was conducted to test whether equilibrium sorption could account for the apparent increase in sorption with time. Apparent K_d (K_{d_app}) values were calculated as the ratio of fluopyram sorbed to soil (µg/g) to the concentration of fluopyram in the liquid 0.01M $CaCl_2$ supernatant phase (µg/mL) at each time point.

Acceptance criteria

The decision on whether a model fit is acceptable or not was based on:

- An assessment of the visual fit of a model with and without time-dependent sorption

- A χ^2-test to assess the goodness of fit and to compare a model with and without time-dependent sorption
- An assessment of the confidence in the parameter estimates

Plots of total mass and liquid phase concentration with time were plotted with plots of residuals and evaluated to allow a visual assessment of the evaluations. Apparent K_d (K_{d_app}) values calculated from the measured data and from the simulated concentrations were plotted against time. The apparent K_d values were evaluated for both equilibrium and non-equilibrium sorption to check that the increase in apparent K_d could not be accounted for by the effect of concentration and the Freundlich coefficient. Model fits were also be evaluated using chi-square (χ^2) error statistics and the relative standard error (RSE) was calculated for each optimised parameter. It is recommended the RSE should be ≤ 0.4.

II. RESULTS

Comparison of the non-equilibrium and equilibrium K_{d_app} fits showed that strong aged-sorption effects occurred for all soils, as evidenced by the equilibrium fit not being able to adequately describe the increased observed in K_d with time. Plots for all soils are provided in the report. Example comparison plots are provided in the figures below for soils Laacher Hof AIIIa and Little Oliver.

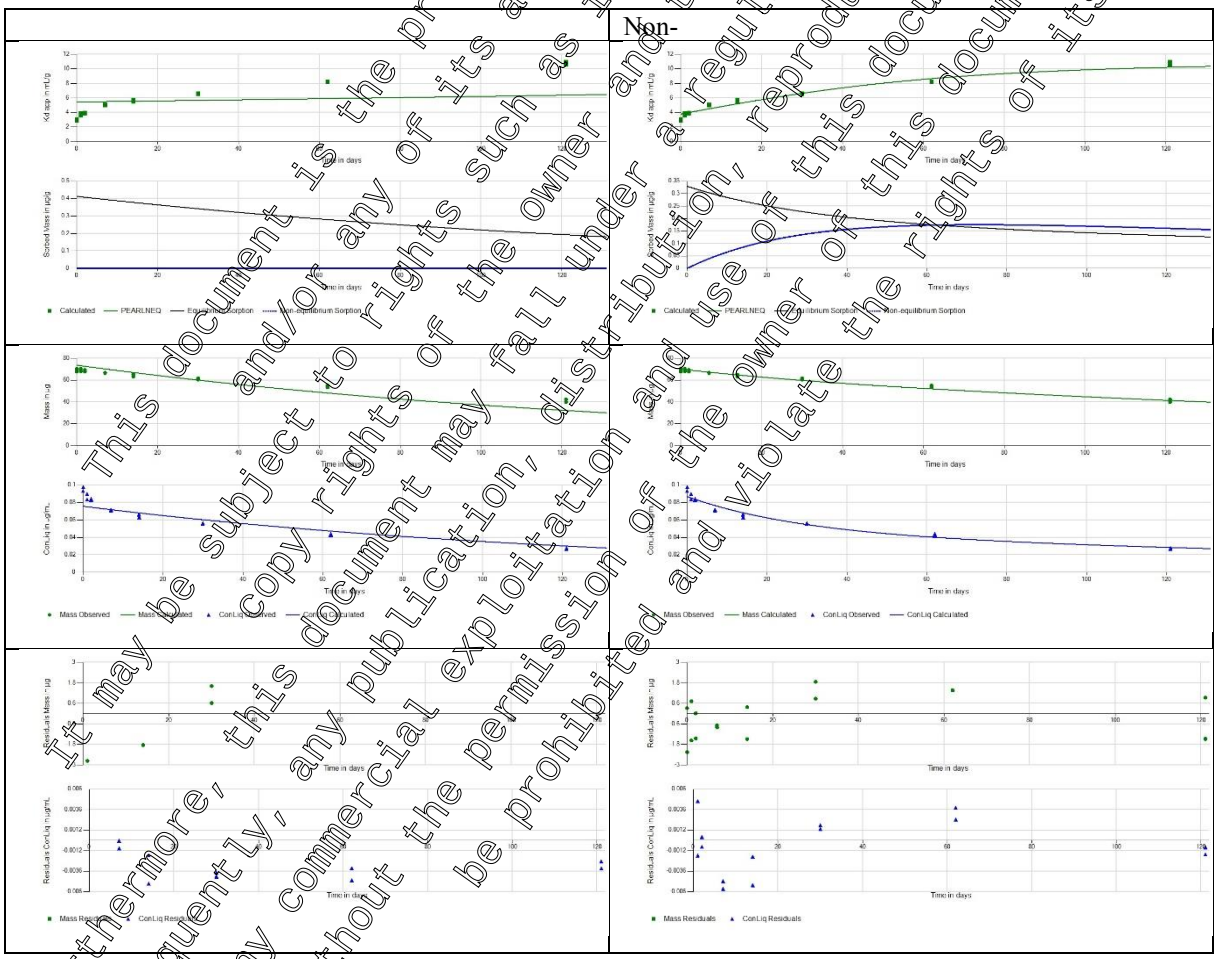


Figure 7.1.3.2-2: Laacher Hof AIIIa - optimised model fits for equilibrium and non-equilibrium sorption

In Little Oliver soil, comparison of the apparent K_d plots also indicated that equilibrium sorption was not able to adequately describe the data and that significant aged-sorption was occurring (see Figure 7.1.3.2-3).

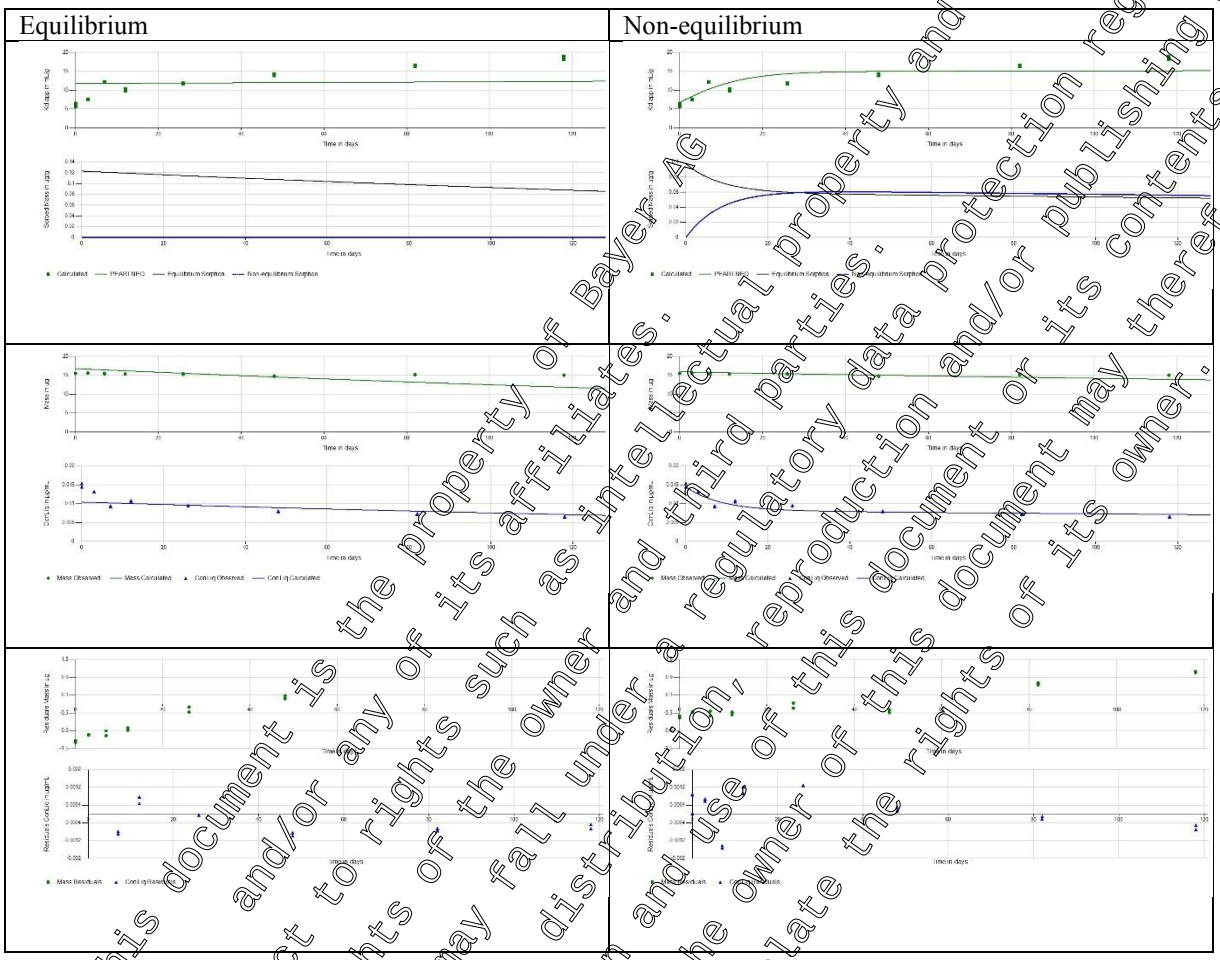
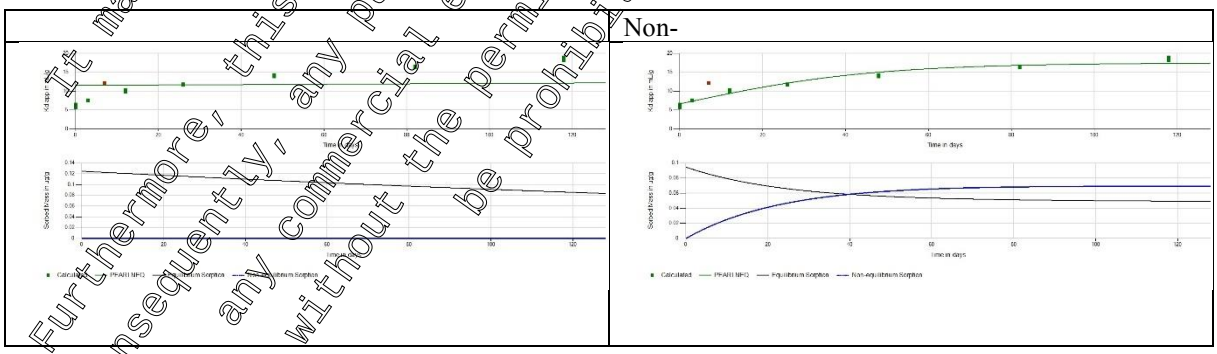


Figure 7.1.3.2-3: Little Oliver - optimised model fits for equilibrium and non-equilibrium sorption

However, it is evident that data at DAT 7 is out of alignment with the remaining data. Thus, an additional evaluation was conducted with DAT 7 excluded, resulting in a significant improvement in the fits as shown in Figure 4. The results with DAT 7 excluded were selected as the endpoints for this soil.



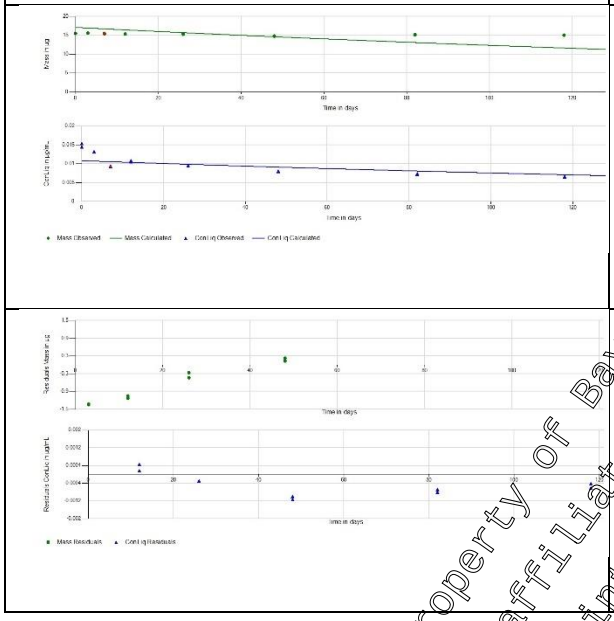
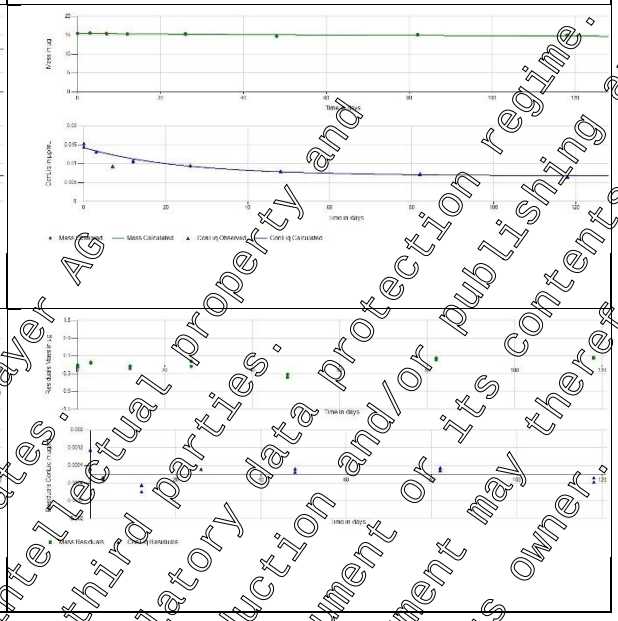
	Non-
	

Figure 7.1.3.2-4: Little Oliver - optimised model fits for equilibrium and non-equilibrium sorption – DAT7 outlier excluded

Model fits were evaluated using chi-square (χ^2) error statistics. In each soil the calculated minimum χ^2 error values for were lower for the non-equilibrium sorption model compared to equilibrium sorption. The relative standard error (RSE) was calculated to be ≤ 0.4 for all optimised parameter with very few exemption were the RSE is slightly above 0.4.

The optimised parameter results are summarised below. Parameter estimations of f_{NE} and k_{des} were robust for all sixteen soils and are suitable for use in exposure modelling.

Table 7.1.3.2-41: Optimised parameter results

#	Soil	f_{NE} (-)	k_{des} (1/d)	DT_{50},eq (d)	FOCUS correction factor	DT_{50},eq 20°C pF2 (d)	Evidence of aged sorption	Robust parameters
1	Hoefchen	0.540	0.02516	156.7	1.0000	156.7	Yes	Yes
2	Laacher Hof AXXa	0.551	0.02450	158.0	1.0000	158.0	Yes	Yes
3	Wurmwiese	0.540	0.07196	171.5	1.0000	171.5	Yes	Yes
4	Laacher Hof AIIIa	0.583	0.02088	112.8	1.0000	112.8	Yes	Yes
5	Hoefchen [1]	0.482	0.03358	145.3	1.0000	145.3	Yes	Yes
6	Laacher Hof AXXa	0.491	0.03746	304.1	1.0000	304.1	Yes	Yes
7	Wurmwiese	0.470	0.03800	170.4	1.0000	170.4	Yes	Yes
8	Dollendorf II	0.350	0.08236	118.3	1.0000	118.3	Yes	Yes
9	Little Oliver [1]	0.910	0.02283	998.7	0.9447	943.5	Yes	Yes
10	Auchy les Mines	0.957	0.01028	774.5	0.9447	731.7	Yes	Yes
11	Urbanowice	0.611	0.01940	952.2	0.7503	778.7	Yes	Yes
12	Charles River Farm	0.716	0.01815	391.9	0.9447	370.2	Yes	Yes
13	Sindos	0.430	0.01946	212.5	0.9447	200.8	Yes	Yes
14	Paradiso San Zenone	0.601	0.02661	256.4	0.9447	242.2	Yes	Yes
15	Hoeltinghausen	0.550	0.04667	472.6	0.9447	446.5	Yes	Yes
16	Hornton	0.785	0.01491	366.7	0.9201	337.4	Yes	Yes
17	Le Thour	0.138	0.13818	150.2	0.9447	141.9	Yes	Yes
18	Brannens	0.323	0.02876	323.1	0.9447	305.2	Yes	Yes
19	Balbiano	0.403	0.01932	290.2	0.9447	274.1	Yes	Yes
20	Almayate East	0.918	0.02180	176.9	0.8902	157.4	Yes	Yes
	Geometric mean	**0.525**	**0.0285**			**252**		

[1] Excluding outlier

III. CONCLUSIONS

The adsorption of fluopyram to soil is known to increase significantly with time under laboratory conditions. Aerobic degradation and time-dependent sorption data obtained for twenty soils was evaluated according to the draft guidance document on aged sorption (Morris *et al.*, 2019) and EFSA PPR Panel Opinion (EFSA, 2018), resulting in mean estimated parameters for fluopyram of 0.525 and 0.0285 1/d for f_{NE} and k_{des}, respectively.

3. Assessment and conclusion

Assessment and conclusion by applicant:
The modelling report was conducted according to current guidance on aged sorption and is considered to be valid to assess the aged sorption of fluopyram in soil.

Assessment and conclusion by RMS:
Outcome and conclusion of the study: RMS should indicate if they agree to the results and conclusions of the APPL

1. Information on the study

Data Point:	KCA 7.1.3.2/07
Report Author:	[redacted]
Report Year:	2021
Report Title:	Fluopyram (FLU) - Aged-sorption parameters – Evaluation of Tier-1 DegT50EQ values from laboratory and field studies
Report No:	VC/21/001B
Document No:	M-762930-01-1
Guideline(s) followed in study:	none
Deviations from current test guideline:	Current Guideline: not applicable
Previous evaluation:	No, not previously submitted
GLP/Officially recognised testing facilities:	No, not conducted under GLP/Officially recognised testing facilities
Acceptability/Reliability:	Yes

2. Full Summary of KCA 7.1.3.2/07

Executive Summary

For inclusion in PECgw exposure assessments lower-tier degradation study data (laboratory and field) must be combined with the aged-sorption data following re-evaluation to estimate $DegT_{50eq}$ values

Data from 4 laboratory aerobic degradation and time-dependent sorption studies in twenty soils for fluopyram was evaluated in a separate report (KCA 7.1.3.2/06; M-762175-01-1) according to the guidance document on aged sorption (European Commission, 2021), resulting in mean aged-sorption parameters of: f_{ne} 0.525; k_{des} 0.0285 1/d.

Existing lower-tier degradation study data for fluopyram from laboratory and field studies have been evaluated to derive $DegT_{50eq}$ values, which when combined with the higher-tier aged-sorption values (KCA 7.1.3.2/06), yield an overall geometric mean normalised $DegT_{50eq}$ of 216.5 days based on field data for use in exposure modelling (in combination with the mean aged-sorption parameters: F_{ne} 0.525; k_{des} 0.0285). The geometric mean normalised $DegT_{50eq}$ based on laboratory data is 254.4 days.

The final results for all normalised (20ºC and pF2) $DegT_{50eq}$ evaluations are summarised in the table below.

Table 7.1.3.2-42: Overall $DegT_{50eq}$ evaluation results – laboratory data

#	Soil	$DegT_{50eq}$ (days)	Derivation
1	Hoefchen	156.7	TDS - PEARLneq
2	Laacher Hof AXXa	158.0	TDS - PEARLneq
3	Wurmwiese	171.5	TDS - PEARLneq
4	Laacher Hof AIIIa	112.8	TDS - PEARLneq
5	Hoefchen	145.3	TDS - PEARLneq
6	Laacher Hof AXXa	304.1	TDS - PEARLneq
7	Wurmwiese	170.4	TDS - PEARLneq
8	Dollendorf II	118.3	TDS - PEARLneq
9	Little Oliver	943.5	TDS - PEARLneq
10	Auchy les Mines	731.7	TDS - PEARLneq
11	Urbanowice	719.7	TDS - PEARLneq
12	Charles River Farm	370.2	TDS - PEARLneq

#	Soil	$DegT_{50eq}$ (days)	Derivation
13	Sindos	200.8	TDS - PEARLneq
14	Paradiso San Zenone	242.2	TDS - PEARLneq
15	Hoeltinghausen	446.5	TDS - PEARLneq
16	Hornton	337.4	TDS - PEARLneq
17	Le Thour	141.9	TDS - PEARLneq
18	Brannens	305.2	TDS - PEARLneq
19	Balbiano	274.1	TDS - PEARLneq
20	Almayate East	157.4	TDS - PEARLneq
21	Springfield	333.8	Lab Tier-1 Refit
22	Porterville	521.5	Lab Tier-1 Refit
23	Argissolo	321.9	$DegT_{50}$ [1]
24	Frankenforst	156.3	Lab Tier-1 Refit
25	Wurmwiese	210.4	Lab Tier-1 Refit
26	Höfchen	200.7	Lab Tier-1 Refit
27	Innerdeich	217.7	Lab Tier-1 Refit
	Geometric mean	**254.4**	

[1] Tier-1 refit not acceptable, standard $DegT_{50}$ x SF1 (0.731) used

Table 7.1.3.2-43: Overall $DegT_{50eq}$ evaluation results – field data

#	Soil	$DegT_{50eq}$ (days)	Derivation
1	Little Oliver	90.9	Field Scaling factor 1
2	Auchy les Mines	505.5	Field Scaling factor 1
3	Urbanowice	429.9	Field Scaling factor 1
4	Charles River Farm	205.3	Field Scaling factor 1
5	Sindos	1000	Default, not corrected
6	Hoeltinghausen	327.3	Field Scaling factor 1
7	Hornton	166.4	Field Scaling factor 1
8	Le Thour	81.7	Field Scaling factor 1
9	Brannens	153.0	Field Scaling factor 1
10	Balbiano	161.6	Field Scaling factor 1
11	Almayate East	130.2	Field Scaling factor 1
12	North Rose, New York	206.0	Field Scaling factor 1
13	Ephrata, Washington	191.5	Field Scaling factor 1
	Geometric mean	**216.5**	

I. METHODS

Degradation in soil under laboratory conditions

The aerobic laboratory degradation and time-dependent sorption of fluopyram has been measured in twenty soils covering a wide range of soil properties (KCA 7.1.1.1/02, M-298296-01-1; KCA 7.1.1.1/05, M-681092-01-1 amended report M-681092-02-1; KCA 7.1.1.1/01, M-298413-01-1; KCA 7.1.1.1/06, M-753426-01-1). Characteristics of the soils used are summarised in the table below.

Table 7.1.3.2-44: Test soils used for the time-dependent sorption testing of fluopyram

#	Soil	Source	Texture (USDA)	pH [1]	OC [%]
1	Hoefchen	Germany	Silt loam	6.6	2.1
2	Laacher Hof AXXa	Germany	Sandy loam	6.6	1.5
3	Wurmwiese	Germany	Loam	5.5	2.0
4	Laacher Hof AIIIa	Germany	Loam	6.6	1.3
5	Hoefchen	Germany	Silt loam	6.7	2.4
6	Laacher Hof AXXa	Germany	Sandy loam	6.2	2.2
7	Wurmwiese	Germany	Sandy loam	5.2	1.8
8	Dollendorf II	Germany	Clay loam	7.3	3.1
9	Little Oliver	UK	Sandy loam	5.5	1.5
10	Auchy les Mines	France	Silt loam	7.5	2.0
11	Urbanowice	Poland	Silt loam	4.9	1.1
12	Charles River Farm	Spain	Clay	7.7	1.6
13	Sindos	Greece	Loam	7.2	1.3
14	Paradiso San Zenone	Italy	Sandy loam	5.4	1.2
15	Hoeltinghausen	Germany	Sand	4.5	0.9
16	Hornton	UK	Loam	5.9	2.1
17	Le Thour	France	Silt loam	7.4	2.8
18	Brannens	France	Sandy loam	4.7	0.6
19	Balbiano	Italy	Sandy loam	7.1	1.7
20	Almayate East	Spain	Loam	7.7	1.2

[1] determined in $CaCl_2$

The aerobic laboratory degradation of fluopyram has been measured in seven soils covering a wide range of soil properties (KCA 7.1.1.1/07, M-761739-01-1; KCA 7.1.1.1/04, M-349303-01-1 amended report M-349303-02-1; KCA 7.1.1.1/03, M-299548-02-1). Physico-chemical properties of the test soils used are summarised below.

Table 7.1.3.2-45: Test soils used for the aerobic degradation testing of fluopyram

#	Soil	Source	Texture (USDA)	pH	OC [%]
1	Springfield	USA	Silty clay loam	6.5	1.7
2	Porterville	USA	Sandy loam	7.9	0.5
3	Argissolo	Brazil	Clay	5.3	2.6
4	Frankenforst	Germany	Silt loam	7.3	2.3
5	Wurmwiese	Germany	Loam	5.1	2.1
6	Hoefchen	Germany	Silt loam	5.7	2.3
7	Innerdeich	Germany	Sandy loam	6.2	1.8

The overall geometric mean normalised laboratory $DegT_{50}$ for fluopyram is 364 days.

Degradation in soil under field conditions

The behaviour of fluopyram was investigated in fourteen terrestrial field soil dissipation trials designed to determine the dissipation under representative European field conditions (KCA 7.1.2.2.1/15, M-758589-01-1; KCA 7.1.2.2.1/14, M-758583-01-1; KCA 7.1.2.2.1/04, M-306809-01-2; KCA 7.1.2.2.1/03, M-306817-01-2). Data for the Paradiso trial were not suitable for evaluation. The table below summarises the locations and soils used in the trials and normalised $DegT_{50}$ values (KCA 7.1.2.2.1/18, M-762154-01-1; KCA 7.1.2.2.1/16, M-761975-01-1; KCA 7.1.2.2.1/17, M-761974-01-1).

Table 7.1.3.2-46: Test soils used for the field dissipation testing of fluopyram

#	Soil	Texture (USDA)	pH	OC [%]	$DegT_{50}$ matrix (d) norm
1	Little Oliver	Sandy clay loam	5.3	1.5	153.8
2	Auchy les Mines	Loam	7.3	1.7	371.6
3	Urbanowice	Silt loam	5.2	1.0	605.3
4	Charles River Farm	Clay	7.8	1.5	306.2
5	Sindos	Loam	6.6	1.5	>1000
6	Hoeltinghausen	Loamy sand	5.56	0.8	453.9
7	Hornton	Silt loam	6.11	2.2	263.7
8	Le Thour	Silt loam	7.50	2.5	83.9
9	Brannens	Sandy loam	4.44	0.8	180.5
10	Balbiano	Loam	7.20	2.0	203.0
11	Almayate East	Silt loam	7.74	1.4	221.3
12	North Rose, New York	Loamy sand	5.9	1.3	281.7
13	Ephrata, Washington	Sandy loam	7.5	0.5	257.4

Adsorption data

Two adsorption batch-equilibrium studies (KCA 7.1.3.1.1/01, M-248464-01-1; KCA 7.1.3.1.1/02, M-753424-01-1) with seventeen soils were performed with [^{14}C] fluopyram. The studies were evaluated by fitting the Freundlich equation, $C_{sorb} = K_f C_{aq}^{1/n}$, to the measured equilibrium concentrations. Soil properties as well as the Freundlich coefficients are given in the table below, with a geometric mean Kom of 134.7 mL/g and average 1/n of 0.843 used for the evaluations.

Table 7.1.3.2-47: Soil adsorption data of fluopyram

#	Soil	Texture (USDA)	pH	OC [%]	K_f (mL/g)	$K_{f,oc}$ (mL/g)	1/n (-)
1	Laacher Hof AXXa	Sandy loam	6.0	1.3	3.03	233.2	0.7645
2	Wurmwiese	Loam	5.4	2.1	4.84	233.8	0.8492
3	Höfchen	Silt loam	6.1	2.6	6.83	260.5	0.8376
4	Pikeville	Loamy sand	5.0	1.1	2.94	267.4	0.8463
5	Stanley	Clay loam	5.4	1.1	4.40	399.6	0.8367
6	Little Oliver	Sandy loam	5.5	1.5	3.99	266.1	0.8793
7	Auchy les Mines	Silt loam	7.5	2.0	3.70	185.1	0.7321
8	Urbanowice	Silt loam	4.9	1.1	2.52	229.3	0.8578
9	Charles River Farm	Clay	7.7	1.6	2.52	157.4	0.8363
10	Sindos	Loam	7.2	1.3	2.47	190.3	0.8548
11	Paradiso San Zenone	Sandy loam	5.4	1.2	1.87	156.0	0.8260
12	Hoeltinghausen	Sand	4.5	0.9	2.88	320.1	0.9179

13	Hornton	Loam	5.9	2.1	5.13	244.1	0.8673
14	Le Thour	Silt loam	7.4	2.8	5.11	182.5	0.8868
15	Brannens	Sandy loam	4.7	0.6	1.45	242.0	0.8944
16	Balbiano	Sandy loam	7.1	1.7	3.64	214.1	0.8392
17	Almayate East	Loam	7.7	1.2	3.34	278.3	0.8083
					Geometric mean	**232.1**	**-**
						Average	**0.8432**

Aged sorption

Data from four aerobic degradation and time-dependent sorption studies in twenty soils for fluopyram (KCA 7.1.1.1/02, M-298296-01-1; KCA 7.1.1.1/05, M-681092-01-1, amended report M-681092-02-1; KCA 7.1.1.1/01, M-298413-01-1; KCA 7.1.1.1/06, M-753426-01-1) was evaluated (KCA 7.1.3.2/06, M-762175-01-1) according to the guidance document on aged sorption (European Commission, 2021), aged-sorption parameters are given in the table below, with a geometric mean of: F_{ne} 0.525; k_{des} 0.0285.

Table 7.1.3.2-48: Aged-sorption data of fluopyram

#	Soil	f_{NE} (-)	k_{des} (1/d)	$DT_{50,eq}$ (d)	$DT_{50,eq}$ 20°C pF2 (d)	Evidence of aged sorption	Robust parameters
1	Hoefchen	0.540	0.02516	156.7	156.7	Yes	Yes
2	Laacher Hof AXXa	0.551	0.02450	158.0	158.0	Yes	Yes
3	Wurmwiese	0.540	0.07196	171.5	171.5	Yes	Yes
4	Laacher Hof AIIIa	0.583	0.02088	112.8	112.8	Yes	Yes
5	Hoefchen	0.482	0.03358	145.3	145.3	Yes	Yes
6	Laacher Hof AXXa	0.491	0.03746	304.1	304.1	Yes	Yes
7	Wurmwiese	0.470	0.03800	170.4	170.4	Yes	Yes
8	Dollendorf II	0.350	0.08236	118.3	118.3	Yes	Yes
9	Little Oliver	0.910	0.02283	998.7	943.5	Yes	Yes
10	Auchy les Mines	0.957	0.01028	774.5	731.7	Yes	Yes
11	Urbanowice	0.611	0.01940	959.2	719.7	Yes	Yes
12	Charles River Farm	0.716	0.01215	391.9	370.2	Yes	Yes
13	Sindos	0.430	0.01946	212.5	200.8	Yes	Yes
14	Paradiso San Zenone	0.601	0.02661	256.4	242.2	Yes	Yes
15	Hoeltinghausen	0.550	0.04667	472.6	446.5	Yes	Yes
16	Hornton	0.785	0.01491	366.7	337.4	Yes	Yes
17	Le Thour	0.138	0.13818	150.2	141.9	Yes	Yes
18	Brannens	0.323	0.02876	323.1	305.2	Yes	Yes
19	Balbiano	0.403	0.01932	290.2	274.1	Yes	Yes
20	Almayate East	0.918	0.02180	176.9	157.4	Yes	Yes
	Geometric mean	**0.525**	**0.0285**	**-**	**252**		

Estimating $DegT_{50eq}$ values from lower-tier $DegT_{50}$ values

The evaluations have been conducted according to the guidance document on aged sorption (European Commission, 2021). Before combining and averaging the degradation endpoints, $DegT_{50eq}$ values need to be calculated for each of the Tier-1 degradation endpoints. Three methods are available to calculate the $DegT_{50eq}$, depending on which information is available from the Tier 1 degradation study. The guidance document on aged sorption recommends that a refit of the aged sorption model to the original data (total mass only) is always the preferred option for the conversion of lower-tier degradation endpoints. If raw data and sufficient information from the Tier 1 study are not available for the performance of an inverse optimisation, scaling factor method 1 is recommended, and finally if not all information for this method is accessible, scaling factor method 2 is to be used.

Refit of residue data

Refit of residues data method. A model, for example PEARLNEQ, can be used to estimate $DegT_{50eq}$ values for lower-tier degradation study data, in an analogous way to a full aged sorption evaluation but using the geometric mean F_{ne} and k_{des} parameters derived from the aged sorption studies, according to the following procedures:

- Calculate the Total mass degradation data at each timepoint in µg. If not directly available then the Total mass data can be derived from the %applied radioactivity data and the mass dosed into the test system (µg). The guidance document on aged sorption (European Commission, 2021) does not recommend adding the non-extractable residue fraction and possible metabolite to the compound at sampling time t = 0, as is required for kinetic analysis of first-tier degradation studies (FOCUS, 2006).
- A PEARLNEQ input file is created using the Total mass data (µg) with inverse optimisation for unweighted data. This is in line with current guidance for first-tier degradation studies (FOCUS, 2006). For the aqueous phase, input 'dummy values' e.g. '99.999' along with a weighting of zero for all timepoints.
- Set the volume of liquid added to zero. Set the volume of liquid in soil (VolLiq), mass of soil and organic matter content as usual.
- Derive the geometric mean F_{ne} and k_{des} parameters from the aged sorption studies and fix these in PEARLNEQ
- If soil-specific $K_{OC/OM}$ (and 1/n) data are available, then the measured K_{OM} and 1/n are used directly in PEARLNEQ. Otherwise, the overall geometric mean K_{OM} and average 1/n values are used. K_{OM} and 1/n are fixed for the evaluation and not optimised.
- Optimise $DegT_{50eq}$ and M_{ini} in PEARLNEQ
- Normalise $DegT_{50eq}$ to FOCUS reference conditions (20°C and pF2).

Combining Tier 1 and aged sorption studies

The guidance document on aged sorption (European Commission, 2021) requires combining all available lower-tier degradation and adsorption parameters with the parameters from the aged sorption studies obtained at Tier 2a for use in the groundwater leaching assessment. The figure below illustrates the flow chart that must be applied to combine the parameters of Tier 1 and the aged sorption studies (Tier 2a) in the case that all soils in the higher-tier experiments were extracted with the same procedure for the determination of total mass (one set of parameters).

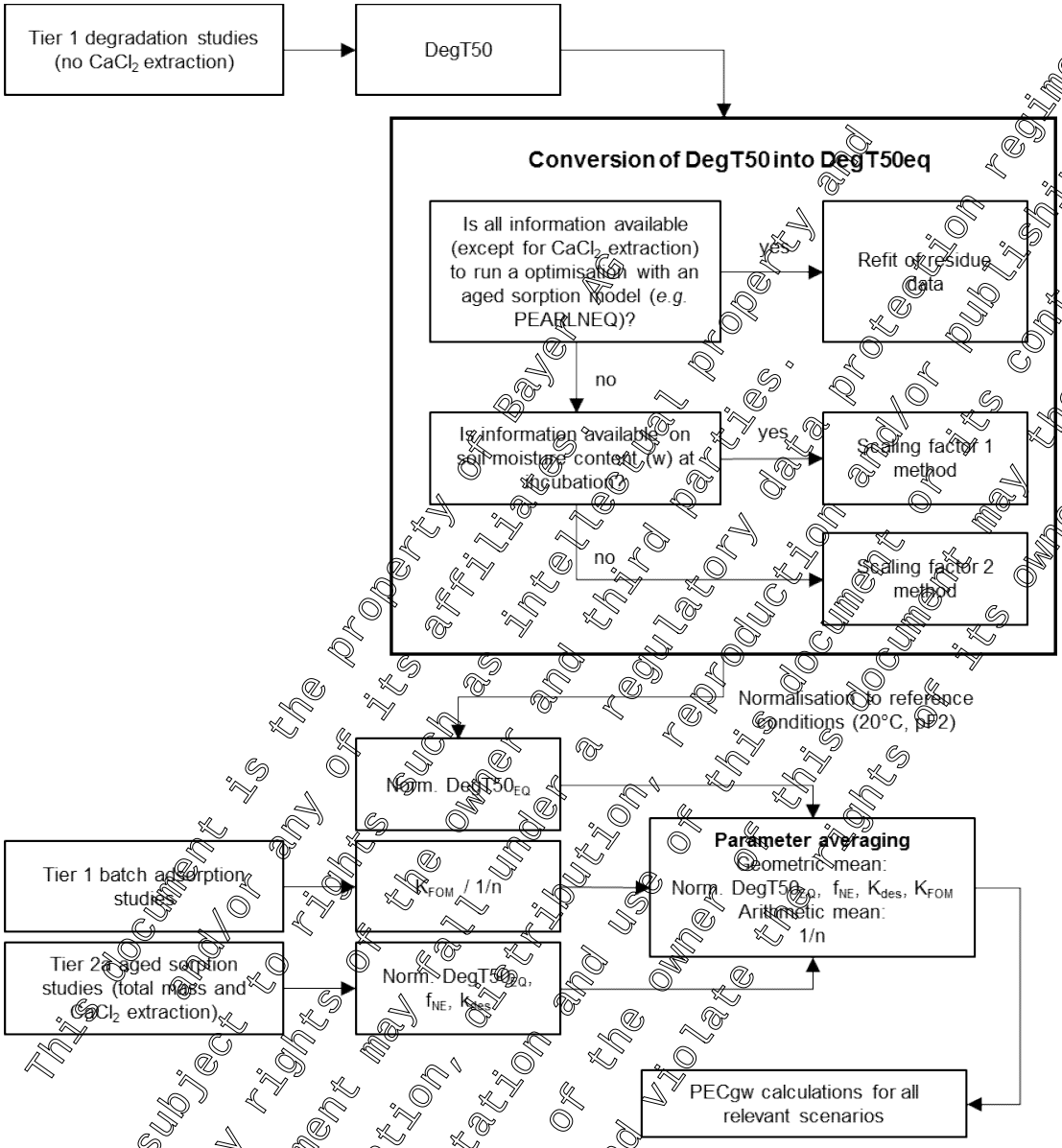


Figure 7.1.3.2- 5: Flow chart for combining Tier 1 and Tier 2a (aged sorption) parameters for groundwater risk assessment

If the $DegT_{50}$ from the lab aged sorption is greater than 240 days, then no comparison is made between the lab $DegT_{50}$ and field $DegT_{50}$ (as per EFSA (2014) guidance). In this situation, only the field $DegT_{50}$, with no correction factor, should be taken forward for use in the aged sorption model.

A number of evaluations have been undertaken to clearly illustrate that aged-sorption processes are relevant for fluopyram under field conditions.

1. Degradation of residues with time

PEARL can be readily be used to simulate the behaviour of fluopyram residues in soil during the field experiment and to evaluate the effects of different input parameters. Direct comparisons can be made *vs.* the measured soil residues with time. The comparisons have been made as a 3-step evaluation:

Simulation with normalised $DegT_{50}$
Simulation with normalised $DegT_{50}$ (un-corrected) with aged-sorption
Simulation with normalised $DegT_{50}$eq (corrected with Scaling Factor 1) with aged-sorption

PEARL simulation comparisons for all EU field trials are provided in the report. An example of simulation plot is provided in the figure below for one soil.

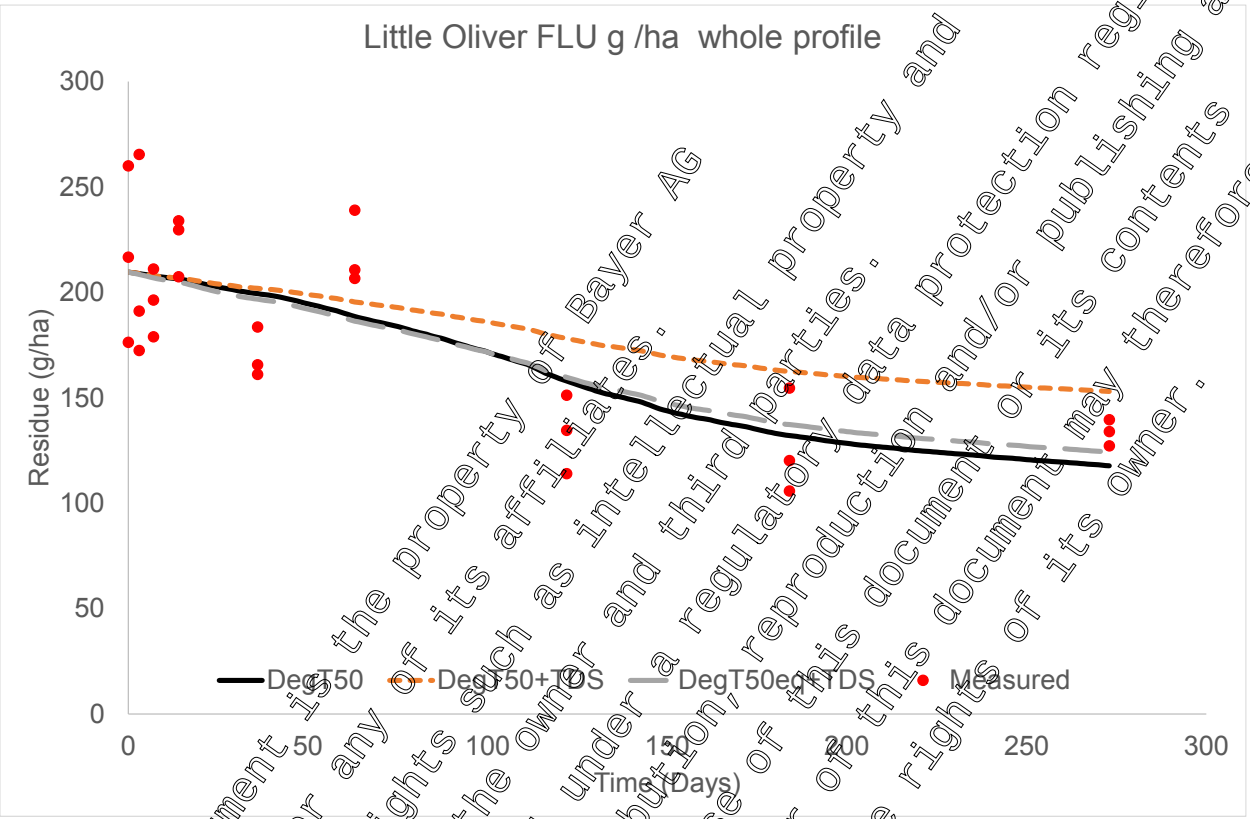


Figure 7.1.3.2- 6: PEARL residue decline simulations – Little Oliver

As expected, PEARL simulations with the normalised $DegT_{50}$ values closely follows the decline of residues with time (cf Timestep normalisation). However, PEARL simulations using the normalised $DegT_{50}$ values with aged-sorption [no correction to $DegT_{50}eq$] significantly over-estimates residues remaining throughout the trials, with an increase of between 104 and 146% at the final timepoint. This is clearly an unacceptable situation with regards to data fitting. Correction of $DegT_{50}$ values to $DegT_{50}eq$ values with Scaling Factor 1 is shown to better simulate the decline of field residues, whilst remaining conservative.

2. Depth profile analysis

The PEARL simulations can also be evaluated to compare the mobility of residues into the profile with time. The field studies reported residues analysed in 10 cm increments, these can then be compared to the predicted movement in the PEARL simulations averaged across 10 cm depth increments at each timepoint. Based on evaluation of the final sampling timepoint of each trial (interim), PEARL over-estimates the mobility of fluopyram in soil compared to the measured field data when aged-sorption is not used. Inclusion of aged-sorption without correction of the $DegT_{50}$ reduces the mobility, but over-estimates the total residue remaining. PEARL depth profile simulations for all EU field trials are provided in the report. An example of simulation plot is provided in the figure below for one soil.

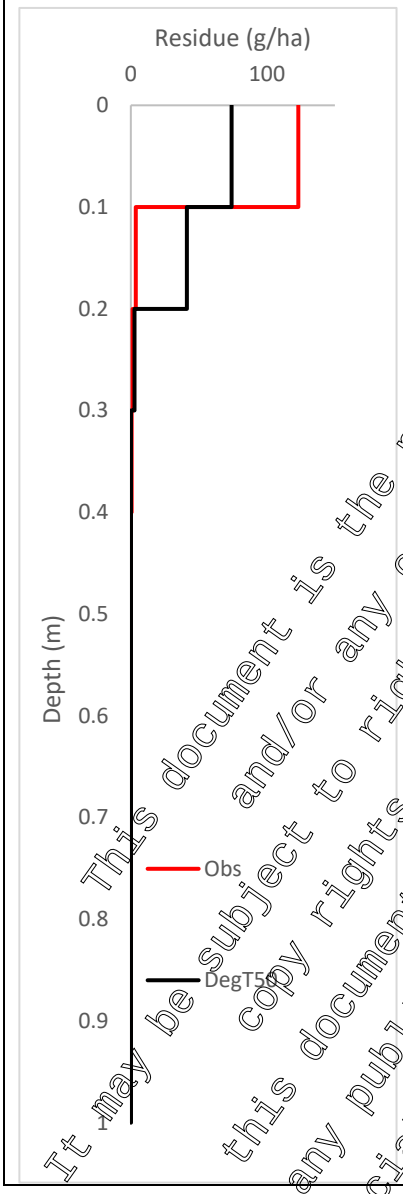
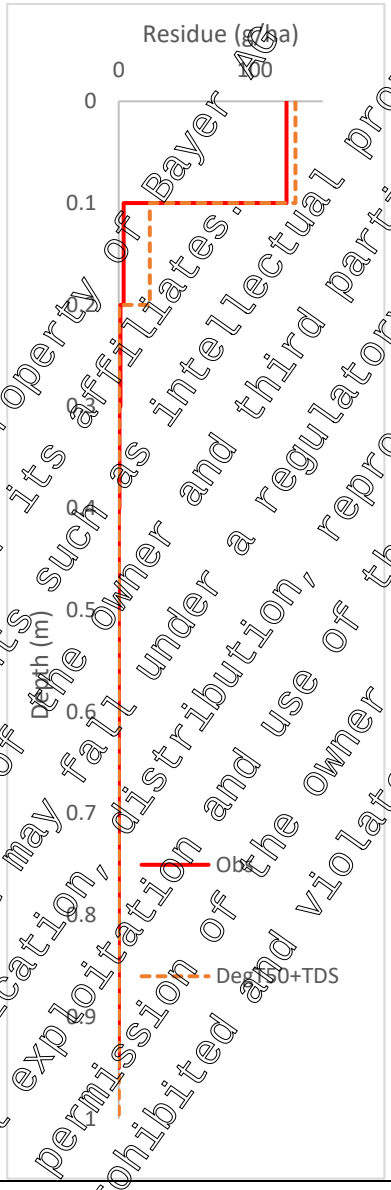
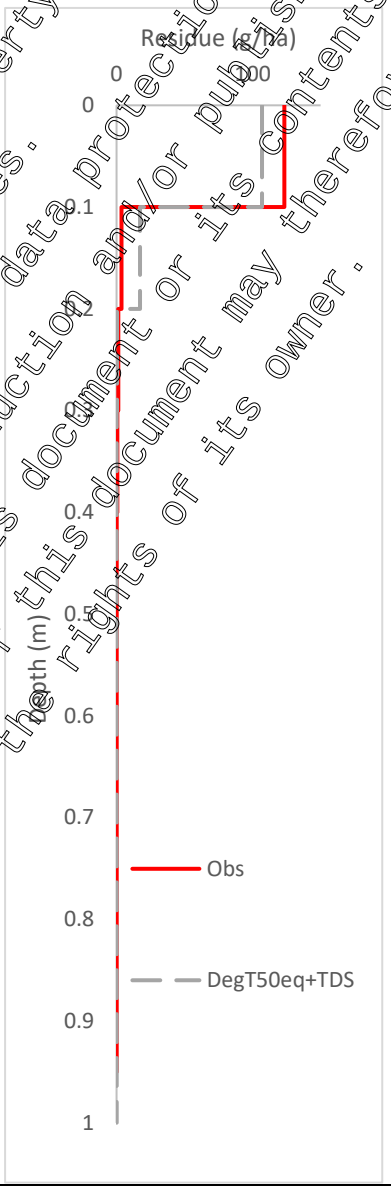
$DegT_{50}$	$DegT_{50}$ + TDS	$DegT_{50}$eq+ TDS
Good total residue match, but mobility higher than observed	Reduced mobility, but total residues over-estimated (130% of $DegT_{50}$ fit)	Reduced mobility, but still higher than observed. Good total residue fit (105% of $DegT_{50}$ fit)
		

Figure 7.1.3.2-7: PEARL depth profile simulations – Little Oliver DAT273

Inclusion of aged-sorption with correction of the $DegT_{50}$ reduces the mobility and results in an improved fit to the total residue remaining. Thus, confirming that inclusion of aged-sorption with correction to $DegT_{50eq}$ is justified for fluopyram.

3. K_{d_app} plots

As part of the European field dissipation trials, calcium chloride extractions were conducted at selected timepoints (0, 0.5, 1, 2, 4 and 6 months), followed by soil extraction. This allows for K_{d_app} values to be calculated for the field soils. K_{f_app} values can additionally be calculated using the 1/n values determined in the OECD 106 ads/des experiments for the same soils. The calculated K_{d/f_app} values for the field trials

can be evaluated to check increases with time and additionally compared to the values derived in the laboratory aged-sorption experiments. K_{d/f_app} plots for all EU field trials are provided in the report. Examples of these plot are provided in and the figure below for one soil.

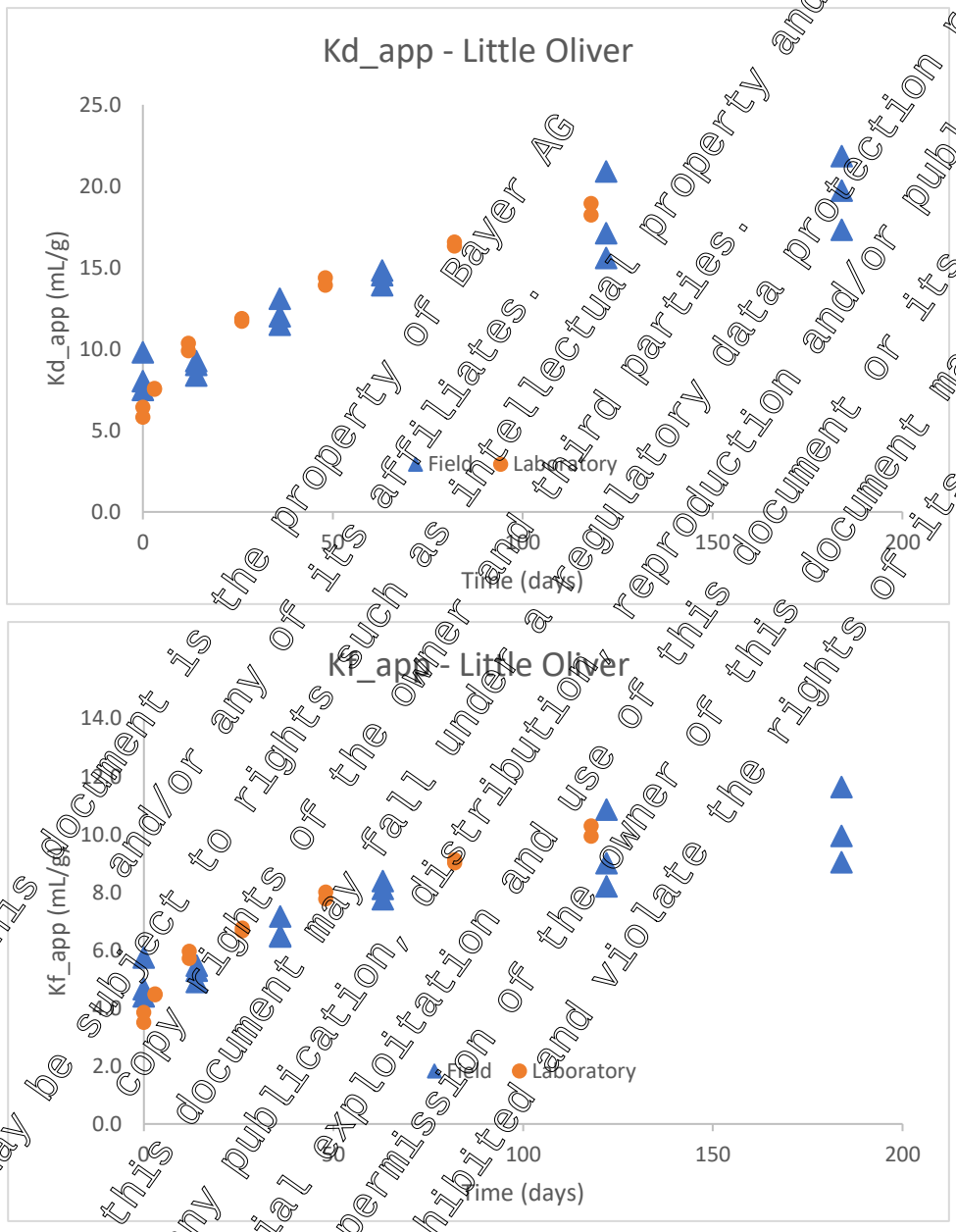


Figure 7.1.3.2- 8: Kd/f_app plots - Little Oliver

The K_{d_app} and K_{f_app} plots show significant ageing of residues in field soils for all trials, except of one. The increase in K_{d_app} and K_{f_app} with time corresponds well to that measured in the laboratory, confirming that aged-sorption is a relevant process in field soils.

II. RESULTS

Refit of residue data

For refit of residue data aerobic degradation data of fluopyram for the seven soils have been evaluated according to the refit procedures. Fluopyram data reported as %AR was converted to total µg by

multiplying the %AR by the dosed mass of fluopyram. Phenyl and pyridyl labelled data were combined as replicates. The mean aged-sorption parameters of F_{ne} 0.525 and k_{des} 0.0285 were used in the refit procedure.

The calculated $DegT_{50eq}$ refit values for the lower-tier laboratory degradation studies are summarised in the table below. The refit for the *Argissolo* soil did not yield a robust parameter estimate. Therefore, a $DegT_{50}eq$ value of 517 days was derived from the standard modelling endpoint DT_{50} value of 707.1 days using Scaling Factor 1 (0.731; derived from: mean K_{om} 134.7 mL/g, f_{om} 0.045, w 0.244 mL/g and f_{ne} 0.525).

Table 7.1.3.2-49: $DegT_{50eq}$ refit values for lower-tier laboratory degradation studies

#	Soil	Temperature (°C)	FOCUS correction factor	$DegT_{50eq}$ (d)	$DegT_{50eq}$ 20°C pF2 (d)
1	Springfield	25	1.0138	329.3	333.8
2	Porterville	25	0.9130	571.2	521.5
3	*Argissolo*	*20*	*0.6227*	*517.0*	*321.9*
4	Frankenforst	20	0.8282	188.5	156.3
5	Wurmwiese	20	0.9270	233.5	216.4
6	Hoefchen	20	0.9270	216.5	200.7
7	Innerdeich	20	0.9270	234.8	217.7

Field $DegT_{50}$ evaluations

Normalised field $DegT_{50}$ values are available for 13 trials, the overall geometric mean normalised laboratory $DegT_{50}$ for fluopyram is 364 days, thus only field data are considered for PEC_{gw} evaluation, but without correction to $DegT_{50}eq$. Where a comparison of laboratory and field degradation data indicated that the two sets of data were from different distributions, then non-correction of the field $DegT_{50}$ to $DegT_{50}eq$ was considered as a conservative approach due to uncertainty if aged-sorption processes were then relevant under field conditions. However, evaluation of the field data for fluopyram clearly indicates that inclusion of aged-sorption processes in the simulation modelling is necessary to describe the observed behaviour. Therefore, correction of field $DegT_{50}$ values to $DegT_{50}eq$ values is justified and appropriate in this case.

Soil-specific K_{om} and F_{ne} values were used where available, else the overall geometric mean K_{om} (134.7 mL/g) and F_{ne} (0.525) values were substituted. The incubation soil moisture content (*w*) was derived from the PEARL simulations conducted for the Timestep normalisation procedure as the average over the experimental period of the study. The $DegT_{50eq}$ values for the 13 field trials calculated with scaling factor 1 are summarised in the table below.

Table 7.1.3.2-50: Normalised field $DegT_{50eq}$ values for fluopyram

Location	$DegT_{50}$ matrix (d) norm	K_{om} (mL/g)	F_{om}	w (mL/g)	F_{ne} (-)	Scaling factor 1	$DegT_{50eq}$ (d)
Little Oliver	153.8	153.5	0.026	0.227	0.910	0.591	90.9
Auchy les Mines	871.6	108.9	0.029	0.216	0.957	0.580	505.5
Urbanowice	605.3	132.7	0.017	0.259	0.611	0.710	429.9
Charles River Farm	306.2	90.0	0.026	0.275	0.716	0.670	205.3
Sindos	>1000	112.5	0.026	0.199	0.430	0.785	1000 [1]
Hoeltinghausen	453.9	180.1	0.014	0.118	0.550	0.721	327.3
Hornton	263.7	142.4	0.038	0.305	0.785	0.631	166.4
Le Thour	83.9	106.4	0.042	0.279	0.138	0.974	81.7
Brannens	180.5	145.2	0.013	0.162	0.323	0.848	153.0
Balbiano	203.0	125.5	0.035	0.240	0.403	0.796	161.6
Almayate East	221.3	159.0	0.025	0.221	0.918	0.588	130.2
North Rose, New York	281.7	134.7	0.022	0.122	0.525	0.731	206.0
Ephrata, Washington	257.4	134.7	0.008	0.104	0.525	0.744	191.5
						Geometric mean	**216.5**

[1] not corrected

Overall $DegT_{50eq}$ summary

The final results for all normalised (20 °C and pF2) $DegT_{50eq}$ evaluations, with overall geometric mean values of 254.4 days for laboratory data and 216.5 days for field data are summarized in the tables below. These $DegT_{50eq}$ values are only valid for use in combination with the mean aged-sorption parameters of F_{ne} 0.525 and k_{des} 0.0285 for FOCUS model exposure calculations.

Table 7.1.3.2-51: Overall $DegT_{50eq}$ evaluation results – laboratory data

#	Soil	DegT50eq (days)	Derivation
1	**Hoefchen**	**156.7**	**TDS - PEARLneq**
2	Laacher Hof AXXa	158.0	TDS - PEARLneq
3	Wurmwiese	171.5	TDS - PEARLneq
4	Laacher Hof AIIIa	112.8	TDS - PEARLneq
5	Hoefchen	145.3	TDS - PEARLneq
6	Laacher Hof AXXa	304.1	TDS - PEARLneq
7	Wurmwiese	170.4	TDS - PEARLneq
8	Dollendorf II	118.3	TDS - PEARLneq
9	Little Oliver	943.5	TDS - PEARLneq
10	Auchy les Mines	731.7	TDS - PEARLneq
11	Urbanowice	719.7	TDS - PEARLneq
12	Charles River Farm	370.2	TDS - PEARLneq
13	Sindos	200.8	TDS - PEARLneq
14	Paradiso San Zenone	242.2	TDS - PEARLneq
15	Hoeltinghausen	446.5	TDS - PEARLneq
16	Hornton	337.4	TDS - PEARLneq
17	Le Thour	141.9	TDS - PEARLneq
18	Brannens	305.2	TDS - PEARLneq

19	Balbiano	274.1	TDS - PEARLneq
20	Almayate East	157.4	TDS - PEARLneq
21	Springfield	333.8	Lab Tier-1 Refit
22	Porterville	521.5	Lab Tier-1 Refit
23	*Argissolo*	321.9	$DegT_{50}$ [1]
24	Frankenforst	156.3	Lab Tier-1 Refit
25	Wurmwiese	216.4	Lab Tier-1 Refit
26	Höfchen	200.7	Lab Tier-1 Refit
27	Innerdeich	217.7	Lab Tier-1 Refit
	Geometric mean	**254.4**	

[1] Tier-1 refit not acceptable, standard $DegT_{50}$ × SF1 (0.731) used

Table 7.1.3.2-52: Overall $DegT_{50eq}$ evaluation results – field data

#	Soil	$DegT_{50eq}$ (days)	Derivation
1	Little Oliver	90.9	Field Scaling factor 1
2	Auchy les Mines	505.5	Field Scaling factor 1
3	Urbanowice	429.9	Field Scaling factor 1
4	Charles River Farm	205.3	Field Scaling factor 1
5	Sindos	1000	Default, not corrected
6	Hoeltinghausen	357.3	Field Scaling factor 1
7	Hornton	166.4	Field Scaling factor 1
8	Le Thour	81.7	Field Scaling factor 1
9	Brannens	153.0	Field Scaling factor 1
10	Balbiano	161.6	Field Scaling factor 1
11	Almayate East	130.2	Field Scaling factor 1
12	North Rose, New York	206.0	Field Scaling factor 1
13	Ephrata, Washington	191.5	Field Scaling factor 1
	Geometric mean	**216.5**	

III. CONCLUSIONS

The geometric mean normalised $DegT_{50eq}$ based on laboratory data is 254.4 days. The overall geometric mean normalised $DegT_{50eq}$ based on field data for use in exposure modelling (in combination with the mean aged-sorption parameters: F_{ne} 0.525; k_{des} 0.0285 1/d) is 216.5 days.

3. Assessment and conclusion

Assessment and conclusion by applicant:
The estimate of $DegT_{50eq}$ was conducted according to current guidance document on aged sorption (European Commission, 2021) and is considered to be valid for groundwater risk assessment.

Assessment and conclusion by RMS:
Outcome and conclusion of the study**:** RMS should indicate if they agree to the results and conclusions of the APPL.

An update of the TDS evaluation will be conducted when the final reports of the studies M-758583-01-1 and M-758589-01-1 are available and will be provided at the latest by end of February 2022.

CA 7.1.4 Mobility in soil

The mobility of fluopyram and its degradation product fluopyram-7-hydroxy in soil is considered to be low as the K_{foc} values determined in the course of adsorption studies are between 156 mL/g to 400 mL/g for fluopyram and between 85 mL/g and 149 mL/g for fluopyram-7-hydroxy.

For the degradation product TFA studies on plant uptake were conducted in either hydroponic systems or container experiments and the TSCF based on inverse modelling using PEST and PEARL was determined, in addition. The results indicate significant uptake of TFA by plants. Majority of TFA proportion was translocated into the shoots of wheat plants. The plant uptake factor (PUF) of TFA determined in wheat plants (five replicates) amounted to 0.05 ± 0.03 at t_1 and 0.18 ± 0.01 at t_{end}. The TSCF of TFA in wheat plants was in the range of 0.11 to 0.19 shortly after the beginning of the equilibration phase (2 - 4 days). It reached an overall mean value of 0.17 (range: 0.15 – 0.20) at the end of the experimental phase (6 - 8 days). Results from inverse modelling achknowledged the observations in the experimental studies could be retrieved quite well by the simulations, i.e. the dynamics of plant uptake and water fluxes were close the measured values. The inverse modelling simulation using a coupling of PEARL and PEST resulted to robust parameter estimation of the transpiration stream concentration factor (TSCF).

1. Information on the study

Data Point:	KCA 7.1.4/01
Report Author:	[redacted]
Report Year:	2018
Report Title:	Determination of the plant uptake of [1-14C]-BCS-AZ56367 (TFA) in wheat plants
Report No:	M-617804967-2
Document No:	M-613317-01-1
Guideline(s) followed in study:	US EPA OCSPP Test Guideline: N/A OECD Test Guideline: N/A
Deviations from current test guideline:	not applicable
Previous evaluation:	No, submitted, not evaluated not applicable (evaluation ongoing)
GLP/Officially recognised testing facilities:	Yes, conducted under GLP/Officially recognised testing facilities
Acceptability/Reliability:	Yes

2. Full summary of KCA 7.1.4/01

Executive Summary

The uptake of [2-^{14}C]trifluoroacetate (TFA) was investigated in wheat plants to determine the plant uptake factor (PUF) and the transpiration stream concentration factor (TSCF).

The test was performed in hydroponic systems consisting of brown glass bottles each containing either approximately 510 mL test solution (nutrient solution plus test item) or pure nutrient solution initially adjusted to a pH value of 6.5. A study application rate of 51.0 µg test item per test system was applied, equal to a test item concentration in test solution of 95.6 µg/L.

Pre-grown wheat plants (BBCH 11-12) were equilibrated in the nutrient solution for 10 days. Starting from BBCH 21 they were exposed to the test solution for a maximum period of 8 days. The incubation time considered to calculate the plant uptake factor data started 2 days after treatment (DAT) and was

over 6 days in total. The incubation time considered to calculate the transpiration stream concentration factor started with the day of application and was over 8 days in total. The test was performed in five replicates with additional four replicates each of plant and stability controls.

During the study, the plants were incubated in a climatic chamber in the greenhouse under controlled temperature, humidity and light conditions (setpoint values: 22/18 °C (day/night), 60% humidity and a day/night cycle of 16 h/8 h).

Wheat plants appeared healthy over the total study duration both in treated and untreated test systems. The wheat plants grew from BBCH 21 at DAT 0 (t_{start}, application and start of equilibration) to BBCH 23-24 at the end of study at DAT 8 (t_{end}).

Mean material balances were 99.4% AR at DAT 4 (range from 99.1 to 99.6% AR) and 99.2% AR at DAT 8 (range from 98.9 to 99.4% AR).

During the incubation period 85.2 to 325.9 mL of the test solution was taken up by the plants. About 5.5 mL of the test solutions were lost due to evaporation, which was determined as the mean of four control replicates. The mean initial concentrations (DAT 0) of TFA in the test solutions amounted to 95.6 µg/L, increasing to 109.8 µg/L at DAT 4 and further increasing to 168.2 µg/L at DAT 8. Root wash desorbed 0.7 µg of the test item from the roots at DAT 4 and 4.2 µg at DAT 8. The separate analysis of roots and shoots showed, that at DAT 4 92.0% and at DAT 8 94.1% of radioactivity taken up is translocated from roots into shoots.

The transpiration stream concentration factor (TSCF) of TFA amounted to 0.17 over the study period. The mean plant uptake factor (PUF) of TFA was determined for wheat plants post equilibration as 0.18 over 6 days.

Replicate No.	**PUF_{wheat}**		**$TSCF_{wheat}$**	
	t_0-t_1	**t_0-t_{end}**	**t_{start}-t_1**	**t_{start}-t_{end}**
1	0.09	0.17	0.10	0.17
2	0.00	0.17	0.12	0.16
3	0.09	0.19	0.10	0.18
4	0.05	0.18	0.11	0.17
5	0.08	0.19	0.12	0.18
Mean	**0.05**	**0.18**	**0.11**	**0.17**

t_{start} = application and start of equilibration at DAT 0
t_0 = end of the equilibration phase at DAT 2
t_1 = interim sampling at DAT 4
t_{end} = end of study at DAT 8

I. MATERIALS AND METHODS

A. MATERIALS

1. Test Item

[1-^{14}C]BCS-AZ56567, sodium trifluoroacetate (TFA)
Batch Code: KML 9173
Specific Activity: 4.08 MBq/mg
Radiochemical Purity: ≥ 98% (HPLC/radio-detector)

2. Test Plants

Wheat plants (variety: Thasos) were pre-grown in perlite (particle size: 0 - 6 mm) in a greenhouse. At growth stage BBCH 11-12, plants were taken out of the perlite and their root system was gently cleaned with untreated nutrient solution. Plants were transferred to brown glass bottles containing approximately 500 mL untreated nutrient solution and acclimatized to aerobic study conditions for 10 days.

B. STUDY DESIGN

1. Experimental Conditions

The hydroponic test system, for determination of the plant uptake factor, consisted of brown glass bottles filled with approximately 510 mL nutrient solution (Hoagland No.2 basal salt mixture containing 2-(N-morpholino)-ethanesulfonic acid (MES) buffer) initially adjusted to a pH of 6.5. The biomass of the plants was determined. Two plants were transferred into each vessel and fixed using polyurethane (PU) foam plugs and a wooden skewer with wire fitting to hold the plant in an upright position. To establish aerobic conditions throughout the study, each flask was aerated with a stream of air.

The test was performed in five replicates with additional four replicates each of plant and stability controls. Beside the treated plant uptake test systems, four test systems also applied with the solvent of the application solution (water) were used to monitor the plant health and the transpiration volume of untreated plants during the study course. Additionally, four test systems without plants were treated with the test item to monitor losses of test solution by evaporation and losses of test item during study course, e.g. due to adsorption to the test vessel surface or hydrolysis (stability controls).

The application solution was applied under stirring onto the surface of the nutrient solution of the prepared test systems. The initial test item concentration in the aqueous test solution was 95.6 µg/L.

During the study, the test systems were incubated in a climatic chamber in the greenhouse (setpoint values: 22/18 °C (day/night), 60% humidity and a day/night cycle of 16 h/8 h). During the definitive test, the light intensity was measured as > 10.0 kLux.

Table 7.1.4- 1: Experimental condition

Parameter		Description
Duration of test		Application: DAT 0 (t_{start}); end of the equilibration phase at DAT 2 (t_0); interim sampling: DAT 4 (t_1); harvest / end of the study: DAT 8 (t_{end})
Test concentrations	Nominal	100 µg/L at study start
	Real	95.6 µg/L at study start
Number of replications		5 replicate vessels for harvesting on DAT 4 (t_1) and DAT 8 (t_{end})
Plants per vessel		2
Growth stage at application		BBCH 21
Growth stage at final harvest		BBCH 23-24
Preparation of test medium	Volume used per vessel	534 to 552 mL (= V_{start})
	Method of preparation	For 1 litre nutrient solution 50% Hoagland nutrient solution, 1.03 g/L MES hydrate buffer (2-(N-morpholino)-ethanesulfonic acid), 0.3 g potassium nitrate and 0.75 ml of 15% ferric EDTA solution were dissolved with tap water and the pH was adjusted to 6.5.

	Target pH	6.5
Test material application	Solvent	ultra-pure water
	Volume of application solution	75.4 µL per vessel
	Application method	Pipette
Test apparatus		Ca 500 mL brown glass bottles
Is there any indication of the test item adsorbing to the walls of the test apparatus?		No, the amount of dissolved radioactivity in the vessel with nutrient solution and test item (no plant) stays constant with time.
Experimental conditions	Temperature	22 °C (day), 18 °C (night)
	Aeration	ventilation tubes connected to a peristaltic pump
	Humidity	Set to 60%
	Lighting	Climatic chamber with day/night cycle (16 h light & 8 h dark)
Other Details		4 additional vessel with nutrient solution and test item (no plant) to determine pH level, dissolved oxygen, loss of nutrient solution via evaporation and to determine the stability of the test item at test end and to show no indication of the test item adsorbing to the walls of the test system. 4 additional vessels with nutrient solution and plants to determine the growth of the plant during the experiment. Determination of weight of plants at start of experiment and at harvesting after carefully patting dry the roots.

2. Sampling

The mass of the test substance and the volume of test solution in the test vessels were determined at the start of the incubation (t_{start}; 0 days after treatment (DAT)), at the end of the equilibration phase (t_0; DAT 2), at the interim sampling (t_1; DAT 4) and at the end of the experiment (t_{end}; DAT 8).

Additionally, the pH of the test solution and the dissolved oxygen level in the test solution was determined in selected vessels.

The plants were processed and analysed at t_1 and t_{end}.

3. Analytical Procedures

The plants were removed from the test vessels, transferred into glass flasks and the roots were gently shaken for about 5 min in approximately 200 mL acetonitrile/water (4/1, v/v) to wash off any compound associated to the root surface. The root wash solution was quantified separately by LSC. The roots were patted dry, the plant then divided into shoots and roots and the fresh weight biomasses were determined gravimetrically. For the test solution remaining in the test vessel the pH value and oxygen saturation was determined. The mass of the test compound in the test solution was calculated from the specific radioactivity and the amount of radioactivity in the test solution. The radioactivity in roots and shoots was determined separately by combustion and subsequent measurement by LSC.

The residual volume of the nutrient solution of the plant controls was determined at DAT 0, 4 and 8. The weight of the total plant (after patting the roots dry) was determined at DAT 8.

The volume of the test solution of stability controls was determined at t_0, t_1 and t_{end} (DAT 2, 4 and 8) gravimetrically. Aliquots of the test solutions of the stability controls were taken and analyzed by LSC. At the end of the study (t_{end}, DAT 8), an aliquot was analyzed by reverse phase HPLC using a Purospher Star RP-18 column, a gradient elution of water acidified with 1% formic acid/acetonitrile acidified with 1% formic acid (starting gradient 1/0, v/v) and Ramona Star radio-detector for confirmation of test item stability.

The Plant Uptake Factor (PUF) was calculated by means of the following equation:

$$PUF = \frac{ln\left(\frac{m_{sol}}{m_0}\right)}{ln\left(\frac{V_{sol}}{V_0}\right)}$$

with:

m_0	= mass of item at start of the experiment (t_0, at end of the equilibration phase, DAT 2)	[µg]
V_0	= volume of test solution at start of the experiment (t_0, at end of the equilibration phase, DAT 2)	[L]
m_{sol}	= mass of test item at a given time t after the start of the experiment	[µg]
V_{sol}	= volume of test solution at given time t after the start of the experiment	[L]

The Transpiration Stream Concentration Factor (TSCF) was calculated by means of the following equation:

$$TSCF = \frac{\ln\left(1 - \frac{m_{shoots}}{m_{shoots} + m_{sol}}\right)}{\ln\left(\frac{V_{sol}}{V_{start}}\right)}$$

with:

V_{sol}	= volume of test solution at given time t after the start of the experiment	[L]
V_{start}	= volume of test solution at start of the equilibration (DAT 0)	[L]
m_{sol}	= mass of test item at a given time t after the start of the experiment	[µg]
m_{shoots}:	= mass of test item in shoots	[µg]

II. RESULTS AND DISCUSSION

A. PLANT CONTROLS

The health and growth of the wheat plants was visually assessed regularly. Wheat plants appeared healthy over the total study duration both in treated and untreated test systems. However, all wheat plants initially showed slight chlorosis due to a lack of magnesium, but until the end of the test period all plants exhibited an excellent plant health. The wheat plants grew from BBCH 21 at DAT 0 to BBCH 23-24 at the end of the study. The plant biomass increase was 208% for untreated and 167% for treated from the start of the experiment to the end of the study.

B. MATERIAL BALANCE

Mean material balances ranged from 99.2 to 99.4% AR indicating there was no significant loss of radioactivity from the test systems or during sample processing. The complete material balances found at all other sampling intervals for all test systems demonstrated that there was no significant loss of radioactivity from the test systems or during sample processing.

Table 7.1.4- 2: Recovery of radioactivity of TFA in wheat and hydroponic solutions after equilibrium period (as % of applied)

Fraction analysed	Replicate	Incubation time (DAT)	
		4 (t_1)	8 (t_{end})
Test solution, aliquot adjusted	1	95.6	77.5
	2	95.7	84.3
	3	96.8	76.8
	4	95.6	75.2
	5	95.9	75.5
	Mean	**95.9**	**77.9**
Root wash solution	1	1.4	7.9
	2	1.3	5.3
	3	1.1	8.6
	4	1.4	9.5
	5	1.3	9.3
	Mean	**1.3**	**8.1**
Test solution + root wash	1	97.0	85.4
	2	97.9	89.8
	3	97.8	85.4
	4	97.2	84.7
	5	97.1	84.8
	Mean	**97.2**	**86.0**
Combustion shoots	1	1.9	12.5
	2	2.1	9.4
	3	1.6	13.2
	4	2.1	13.5
	5	2.2	13.8
	Mean	**2.0**	**12.4**
Combustion roots	1	0.2	1.3
	2	0.2	0.6
	3	0.1	0.8
	4	0.2	0.7
	5	0.1	0.5
	Mean	**0.2**	**0.8**
Total in plant	1	2.1	13.7
	2	2.3	9.7
	3	1.8	14.0
	4	2.2	14.2
	5	2.3	14.3
	Mean	**2.1**	**13.2**
Total recovery	1	99.1	99.1
	2	99.2	99.4
	3	99.6	99.4
	4	99.4	98.9
	5	99.5	99.2
	Mean	**99.4**	**99.2**

C. STABILITY OF TEST ITEM

The stability of the test item was confirmed by HPLC analysis of an aliquot of the stock solution and at the end of the study in the control test solution.

D. FINDINGS

The experiment with [1-^{14}C]BCS-AZ56567 (TFA) exhibited for the total experimental time period a water loss per test system ranging from 85.2 to 325.9 mL resulting in a mean transpiration stream of 92 mL on DAT 4 (t1) and 291 mL on DAT 8 (t_{end}). The control samples without plants did result in a calculated evaporation of – 0.49 mL on DAT 4 (t_1) and gave a mean loss of 5.5 mL by evaporation at the end of the study. Those values have been considered in the calculation of the transpiration.
The mean pH values of the test solutions increased within two pH units of the system initially buffered to pH 6.5 to mean values of 7.2 (7.1 – 7.3) on DAT 4 (t_1) and 8.3 (7.8 – 8.5) on DAT 8 (t_{end}).

The mean initial concentration of test item in the test solutions at start of the equilibration on DAT 0 (t_{start}) amounted to 95.6 µg/L, increasing to 109.8 µg/L at DAT 4 (t_1) and further increasing to 168.2 µg/L at DAT 8 (t_{end}). The mass of the test item decreased from 52.0 µg at DAT 0 to 50.6 µg at DAT 4 and further decreased to 39.9 µg at DAT 8.

On average the root wash gave 0.7 µg of the test item from the roots at DAT 4 (t_1) and 4.2 µg at DAT 8 (t_{end}). Recovery of total applied radioactivity was found in mean as 99.4% at DAT 4 and 99.2% at DAT 8. The separate analysis of roots and shoots showed, that at DAT 4 92.0% and at DAT 8 94.1% of radioactivity taken up is translocated from roots into shoots.

The transpiration stream concentration factor (TSCF) of TFA amounted to 0.17 over the study period. The plant uptake factor (PUF) of TFA was determined for wheat plants post equilibration as 0.18 over 6 days (see Table below).

Table 7.1.4- 3: Transpiration stream concentration factor (TSCF) of TFA

Results TSCF calculation	**t_{start}-t_1**					
Sample ID	**V start [mL]**	**m start [µg]**	**V sol [mL]**	**m sol [µg]**	**m shoots [µg]**	**TSCF**
PT9	547.90	51.63	448.93	50.07	1.01	0.10
PT10	543.62	52.11	453.47	50.54	1.08	0.12
PT11	542.80	52.05	460.14	50.93	0.84	0.10
PT12	550.08	52.09	456.60	50.61	1.08	0.11
PT13	552.33	51.70	457.23	50.23	1.12	0.12
mean	**547.3**	**51.9**	**455.28**	**50.47**	**1.02**	**0.11**
SD	3.67	0.21	3.81	0.30	0.10	0.01
CV %	0.67	0.40	0.84	0.60	9.78	7.39
Results TSCF calculation	**t_{start}-t_{end}**					
Sample ID	**V start [mL]**	**m start [µg]**	**V sol [mL]**	**m sol [µg]**	**m shoots [µg]**	**TSCF**
PT14	535.73	51.70	245.20	44.22	6.45	0.17
PT15	542.76	51.77	294.48	46.60	4.74	0.16
PT16	539.08	51.94	239.16	44.50	6.87	0.18
PT17	547.63	52.09	231.78	44.29	7.04	0.17
PT18	533.35	52.26	231.52	43.95	7.15	0.18
mean	**539.5**	**52.0**	**248.42**	**44.71**	**6.45**	**0.17**
SD	5.07	0.20	23.58	0.96	0.89	0.01
CV %	0.94	0.39	9.49	2.15	13.74	4.36

with:
V_t = volume of test solution at given time t after the start of the experiment
V_{start} = volume of test solution at start of the equilibration (t_{start}, DAT 0)
m_{sol} = mass of test item at a given time t after the start of the experiment
m_{shoots}: = mass of test item in shoots
m_{start} = mass of test item in the test solution at the start of the equilibration (for comparison only)

Table 7.1.4- 4: Plant Uptake Factors and Transpiration Stream Concentration Factors of TFA in wheat

Replicate No.	PUF_{wheat}		$TSCF_{wheat}$	
	t_0-t_1	t_0-t_{end}	t_{start}-t_1	t_{start}-t_{end}
1	0.09	0.17	0.10	0.17
2	0.00	0.17	0.12	0.16
3	0.03	0.19	0.10	0.18
4	0.05	0.18	0.11	0.17
5	0.08	0.19	0.12	0.18
Mean	**0.05**	**0.18**	**0.11**	**0.17**

t_{start} = application and start of equilibration at DAT 0
t_0 = end of the equilibration phase at DAT 2
t_1 = interim sampling at DAT 4
t_{end} = end of study at DAT 8

III. CONCLUSIONS

The good plant health indicated by intense biomass increase and water consumption throughout the testing period demonstrated a reliable and robust test system for the PUP/TSCF determination of the test item. Aerobic conditions were maintained throughout the experimental period. The mean pH values of the test solutions increased within two pH units of the system initially buffered to pH 6.5. As for the results, deviations between the values of individual test replicates were low and the overall radioactive recovery was very good (by > 99%). The test item was translocated into the shoots of wheat plants (92.0 and 94.1% of radioactivity which was taken up was translocated from roots into shoots after 4 and 8 days, respectively). The mean TSCF for TFA amounted to 0.17 over the study period of 8 days. The mean PUF for TFA was determined for wheat plants post equilibration as 0.18 over 6 days.

The study was conducted the year before the "Interim study design to determine uptake of chemicals by plant roots" ECPA/IVA Working Group "Plant uptake factor" (2019) was available. Many criteria that are part of that study design are part of this study that was conducted according on earlier versions: Equilibration of the plants prior to test item application, emphasis on increase of the biomass during the course of the study, number of replicates, control plants without test item, recording of the growth conditions with respect to oxygen, light, climate conditions and the pH value. As carry-over of prior plant uptake designs this study still calculated the plant uptake factor.

3. Assessment and conclusion

Assessment and conclusion by applicant:
The study and its data are considered to be valid and reliable for use in risk assessment.

Assessment and conclusion by RMS:
Outcome and conclusion of the study: RMS should indicate if they agree to the results and conclusions of the APPL.

1. Information on the study

Data Point:	KCA 7.1.4/02
Report Author:	[redacted]
Report Year:	2021
Report Title:	Determination of the plant uptake of [1-14C]BCS-AZ56587 in wheat
Report No:	S19-22291
Document No:	M-762082-01-1
Guideline(s) followed in study:	US EPA OCSPP Test Guideline: N/A OECD Test Guideline: N/A
Deviations from current test guideline:	not applicable
Previous evaluation:	No, not previously submitted
GLP/Officially 589ecognized testing facilities:	Yes, conducted under GLP/Officially 589ecognized testing facilities
Acceptability/Reliability:	Yes

2. Full summary of KCA 7.1.4/02

Executive Summary

The uptake of [1-^{14}C]trifluoroacetate (TFA) was investigated in wheat plants and used to determine the transpiration stream concentration factor (TSCF). The study was conducted in compliance with the "Interim study design to determine uptake of chemicals by plant roots" ECPA/IVA Working Group "Plant uptake factor" (2019).

An application rate of 130.4 µg [1-^{14}C]trifluoroacetate per test system was used, equivalent to mean initial concentration of 130.2 µg/L (equal to 0.96 µM) of nutrient solution.

The test was performed in hydroponic systems consisting of brown glass bottles each containing either approximately 1000 mL test solution (nutrient solution plus test item) or pure nutrient solution. The nutrient solutions were adjusted to a pH value of 6.5 at the start of the experiments. The oxygen content of the nutrient solutions was recorded at the start and the sampling dates. Pre-grown wheat plants (BBCH 10) were equilibrated in nutrient solution for 10 days. Starting at BBCH 12 they were exposed to the test solution for up to 6 days with 3 samplings after 2 (t_2), 4 (t_4) and 6 (t_6) days.

During the study, the wheat plants were incubated in a climatic chamber under controlled temperature, humidity and light conditions (22/18 °C (day/night), 68.8% humidity and a day/night cycle of 16 h/8 h). Wheat plants remained healthy in both treated and untreated test systems throughout the study. Wheat plants grew from BBCH 12 at t_0 (application) to BBCH 23-24 at t_6 (end of study at DAT-6).

Mean mass balances were 99% AR (and ranged from 94 to 101% AR). For t_2 the mean balance was 97%, for t_4 and t_6 100%.

The transpiration stream concentration factor (TSCF) of TFA in wheat plants amounted to 0.18 ± 0.02 at t_2, 0.17 ± 0.01 at t_4 and 0.17 ± 0.02 at the end of the study (t_6) resulting in a mean of 0.17.

Replicate No.	$TSCF_{wheat}$		
	t_0-t_2	t_0-t_4	t_0-t_6
1	(0.53)*	0.17	0.16
2	0.19	0.16	0.16
3	0.19	0.17	0.16
4	0.16	0.20	0.16
5	0.18	0.16	0.15
6	0.16	0.17	0.20
mean	**0.18**	**0.17**	**0.17**
SD	0.02	0.01	0.02
CV [%]	9.16	7.19	11.46
TSCFwheat: mean over all determined values		**0.17**	

t_0= start of uptake at DAT-0
t_2 = interim sampling at DAT-2
t_4 = interim sampling at DAT-4
t_6 = end of study at DAT-6
* Replicate was not included into calculations due to evidence (Nalimov test) for statistical outlier

3. MATERIALS AND METHODS

A. MATERIALS

1. Test Item

[1-^{14}C]BCS-AZ56560, sodium trifluoroacetate (TFA)
Batch number (origin ID): KLM 9173
Specific radioactivity: 4.08 MBq/mg
Radiochemical purity: ≥ 99% (HPLC with radio-detector)

2. Test System

Nutrient solution: Plants were maintained hydroponically in a nutrient solution (50% Hoagland No. 2 basal salt mixture containing Fe(III)-EDTA and 2-(N-morpholino)-ethanesulfonic acid (MES) buffer). The nutrient solution was adjusted to a pH value of 6.7 at the start of the experiments.

Plants: Wheat plants (variety: Thasos) were grown in perlite in a growth chamber until reaching BBCH growth stage 10. Perlite was then removed from the root system by washing with untreated nutrient solution and plants were carefully transferred to the hydroponic system into 350 mL vessels (two wheat plants per vessel). After 10 days at BBCH 12, which is regarded as at the start of the definitive test, the plants were transferred to 1000 mL vessels. The vessels were aerated with a stream of air. The oxygen content of the nutrient solutions was recorded at the start and the sampling dates.

During the study, the plants were incubated in a climatic chamber under controlled temperature, humidity and light conditions (22/18 °C (day/night), 68.8% humidity and a day/night cycle of 16 h/8 h). During the definitive test, the light intensity was measured as > 27.0 kLux.

Wheat plants remained healthy in both treated and untreated test systems throughout the study. Wheat plants grew from BBCH 12 at t_0 (application) to BBCH 23-24 at t_6 (end of study at day 6) with a biomass increase >100% in treated and untreated plants.

B. STUDY DESIGN

1. Experimental Conditions:

The study was conducted in compliance with the latest guidance "Interim study design to determine uptake of chemicals by plant roots" ECPA/IVA Working Group "Plant uptake factor" (2019).

The definitive test was performed in hydroponic systems consisting of brown glass bottles each containing either approximately 1000 mL test solution (nutrient solution plus test item) or pure nutrient solution with two plants per vessel. The root system of the plants was fully submerged. Each bottle was and equipped with aeration and fixation equipment.

Pre-grown wheat plants (BBCH 10) were equilibrated in nutrient solution for 10 days. Starting from BBCH 12 they were exposed to the test solution for a maximum period of 6 days. Therefore, the incubation time considered to calculate the transpiration stream concentration (TSCF) factor was over 6 days.

For the preparation of the application solution radiolabelled (1.04 mg) and non-labelled (1.80 mg) test item was dissolved in 7.30 mL acetonitrile/water (1:1, v:v). The final concentration in the application solution was measured by LSC to be 0.380 mg [1-^{14}C]trifluoroacetate / mL.

An application rate of 130.4 µg [1-^{14}C]trifluoroacetate per test system was used, equivalent to mean initial concentration of 130.2 µg/L (equal to 0.96 µM) of nutrient solution.

Table 7.1.4- 5: Experimental parameters

Parameter		Description
Duration of test		Application: day 0 (t_0); 1st interim sampling: day 2 (t_2); 2nd interim sampling: day 4 (t_4); 3rd harvest / end of the experiment: day 6 (t_6)
Test concentrations	Nominal	135.6 µg/L (1µM)
	Real	130.2 µg/L (0.96 µM) at study start
Number of replications		6 replicate vessels for harvesting on day 2 (t_2), day 4 (t_4), and day 6 (t_6)
Preparation of test medium	Volume used per vessel	1000 mL
	Method of preparation	For 1 litre nutrient solution 50% Hoagland nutrient solution, 6.6 g/L MES hydrate buffer (2-(N-morpholino)-ethanesulfonic acid) and 11.25 mg/L Fe(III)-EDTA was dissolved with tap water and pH was adjusted to 6.5 using potassium hydroxide.
	Target pH	6.5
Test material application	Solvent	acetonitrile/water (1:1; v:v)
	Volume of application solution	358 µL per vessel
	Application method	Pipette
Test apparatus		2000 mL brown glass flasks
Is there any indication of the test item adsorbing to the walls of the test apparatus?		No, the amount of dissolved radioactivity in the vessel with nutrient solution and test item (no plant) stays constant with time.
Experimental conditions	Temperature	22 °C (day), 18 °C (night)
	Aeration	Linear membrane pump equipped with aeration tubes (0.5 cm diameter), humidity of pumped air equal to the humidity in the chamber
	Humidity	average 68.8%
	Lighting	Climatic chamber with day/night cycle (16 h light & 8 h dark)

Other Details	Additional vessels with nutrient solution only to determine pH level, dissolved oxygen and loss of nutrient solution via evaporation. Additional vessel with nutrient solution and test item (no plant) to determine the stability of the test item at test end and to show no indication of the test item adsorbing to the walls of the test system. Additional vessels with nutrient solution and plants to determine the growth of the plant during the experiment. Determination of weight of plants at start of experiment after carefully patting dry the roots.

2. Sampling

Analyses were conducted at 0 (t_0), 2 (t_2), 4 (t_4) and 6 days (t_6) after treatment. At each sampling, radioactivity in the test solution, pH, oxygen saturation and volume of the solutions as well as biomass of the plants (i.e. weight of the plants) was determined.

For the determination of radioactivity in the test solution aliquots of about 2 mL were removed from each treated vessel. Additional samples were taken at the end of the study for the stability of the test item from the vessel treated but without plant. The volume of the aliquots was recorded by weighing the vessels.

Treated plants were processed and analysed 2 (t_2), 4 (t_4) and 6 days (t_6) after treatment. The biomass development of plant roots and shoots in the presence of test item was evaluated when sampled. Control plants grown in systems without test item were processed and analysed on day 0, 2, 4 and 6 (t_0, t_2, t_4 and t_6) to determine biomass development in roots and shoots. 3 replicates (4 replicates at day 0) were taken at each timepoint.

Three vessels containing nutrient solution only (without plants) were used to measure pH, oxygen saturation and evaporation during incubation. One vessel had been inoculated on day 0 (t_0) by dipping the roots of a test plant into the nutrient solution for 10 seconds and was prepared without plants but treated with test item to monitor stability of the test item as well as pH level during incubation. Results for this vessel were not used for the determination of the evaporation.

3. Analytical Procedures

At each sampling date the volume of the test solution in individual test systems was determined by weighing. The plants were removed from the test vessels and any compound associated with the root surface was removed by gently shaking the roots in approximately 200 mL acetonitrile/water 4/1 (v/v) for 5 minutes. Roots were patted dry, plants divided into shoot and roots and the fresh weight biomasses were determined by weighing.

The pH and oxygen saturation of the test solution present in the test vessel were measured, and the radioactivity determined by LSC by analysing in triplicate (3 x 500 µL) from each sampled aliquot. Radioactivity taken up into root tissues as well as radioactivity allocated to the shoots was determined by combustion in an oxygen atmosphere using an oxidizer.

Plant controls were divided into shoot and roots and the fresh weight biomasses were determined by weighing as described above.

The volume of the test solution in the stability control was determined at t_0, t_2, t_4 and t_6 by weighing the test vessels. Aliquots were taken and analysed by LSC. At the end of the study on day 6(t_6), an aliquot was analysed by HPLC with radiodetection to confirm the test item stability.

pH, oxygen saturation and evaporation during incubation (by weighing) were monitored on each sampling day in the three control vessels without plants or test item. pH and oxygen saturation were monitored on each sampling day in the vessels with plants.

Aerobic conditions were maintained throughout the experimental period. The pH-values remained in an adequate range for treated (6.49 to 7.00), for untreated (6.50 to 6.93) and control test systems (6.50 to 6.90) of the system initially buffered to pH 6.5.

The identity of the test item was confirmed in stock solution by HPLC-MS/MS) including accurate mass determination.

II. RESULTS AND DISCUSSION

A. Data

The transpiration stream concentration factor (TSCF) of TFA in wheat plants was calculated from 6 replicates (5 replicates at t_2) and amounted to 0.16 ± 0.01 at t_2, 0.17 ± 0.01 at t_4 and 0.17 ± 0.02 at the end of the study (t_6) resulting in a mean of 0.17.

Table 7.1.4- 6: Transpiration stream concentration factor (TSCF) for TFA

Results TSCF calculation	t_2				
Sample ID	**V sol-0 [L]**	**V sol$_A$-2 [L]**	**m sol-2 [µg]**	**m shoots-2 [µg]**	**TSCF**
391TP14	0.9971	0.9911	125.90	0.3984	0.53*
391TP15	0.9998	0.9913	124.83	0.2016	0.19
391TP16	0.9980	0.9834	130.59	0.3439	0.19
391TP17	1.0009	0.9853	126.37	0.3153	0.16
391TP18	0.9973	0.9795	128.49	0.4184	0.18
391TP19	1.0021	0.9828	125.59	0.3918	0.16
mean	**0.9992**	**0.9856**	**125.29**	**0.3449**	**0.18**
SD	0.0020	0.0048	2.61	0.0799	0.02
CV %	0.20	0.48	2.09	23.15	9.16
Results TSCF calculation	t_4				
Sample ID	**V sol-0 [L]**	**V sol$_A$-4 [L]**	**m sol-4 [µg]**	**m shoots-4 [µg]**	**TSCF**
391TP20	0.9968	0.9665	131.0664	1.1829	0.17
391TP21	0.9982	0.9683	131.7057	0.6470	0.16
391TP22	0.9969	0.9524	128.9708	1.0068	0.17
391TP23	0.9994	0.9752	134.1085	0.6396	0.20
391TP24	1.0000	0.9484	129.3733	1.1350	0.16
391TP25	1.0009	0.9583	130.9065	0.9787	0.17
mean	**0.9987**	**0.9582**	**131.0222**	**0.9325**	**0.17**
SD	0.0017	0.0114	1.8405	0.2372	0.01
CV %	0.17	1.19	1.40	25.43	7.19
Results TSCF calculation	t_6				
Sample ID	**V sol-0 [L]**	**V sol$_A$-6 [L]**	**m sol-6 [µg]**	**m shoots-6 [µg]**	**TSCF**
391TP26	0.9963	0.9155	127.9601	1.7914	0.16
391TP27	0.9989	0.9062	129.3160	2.0390	0.16
391TP28	0.9975	0.9342	131.2903	1.3735	0.16
391TP29	1.0001	0.9196	126.8398	1.7352	0.16
391TP30	0.9962	0.8856	129.2318	2.2295	0.15
391TP31	1.0004	0.9387	131.1206	1.7019	0.20
mean	**0.9982**	**0.9166**	**129.2921**	**1.8117**	**0.17**
SD	0.0018	0.0194	1.7394	0.2955	0.02
CV %	0.18	2.11	1.35	16.31	11.46

V sol-0: volume of test solution on day 0 [L]
V sol$_A$-x: volume of test solution on day 2 (V sol$_A$-2), day 4 (V sol$_A$-4) and day 6 (V sol$_A$-6), corrected due to evaporation and aliquot volume [L]
m sol- : mass of test item in solution, at the end of the equilibration phase on day 2 (m sol-2), day 4 (m sol-4) or at the end of the experiment on day 6 (m sol-6) [µg]
m shoots- : mass of test item in the shoot, at the end of the equilibration phase on day 2 (m shoots-2), day 4 (m shoots-4) or at the end of the experiment on day 6 (m shoots-6) [µg]
*Replicate was not included into calculations due to evidence (Nalimov test) for statistical outlier

Good plant health, as shown by the intense biomass increase and water consumption during the study, demonstrated the test system provided a reliable and robust method to calculate TSCF for TFA.

B. Mass Balance

Mean mass balances were 99% AR (and ranged from 94 to 101% AR). For t_2 the mean balance was

97%, for t_4 and t_6 100%.

There were no signs for losses of radioactivity from the test systems or during sample processing. No adsorption of TFA to the walls of the test systems was observed throughout the test.

C. Translocation of the test item

During the incubation period 15.3 to 81.6 mL of the test solution was taken up by the plants. About 25.0 mL of the test solutions were lost due to evaporation after 6 days.

The mean initial concentrations on day 0 (t_0) of [1-^{14}C]trifluoroacetate in the test solutions was 130.2 µg/L (0.96 µM), decreasing to 129.1 µg/L (0.93 µM) at t_2 (first interim sampling at day 2) and slightly increasing to 137.0 µg/L (1.01 µM) at t_4 (second interim sampling at day 4) and 143.1 µg/L (1.05 µM) at t_6 (end of study at day 6). Root wash desorbed 1.2 µg of the test item from the roots at t_2, 2.3 µg at t_4 and 2.3 µg at t_6. The separate analysis of roots and shoots showed that at t_2 > 75.0%, at t_4 87.5% and at t_6 88.9% of radioactivity taken up by the plants was translocated from roots into shoots.

No degradation of TFA was observed at the end of the study in test solution from the stability control (without plants).

III. CONCLUSIONS

TFA was translocated into the shoots of wheat plants, with > 75, 87.5 and 88.9% of the radioactivity taken up by the plants translocated from roots into shoots after 2, 4 and 6 days, respectively. The TSCF for TFA amounted to 0.18 ± 0.02 at day 2 (t_2), 0.17 ± 0.01 at day 4 (t_4) and 0.17 ± 0.02 at the end of the study on day 6 (t_6) resulting in a mean of 0.17.

3. Assessment and conclusion

Assessment and conclusion by applicant: The study is considered valid to assess the TSCF of TFA in plants.

Assessment and conclusion by RMS: Outcome and conclusion of the study: RMS should indicate if they agree to the results and conclusions of the APPL.

1. Information on the study

Data Point:	KCA 7.1.4/03
Report Author:	[redacted]
Report Year:	2018
Report Title:	Translocation and uptake of [1-14C]-BCS-AZ56567 in soil, percolate and winter wheat plants
Report No:	M99904993-2
Document No:	M-612246-01-1
Guideline(s) followed in study:	US EPA OCSPP Test Guideline: N/A OECD Test Guideline: N/A
Deviations from current test guideline:	not applicable
Previous evaluation:	No, submitted, not evaluated not applicable (evaluation ongoing)
GLP/Officially 596ecognized testing facilities:	Yes, conducted under GLP/Officially 596ecognized testing facilities
Acceptability/Reliability:	Yes

2. Full summary of KCA 7.1.4/03

Executive Summary

The translocation and uptake of [4-^{14}C]trifluoroacetate (TFA) was investigated in soil, percolate and winter wheat plants for a time period of 228 days after application onto soil. The study was conducted in a roofed vegetation hall under outdoor conditions in a 1 m² planting container.

The test item was applied onto bare soil between the wheat plants when the plants had reached the growth stage BBCH 12-14 45 days after sowing. A study application rate of 62 g test item/ha was applied.

Used soil Monheim 4 was classified as a sandy loam soil according to USDA classification.

Soil	Source	Texture (USDA)	pH [1]	OC [%]
Monheim 4	North Rhine-Westphalia, Germany	Sandy loam	6.6	1.3

[1] pH value was derived from aqueous 0.1 M CaCl₂ suspension (1:2)

For wheat plants five sampling intervals were distributed over a period of 228 days after application. At each sampling interval approximately 10 randomly selected plants were removed from soil and processed 38, 92, 150, 169 and 228 days after treatment (DAT), corresponding to BBCH growth stages of 21-22, 24-25, 32-33, 59 and 89-92. After the final harvest 10 soil cores were randomly taken to a depth of 47 cm using a boring rod (Ø 20 mm) and separated into soil layers of 0-10, 10-30 and 30-47 cm. Aliquots of percolate were analyzed whenever 5 L of percolate were collected over the whole study period.

Wheat plants appeared healthy over the total study duration. The plants grew from BBCH 12-14 at day of application to BBCH 89-92 at the last sampling interval. The total recovered radioactivity (material balance) was 103.4% AR. Radioactive residues in total plants increased from DAT 38 to DAT 228 (study end) from 4.3 to 52.1% AR. Radioactivity in shoots increased from 3.5% AR at DAT 38 to 52.1% AR at DAT 228, whereas radioactivity in roots decreased from DAT 38 to DAT 228 from 0.9 to 0.1% AR. From DAT 92 onwards ≥ 98.6% of the radioactivity taken up by wheat plants had translocated from roots to shoots.

Radioactive residues in total soil amounted to 17.3% AR at study end (DAT 228). The distribution of radioactivity in the different soil layers was 4.1, 6.2 and 7.1% AR for soil layers 0-10, 10-30 and 30 – 47 cm, respectively.
The total radioactive residues in percolate of the planting container amounted to 33.9% AR at study end (DAT 228). Radioactive residues in the collected single percolate fractions increased from 0.3% AR at DAT 37 to 5.0% AR at DAT 95 and decreased to 0.6% AR towards study end (DAT 228). In total 58.1 L percolate were collected.

3. MATERIALS AND METHODS

A. MATERIALS

1. Test Item

[1-^{14}C]BCS-AZ56567, sodium trifluoroacetate (TFA)

Sample ID:	KML 9173
Specific Activity:	4.08 MBq/mg
Radiochemical purity:	≥98% (HPLC with radio-detector)

2. Test Soil

The uptake and translocation behaviour of TFA was investigated after application to a European soil. Detailed soil characteristics are presented in the table below.

Table 7.1.4- 7: Physico-chemical properties of test soil

Parameter	Soil
Soil designation	Monheim 4
Country	Germany
Textural Classification (USDA)	Sandy loam
Sand [50 – 2000 µm] (%)	74
Silt [2 – 50 µm] (%)	18
Clay [< 2 µm] (%)	8
pH (soil/H_2O 1/1)	7.0
pH (soil/0.01M $CaCl_2$ ½)	6.6
pH (saturated paste)	6.9
pH (soil/1 N KCl 1/1)	6.5
Organic carbon (%)	1.3
Organic matter (%)[1]	2.2
Cation exchange capacity (meq/100 g)	7.6
Water holding capacity (WHC)	
at 1 cm of water (%)[2]	38.9
at 1/10 bar (pF 2.0) (%)	16.9
Bulk density (disturbed) (g/cm^3)	1.24

[1] % organic matter = % organic carbon x 1.724
[2] The maximum water holding capacity is not reported.

3. Test Plants

The study was carried out using winter wheat plants (Triticum aestivum cv. Kerubino).

B. STUDY DESIGN

1. Experimental Conditions

The study design consisted of 1 m^2 planting container filled with a 47 cm layer of Monheim 4 soil underlaid with a gravel layer of 10 cm. The container was connected to 5 L plastic bottles for collecting the percolate. Prior to sowing, the container was kept outdoors and irrigated by rainfall. Shortly before sowing with winter wheat plants, the soil was cultivated to a depth of approximately 15 cm depth according to good agricultural practice. Wheat plants were sown in 10 rows at a seed density of 500 seeds/m^2. After sowing, the test system was moved to a roofed vegetation hall under outdoor conditions to allow natural temperature and light conditions for growth. The climatic conditions were recorded. Irrigation was performed prior to application with 1 L every three days. Post application, irrigation was performed shortly after rainfall events considering measured rainfall amounts. Daily temperature, humidity and irrigation data were recorded. Fertilisation and plant protection products were applied throughout the test period, none of which are chemically related to TFA.

The water balance was monitored by weighing the container after irrigation and after each plant sampling.

Application solution was prepared by dissolving [1-^{14}C]trifluoroacetate (TFA) in 5 mL water, resulting in a nominal concentration of 1.7 mg/mL. An aliquot of 3.79 mL of this solution was applied to 50 g quartz sand. The quartz sand was mixed with 1 kg air dried Monheim 4 soil and homogenised for 30 minutes in a tumble mixer. This treated soil was then evenly distributed between the plants within the container, giving a nominal application rate of 6.3 mg/m^2.

2. Sampling

For confirmation of application rate and homogeneity, an aliquot of the treated soil was immediately sampled for analysis.

Approximately 10 individual randomly selected plants were removed from soil for analysis at 38, 92, 150, 169 and 228 days after treatment (DAT), corresponding to BBCH growth stages of 21-22, 24-25, 32-33, 59 and 89-92. Remaining soil was washed off using water and the roots were patted dry. Plant material was separated into roots and shoots and homogenised in liquid nitrogen. Prior to analysis it was stored for a maximum of 25 days at ambient temperature.

At DAT 228, 10 randomly distributed soil cores were taken to a depth of 47 cm using a boring rod (diameter 20 mm). To facilitate sampling the soil was irrigated for two days with a total of 20 L water prior to taking the soil cores. Soil cores were separated into 0-10, 10-30 and 30-47 cm horizons, air dried, homogenised and stored at ambient temperature in the laboratory for four days.

Samples of percolate were analysed at DAT 37, 39, 63, 73, 80, 85, 93, 95, 98, 101, 140 and 228. Sampling was performed whenever 5 L of percolate had been collected, where upon the 5 L collection vessel was removed and replaced with an empty vessel. Aliquots were then taken from the full vessel for immediate analysis.

3. Analytical Procedures

Plant material was separated into roots and shoots and fresh weights of the plant material were determined gravimetrically. Roots and shoots were homogenised with liquid nitrogen. Radioactivity in roots and shoots was determined separately by combustion and subsequent liquid scintillation counting (LSC).

Aliquots of the air-dried and homogenised soil were analysed by combustion and subsequent measurements by LSC. Radioactivity in percolate was analysed directly by LSC.

Identity of TFA was confirmed using reverse-phase HPLC/MS using a Nucleodur Gravity C18 column, gradient elution of water acidified with 0.1% formic acid/acetonitrile acidified with 0.1% formic acid (starting gradient 95/5, v/v). Mass spectrometry was performed with electrospray ionization mass spectrometry in single stage mode (ESI-MS).

II. RESULTS AND DISCUSSION

A. CONFIRMATION APPLICATION RATE AND HOMOGENITY

Homogeneity of application was determined by combustion LSC of treated soil. The mean of 6.17 mg/g was recovered and was set to 100% applied radioactivity (AR).

B. MATERIAL BALANCE

The total recovered radioactivity (material balance) was 103.4% AR at study end. The complete material balances found at the end of the study demonstrated that there was no significant loss of radioactivity from the test system or during sample processing.

C. DISTRIBUTION OF RADIOACTIVITY IN PLANTS

Radioactive residues in total plants increased from DAT 38 to DAT 228 (study end) from 4.3 to 52.1% AR. Radioactivity in shoots increased from 3.5% AR at DAT 38 to 52.1% AR at DAT 228, whereas radioactivity in roots decreased from DAT 38 to DAT 228 from 0.9 to 0.1% AR. From DAT 92 onwards ≥ 98.6% of the radioactivity taken up by wheat plants had translocated from roots to shoots.

D. RESIDUES IN SOIL

Radioactive residues in total soil amounted to 17.3% AR at study end (DAT 228). The distribution of radioactivity in the different soil layers was 4.1, 6.2 and 7.1% AR for soil layers 0-10, 10-30 and 30 – 47 cm, respectively.

E. PERCOLATE

The total radioactive residues in percolate of the planting container amounted to 33.9% AR at study end (DAT 228). Radioactive residues in the collected single percolate fractions increased from 0.3% AR at DAT 37 to 5.0% AR at DAT 95 and decreased to 0.6% AR towards study end (DAT 228). In total 58.1 L percolate were collected.

Table 7.1.4- 8: Distribution of radioactivity in percolate (% AR)

DAT	Volume (mL)	LSC aliquot		Total Recovery	
		(mL)	(dpm)	(dpm)	(% AR)
37	4989.2	10	9277	4628481	0.3
39	5138.8	5	5951	6116200	0.4
63	5202.0	5	17191	17885516	1.2
73	5064.0	5	29668	30047750	2.0
80	5224.1	5	47023	49130571	3.3
85	5251.4	5	52557	54779110	3.6
93	5295.5	5	58224	61665038	4.1
95	5208.4	5	73105	76152016	5.0
98	4764.7	5	76484	72838773	4.8
101	5064.2	5	76091	77068008	5.1
140	5055.4	5	53180	53769234	3.6
228	1863.2	5	22972	8560286	0.6
Total	**58077.9**	**-**	**-**	**512640985**	**33.9**

DAT: Days After Treatment; dpm: disintegrations per minute

F. IRRIGATION

The irrigation volume was recorded a about 120 individual datapoints. The container was irrigated with a cumulative total of 477.5 L.

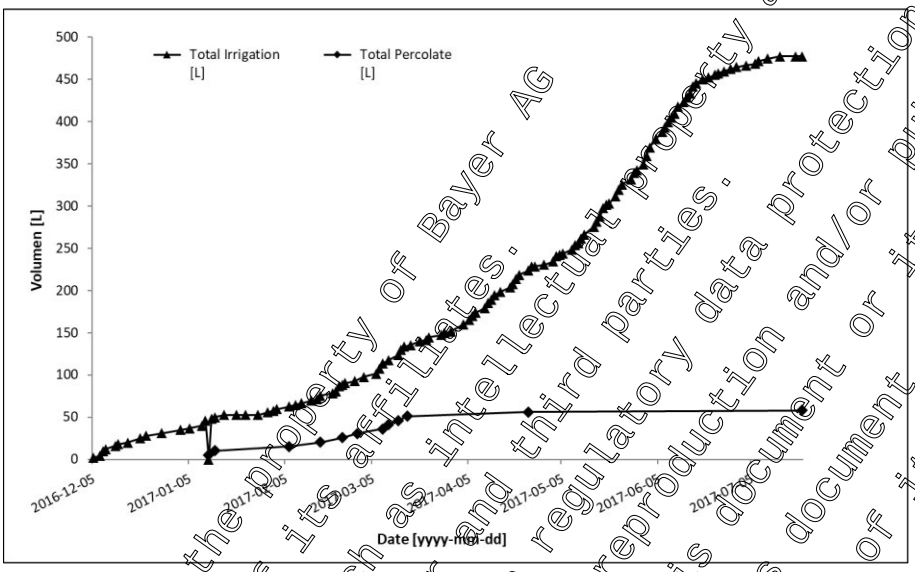


Figure 7.1.4- 1: Irrigation and percolate

Table 7.1.4- 9: Summary of radioactivity in plants, percolate and soil (values given in % AR)

Compound		DAT 37	38	39	63	73	80	85	92	93	95	98	101	140	150	169	228
Plants	Shoots	n.a.	3.5	n.a.	n.a.	n.a.	n.a.	n.a.	27.0	n.a.	n.a.	n.a.	n.a.	n.a.	21.6	48.9	52.1
	Roots	n.a.	0.9	n.a.	n.a.	n.a.	n.a.	n.a.	0.4	n.a.	n.a.	n.a.	n.a.	n.a.	0.1	0.2	0.0
	Total	n.a.	4.3	n.a.	n.a.	n.a.	n.a.	n.a.	27.4	n.a.	n.a.	n.a.	n.a.	n.a.	21.7	49.1	52.1
Percolate	Single fractions	0.3	n.a.	0.4	1.3	2.0	3.3	3.6	n.a.	4.1	5.0	4.8	5.1	3.6	n.a.	n.a.	0.6
	Sum of fractions	0.3	n.a.	0.7	1.9	3.9	7.1	10.8	n.a.	14.8	19.9	24.7	29.8	33.4	n.a.	n.a.	33.9
Soil	0-10 cm	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	4.1
	10-30 cm	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	6.2
	30-47 cm	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	7.1
Material Balance [1]		-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	**103.4**

n.a.: not analysed

[1] The material balance was established at study end (DAT 228) when the residues in soil were determined.

III. CONCLUSIONS

At study end, 52.1% of applied radioactivity was taken up into plants. The test item was translocated into the shoots of wheat plants (from DAT 92 onwards, ≥98.6% of radioactivity that was taken up had translocated). Total radioactive residues in soil and percolate amounted to 17.3% AR and 33.9% AR, respectively.

3. Assessment and conclusion

Assessment and conclusion by applicant: The study and its data are considered to be valid and reliable for use in risk assessment

Assessment and conclusion by RMS: Outcome and conclusion of the study: RMS should indicate if they agree to the results and conclusions of the APPL.

1. Information on the study

Data Point:	KCA 7.1.4/04
Report Author:	[redacted]
Report Year:	2018
Report Title:	Determination of the TSCF for the plant uptake of trifluoroacetic acid (TFA) in wheat plants based on inverse modelling with PEST/PEARL - Tier 4. Compound/crop specific uptake under dynamic outdoor conditions during a whole vegetation period
Report No:	EnSa-17-0698
Document No:	M-613672-01-1
Guideline(s) followed in study:	none
Deviations from current test guideline:	not applicable
Previous evaluation:	No, submitted, not evaluated not applicable (evaluation ongoing)
GLP/Officially recognised testing facilities:	No, not conducted under GLP/Officially recognised testing facilities
Acceptability/Reliability:	Yes

2. Full summary of KCA 7.1.4/04

Executive Summary

The plant uptake and translocation of [1-^{14}C]trifluoroacetate (TFA) was investigated in a container outdoor study with 1 m^2 surface in a roofed vegetation hall for a time period of 228 days, cropped with winter wheat. A detailed description of the trial can be found under KCA 7.1.4/03 (M-612246-01-1). The test substance was applied in at a nominal rate of 62 g/ha.

The dynamics of the substance mass partition was measured in the plants and in the water percolating through the outlet of the container. At termination of the trial, the mass in the remaining soil was quantified. A mass balance of 101.2 % of the applied rate was achieved. At the end of the study period, 52.1 % of the active substance was found in the whole plants (99 % of it in the shoots).

Modelling of the translocation and uptake of TFA was conducted with FOCUS PEARL 4.4.4 considering root uptake processes as routinely applied for standard FOCUS modelling (FOCUS 2009, 2014). The circumstances of the trial in terms of meteorological conditions, soil properties, crop development, and irrigation schedule were implemented as adequate as possible. Based on the observed mass/water fluxes and plant uptake dynamics the corresponding model parameters were estimated.

The observations in the trial were simulated in a realistic yet conservative manner in simulations when compared to measured experimental values (i.e. the dynamics of plant uptake and water fluxes were

close the measured values). The inverse modelling simulation using a coupling of PEARL and PEST (Doherty 2002) resulted to robust parameter estimation of the transpiration stream concentration factor (TSCF) as $TSCF_{wheat}$ = 0.31 ± 0.11 with a relative standard error (RSE) <0.4.

The results demonstrate that TFA is taken up by plant roots under dynamic outdoor conditions. The inverse modelling technique allows a robust estimation of the TSCF as effective value for a whole growing season (e.g. 228 days) with a calculated RSE <0.4. The result suggests that Briggs based estimation of TSCF tend to be over conservative in case of small polar substances like TFA. Results also indicate that observed relationships of the plant uptake by Briggs *et al.* (1982) and Dettenmaier *et al.* (2009) may not be limited to neutral compounds but are also applicable for ionisable organic chemicals. Uptake experiments under cropped outdoor conditions may be suitable as higher tier to derive a refined TSCF (e.g. as Tier-4).

I. MATERIAL AND METHODS

The plant uptake and translocation of [1-^{14}C]trifluoroacetate (TFA) was investigated in a container outdoor study with 1 m^2 surface in a roofed vegetation hall for a time period of 228 days, cropped with winter wheat. The test substance was applied at a rate of 62 g/ha.

The dynamics of the substance mass partition was measured in the plants and in the water percolating through the outlet of the container. At termination of the trial, the mass in the remaining soil was quantified. A mass balance of 103.4 % of the applied rate was achieved. At the end of the study period, 52.2 % of the applied radioactivity was taken up by the plants. 52.1% were found in the shoots, 0.05% in the roots.

Additionally, to the container with applied radio-labelled test substance, two separate non-GLP containers of the same dimensions were run without substance application but same cereal growing conditions. These additional containers were used to monitor plant development, especially the spring point (i.e. the time when the winter wheat plants start rapid growth) and scaling the Haude-derived evapotranspiration via PEARL factor *FacEvp* with the goal to meet the actual observed cumulative water fluxes.

Crop definition
Modelling of the translocation and uptake of TFA was conducted with FOCUS PEARL 4.4.4 considering root uptake processes as routinely applied for standard FOCUS modelling (FOCUS 2009, 2014). The absolute values for the leaf area index (LAI), the crop coefficient (kc-factor), and the relation between spring point and maximum LAI were left unchanged. Furthermore, the dynamics of the rooting density was not modified. Standard FOCUS assumption of constant root density up to rooting depth was assumed.

Table 7.1.4- 10: Crop definition, adapted from FOCUS to meet trial conditions

Stage	Date (day/month)	Julian day	Day after emergence	Relative crop time	Leaf Area Index	kc[1]	Rooting depth (m)	BBCH[2]
Sowing	21/10	294	-20					0
Emergence	10/11	314	0	0	0	1.05	0	9
Spring point	25/02	56	107	0.423	0.1	1.05	0.20	
Max. LAI	24/03	83	134	0.530	3.8	1.05	0.47	40
Max. LAI	25/03	84	135	0.534	3.8	1.1	0.47	40
Max. LAI	23/05	143	194	0.767	3.8	1.1	0.47	
Senescence	24/05	144	195	0.771	3.8	0.7	0.47	60
Harvest	21/07	202	253	1.00	3.8	0.7	0.47	90

[1] Crop evaporation coefficient
[2] Derived from observation in the trials, not part of the modelling process

Modelling domain and soil definition
The modelling domain was defined with a length of 47 cm as given by the dimension of the soil container. The soil texture was: 74 % sand, 18 % silt, and 8 % clay, with an organic matter content of 2.2 %. The hydrological properties were parameterized using the van-Genuchten/Mualem formulation with the Rosetta continuous pedotransfer function. Initial estimates of the hydrologic parameters assume undisturbed soils.

For a better representation the observed leached mass at the bottom of the domain, the initial estimates of θ_{sat} and the dispersion length were adjusted from the originally estimated 0.41 to 0.25 and the value for the dispersion length was changed from the FOCUS default of 5 cm to 10 cm. In this manner, some presence of immobile water fractions may have been accounted for. The lower boundary condition "lysimeter" or "free drainage" was chosen.

Meteorological conditions and evaporation
The outdoor container study was conducted in a roofed vegetation hall which to large extend open to the surrounding climatic conditions. The meteorological conditions in terms of minimum and maximum temperature and relative humidity were monitored during the study period and used in the PEARL simulations. The container setup was initially irrigated, and after substance application, daily irrigation was conducted following the natural outside rainfall patterns.

In a warm-up period, the measurements from the weather station "Hoefchen" (from Jan 2016 to Oct 2016) and the standard FOCUS scenario Hamburg was used (4 years: 2012 – 2016), respectively. The warm-up period was considered in order to establish in the PEARL evaluation a meaningful soil condition at time point of application.

The potential evapotranspiration was calculated using the formulation of Haude (as described in Klein 2012), applying the measurements of temperature and relative humidity.

Modelling procedure
The preparation of the inverse modelling procedure:
- Forward simulations including all input parameters of the trial (soil, weather, crop definition etc.).
- Simulation period is from day of application (5th December) until harvest of wheat plants at the end of the study (DAT 228).
- Additional warm-up period of 4 years considered.
- PEARL evapotranspiration adjustment factor (*FacEvp*) adjusted manually to 1.095 to meet the mean volume of water leached at the bottom of two parallel containers, not spiked with radio-labelled TFA (i.e. 53 mm).

- In the PEST setup (.pst file), the five measured up-taken masses were used in the objective function, weighted by the days after treatment, i.e. 38, 92, 150, 169, and 228. Hence, the fact that the last sampling point is an "integral" of the preceding is implicitly taken into account.
- The TSCF was implemented with the best estimator of the PEST calculated standard 95 % confidence interval.

In order to characterize the uncertainty of the estimated TSCF the relative standard error (RSE) was considered. The relative standard error (RSE) should be calculated for each optimised parameter. The RSE is simply calculated according to the equation below. A reliable parameter estimation can be assumed in case RSE is <0.4.

$$RSE = \frac{95\%confidence\,interval}{4 * \upsilon}$$

Where ν is the fitted parameter value. The confidence interval (upper limit minus lower limit) is divided by a factor 4 to calculate the estimated standard deviation (or standard error) of the parameter fit. This is because the width of the 95 % confidence interval equals 4 times the standard deviation based on a normal distribution (the fitted value plus or minus 2 × the standard deviation). The lower and upper boundary of the PEST calculated 95 % confidence interval was employed for the RSE calculation.

II. RESULTS AND DISCUSSION

Water Balance

Initial estimation with the Haude equation (applying the measurements of temperature and relative humidity) resulted to a slight under estimation of the potential evapotranspiration. Thus, the dynamic water fluxes of the two parallel non-GLP container are employed to calibrate the Haude estimation to reflect the specific experimental circumstances.

The cumulated water percolated through the bottom of the containers is shown in the figure below.

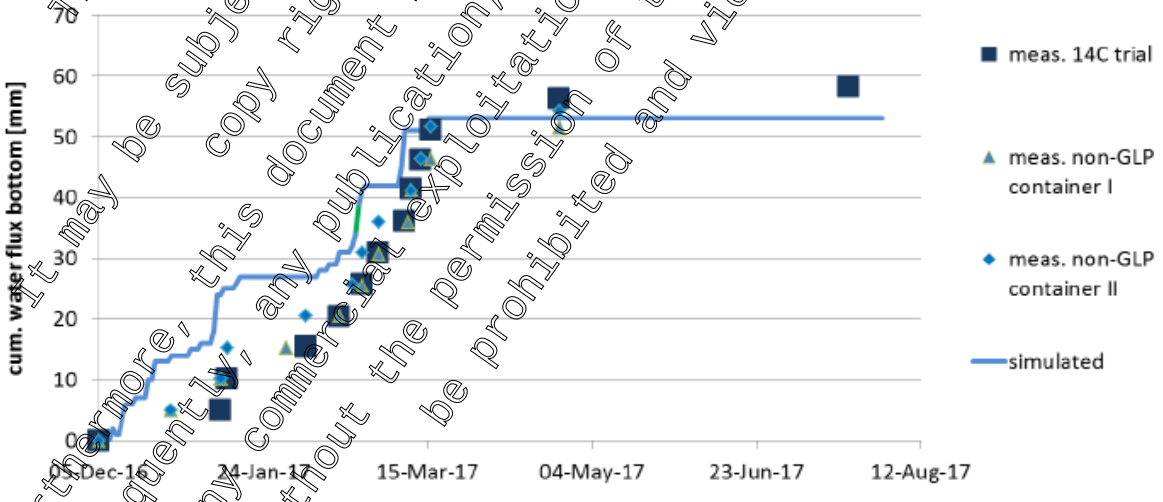


Figure 7.1.4- 2: Cumulative water fluxes at the bottom of the plant containers: measurements (markers) vs. simulation (line). Three container setups were run: one with ^{14}C-labelled TFA application and two without ("non-GLP containers"). The simulation was adjusted to meet the mean outflow volume of the two non-GLP containers, i.e. 53 mm.

Mass flux at the bottom of the soil core

The simulation with a value of θ_{sat} of 0.25 and a dispersion length of 10 cm showed a considerably better representation of the measurements than the one with θ_{sat} = 0.41 and dispersion length = 5 cm. The lower value for θ_{sat} aims to intrinsically take a fraction of immobile water into account, while the increased value for the dispersion length aims to lead to an accelerated breakthrough of the substance.

Additional simulations confirmed that the adjustment of the two hydrological parameters had no significant influence in the simulated water balance.

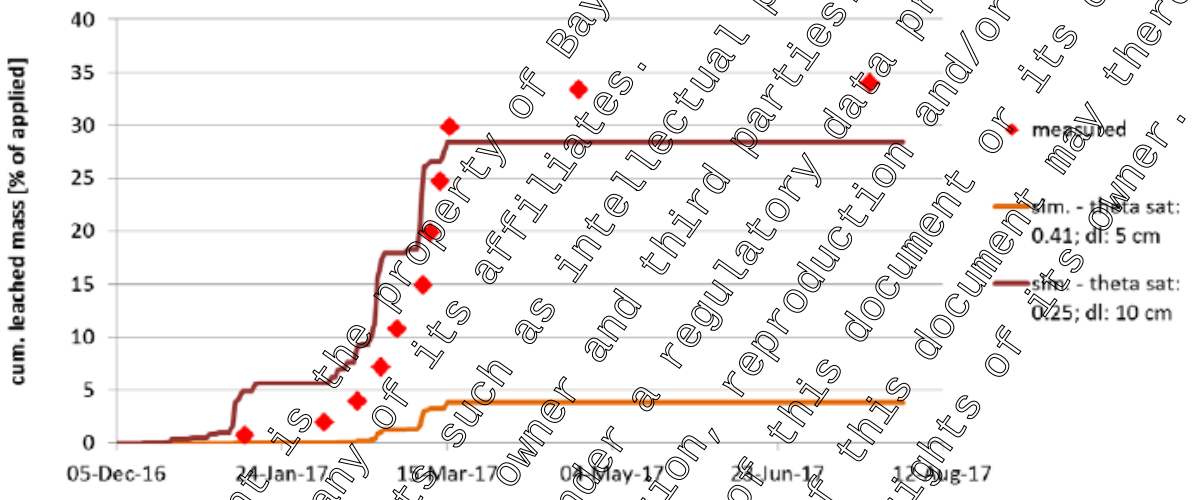


Figure 7.1.4- 3: Cumulative substance amount measured at the outlet of the container – measurements (markers) and the two alternative simulations (lines). To meet the observed measurements, the estimated value for the van-Genuchten- Mualem parameter θ_{sat} of 0.41 was manually modified to 0.25, and the "standard" FOCUS parameter value for the dispersion length of 5 cm was altered to 10 cm.

Inverse estimate of TSCF

The definite inverse parameter estimation of the TSCF was started after establishment of good agreement between simulated and measured water balance and simulated and measured mass fluxes during the experiment. The dynamics of measured and simulated plant uptake after inverse TSCF optimization is shown below.

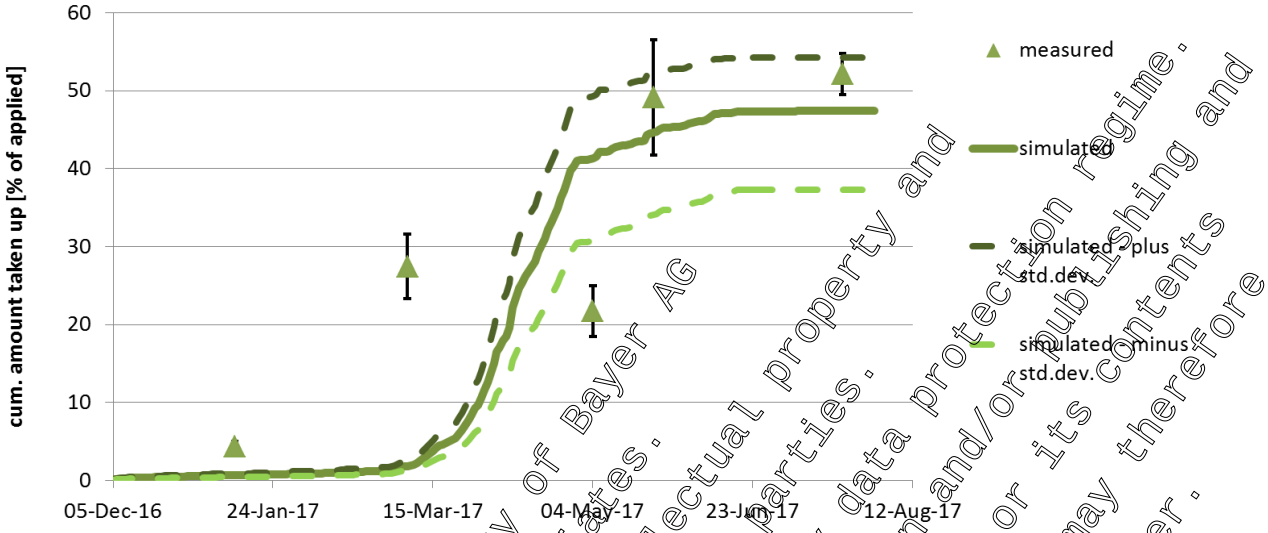


Figure 7.1.4- 4: Masses taken up by the winter wheat plants: measurements (markers, including error indicators) vs. inverse simulations (lines). Besides a simulation using the best estimator for the TSCF, simulations applying plus/minus one standard deviation are drawn.

The error indicators in the figure above mark the estimated 15 % experimental uncertainty in the first four samplings and a smaller 5 % uncertainty for the last sampling point, indicating the cumulative character of the last measurement.

The inverse parameter estimation of the transpiration stream concentration factor (TSCF) resulted to an estimated TSCF of 0.31 (see below). The relative standard error (RSE) of the estimation procedure was calculated as 0.36 based on the width of the PEST calculated 95 % confidence interval (giving a range of 0.527-0.089). This leads to standard error for the determined TSCF of 0.11.

In terms of cumulative masses taken up, the simulated values were found to be below the measurements representing an underestimation of the true uptake. Hence, the modelling remains conservative in terms of dynamics during the whole wheat growing season.

III. CONCLUSIONS

The observations in the trial were simulated in a realistic yet conservative manner in simulations when compared to measured experimental values (i.e. the dynamics of plant uptake and water fluxes were close the measured values). The inverse modelling simulation using a coupling of PEARL and PEST (Doherty 2002) resulted to robust parameter estimation of the transpiration stream concentration factor (TSCF) with a relative standard error (RSE) <0.4. The definite inverse parameter estimation of the TSCF was started after establishment of good agreement between simulated and measured water balance and simulated and measured mass fluxes during the experiment.

The results demonstrate that TFA is taken up by plant roots under dynamic outdoor conditions. Inverse modelling technique allows a robust estimation of the TSCF as effective value for a whole growing season (e.g. 228 days) with a calculated RSE <0.4. Briggs based estimation of TSCF tend to be over conservative in case of small polar substances like TFA. Results also indicate that observed relationships by Briggs *et al.* (1982) and Dettenmaier *et al.* (2009) may be not limited to neutral compounds but are also applicable for ionisable organic chemicals. Uptake experiments under cropped outdoor conditions may be suitable as higher tier to derive a refined TSCF (e.g. as Tier-4).

3. Assessment and conclusion

Assessment and conclusion by applicant:
The study and its data are considered to be valid and reliable for use in risk assessment

Assessment and conclusion by RMS:
Outcome and conclusion of the study: RMS should indicate if they agree to the results and conclusions of the APPL.

A new container study is ongoing to determined the TSCF for TFA. After its finalization, the corresponding study report plus relevant new kinetic evaluation will be submitted with the planned dossier update at the latest by end of February 2022.

CA 7.1.4.1 Column leaching studies

CA 7.1.4.1.1 Column leaching of the active substance

No column leaching studies with fluopyram have been performed. Studies are not required under Commission Regulation (EU) No 283/2013 in accordance with Regulation (EC) No 1107/2009 since 17 Kfoc values > 25 mL/g were obtained in the course of several adsorption studies.

CA 7.1.4.1.2 Column leaching of metabolites, breakdown and reaction products

No column leaching studies with fluopyram-7-OH have been performed. Studies are not required under Commission Regulation (EU) No 283/2013 in accordance with Regulation (EC) No 1107/2009 since four K_{foc} values > 25 mL/g were obtained in the course of an adsorption study.

A soil column leaching study with TFA was performed and is summarised below.

1. Information on the study

Data Point:	KCA 7.1.4.1.2/01
Report Author:	[redacted]
Report Year:	2014
Report Title:	[1-14C]trifluoroacetate: Soil column leaching
Report No:	EnSa-14-0050
Document No:	M-477737-01-1
Guideline(s) followed in study:	OECD Test Guideline No. 312; US EPA OCSPP Test Guideline No. 835.1240
Deviations from current test guideline:	Current Guideline: OECD 312 (2004) Interaction of the test item with the column material was not investigated, but as the mass balance is good and nearly no retention of the test item was observed this deviation can be regarded as negligible.
Previous evaluation:	yes, evaluated and accepted RAR flurtamone (2016)
GLP/Officially recognised testing facilities:	Yes, conducted under GLP/Officially recognised testing facilities
Acceptability/Reliability:	Yes

2. Full summary of KCA 7.1.4.1.2/01

Executive Summary

The adsorption behaviour of [1-^{14}C]trifluoroacetate was studied in four different soils in the dark in the laboratory at 20.1°C using two different soil column leaching experiments. Four different soils were used for the study:

Soil ID	Source	Texture (USDA)	pH[1]	OC [%]
AX	Monheim, Germany	loamy sand	6.2	1.8
DD	Blankenheim, Germany	loam	7.4	5.2
HH	Burscheid, Germany	silt loam	6.5	1.6
WW	Monheim, Germany	sandy loam	5.3	1.9

[1] measured in $CaCl_2$ solution

[1-^{14}C]trifluoroacetate (TFA) was applied at a nominal application rate of 11.0 µg per soil column. Additional soil columns were treated with [triazine-UL-^{14}C]atrazine used as reference item to check the test conditions with a moderately mobile reference item. Tritiated water ($^{3}H_2O$) was added as a tracer to the application solutions of the test item and the reference item to check the hydraulic conditions during the study.

Two different test designs were used for this soil column leaching study. Test design A reflected the test item distribution in the leachate as well as in the soil column after 200 mm artificial rain over a period of approx. 48 hours, whereas test design B delivered detailed information of the test item distribution only in the leachate by using a larger irrigation volume.

The test and reference items were sufficiently stable throughout the study.

Material balances for the test item were between 99.4 to 103.8% of the applied radioactivity [% AR] in all soil columns using test design A and between 93.2 to 105.2% AR using test design B. Material balances for the tracer and the reference item were between 89.1 to 105.5% AR and between 96.8 to 104.3% AR, respectively, in all soil columns and both test designs.

Using test design A, 62.0 to 97.0% AR of the test item were found in the leachate of the single soil columns. The maximum amount of test item was found in the fourth to fifth leachate fraction of each

soil column. 58.2 to 90.3% AR of the tracer were found in the leachate of the respective soil columns. The maximum amount of tracer was found in the fourth to fifth leachate fraction, i.e. after elution of approximately one saturation volume, demonstrating suitable hydrodynamic properties of the soil columns. The residual amounts of test item and tracer were almost equally distributed in the corresponding soil columns.

The maximum amount of reference item was found in the first segment of each soil column using test design A, but translocation of the reference item in deeper soil column segments could also be observed, demonstrating the suitable hydrodynamic properties of the soil columns. Only minor amounts of the reference item (< 1% AR) were found in the corresponding leachates of the single soil columns, whereas 45.1 to 93.9% AR of the tracer where found in the leachates.

Using test design B the applied radioactivity of test item and tracer was completely recovered in the leachates of the respective soil columns. The soil segments of the soil columns run with test design B were not further investigated.

The soil adsorption coefficients (K_d) for the reference item calculated according to Lambert, Hamaker and McCall ranged from 5.1 to 6.3 mL/g in the investigated soils (mean: 5.6 mL/g). The respective organic carbon normalized soil adsorption coefficients (K_{oc}) were in the range of 120.4 to 337.1 mL/g (overall mean: 258.4 mL/g).

The mobility of the test item [1-^{14}C]trifluoroacetate was determined to be almost identical to the mobility of the tracer in all soil columns, and for both test designs. In conclusion, it is expected that both compounds are very mobile in soil.

By using test design A it was measured that neither TFA nor the tracer had a Koc much differing from zero in any of the soils. Test design B resulted in Koc data for the tracer as well as for TFA indicating a weak retardation in all four soils. However, just an unknown technical reason when using test design B could explain that the tracer did not show a Koc differing from zero in all soils.

I. MATERIALS AND METHODS

A. MATERIALS

1. Test Item

[1-^{14}C]trifluoroacetate, (sodium salt of trifluoroacetic acid,)
Specific activity 5.48 MBq/mg
Radiochemical purity > 98% HPLC with radioactivity detector

2. Test soils

The soils were sampled fresh from the fields (upper horizon of 0 to 20 cm), sieved to a particle size of ≤ 2 mm and stored at ≤ 8 °C for 18 days. The soils were air-dried for 5 days at ambient temperature and stored in the laboratory at ambient temperature until column preparation. The soils were taken from agricultural areas representing different geographical origins and different soil properties as required by the guidelines. Soil characteristics are summarised in the table below.

Table 7.1.4.1.2- 1: Physico-chemical properties of test soils

Parameter	Results / Units			
Soil abbreviation/ soil ID	**AX**	**DD**	**HH**	**WW**
Geographic Location				
City	Monheim	Blankenheim	Burscheid	Monheim
State	North-Rhine Westphalia	North-Rhine Westphalia	North-Rhine Westphalia	North-Rhine Westphalia
Country	Germany	Germany	Germany	Germany
Soil Taxonomic Classification (USDA)	sandy, mixed, mesic Typic Cambudoll	fine-loamy, mixed, active, frigid Typic Eutrudept	loamy, mixed, mesic Typic Argudalf	loamy, mixed, mesic Typic Argudalf
Soil Series	no information available			
Textural Class (USDA)				
Sand [%] [50 µm – 2 mm]	78	39	19	67
Silt [%] [2 µm – 50 µm]	16	36	64	28
Clay [%] [< 2 µm]	6	25	17	15
pH				
- in $CaCl_2$ (soil/$CaCl_2$ 1/2)	6.2	7.4	6.5	5.3
- in water (soil/water 1/1)	6.5	7.5	6.7	5.5
- in water (saturated paste)	6.6	7.4	6.8	5.5
- in KCl	6.0	7.1	6.1	4.9
Organic Carbon [%]	1.8	5.2	1.6	1.9
Organic Matter [%] [1]	3.1	9.0	2.8	3.3
Cation Exchange Capacity [meq/100 g]	9.4	22.3	12.2	9.9
Water Holding Capacity				
maximum [g H_2O *ad* 100 g soil dw]	43.8	79.3	51.8	60.2
at 0.1 bar (pF 2.0) [%]	13.3	38.2	26.5	20.9
Bulk Density (disturbed) [g/cm³]	1.22	1.01	1.12	1.13

USDA: United States Department of Agriculture, dw: dry weight
[1] calculated as: OM [%] = OC [%] · 1.724

B. STUDY DESIGN

1. Experimental Conditions

Two different test designs were used for this soil column leaching study. Test design A reflected the test item distribution in the leachate as well as in the soil column, whereas test design B delivered detailed information of the test item distribution only in the leachate by using a larger irrigation volume. Test design A was run once with the test item plus tracer and once with the reference item plus tracer (duplicate soil columns each). The soil columns were eluted under saturated conditions with 392 mL (equal to 200 mm) artificial rain over a period of approx. 48 hours at a constant flow rate. Test design B was run only with the test item plus tracer (duplicate soil columns). The soil columns were eluted under saturated conditions with 984 mL (equal to 502 mm) artificial rain over a period of approx. 120 hours at a constant flow rate.

The test systems consisted of glass columns (45 cm length and 5 cm inner diameter) filled with soil to a height of approx. 30 cm. The glass columns were connected to a reservoir containing the artificial rain solution (0.01 M aqueous calcium chloride) as well as to a peristaltic pump and a fraction collector. The desired flow rate of the artificial rain was regulated on the pre-column side by a peristaltic pump. The

flow of the percolate was regulated on the post-column side in the same way. This set-up allowed controlling and maintaining a constant level of supernatant water on top of the soil and hence, saturated flow conditions as required for the calculation of adsorption coefficients according to the chromatographic theory.
For preparation of the test systems, a layer of quartz wool followed by a layer of washed sea sand was placed in the lower, conical end of the glass column to later retain the soil within the column. Afterwards, each column was dry packed with the sieved, air-dried soils to a height of approx. 30 cm, while gently vibrating. 678 to 856 g of air-dried soil was used per column.

For equilibration, the soil columns were saturated with an upward flow of artificial rain (total volume 400 mL per soil column), establishing a supernatant solution of 10-20 mm above soil surface. The soil columns were allowed to soak for approx. 16 hours in a temperature-controlled walk-in climatic chamber at 20 ± 2°C in the dark prior to application.

The amount of TFA was added at a nominal application rate of 11.0 µg test item per soil column. All application solutions were prepared in water. One application solution contained the test item and the tracer side by side; the other application solution contained the reference item and the tracer side by side. For the application, the artificial rain solution levels were adjusted to the soil surface levels and 500 µL of the respective application solution were applied dropwise onto the soil surface of the respective soil columns. The application rate and the homogeneity of the application solution were determined by LSC before, during and after the application of the soil columns. The stability of the test item and the reference item in the application solutions was determined by HPLC/radiodetection, before and after application

After application, a glass frit glued to an upside-down glass funnel was placed onto the top of each soil column in order to avoid whirling up the soil during the leaching test and to achieve a uniform moistening of the soil surface. The glass columns were then connected to the artificial rain reservoirs as well as to the peristaltic pumps and the fraction collector. The soil was overlaid manually with approx. 20 mL of artificial rain and a saturated flow of approx. 8.2 mL/h was established using the peristaltic pumps. A supernatant of approx. 10-20 mm was maintained above the soil layer throughout the experiment.

All experiments were performed in duplicate in a temperature-controlled walk-in climatic chamber at 20.1°C in the dark.

2. Sampling

The leachate was sampled in constant time intervals using a time-controlled automatic fraction collector. For test design A the leachate fractions were sampled in intervals of 6 hours (approx. 50 mL/fraction) using a total irrigation volume of 392 mL. For test design B the leachate fractions were sampled in intervals of 6 hours (approx. 50 mL/fraction) within the first 48 hours of irrigation (equal to a irrigation volume of approx. 400 mL) afterwards they were sampled in intervals of 12 hours (approx. 100 mL/fraction) until end of irrigation using a total irrigation volume of 984 mL

After draining, the soil columns were deep-frozen and cut each into 5 segments of approx. 6 cm height for further analysis (test design A only).

3. Analytical Procedures

Volume and the pH-value of each leachate fraction was determined. Single soil segments were extracted four times at ambient temperature using acetonitrile/ water (1:1, v/v). After each extraction step, supernatant and soil were separated by centrifugation and decantation.

The radioactivity content in leachate fractions and soil extracts was determined by liquid scintillation counting. Additionally, selected leachate fractions and soil extracts were analysed by

HPLC/radiodetection. Non-extractable residues were determined by combustion/ liquid scintillation counting.

The identity of the test item was elucidated by IC-MS/MS and the identity of the reference test item was elucidated by HPLC-MS/MS, both including accurate mass determination.

The adsorption values for leaching compounds (i.e. the test item TFA) were calculated according to Ketelle, B.H. et al (1947) and Swoboda, A.R. et al (1968).

The adsorption values for non-leaching compounds (i.e. the reference item atrazine) were calculated according to Lambert, S.M. et al. (1965) and according to Hamaker, J.W. (1975) McCall, P.J. (1981). The results of each mathematical model were averaged.

II. RESULTS AND DISCUSSION

A. MATERIAL BALANCE

Material balances for the test item were between 99.4 to 103.8% of the applied radioactivity [% AR] in all soil columns using test design A and between 93.2 to 105.2% AR using test design B. Material balances for the tracer and the reference item were between 89.1 to 105.5% AR and between 96.8 to 104.3% AR, respectively, in all soil columns and both test designs.

B. DEGRADATION OF TEST ITEM

The test item was sufficiently stable throughout the study, as demonstrated by HPLC/radiodetection analysis of selected leachate fraction and soil column segment extracts.

C. FINDINGS

Using test design A, 62.0 to 97.0% AR of the test item were found in the leachate of the single soil columns. The maximum amount of test item was found in the fourth to fifth leachate fraction of each soil column. 58.2 to 90.3% AR of the tracer were found in the leachate of the respective soil columns. The maximum amount of tracer was found in the fourth to fifth leachate fraction, i.e. after elution of approximately one saturation volume, demonstrating suitable hydrodynamic properties of the soil columns. The residual amounts of test item and tracer were almost equally distributed in the corresponding soil columns.

The maximum amount of reference item was found in the first segment of each soil column using test design A, but translocation of the reference item in deeper soil column segments could be also observed, demonstrating the suitable hydrodynamic properties of the soil columns. Only minor amounts of the reference item (< 1% AR) were found in the corresponding leachates of the single soil columns, whereas 45.1 to 93.9% AR of the tracer where found in the leachates.

Using test design B, the applied radioactivity of test item and tracer was completely recovered in the leachates of the respective soil columns. The maximum amount of test item was found in leachate fraction 8 of soil AX, in leachate fraction 3 of soil DD, in leachate fraction 9 of soil HH, and in leachate fraction 3 or 10 of soil WW. The tracer peak was likewise found in leachate fraction 7 to 9 of soil AX, in leachate fraction 3 to 4 of soil DD, in leachate fraction 9 of soil HH and in leachate fraction 3 or 10 of soil WW. The soil segments of the soil columns run with test design B were not further investigated, as the applied radioactivity of test item was completely recovered in the leachate.

The soil adsorption coefficients (K_d) for the reference item atrazine, calculated according to Lambert, Hamaker and McCall, ranged from 5.1 to 6.3 mL/g in the investigated soils (mean: 5.6 mL/g). The respective organic carbon normalized soil adsorption coefficients (K_{OC}) were in the range of 120.4 to 337.1 mL/g (overall mean: 258.4 mL/g).

The mobility of the test item TFA was determined to be almost identical to the mobility of the tracer in all soil columns and in both test designs. Thus, virtually no adsorption was determined for the test item, when calculation was performed according to Ketelle and Swoboda. According to the Briggs classification system, the mobility of TFA can be classified as "very mobile" in all soils.

The soil adsorption coefficients (K_d) and the respective organic carbon normalized soil adsorption coefficients (K_{OC}) of test and reference item are presented in the tables below.

Table 7.1.4.1.2- 2: Adsorption coefficients of test, reference item and of tracer in soils (test design A)

Soil	Replicate	Columns test item + tracer				Columns reference item + tracer			
		[1-^{14}C]trifluoroacetate (TFA)		^3H_2O		[triazine-UL-^{14}C]atrazine		^3H_2O	
		K_d [mL/g]	K_{OC} [mL/g]	K_d [mL/g]	K_{OC} [mL/g]	K_d [mL/g]	K_{OC} [mL/g]	K_d [mL/g]	K_{OC} [mL/g]
AX	1	0.0	0.0	0.0	0.0	5.0	278.4	0.0	0.0
	2	0.0	0.0	0.0	0.0	5.1	284.1	0.1	5.7
	Mean	**0.0**	**0.0**	**0.0**	**0.0**	**5.1**	**281.3**	**0.1**	**2.9**
DD	1	0.0	0.0	0.0	0.0	6.3	120.9	0.0	0.0
	2	0.0	0.0	0.0	0.0	6.2	119.8	0.0	0.0
	Mean	**0.0**	**0.0**	**0.0**	**0.0**	**6.3**	**120.4**	**0.0**	**0.0**
HH	1	0.0	0.0	0.0	0.0	5.4	337.1	0.2	11.1
	2	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	Mean	**0.0**	**0.0**	**0.0**	**0.0**	**5.4**	**337.1**	**0.2**	**11.1**
WW	1	0.0	0.0	0.0	0.0	5.5	289.9	0.2	8.5
	2	0.0	0.0	0.0	0.0	5.7	299.9	0.0	3.0
	Mean	**0.0**	**0.0**	**0.0**	**0.0**	**5.6**	**294.9**	**0.0**	**5.8**
Overall Mean		**0.0**	**0.0**	**0.0**	**0.0**	**5.6**	**258.4**	**0.1**	**4.9**

n.d. not determined

Table 7.1.4.1.2- 3: Adsorption coefficients of the test item and tracer in soils (test design B)

Soil	Replicate	Columns test item + tracer			
		[1-^{14}C]trifluoroacetate (TFA)		^3H_2O	
		K_d [mL/g]	K_{OC} [mL/g]	K_d [mL/g]	K_{OC} [mL/g]
AX	1	0.1	5.3	0.1	5.8
	2	0.1	3.6	0.1	4.5
	Mean	**0.1**	**4.5**	**0.1**	**5.2**
DD	1	0.0	0.0	0.0	0.0
	2	0.0	0.0	0.0	0.0
	Mean	**0.0**	**0.0**	**0.0**	**0.0**
HH	1	0.2	14.2	0.2	15.1
	2	0.1	8.4	0.2	10.7
	Mean	**0.2**	**11.3**	**0.2**	**12.9**
WW	1	0.3	14.2	0.2	11.1
	2	0.0	0.0	0.0	0.0
	Mean	**0.2**	**7.1**	**0.1**	**5.6**
Overall Mean		**0.2**	**9.1**	**0.1**	**5.9**

III. CONCLUSIONS

The mobility of the test item [1-^{14}C]trifluoroacetate was determined to be almost identical to the mobility of the tracer in all soil columns, and for both test designs. In conclusion, it is expected that both compounds are very mobile in soil.

By using test design A it was measured that neither TFA nor the tracer had a Koc much differing from zero in any of the soils. Test design B resulted in koc data for the tracer as well as for TFA indicating a weak retardation in all four soils. However, just an unknown technical reason when using test design B could explain that the tracer did not show a Koc differing from zero in all soils.

3. Assessment and conclusion

Assessment and conclusion by applicant: The study and its data are considered to be valid and reliable for use in risk assessment.

Assessment and conclusion by RMS: Outcome and conclusion of the study. RMS should indicate if they agree to the results and conclusions of the APPL.

CA 7.1.4.2 Lysimeter studies

No lysimeter studies with fluopyram have been performed. Studies are not required under Commission Regulation (EU) No 283/2013 in accordance with Regulation (EC) No 1107/2009.

CA 7.1.4.3 Field leaching studies

No field leaching studies with fluopyram were performed. Studies are not required under Commission Regulation (EU) No 283/2013 in accordance with Regulation (EC) No 1107/2009. A comprehensive set of laboratory data on degradation and adsorption of parent active substance and relevant degradation products to soil allow for an assessment of the mobility of all significant residues under various environmental conditions by the use of computer simulations as given, for example, by the FOCUS scenario approach. Such transfer calculation is more flexible and allows for adaptation to site or country specific climate and soil conditions, overcoming the limitations of a field leaching experiment.

CA 7.2 Fate and behaviour in water and sediment

The fate and behaviour of fluopyram in the aquatic environment has been investigated in a comprehensive series of laboratory studies. The laboratory studies (except the quantum yield investigation) were all conducted with ^{14}C-labelled active substance. When required to fully define the fate of the molecule, studies have been separately performed with labelling in each of the two rings; uniformly labelled phenyl-ring or labelled in the 2- and 6-positions of the pyridyl-ring.

CA 7.2.1 Route and rate of degradation in aquatic systems (chemical and photochemical degradation)

1. Information on the study

Data Point:	KCA 7.2.1/01
Report Author:	[redacted]
Report Year:	2021
Report Title:	Fluopyram - Effect of water treatment processes on the nature of residues present in groundwater and surface water
Report No:	EnSa-21-0047
Document No:	M-763244-01-1
Guideline(s) followed in study:	--
Deviations from current test guideline:	Current Guideline: not applicable
Previous evaluation:	No, not previously submitted
GLP/Officially recognised testing facilities:	not applicable
Acceptability/Reliability:	Yes

2. Full summary of KCA 7.2.1/01

An assessment of the potential impact of drinking water treatment, considering both the exposure aspects and transformation chemistry, has been prepared for fluopyram.

The first step in the assessment was a review of the predicted exposure concentrations at the field level for groundwater and surface water. This was refined by a review of the predicted exposure situation at raw water abstraction points and finally the impact of mechanical, physical, biological steps conducted prior to the eventual chemical steps on the predicted exposure situation at the chemical stages of raw water processing was assessed.

Exposure of the groundwater recharge at 1 m depth beneath the treated field was predicted to reach the following maximum concentrations across all representative uses:

- Below threshold (< 0.1 µg/L) for the parent substance fluopyram (max. 0.092 µg/L) and its metabolite fluopyram-7-hydroxy (max. 0.027 µg/L).
- Max. 3.718 µg/L for metabolite TFA

Exposure of shallow surface water directly adjacent to the treated field was predicted to reach maximum concentrations of

- Max. 4.83 µg/L for the parent substance fluopyram,
- Max. 0.315 µg/L for metabolite fluopyram-7-hydroxy
- Max. 1.63 µg/L for metabolite TFA.

Attenuation factors from conservative field scale predictions to actual exposure situation at drinking water abstraction points will be significant. In groundwater the trigger for further assessment is not breached even at the field scale for the parent molecule and its metabolites fluopyram-7-hydroxy. For metabolite TFA an attenuation factor as low as 38 would be sufficient to ensure the parametric value of 0.1 µg/L was not reached at the raw water abstraction point. This is at the lower end of precedent values commonly agreed as reasonable for such a process. In surface water assuming an exposure level at the

maximum predicted across all representative uses, an attenuation factor of 49 would suffice for potential exposure below 0.1 µg/L for any fluopyram-derived residue at the abstraction point, also within agreed attenuation factors.

Thus, it is unlikely that any fluopyram-derived components would under realistic conditions be present in raw water abstracted for drinking water production from groundwater or surface water at concentration levels requiring further assessment on their processing behaviour. An evaluation of public monitoring data confirms that findings of fluopyram are rare with exceedance above the regulatory groundwater trigger of 0.1 µg/L at only 0.048% (9 samples of 18,855 analyses) and above the surface water Tier 1-RAC-SW (5 µg/L) at 0.098% (8 samples out of 9,187 analyses).

The metabolite TFA, trifluoroacetate, is a confirmed or suspect common terminal degradate of a large number (>1 million) and wide range of chemicals including hydrofluorocarbons used as refrigerants, pharmaceuticals, pesticides and polymers, and is a high production volume chemical used as synthesis building block. Although environmental detects of this component are rather frequent and may exceed the threshold of 0.1 µg/L, individual substance fluopyram is expected an only minor contributor.

According to public literature data, adsorptive pre-conditioning of raw water, often preceding the chemical-oxidative stages of a drinking water facility, might attenuate concentrations of fluopyram parent, but unlikely of metabolite TFA. For the latter, removal can only be achieved in waterworks applying reverse-osmosis technology.

The next step in the assessment was a review of the behaviour of fluopyram residues upon chemical-oxidative water treatment. For the production of public drinking water, raw water is sourced from groundwater and/or surface water and is processed for purification and disinfection typically by a sequence of mechanical, physical, biological, and eventually chemical treatment steps. The chemical steps can be summarised as an exposure of pre-cleaned raw water to chemical oxidants, aiming for a transformation or mineralization of unwanted matrix components and micropollutants (e.g. to remove colour, odour, toxicity, and/or to meet other quality parameters), and for the inactivation of microbial life (i.e. control of waterborne diseases). In practice, two major groups of chemical reagents are in use; ozone-based treatment and chlorine-based treatment.

Literature review did not identify publications alerting of real-world detects of water treatment by-products possibly linked to fluopyram. A research article was discussed which investigates on the kinetics of chemico-oxidative transformation of fluopyram under harsh 'advanced oxidation process (AOP)'-type conditions. This data seems to indicate an only moderate susceptibility of fluopyram for oxidative processing in general and lets expect low to negligible transformation under exposure × time conditions as would typically prevail upon a regular ozone-based drinking water processing. Nevertheless, the study provides mechanistic insights into direction and routes of radical-driven breakdown under extreme conditions, by forcing fluopyram degradation via a novel process of 'ozone-enhanced microbubbles treatment (OMBT)'. The experiments were accompanied by analytical investigations and supportive quantum chemical calculations. In a subsequent (eco)toxicity QSAR analysis, none of the thereby proposed degradate structures triggered specific alerts for genotoxicity potential nor for acute toxicity classification, suggesting their likely non-relevance.

Further research reported on the water treatability of metabolite TFA. The investigations clearly demonstrate in laboratory and waterworks practice the molecule's recalcitrance to any ozone or chlorine-based chemico-oxidative processing. This implies the absence of any treatment by-products originating from this metabolite.

A systematic expert judgement analysis was made to assess the chemical structures of fluopyram and its environmental degradates fluopyram-7-hydroxy and TFA for motifs specifically alerting for a risk of forming N-nitrosamine type byproducts upon oxidative water processing. Different classes of

compounds have been assayed for their potential to form nitrosodimethylamine (NDMA) upon ozone treatment. Three types of structural moieties appear to have relevance as eventual NDMA precursors which can serve as structure alerts for screening purposes; N,N-dimethylhydrazine (UDMH) derivatives, N,N-dimethylsulfamide (DMS) derivatives and N,N-dimethylaminocarbamate (DMAC) derivatives. The structures of fluopyram and its metabolites do not match any of these precursor motifs. The compounds do not include any substructure moieties that would be expected prone to cleavage forming UDMH, DMS or DMAC. Also, a pre-requisite dimethyl-substituted amine moiety is not present in the molecule family. No environmental transformation reactions are known that might convert these components to form one of the alerting motifs. Fluopyram and its metabolites also do not include any homologues or analogues to the alerting core structure moieties potentially giving rise to similar N-nitroso components, no environmental transformation reactions are known that might convert such compound class to form one of the alerting motifs.

I. MATERIALS AND METHODS

Environmental residues relevant for assessment of fluopyram
The proposed residue definition in the fluopyram submission (2021) for risk assessment for groundwater includes fluopyram, fluopyram-7-hydroxy (M08), and trifluoroacetate (TFA). The proposed residue definition for risk assessment for surface water includes the same three components.

An assessment of the potential impact of drinking water treatment, considering both the exposure aspects and transformation chemistry, has been prepared for fluopyram and its metabolites.

For drinking water production, raw water is sourced from dedicated groundwater and surface water areas and is often processed for purification and disinfection. Typically, a sequence of mechanical, physical, biological, and eventually chemical treatment steps is applied, adapted to specific raw water type and quality. The chemical steps can be described as exposure of pre-cleaned raw water to chemical oxidants, aimed at transformation or mineralisation of unwanted matrix components and micropollutants (e.g. to remove colour, odour, toxicity, and/or to meet other quality parameters), and for the inactivation of microbial life (i.e. control of waterborne diseases).

In practice, two major groups of chemical reagents are in use, ozone or chlorine-based treatments. The benefit of such treatment for the inactivation of disease-bearing microbes and the conversion of unwanted pollutants to less critical components usually by far outweighs the general risk from "disinfection by-product (DBP)" formation, i.e. an unintended generation of toxic substances from the conversion of previously innocuous components. From a regulatory perspective in the drinking water context, parametric values for certain indicator components or component groups apply at the point at which drinking water emerges from taps used for human consumption, i.e. after having passed through all processing stages.

N-nitrosodimethylamine (NDMA) is a specific DBP of particular toxicological concern with identified precursors which included pesticide substances and/or their residues. Thus, particular consideration is also given to the possibility of forming NDMA and related N-nitrosamine type by-products.

A. Identification of residues exposed to the chemical-oxidative stages of drinking water treatment
The exposure situation was reviewed first at the field boundary level, then at the location of potential raw water abstraction points, and after the primary physical/adsorptive water processing stages typically preceding the chemical-oxidative treatment.

The assessment aimed to identify any components which could not be excluded as being present in excess of a threshold concentration of 0.1 µg/L at the chemical-oxidative stages of water treatment, and which would therefore require subsequent considerations on their transformation behaviour upon treatment.

The parametric value of 0.1 µg/L was selected for consistency with the non-relevance assessment of groundwater metabolites. Such an approach has been in a number of recent EFSA decisions. This is considered to be a very protective selection in view of the chemical parameters defined in European water regulation for surrogate DPBs (i.e. 10 µg/L for bromate, 100 µg/L for THMs, 80 µg/L being proposed for HAAs) ensuring that even in a very worst case only a minimal fraction of a water's total DPB burden might be associated with a particular pesticide residue

B. Assessment of the behaviour of fluopyram residues upon chemical-oxidative water treatment
The next step was an assessment of the behaviour of fluopyram residues upon chemical-oxidative water treatment.

Exposure of raw water abstracted for drinking water production to fluopyram is predicted to be typically low, at levels not triggering concern. However, possible transformation upon processing were assessed to 1) check for any specific alerts in public literature related to the behaviour of fluopyram chemistry upon ozone- or chlorine-based drinking water processing and 2) an evaluation via structured and systematic expert assessment for potentially alerting moieties to exclude risk of NDMA, or homologous N-nitrosamine type by-product generation from fluopyram residues upon chemico-oxidative water processing.

II. RESULTS AND DISCUSSION

A. Identification of residues exposed to the chemical-oxidative stages of drinking water treatment
1. Predicted exposure concentrations at the field level
The first step was a review of the groundwater and surface water exposure situation at the field scale level for fluopyram and its metabolites based on the PEC_{gw} and PEC_{sw} values predicted for the most critical 'representative use' for EU Annex I inclusion.

Groundwater: With regard to groundwater exposure, reference is made to the assessments presented for the representative uses in apples, spring cereals, winter cereals, and vines according to Good Agricultural Practice (GAP) under European cropping conditions. Exposure of groundwater recharge at the field level was calculated using the FOCUS groundwater scenarios and the simulation models PEARL 4.4.4., PELMO 5.5.3, and MACRO (refer to the respective Documents MCP, Section 9, Point CP 9.2.4.1 for details). The assessment comprised different Tier levels and was presented for different use rotation scenarios (annual applications, applications only every 2nd or every 3rd year).

In the present context of assessing for a potential impact of drinking water processing, according Regulation (EU) 1107/2009 Art. 4 (3b) *having regard to realistic conditions of use,* results from the most realistic simulations are considered relevant, i.e. Tier 2a 2. These are summarised for all representative uses in Doc. N4, reproduced for overview here below:

Table 7.2.1- 1: Maximum FOCUS PECgw results of fluopyram and its metabolites (in µg/L for the uses assessed)

– Tier 2a 2: annual application

Use pattern	Fluopyram	Fluopyram-7-hydroxy	Trifluoroacetic acid
Apples I, 1×75 g a.s./ha	(0.124)	(0.033)	(6.349)
Apples II, 1×75 g a.s./ha	(0.131)	(0.034)	(6.281)
Apples III, 1×75 g a.s./ha	(0.133)	(0.036)	(6.149)
Spring Cereals I, 1×39 g a.s./ha	0.006	0.004	0.731
Spring Cereals II, 1×78 g a.s./ha	0.029	0.012	1.362
Winter Cereals I, 1×39 g a.s./ha	0.009	0.005	1.117
Winter Cereals II, 1×78 g a.s./ha	0.036	0.013	2.227
Vines I, 2×50 g a.s./ha	(0.176)	(0.046)	(5.965)
Vines II, 2×50 g a.s./ha	**0.092**	**0.027**	**3.718**

– Tier 2a 2: application every 2nd year

Use pattern	Fluopyram	Fluopyram-7-hydroxy	Trifluoroacetic acid
Apples I, 1×75 g a.s./ha	0.050	0.015	3.668
Apples II, 1×75 g a.s./ha	0.053	0.015	3.389
Apples III, 1×75 g a.s./ha	0.053	0.015	3.645
Spring Cereals I, 1×39 g a.s./ha	0.003	0.002	0.390
Spring Cereals II, 1×78 g a.s./ha	0.013	0.005	0.779
Winter Cereals I, 1×39 g a.s./ha	0.004	0.002	1.173
Winter Cereals II, 1×78 g a.s./ha	0.013	0.005	2.346
Vines I, 2×50 g a.s./ha	0.060	0.019	3.344
Vines II, 2×50 g a.s./ha	0.030	0.010	2.051

– Tier 2a 2: application every 3rd year

Use pattern	Fluopyram	Fluopyram-7-hydroxy	Trifluoroacetic acid
Apples I, 1×75 g a.s./ha	0.026	0.008	2.371
Apples II, 1×75 g a.s./ha	0.027	0.008	2.128
Apples III, 1×75 g a.s./ha	0.028	0.009	2.362
Spring Cereals I, 1×39 g a.s./ha	0.002	0.001	0.265
Spring Cereals II, 1×78 g a.s./ha	0.006	0.003	0.530
Winter Cereals I, 1×39 g a.s./ha	0.002	0.001	0.670
Winter Cereals II, 1×78 g a.s./ha	0.007	0.003	1.337
Vines I, 2×50 g a.s./ha	0.021	0.011	2.187
Vines II, 2×50 g a.s./ha	0.015	0.006	1.382

in brackets: not relevant in present context (parent < 0.1 µg/L)
bold/underlined: maximum values

For assessment of water processing risk the conclusion can safely focus on results from those scenario simulations that would in practice allow for a successful products registration, i.e. where the exposure predicted for the parent substance would fulfil European acceptability criteria not exceeding the parametric cut-off value of 0.1 µg/L. For these combinations, exposure of the groundwater recharge in 1 m depth underneath the treated field was predicted to reach maximum concentrations of:

Fluopyram: 0.092 µg/L [Vines II, 2×50 g a.s./ha]
Fluopyram-7-hydroxy: 0.027 µg/L [Vines II, 2×50 g a.s./ha]
Trifluoroacetate: 3.718 µg/L [Vines II, 2×50 g a.s./ha]

Surface water: With regard to surface water, reference is made to the exposure modelling presented for the representative uses in apples, spring cereals, winter cereals, and vines according to Good Agricultural Practice (GAP) under European cropping conditions. Exposure of surface water at the field level was calculated using the FOCUS suite of surface water scenarios and the simulation models PRZM 4.3.1, MACRO 5.5.4, and TOXSWA 5.5.3 (refer to the respective Documents MCP, Section 9, Point CP 9.2.5 for details). The assessment comprised different FOCUS Steps, and Tier levels.

In the present context of assessing for a potential impact of drinking water processing, according Regulation (EU) 1107/2009 Art. 4 (3b) *having regard to realistic conditions of use* prediction results for the European environmental scenarios for an unmitigated use (FOCUS Step 3) under most realistic modelling assumptions (Tier 2) are considered relevant. A summary of data calculated for the use representating the worst case is tabulated below:

Table 7.2.1- 2: Spring cereals I - early - 0.039 kg a.s./ha (DGR I / PMT I) [M-763440-01-1/M-763464-01-1]

Step 3		Max PEC_{sw} (µg/L)		
Scenario FOCUS	**Waterbody**	**Fluopyram**	**Fluopyram-7-hydroxy**	**Trifluoroacetate**
D1	Ditch	1.01	0.095	0.191
D1	Stream	0.631	0.059	0.119
D3	Ditch	0.247	<0.001	0.350
D4	Pond	0.249	0.023	0.548
D4	Stream	0.249	0.022	0.230
D5	Pond	0.208	0.025	0.768
D5	Stream	0.223	0.019	0.303
R4	Stream	0.259	0.002	0.001

Table 7.2.1- 3: Spring cereals II - early - 0.078 kg a.s./ha (DGR II / PMT II) [M-763440-01-1/M-763464-01-1]

Step 3		Max PEC_{sw} (µg/L)		
Scenario FOCUS	**Waterbody**	**Fluopyram**	**Fluopyram-7-hydroxy**	**Trifluoroacetate**
D1	Ditch	2.04	0.183	0.378
D1	Stream	1.28	0.115	0.235
D3	Ditch	0.495	<0.001	0.699
D4	Pond	0.523	0.049	1.09
D4	Stream	0.523	0.044	0.458
D5	Pond	0.470	0.051	1.53
D5	Stream	0.455	0.039	0.603
R4	Stream	0.558	0.005	0.002

Table 7.2.1- 4: Winter cereals I - early - 0.039 kg a.s./ha (DGR III / PMT III) [M-763440-01-1/M-763464-01-1]

Step 3		Max PEC_{sw} (µg/L)		
Scenario FOCUS	Waterbody	Fluopyram	Fluopyram-7-hydroxy	Trifluoroacetate
D1	Ditch	1.80	0.133	0.372
D1	Stream	1.15	0.085	0.168
D2	Ditch	2.29	0.171	0.198
D2	Stream	1.44	0.110	0.142
D3	Ditch	0.247	0.001	0.382
D4	Pond	0.319	0.029	0.666
D4	Stream	0.324	0.028	0.289
D5	Pond	0.202	0.025	0.818
D5	Stream	0.220	0.020	0.341
D6	Ditch	0.357	0.022	0.419
R1	Pond	0.017	<0.001	<0.001
R1	Stream	0.163	0.002	<0.001
R3	Stream	0.236	0.005	0.002
R4	Stream	0.413	0.007	<0.001

Table 7.2.1- 5: Winter cereals I - late - 0.039 kg a.s./ha (DGR III / PMT IV) [M-763440-01-1/M-763464-01-1]

Step 3		Max PEC_{sw} (µg/L)		
Scenario FOCUS	Waterbody	Fluopyram	Fluopyram-7-hydroxy	Trifluoroacetate
D1	Ditch	0.403	0.041	0.050
D1	Stream	0.253	0.026	0.031
D2	Ditch	0.296	0.030	0.045
D2	Stream	0.253	0.019	0.030
D3	Ditch	0.048	<0.001	0.097
D4	Pond	0.064	0.005	0.113
D4	Stream	0.214	0.006	0.050
D5	Pond	0.029	0.004	0.132
D5	Stream	0.231	0.004	0.051
D6	Ditch	0.249	0.005	0.090
R1	Pond	0.035	<0.001	<0.001
R1	Stream	0.163	0.002	<0.001
R3	Stream	0.229	0.006	0.003
R4	Stream	0.163	0.003	<0.001

Table 7.2.1- 6: Winter cereals II - early - 0.078 kg a.s./ha (DGR IV / PMT V) [M-763440-01-1/M-763464-01-1]

Step 3		Max PEC_{sw} (µg/L)		
Scenario FOCUS	Waterbody	Fluopyram	Fluopyram-7-hydroxy	Trifluoroacetate
D1	Ditch	3.60	0.250	0.541
D1	Stream	2.31	0.160	0.334
D2	Ditch	**4.83**	**0.315**	0.395
D2	Stream	3.06	0.219	0.280
D3	Ditch	0.494	0.001	0.765
D4	Pond	0.655	0.060	1.32
D4	Stream	0.673	0.055	0.574
D5	Pond	0.485	0.051	**1.63**
D5	Stream	0.451	0.038	0.681
D6	Ditch	0.708	0.042	0.836
R1	Pond	0.034	<0.001	<0.001
R1	Stream	0.325	0.005	<0.001
R3	Stream	0.497	0.010	0.003
R4	Stream	0.835	0.013	0.002

Table 7.2.1- 7: Winter cereals II - late - 0.078 kg a.s./ha (DGR IV / PMT VI) [M-763440-01-1/M-763464-01-1]

Step 3		Max PEC_{sw} (µg/L)		
Scenario FOCUS	Waterbody	Fluopyram	Fluopyram-7-hydroxy	Trifluoroacetate
D1	Ditch	0.933	0.079	0.098
D1	Stream	0.584	0.050	0.064
D2	Ditch	0.623	0.060	0.089
D2	Stream	0.504	0.037	0.059
D3	Ditch	0.496	0.001	0.194
D4	Pond	0.136	0.011	0.226
D4	Stream	0.427	0.011	0.100
D5	Pond	0.064	0.009	0.262
D5	Stream	0.461	0.008	0.102
D6	Ditch	0.498	0.009	0.180
R1	Pond	0.072	<0.001	<0.001
R1	Stream	0.351	0.003	0.001
R3	Stream	0.504	0.010	0.006
R4	Stream	0.327	0.005	0.001

For the purpose of assessing for water processing risk, the maximum concentration of each component from all representative uses is taken into further consideration:

Fluopyram: 4.83 µg/L [Winter cereals II - early - 0.078 kg a.s./ha, D2 ditch]
Fluopyram-7-hydroxy: 0.315 µg/L [Winter cereals II - early - 0.078 kg a.s./ha, D2 ditch]
Trifluoroacetate: 1.63 µg/L [Winter cereals II - early - 0.078 kg a.s./ha, D5 pond]

2. Predicted exposure situation at raw water abstraction points

The second step was a review of the exposure situation expected at raw water abstraction points of relevance for technical drinking water production. Raw water for drinking water purposes will usually be abstracted from protected groundwater and surface water sources that are dedicated for this use.

Until a water is abstracted for drinking water production, in addition to biodegradation therefore a significant attenuation via mixing in volume and time will likely apply to the maximum local exposure concentrations predicted by the PPP regulatory field scale models. Moreover, it has to be considered that a drinking water catchment will unlikely consist entirely of arable land, a particular active substance will be used only on specific crop types that are usually not simultaneously grown on the entirety of a catchment's area, and will be applied only seasonally a with penetration in its market notably below 100 %.

The attenuation factor from conservative field scale predictions to actual exposure situation at drinking water abstraction points will hence be significant. In recent EU reviews dilution factors have been proposed and accepted by Rapporteur Member States and EFSA within an overall range from 1:10 – 1:1000000 for various active substances.

Concerning potential presence in groundwater, for the parent molecule and its metabolite fluopyram-7-hydroxy the parametric threshold of 0.1 µg/L is not breached even at the field scale. For metabolite TFA an attenuation by factor 38, based on maximum PEC_{gw} of TFA (3.718 µg/L / 0.1 µg/L ~ 38), upon the water transfer (max. $PEC_{gw,field}$ → $PEC_{raw\ water\ abstraction\ point}$) would suffice to not reach threshold at the raw water abstraction point. This is at the lower end of precedent values commonly agreed reasonable for such processes.

Concerning surface water, the predicted exposure at the edge-of-field scale slightly exceeds the conservative assessment threshold for all three compounds. However, attenuation upon the water transfer (max. $PEC_{sw,edge-of-field}$ → $PEC_{raw\ water\ abstraction\ point}$) by factor 49 (fluopyram parent), 3.2 (fluopyram-7-hydroxy), or 17 (TFA) would suffice to reach exposure below the parametric value of 0.1 µg/L at the abstraction point (based on maximum PECsw of fluopyram (4.83 µg/L / 0.1 µg/L ~ 49), fluopyram-7-hydroxy (0.315 µg/L / 0.1 µg/L ~ 3.2), TFA (1.63 µg/L / 0.1 µg/L ~ 17)). Also such required attenuation upon PECsw → PECraw water transfer would be at the lower end of agreed precedence.

Hence, it is unlikely that any fluopyram-derived components would under realistic conditions be present in raw water abstracted for drinking water production from ground water or surface water at concentration levels requiring further assessment on their processing behaviour.

3. Environmental monitoring information

A review of publicly available environmental monitoring information was conducted on the spread of fluopyram covering soil, groundwater, surface water, drinking water, sediment and air (see KCA 7.5/01, M-759463-02-1). The results from the groundwater monitoring data search indicate that fluopyram concentrations above the regulatory trigger of 0.1 µg/L are rare (0.048%, 9 out of 18,855 analyses) with a maximum concentration of 0.25 µg/L.

The results from the surface water monitoring data search indicate that fluopyram concentrations above the Tier 1-RAC-SW (5 µg/L) are also rare (0.098%, 8 out of 9,187 analyses) and the highest value was 12 µg/L.

Concerning metabolites, the sole analyte publicly monitored was found to be TFA. TFA is a known or suspect common degradate of a large number (> 1 million) and wide range of chemicals including hydrofluorocarbons used as refrigerants, pharmaceuticals, pesticides and polymers, and in substance is a high production volume chemical used as synthesis building block. As TFA may hence be significantly contributed also from non-agricultural sources, the results of the search for public monitoring data for TFA were presented in an independent report (see KCA 7.5/06, M-761706-02-1). In the frame of the guidance document for the assessment of the relevance of pesticide metabolites in groundwater within the EU (Sanco/221/2000 rev. 10 Feb 2003), TFA was classified as a non-relevant metabolite (threshold 10 µg/L). For surface water, the Tier 1-RAC-SW is 120 µg/L. Although the results from ground and surface water analysis revealed frequent detects (n=19 of 32 for groundwater, n=366 of 417 for surface water), a compliance rate of 100% with the above thresholds was given. The maximum individual reported concentration was 4.4 µg/L in groundwater, and 17 µg/L in surface water.

From this exhaustive collation of public monitoring datasets, it can be concluded that for the overwhelming majority of environments and sampling times in Europe the exposure of fluopyram is confirmed to be low and within the expectable levels from exposure modelling. It should be emphasized that these data aim to reflect the general situation of diverse ground and surface waters, with no focus to drinking water abstraction points that typically enjoy specific protection.

4. Predicted exposure at the chemical stages of raw water processing

Before being subjected to chemical-oxidative treatment steps, raw water is often conditioned by various physico-biological and/or adsorptive stages such as bank filtration, sand filtration, flocculation, or activated carbon filtering.

No specific data directly describing a possible impact of these processes on fluopyram residues was found available in the public literature. Indicative information could be derived from an article summarising aquatic monitoring activities in the Netherlands (Sjerps et al. 2019, cf. KCA 7.5/02) reporting on frequent analytically detectable residues of fluopyram in surface water (38/46 samples) and dune filtrate (3/4 samples), whereas in notable difference found never detectable quantities in any river bank filtrate (0/10) nor groundwater (0/90) sample. This may indicate that in particular slower filtration processes through carbon-rich media such as soil could possibly reduce fluopyram residues, while a pure sand filtration might have only little impact on concentrations possibly present. In consequence, also activated carbon-based technology might be expected to help reduce fluopyram residues, whilst simple sand filtration or flocculation processes are likely of little impact.

Concerning metabolite TFA, in difference no significant reduction via adsorptive processes would be expected based on the component's physico-chemical properties (low pKa, ionic component of very high polarity, lack of easy biodegradation). Triggered by the widespread occurrence of this component from a plethora of sources, laboratory-, pilot- and full-scale experiments for the treatability of TFA during drinking water production were conducted by Scheurer et al. (2017). These confirmed the expectation of no efficient removal via activated carbon filtration and concluded that also ion exchange techniques could not be economically operated for TFA reduction in practice. In difference, a very good rejection of TFA by reverse osmosis to below detection limits was observed despite of its relatively low molecular weight. The authors speculated that charge interactions could be responsible for this effect, assuming that the negatively charged TFA is rejected by the negatively charged membrane surface. Rejection of TFA tended to be comparable to divalent ions such as calcium or sulphate.

5. Overview of exposure situation

As outlined above, *consequent on application consistent with good plant protection practice and having regard to realistic conditions of use (Reg. 1107/2009, Art. 4),* residues of the active substance fluopyram and its metabolite fluopyram-7-hydroxy would rarely be expected to reach the chemico-oxidative stages of drinking water processing facilities at concentrations considered to raise generic concern over potential by-products formation. Risk from substances resulting from water treatment can therefore be considered as addressed based on low exposure at the chemical water treatment stages.

Concerning metabolite TFA, the individual exposure contribution from plant protection uses of substance fluopyram is also expected unlikely to reach assessment threshold in raw water for drinking water production. Nevertheless, TFA is a terminal degradate shared with a plethora of chemicals having widespread uses, from manifold industrial sectors. On cumulated basis over all sources, a TFA exposure of raw water for drinking water production may therefore nevertheless apply.

B. Assessment of the behaviour of fluopyram residues upon chemical-oxidative water treatment

1. Literature information related to fluopyram behaviour upon water treatment

Amongst the exhaustive literature information collected upon public data search for substance fluopyram, one article specifically reported on the compound's behaviour under conditions of chemical-oxidative water processing: Li et al (2020) tested the treatability of aqueous fluopyram via 'Advanced Oxidation Processes (AOP)', comparatively applying the methodologies ozonation, microbubbles treatment (MCB), and their combination to 'ozone enhanced microbubbles treatment (OMBT)'.

Whilst ozone oxidation is a technology commonly in use at public drinking water treatment facilities, MCB and OMBT represent explorative AOP-type technologies at early laboratory-experimental stages. According to the authors, microbubbles are tiny bubbles that are typically 10-50 µm (and always <

200 µm) in diameter. They have unique characteristics such as self-pressurization, the capacity for generating free radicals, and the presence of a negative charge, and have therefore recently attracted research attention. Microbubbles help accelerate the gas-liquid transformation efficiency, and by gradually shrinking in size break up in the liquid phase and produce hydroxyl radicals. This process gives water containing microbubbles strong oxidation ability. A combination with ozone was expected to further promote such radical formation processes.

In the present context, i.e. by-products assessment in the scope of Regulation (EU) 1107/2009, Article 4, the following conclusions are drawn from the above publication:

- Fluopyram is only moderately susceptible for a degradation upon standard ozone-based technology as is currently in use at drinking water treatment facilities. According Roeske (2007) typical contact times being applied for the technical scale drinking water treatment with ozone are ca. 1-2 min where ozone is used for pre-oxidation prior to filtering/flocculation, or ca. 4 min where ozone is used post-filtering. For safe disinfection, a *Ct value* (i.e. residual ozone concentration in mg/L multiplied by time in minutes) as low as 1.6 is recommended (e.g. 0.4 mg/L × 4 min). Comparison to the half-life time of fluopyram of 1.7 hours reported by Li et al (2017) for the regular ozone incubations lets expect only negligible degradation upon waterworks treatment conditions, and evidently suggests as well negligible generation of potential by-products. Moreover, it is to be noted that the experiment was held in absence of further matrix constituents that would in a natural raw water possibly compete for ozone and/or radical reaction.

- Nevertheless, the paper gives valuable insights into the general behaviour of fluopyram when being exposed to a highly oxidative radical environment, clearly exceeding current standard practices. Under extreme oxidative conditions, fluopyram degrades via routes of hydroxylation and molecule cleavage consistent with expectations from quantum chemistry insights. It thereby forms degradates which in QSAR toxicity and ecotoxicity prediction tools do not trigger alerts specifically different to those resulting for the parent compound. In particular, none of the degradates was suspect for Ames mutagenicity, nor would qualify for an acute toxicity classification.

2. Literature information related to metabolite TFA behaviour upon water treatment

Triggered by the ubiquity of component TFA from a plethora of sources, and its occurrence in certain raw waters for drinking water production a comprehensive set of laboratory-, pilot- and full-scale experiments for the treatability during drinking water production were conducted by Scheurer et al. (2017). Apart from experiments on adsorptive processes, ion exchange and reverse osmosis as were discussed before under point A.5, the authors also studied the impact of chemico-oxidative technologies.

In the present context, i.e. by-products assessment in the scope of Regulation (EU) 1107/2009, Article 4, the following conclusions are drawn from their publication:

- Metabolite TFA is not subject to any transformation upon chemico-oxidative water processing such as ozonation or chlorination, i.e. will readily pass through the technical water treatment stages without a formation of by-products relevant for assessment here.

- Substance TFA itself may however be regarded as a possible by-product of water treatment, as it may in theory be formed upon the biological and/or chemico-oxidative processing of chemicals where the structure includes a C-CF_3 motif. For fluopyram a such potential for TFA generation was demonstrated to hold true in particular upon ozone oxidation, via model experiments. However, under practice operation conditions in terms of ozone concentration × time as are typically applied at drinking water treatment facilities, only negligible overall conversion of fluopyram is expected (cf. data interpretation and discussion under point B.1

before). Therefore, and in view of the typically very low fluopyram exposure concentration of raw water (cf. discussed under point A before), it is clearly not expected that the route of ozone-based water processing would contribute significant amounts of fluopyram-derived TFA as a treatment by-product. (Nevertheless, toxicological assessment of component TFA is found provided in Document N 4 (version Feb. 2021), due to its role as a groundwater metabolite.)

3. Evaluation for possible risk of N-nitrosamine generation

Amongst the broad palette of common disinfection by-products from oxidative treatments, specifically component N-nitrosodimethylamine (NDMA) is of particular practical interest due to occasional occurrences in processed waste- and drinking waters, and its toxicological relevance as a suspect human carcinogen.

In a systematic assessment, the chemical structures of fluopyram and its metabolites fluopyram-7-hydroxy and TFA were found to not match any of the previously known precursors of N-nitrosodimethylamine (NDMA). The compounds do not include any substructure moieties that would be expected prone to cleavage forming N,N-dimethylhydrazine (‘unsymmetrical dimethylhydrazine’, UDMH), N,N-dimethyl sulfamide (DMS) or N,N-dimethyl-O-aminocarbamate (DMAC). Also a pre-requisite dimethyl-substituted amine moiety is not present in the molecule family. No environmental transformation reactions are known that might convert these components to form one of the alerting motifs. Moreover, fluopyram and its metabolites do not include any homologues or analogues to the UDMH, DMS, DMAC alerting core structure moieties, letting exclude also a potential risk of similar-like forming homologous N-nitrosamine type by-products.

III. CONCLUSION

In the scope of Regulation (EU) 1107/2009, Article 4(3b), an investigation was made to assess for the potential risk of by-products formation from environmental residues of the active substance fluopyram upon drinking water treatment. The assessment was based on,

- An estimation of the potential quantity of residues of fluopyram in raw water for the production of drinking water,
- A review and discussion of available literature information investigating the behaviour of fluopyram and its metabolite TFA under chemico-oxidative water treatment conditions, and
- A systematic analysis of fluopyram’s and its degradates’ chemistry for the risk of forming N-nitrosamine type by-products via known precedent routes.

In overall conclusion, this analysis did not reveal alert for any particular risk linked to transformation by-products upon the technical processing of drinking water, neither from the quantitative nor the qualitative perspective.

Specifically,

- It is not expected that residues of or formed from fluopyram would regularly reach the chemico-oxidative stages of drinking water processing facilities at concentrations triggering further assessment, based on the prediction of field scale exposure and considering natural attenuation upon the catchment transfer.
- Literature review did not identify publications alerting of real-world detects of water treatment by-products possibly linked to fluopyram.
- A research article was discussed which investigates on the kinetics of chemico-oxidative transformation of fluopyram under harsh ‘Advanced Oxidation Process’-type conditions. This data seems to indicate an only moderate susceptibility of fluopyram for oxidative processing in general and lets expect low to negligible transformation under exposure × time conditions as would typically prevail upon regular ozone-based drinking water processing. Nevertheless, the study provides mechanistic insights into direction and routes of radical-driven breakdown under

extreme conditions, by forcing fluopyram degradation via a novel process of ozone-enhanced microbubbles treatment (OMBT). The experiments were accompanied by analytical investigations and supportive quantum chemical calculations. In a subsequent (eco)toxicity QSAR analysis, none of the thereby proposed degradate structures triggered specific alerts for genotoxicity potential nor for acute toxicity classification, suggesting their likely non-relevance.

- Further research reported on the water treatability of metabolite TFA. The investigations clearly demonstrate in laboratory and waterworks practice the molecule's recalcitrance to any ozone or chlorine-based chemico-oxidative processing, which implies the absence of further treatment by-products originating from this metabolite.
- A systematic expert judgement analysis was made to assess the chemical structures of fluopyram and its environmental degradates fluopyram-7-hydroxy and TFA for motifs specifically alerting for a risk of forming N-nitrosamine type by-products upon ozone and chlorine water processing. Via a structured stepwise approach, an in-depth comparison of the molecules' chemistries to known N-nitrosamine precursor motifs was made but did not identify any analogies leading into possible concern.

3. Assessment and conclusion

Assessment and conclusion by applicant: The position paper is considered to be valid to aid assessment of the potential impact of drinking water treatment.

Assessment and conclusion by RMS: Outcome and conclusion of the study: RMS should indicate if they agree to the results and conclusions of the APPL.

CA 7.2.1.1 Hydrolytic degradation

Fluopyram is hydrolytically stable under acidic, neutral and alkaline conditions at 50 °C and no hydrolysis half-life could be calculated. Accordingly, hydrolysis can be considered as no relevant degradation pathway of fluopyram and no further degradation products have to be considered.

1. Information on the study

Data Point:	KCA 7.2.1.1/01
Report Author:	[redacted]
Report Year:	2006
Report Title:	[14C]-AE C656948: Aqueous hydrolysis at pH 4, 7 and 9
Report No:	CX/06/015
Document No:	M-282473-01-1
Guideline(s) followed in study:	EU 91/414/EEC amended by 94/37/EEC, Section 8.2.1 and 95/36/EC, Section 7.2.1.1; US EPA, Subdivision N, Section 161-1 [OPPTS 835.2120]; Canadian PMRA DACO Number 8.2.3.3; Japanese MAFF 12 Nousan 8147; OECD 111
Deviations from current test guideline:	Current Guideline: OECD 111 (2004) Sterility checks of the samples showed some minor contamination seen at time zero at pH 4 and pH 7. Sterility was proven for all other samplings.
Previous evaluation:	yes, evaluated and accepted DAR (2011)
GLP/Officially recognised testing facilities:	Yes, conducted under GLP/Officially recognised testing facilities
Acceptability/Reliability:	Yes

2. Full summary of KCA 7.2.1.1/01

Executive Summary

The hydrolytic route and rate of degradation of [phenyl-UL-^{14}C]fluopyram were investigated in sterile aqueous buffer solutions at three pH values (4, 7, and 9) in the laboratory at 50 °C in the dark for 5 days. The test was performed in static systems consisting of 8 mL screw-capped test vessels each containing test solution sealed by sample caps. The final test substance concentration was 1.01 µg/mL. Carbon dioxide and volatile organic compounds were not collected since they were not expected.

Duplicate samples were processed and analyzed 0, 0.1, 2 and 5 days after treatment (DAT).

Mean material balances ranged from 95.0 to 104.7% AR for pH 4, 95.9 to 103.1% AR for pH 7, and 95.5 to 103.1% AR for pH 9 during the study (DAT-0 to DAT-5).

Fluopyram was found to be stable at pH 4 under the conditions tested with no degradation products detected. At pH 7, one minor degradation product was detected at a maximum of 1.6% AR at DAT-5. At pH 9 the same minor degradation product was detected reaching 1.2% AR at DAT-5 and one further minor metabolite was detected at 0.5% in a single flask at DAT-2.

Fluopyram is considered to be hydrolytically stable under acidic, neutral and alkaline conditions. No half-life was to be calculated due to hydrolytic stability of the test item. Due to stability at 50 °C, hydrolytic stability at 25 °C is assumed, therefore no further test were conducted.

I. MATERIALS AND METHODS

A. MATERIALS

1. Test item

[phenyl-UL-^{14}C]AE C656948 (fluopyram)
Batch No.: BECH 1910
Specific Activity: 3.85 MBq/mg
Radiochemical Purity: >99% (HPLC/radiodetection)

2. Test system

The study was carried out using three buffer solutions: 0.01 M sodium acetate buffer solution adjusted to pH 4.0, 0.01 M tris(hydroxymethyl) aminomethane hydrochloride buffer solution adjusted to pH 7.0 and 0.01 M di-sodium tetraborate buffer solution adjusted to pH 9.0. Buffers were chosen to minimise the possibility of interaction with the test item under the reaction conditions. After preparation, the buffers were sterilized by filtration and collected in a sterilized glass bottle. Sterility was checked by incubation of the buffer solutions on agar plates. Afterwards, the oxygen content was depleted by a constant nitrogen flow for approximately five minutes.

B. STUDY DESIGN

1. Experimental conditions

Static test systems were used, consisting of screw-capped test vessels (8 mL capacity) each containing test solution and sealed by sample caps. All glassware was sterilized prior to use by autoclaving for 20 minutes at 121 °C and stored in a laminar flow cabinet to ensure the sterility was maintained. Aqueous buffer solutions were sterilized by filtration through a 0.22 µm Millipore Steritop sterile filter.

Before application of the test item, 7 mL aliquots of the respective buffer solutions were added into the test vessels for each pH. Test solutions were prepared by diluting 72 µL of the treating solution, with a nominal concentration of 100 µg/mL of [phenyl-UL-^{14}C]fluopyram prepared in acetonitrile/water (50:50, v/v), in the sterile buffer solutions. The actual test substance concentration was 1.01 µg/mL and the acetonitrile content was 0.51% (v/v). The pH values of the buffer solutions were measured at time of preparation and at each sampling interval in the control buffers, which were also incubated at 50°C.

Afterwards, test vessels were closed and placed in a dry block heater maintained at 50 ± 0.5°C. Temperature was recorded at each sampling interval. Test systems were incubated under absence of oxygen in the dark for 5 days.

2. Sampling

Duplicate test systems were taken at 0, 0.1, 2 and 5 days after treatment (DAT). Sample processing and analysis was conducted immediately after sampling. No attempts were made to collect volatiles. A sterility check was performed with the initial test solutions and at DAT-2 and DAT-5.

3. Analytical procedures

At each sampling interval, aliquots of the test solutions were solved in an appropriate LSC cocktail and radioactivity was determined by liquid scintillation counting (LSC). Additionally, pH values were controlled at each sampling interval. At each sampling interval, the samples of the test solution were characterized by high performance liquid chromatography (HPLC) with radiodetection to quantify the amount of test item and eventual degradation products present in the water. Additionally, the stock treatment solution was analysed by HPLC to determine the purity. Selected samples were also analysed by thin layer chromatography (TLC) to confirm the identity of the fluopyram.

The limit of quantification (LOQ) for LSC measurement was 0.04% AR. The LOQ for the HPLC/radiodetection method was 1% AR.

II. RESULTS AND DISCUSSION

A. DATA

Radioactive mass balance and distribution of [phenyl-UL-^{14}C]fluopyram and metabolites in water are summarised in Table 7.2.1.1-1 to Table 7.2.1.1-3. The temperatures recorded were within ± 0.5°C of the nominal temperatures throughout the study. The pH values measured were all within 0.1 units of the nominal values.

Table 7.2.1.1-1: Hydrolytic degradation of fluopyram at pH 4 and 50 °C

Compound	Replicate No.	DAT 0	DAT 0.1	DAT 2	DAT 5
Fluopyram	A	96.15	96.95	98.71	104.98
	B	93.83 [1]	97.79	104.72	104.39
	Mean	**94.99**	**97.37**	**101.71**	**104.68**
Total % recovery	A	96.15	96.95	98.71	104.98
	B	93.83 [1]	97.79	104.72	104.39
	Mean	**94.99**	**97.37**	**101.71**	**104.68**

n.d.: not detected, DAT: days after treatment

[1] By error, in the reports, two different values (93.83 and 98.93) were listed. Considering the mean value, only 93.83 is expected to be the correct value.

Table 7.2.1.1-2: Hydrolytic degradation of fluopyram at pH 7 and 50 °C

Compound	Replicate No.	DAT 0	DAT 0.1	DAT 2	DAT 5
Fluopyram	A	95.64	96.86	98.44	102.04
	B	96.16	96.55	97.51	100.91
	Mean	**95.90**	**96.71**	**97.96**	**101.48**
Unknown 1	A	n.d.	n.d.	0.98	1.35
	B	n.d.	n.d.	1.63	1.83
	Mean	**n.d.**	**n.d.**	**1.30**	**1.59**
Total % recovery	A	95.64	96.86	99.39	103.39
	B	96.16	96.55	99.14	102.75
	Mean	**95.90**	**96.71**	**99.27**	**103.07**

n.d.: not detected, DAT: days after treatment

Table 7.2.1.1-3: Hydrolytic degradation of fluopyram at pH 9 and 50 °C

Compound	Replicate No.	DAT 0	DAT 0.1	DAT 2	DAT 5
Fluopyram	A	95.75	97.47	94.78	102.75
	B	95.33	96.13	97.83	100.93
	Mean	**95.54**	**96.80**	**96.30**	**101.84**
Unknown 1	A	n.d.	n.d.	0.73	1.15
	B	n.d.	n.d.	1.72	1.31
	Mean	**n.d.**	**n.d.**	**1.22**	**1.23**
Unknown 2	A	n.d.	n.d.	0.51	n.d.
	B	n.d.	n.d.	n.d.	n.d.
	Mean	**n.d.**	**n.d.**	**0.25**	**n.d.**
Total % recovery	A	95.75	97.47	96.02	103.90
	B	95.33	96.13	99.54	102.25
	Mean	**95.54**	**96.80**	**97.78**	**103.07**

n.d.: not detected, DAT: days after treatment

B. MATERIAL BALANCE

Mean material balances at 50°C ranged from 95.0 to 104.7% AR for pH 4, 95.9 to 103.1% AR for pH 7, and 95.5 to 103.1% AR for pH 9 during the study (DAT-0 to DAT-5).

C. RESIDUES IN TEST SOLUTION
As shown by the complete material balances for all test conditions at all sampling intervals, the radioactivity was completely recovered in the test solutions. No adsorption was found on the apparatus walls.

D. VOLATILE RADIOACTIVITY
Carbon dioxide and volatile organic compounds were not collected.

E. TRANSFORMATION OF THE TEST ITEM
Fluopyram was found to be stable at pH 4 under the conditions tested with no degradation products detected. At pH 7 one degradation product was detected and reached a maximum of 1.6% AR (mean value) at DAT-5. At pH 9 the same minor degradation product was detected reaching 1.2% AR at DAT-5 and additionally, one further minor metabolite was detected at 0.5% in a single flask at DAT-2.

F. KINETICS
Fluopyram was found to be hydrolytically stable over the duration of the study, thus no DT_{50} or DT_{90} values could be determined.

III. CONCLUSIONS

From the very little hydrolytic decomposition observed under the test conditions, fluopyram is considered to be stable to hydrolysis with no requirements for further testing, in particular, at lower temperatures or a second position of radiolabel.

3. Assessment and conclusion

Assessment and conclusion by applicant: The study is considered to be valid and reliable.

Assessment and conclusion by RMS: Outcome and conclusion of the study. RMS should indicate if they agree to the results and conclusions of the APPL.

CA 7.2.1.2 Direct photochemical degradation

The UV-VIS absorption spectrum of a solution containing fluopyram showed one maximum at 270 nm (abs 0.1149) and a shoulder at 216 nm (abs 0.3623). The absorption of light by fluopyram terminates at above 292 nm and does not extend into the range of wavelengths relevant for the environment. It can be concluded that the direct interaction of fluopyram in aqueous solution with sunlight is unlikely (KCA 7.2.1.2/02).

However, in the rather artificial photo-transformation study of fluopyram in pure sterile buffer of pH 7 (KCA 7.2.1.2/01), a slow but continuous photolytic degradation of fluopyram was observed. The experimental half-lives (SFO) were 21.0 (phenyl-label) and 25.0 days (pyridyl-label), corresponding to 52.1 and 62.5 solar days at Phoenix, AZ, USA or 81.0 and 97.0 solar days at Athens, Greece, respectively. Thereby, one degradation product was formed at > 5% AR and identified as fluopyram-lactam. Fluopyram-lactam was observed at a maximum of 12.8% in the experiment using [phenyl-UL-^{14}C]fluopyram and 12.4% using [pyridyl-2,6-^{14}C]fluopyram by the end of the experimental phase after 13 experimental days.

In a related position paper, filed under data point KCA 7.2.1.2/03, before-menioned results are explained in more detail.

Finally, confirmation is given by study KCA 7.2.1.3/01 (photolytic degradation of fluopyram in natural water) where degradation of fluopyram was relatively slow under environmental conditions, and no degradation product was detected at > 5% AR. The maximum amount of lactam was 1.0 to 1.2% of AR, only. Since this study is regarded as highest tier of information, it can be concluded that photolytic transformation will only be a minor contributor to the overall fate of fluopyram under natural outdoor conditions, and no photolytic metabolite has to be included in residue definition for aquatic risk assessments.

1. Information on the study

Data Point:	KCA 7.2.1.2/01
Report Author:	[redacted]
Report Year:	2008
Report Title:	[14C]-AE C656448: Aqueous photolysis in buffer at pH 7
Report No:	CX/06/016
Document No:	M-297180-02-1
Guideline(s) followed in study:	EU 91/414/EEC amended by 94/37/EC, US EPA Subdivision N, Section 161-2; Canadian PMRA DACO Number 8.2.3.3.2; Japanese "Nouyaku 814" J-MAFF 2-6-2 and 13 Sa'san No. 1986; SETAC Europe March 1995, Section 10; OECD Draft August 2000
Deviations from current test guideline:	Current Guideline OECD 316 (2008) Limit of Detection was not reported (but limit of Quantitation was reported)
Previous evaluation:	yes, evaluated and accepted DAR (2012)
GLP/Officially recognised testing facilities:	Yes, conducted under GLP/Officially recognised testing facilities
Acceptability/Reliability:	Yes

2. Full summary of KCA 7.2.1.2/01

Executive Summary

The photolytic route and rate of degradation of [phenyl-UL-^{14}C] and [pyridyl-2,6-^{14}C]fluopyram were studied in sterile aqueous buffer solution (0.02 M phosphate, pH 7) under exposure to simulated sunlight (< 290 nm cut-off filter) and aerobic conditions in the laboratory at 25 ± 2 °C for 13 days.

The test was performed in static systems consisting of quartz glass vessels each containing 18 mL of test solution. During the study no volatile traps were used. The vessels were instead sealed with a stopper.

An actual study application rate of 0.96 mg/L ([phenyl-UL-^{14}C] label) and 0.99 mg/L ([pyridyl-2,6-^{14}C]label) was applied into the buffer solutions.

13 days of incubation under exposure to simulated sunlight were equivalent to 31.8 and 49.3 solar summer days in Phoenix (Arizona, USA) and Athens (Greece), respectively. For comparison, additional samples were incubated in the dark.

Duplicate samples were processed and analysed 0, 0.25, 1.25, 3, 6, 9 and 13 days after treatment (DAT) for irradiated samples using both labels. For dark samples, only one time point (DAT-13) was chosen applying label A. Samples of DAT-0 were processed and analysed immediately after application and were identical for irradiated and dark samples.

For label A, mean material balance ranged from 95.9 to 99.6% of the applied radioactivity (% AR) for irradiated test systems and was at 96.7% AR for dark test systems. For label B, mean material balance ranged from 96.8 to 100.1% AR for irradiated test systems.

In irradiated samples containing label A, the parent compound decreased from 99.5% AR at DAT-0 to 63.9% of the applied at the end of the irradiation. Amount of label A varied between 96.5 and 96.9% AR for DAT-13 in dark samples. In label B irradiated samples, the parent compound decreased from 100.1% of the applied amount at DAT-0 to 71.5% AR at DAT-13.

For label A, one degradation product was formed at > 5% AR and was identified as fluopyram-lactam. The level of fluoypram-lactam reached a maximum of 12.8% by the end of the experimental phase. As characterised by run time in HPLC the same degradation product was formed for label B and was identified as fluopyram–lactam with a maximum of 12.4% by the end of the study.

The experimental DT_{50} values of fluopyram in irradiated and in dark samples were calculated with a simple first order model. The half-life and DT_{90} were 21.0 and 69.7 days for [phenyl-UL-^{14}C]fluopyram ; 25.0 and 83.2 days for [pyridyl-2,6-^{14}C]fluopyram assuming a simple first order kinetic model.

I. MATERIALS AND METHODS

A. MATERIALS

1. Test Items

[phenyl-UL-^{14}C]fluopyram
Sample ID: BECH 1910
Specific Activity: 3.85 MBq/mg
Radiochemical Purity: >99% (HPLC/radio-detection)

[pyridyl-2,6-^{14}C]fluopyram
Sample ID: BECH 1905
Specific Activity: 3.85 MBq/mg
Radiochemical Purity: >98% (HPLC/radio-detection)

2. Test Water

The buffer was selected in order to be transparent over the spectral range of interest (290 – 800 nm), to be of low volatility and to minimise the possibility of interactions with the test item. The study was carried out using an approximately 0.02 M phosphate buffer solution at pH 7. The buffer solution was prepared by diluting 76 mL of disodium hydrogen phosphate solution ($Na_2HPO_4 \times 12\ H_2O$, 0.1 M) and 48 mL of sodium dihydrogen phosphate solution ($NaH_2PO_4 \times 2\ H_2O$, 0.1 M) to 800 mL with deionised water. The solution was adjusted to pH 7 using sodium dihydrogen phosphate solution (0.1 M) and diluted to 1 liter with deionised water. The buffer was sterilised by filtration and was then re-oxygenated.

B. STUDY DESIGN

1. Experimental Conditions

The static test system for photolytic degradation in water consisted of quartz glass vessels (50 mm x 28 mm x 2 mm). No volatile traps were used in this study. The photolysis vessels were tightly sealed to prevent any losses of radioactivity. The test equipment was either sterilised by autoclaving (glassware, agar) or by rinsing with methanol and air dried in a laminar flow cabinet (pipettes, pipettes tips).

The nominal application rate of the test item was chosen to be 1 mg/L (actual: 0.96 mg/L ([phenyl-UL-^{14}C]label) and 0.99 mg/L ([pyridyl-2,6-^{14}C]label). In order to maintain sterility, the treatment was

carried out in a laminar flow cabinet. 18 mL aliquots of the buffer solution were added into the test vessels, the stopper was removed from the vessel and the water surface was treated with 270 µL (label A) or 190 µL (label B) of the treatment solution. The vessels were then closed tightly.

The irradiated test systems were continuously irradiated under artificial sunlight for 13 days at 25 ± 2°C in a Heraeus Suntest® unit containing a xenon lamp simulating natural sunlight. A water/ethylene glycol mixture circulating through the water jacket dissipated the heat generated by the xenon source to ensure a constant temperature through the incubation. The light emission was filtered with a 290 nm cut-off UV-filter, which eliminated all wavelengths < 290 nm. The intensity of the xenon lamp was monitored at the beginning and the end of the overall test period using an irradiance sensor. The light intensity was calculated as 516 W/m^2 ([phenyl-UL-^{14}C]label) and 521 W/m^2 ([pyridyl-2,6-^{14}C]label) for 290 to 800 nm. The radiation intensity and exposure time under experimental conditions can be related to natural solar radiation at e.g. Phoenix (Arizona, USA) or Athens (Greece), representing extraordinary conditions. At this light intensity, one day under Suntest® are equivalent to ca. 2.5 days at Phoenix, Arizona (33.26°N) and to ca. 3.9 days at Athens, Greece (38.03°N).

The dark test systems were only applied with label A and incubated in a climatic cabinet in the dark for 13 days at 25 ± 2°C.

The sterility of the buffer was checked prior to study by aseptically pipetting 50 µL of aqueous solution onto a nutrient agar plate. Additionally, checks of individual samples for sterility were conducted at all sampling points throughout the study.

2. Sampling

For both labels, duplicate samples were processed and analysed 0, 0.25, 1.25, 3, 6, 9 and 13 days after treatment (DAT) for irradiated samples. Dark samples were processed and analysed after 13 days. Samples of DAT-0 were processed and analysed immediately after application and were identical for irradiated and dark samples.

3. Analytical Procedures

At each sampling interval the radioactivity of the test solution was determined by liquid scintillation counting (LSC) of two aliquots. All samples were directly investigated by HPLC without any concentration or extraction. A non-radiolabelled certified reference standard was included as a chromatographic marker.

The limit of quantification (LOQ) for the LSC method was 0.04% AR. The LOQ for the HPLC/radio-detection method was 1.74% AR.

Test item identity was confirmed by HPLC-MS(/MS) including accurate mass determination. Selected samples from this study were analysed to confirm the identity of fluopyram and the metabolite of interest.

The degradation kinetics of fluopyram was determined according to FOCUS guidance document using the software KinGUI 1.0 using a single first order kinetic model (SFO). Model input datasets were the residual amounts found in each replicate test system at each sampling interval. The initial recovery at DAT-0 was included in the parameter optimization procedure, but for optimal goodness of fit, the value was allowed to be estimated by the model. DT_{50} and DT_{90} values were calculated from the resulting kinetic parameters.

II. RESULTS AND DISCUSSION

A. DATA

Results indicated that the anticipated standardised conditions were maintained over the duration of the laboratory study. No colonies were observed on any of the nutrient agar plates for samples. Radioactive mass balance and distribution of [phenyl-UL-^{14}C], [pyridyl-2,6-^{14}C]fluopyram and metabolites in soil extracts are summarised in Table 7.2.1.2-1 to Table 7.2.1.2-3 for irradiated and dark samples.

Table 7.2.1.2-1: Photodegradation of [phenyl-UL-^{14}C]fluopyram in buffer solution (mean values expressed as % AR) – irradiated samples

Compound	Source	Replicate	DAT						
			0 [1]	0.25	1.25	3	6	9	13
Fluopyram	Irradiated	A	99.3	100.2	96.2	91.0	77.0	71.9	60.6
		B	99.8	99.0	92.4	94.4	89.4	77.8	67.2
		Mean	**99.5**	**99.6**	**94.3**	**92.7**	**83.2**	**74.8**	**63.9**
Unknown 2	Irradiated	A	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	2.1
		B	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	1.5
		Mean	**n.d.**	**n.d.**	**n.d.**	**n.d.**	**n.d.**	**n.d.**	**1.8**
Unknown 3	Irradiated	A	n.d.	n.d.	n.d.	n.d.	n.d.	2.3	3.4
		B	n.d.	n.d.	n.d.	n.d.	n.d.	1.0	2.5
		Mean	**n.d.**	**n.d.**	**n.d.**	**n.d.**	**n.d.**	**1.7**	**3.0**
Unknown 4	Irradiated	A	n.d.	n.d.	n.d.	1.4	2.5	3.1	4.1
		B	n.d.	n.d.	n.d.	1.5	1.8	4.1	3.9
		Mean	**n.d.**	**n.d.**	**n.d.**	**1.5**	**2.1**	**3.6**	**4.0**
Unknown 5	Irradiated	A	n.d.	n.d.	n.d.	0.8	2.0	2.6	2.6
		B	n.d.	n.d.	n.d.	n.d.	1.1	1.0	1.5
		Mean	**n.d.**	**n.d.**	**n.d.**	**0.4**	**1.5**	**1.8**	**2.0**
Unknown 7	Irradiated	A	n.d.	n.d.	n.d.	0.9	2.6	2.0	3.5
		B	n.d.	n.d.	n.d.	n.d.	n.d.	1.8	2.8
		Mean	**n.d.**	**n.d.**	**n.d.**	**0.4**	**1.3**	**1.9**	**3.1**
Unknown 8	Irradiated	A	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	2.2
		B	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	1.4
		Mean	**n.d.**	**n.d.**	**n.d.**	**n.d.**	**n.d.**	**n.d.**	**1.8**
Fluopyram-lactam	Irradiated	A	n.d.	n.d.	2.1	4.3	9.8	11.5	14.2
		B	n.d.	n.d.	1.2	3.3	6.0	9.0	11.5
		Mean	**n.d.**	**n.d.**	**1.6**	**3.8**	**7.9**	**10.3**	**12.8**
Unknown 10	Irradiated	A	n.d.	n.d.	n.d.	n.d.	2.1	1.9	1.6
		B	n.d.	n.d.	n.d.	n.d.	1.4	1.3	1.7
		Mean	**n.d.**	**n.d.**	**n.d.**	**n.d.**	**1.8**	**1.59**	**1.6**
Unknown 11	Irradiated	A	n.d.	n.d.	n.d.	n.d.	1.8	1.5	2.1
		B	n.d.	n.d.	n.d.	n.d.	0.6	1.1	1.7
		Mean	**n.d.**	**n.d.**	**n.d.**	**n.d.**	**1.2**	**1.3**	**1.9**
Total recovery [2]	Irradiated	A	99.3	100.2	98.3	98.3	97.9	96.6	96.3
		B	99.8	99.0	93.6	99.2	100.2	97.1	95.6
		Mean	**99.5**	**99.6**	**96.0**	**98.8**	**99.0**	**96.9**	**95.9**

n.d.: not detected, DAT: days after treatment
[1]DAT-0 samples were identical for irradiated and dark samples.
[2]Material balance was identical.

Table 7.2.1.2-2: Photodegradation of [phenyl-UL-^{14}C]fluopyram in buffer solution (mean values expressed as % AR) – dark samples

Compound	Source	Replicate	DAT
			13
Fluopyram	Dark	A	96.9
		B	96.5
		Mean	**96.7**
Total recovery	Dark	A	96.9
		B	96.5
		Mean	**96.7**

Table 7.2.1.2-3: Photodegradation of [pyridyl-2,6-^{14}C]fluopyram in buffer solution (mean values expressed as % AR) – irradiated samples

Compound	Source	Repli-cate	DAT						
			0[1]	0.25	1.25	3	6	9	13
Fluopyram	Irradiated	A	100.1	98.2	97.2	94.6	95.5	76.7	69.2
		B	100.1	99.1	97.1	93.7	80.7	71.0	73.8
		Mean	**100.1**	**98.6**	**97.2**	**94.1**	**88.0**	**73.8**	**71.5**
Unknown 1	Irradiated	A	n.d.	n.d.	n.d.	n.d.	n.d.	2.1	2.3
		B	n.d.	n.d.	n.d.	n.d.	n.d.	2.0	3.8
		Mean	**n.d.**	**n.d.**	**n.d.**	**n.d.**	**n.d.**	**2.1**	**3.0**
Unknown 2	Irradiated	A	n.d.	n.d.	n.d.	n.d.	n.d.	2.1	2.8
		B	n.d.	n.d.	n.d.	n.d.	2.3	3.3	2.0
		Mean	**n.d.**	**n.d.**	**n.d.**	**n.d.**	**1.1**	**2.7**	**2.4**
Unknown 5	Irradiated	A	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
		B	n.d.	n.d.	n.d.	0.4	n.d.	n.d.	n.d.
		Mean	**n.d.**	**n.d.**	**n.d.**	**0.2**	**n.d.**	**n.d.**	**n.d.**
Unknown 6	Irradiated	A	n.d.	n.d.	n.d.	n.d	n.d.	1.3	1.7
		B	n.d.	n.d.	n.d.	n.d	n.d.	1.5	1.94
		Mean	**n.d.**	**n.d.**	**n.d.**	**n.d**	**n.d.**	**1.4**	**1.8**
Unknown 7	Irradiated	A	n.d.	n.d.	n.d.	n.d.	n.d.	1.5	4.1
		B	n.d.	n.d.	n.d.	0.5	1.3	2.6	2.3
		Mean	**n.d.**	**n.d.**	**n.d.**	**0.2**	**0.6**	**2.1**	**3.2**
Fluopyram-lactam	Irradiated	A	n.d.	n.d.	1.6	3.4	4.8	9.4	14.1
		B	n.d.	n.d.	0.9	3.6	6.7	10.5	10.7
		Mean	**n.d.**	**n.d.**	**1.3**	**3.5**	**5.7**	**9.9**	**12.4**
Unknown 10	Irradiated	A	n.d.	n.d.	n.d.	n.d.	n.d.	1.6	2.4
		B	n.d.	n.d.	n.d.	n.d.	n.d.	2.2	1.6
		Mean	**n.d.**	**n.d.**	**n.d.**	**n.d.**	**n.d.**	**1.9**	**2.0**
Unknown 11	Irradiated	A	n.d.	n.d.	n.d.	n.d.	n.d.	1.6	1.9
		B	n.d.	n.d.	n.d.	n.d.	1.3	2.2	2.3
		Mean	**n.d.**	**n.d.**	**n.d.**	**n.d.**	**0.7**	**1.9**	**2.1**
Unknown 12	Irradiated	A	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	1.5
		B	n.d.	n.d.	n.d.	n.d.	1.3	n.d.	0.9
		Mean	**n.d.**	**n.d.**	**n.d.**	**n.d.**	**0.7**	**n.d.**	**1.2**
Unknown 13	Irradiated	A	n.d.	n.d.	n.d.	n.d.	n.d.	1.3	2.2
		B	n.d.	n.d.	n.d.	n.d.	n.d.	2.1	1.5
		Mean	**n.d.**	**n.d.**	**n.d.**	**n.d.**	**n.d.**	**1.7**	**1.8**
Unknown 14	Irradiated	A	n.d.	n.d.	n.d.	n.d.	n.d.	0.8	n.d.
		B	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
		Mean	**n.d.**	**n.d.**	**n.d.**	**n.d.**	**n.d.**	**0.4**	**n.d.**
Total recovery	Irradiated	A	100.1	98.2	98.8	98.0	100.1	98.3	99.9

Compound	Source	Repli-cate	DAT						
			0 [1]	0.25	1.25	3	6	9	13
		B	100.1	99.1	98.0	97.3	93.5	97.3	97.1
		Mean	**100.1**	**98.6**	**98.4**	**97.6**	**96.8**	**97.8**	**98.5**
Material balance	Irradiated	A	100.1	98.2	98.8	97.9	100.1	98.3	102.2
		B	100.1	99.1	98.0	98.2	93.5	97.3	100.8
		Mean	**100.1**	**98.6**	**98.4**	**98.0**	**96.8**	**97.8**	**101.5**

n.d.: not detected, DAT: days after treatment
[1] DAT-0 samples were identical for irradiated and dark samples.

B. MATERIAL BALANCE

For [phenyl-UL-^{14}C]fluopyram, mean material balance ranged from 95.9 to 99.6% of the applied radioactivity (% AR) for irradiated test systems and was at 96.7% AR for dark test systems. For [pyridyl-2,6-^{14}C]fluopyram, mean material balance ranged from 96.8 to 100.1% AR for irradiated test systems. The complete material balances found at all sampling intervals for both irradiated and dark samples demonstrated that there was no significant loss of radioactivity from the test systems or during sample processing.

C. VOLATILES

No volatiles were measured during the study.

D. DEGRADATION OF TEST ITEM

In irradiated samples containing label A, the parent compound decreased from 99.5% AR at DAT-0 to 63.9% of the applied at the end of the irradiation. Amount of label A varied between 96.5 and 96.9% AR for DAT-13 in dark samples. In the label B irradiated samples, the parent compound decreased from 100.1% of the applied amount at DAT-0 to 71.5% AR at DAT-13.
For label A, one degradation product was formed at 12.5% AR and was identified as fluopyram-lactam. The level of fluopyram-lactam reached a maximum of 12.8% by the end of the experimental phase. Furthermore, eight minor degradation products were detected, but none exceeded 4.0% AR at the end of the study. As characterised by run time in HPLC the same degradation product was formed for label B and was identified as fluopyram–lactam. The level of fluopyram-lactam reached a maximum of 12.4% by the end of the study. Ten minor degradation products were detected, but none exceeded 3.2% AR at the end of the study.

F. Kinetics

The experimental DT_{50} values of fluopyram in irradiated and in dark samples were calculated with a simple first order model. The half-life and DT_{90} were 21.0 and 69.7 days (phenyl label); 25.0 and 83.2 days (pyridyl label) assuming a simple first order kinetic model. The statistical parameter and visual fits are summarized in the tables below.

Table 7.2.1.2-4: Kinetic parameter of [phenyl-UL-^{14}C]fluopyram in irradiated samples

Kinetic model	DT_{50} actual	DT_{90} actual	DT_{50} fast / slow	VA	χ^2err / SWARC	k_1	k_2	g	t-test k_1 / k_2	95th CI of k_1	95th CI of k_2
	(d)	(d)	(d)		(% / -)	(1/d)	(1/d)	(-)	(-)	(1/d)	(1/d)
SFO	21.0	69.7	-	+	1.1 / -	0.0330	-	-	<0.001 / -		-

VA = visual assessment, + = good, o = acceptable, - = poor
SWARC = Scaled Weighted Area under Residue Curve
CI = confidence interval

Trigger Endpoints: SFO fit is statistically (χ^2err <15%, t-test <0.05) good and visually acceptable. Consequently, **SFO** degradation model is appropriate for trigger endpoints.

SFO

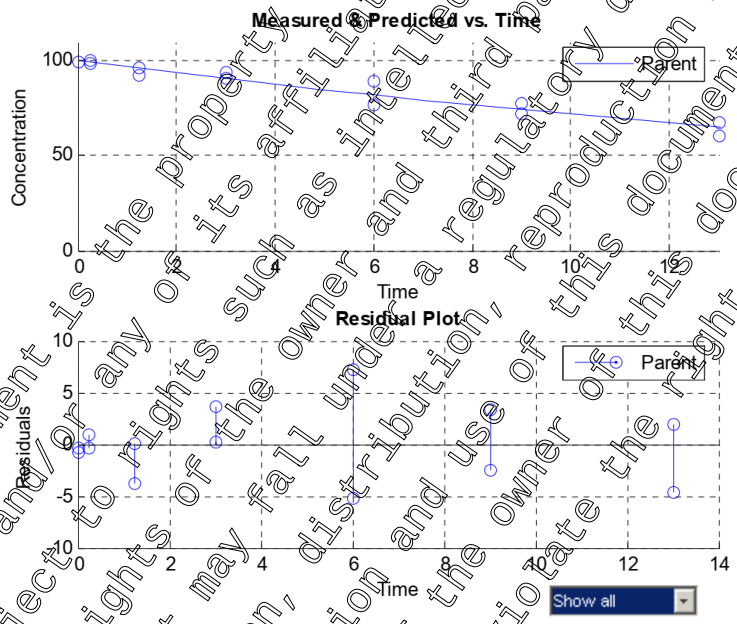


Table 7.2.1.2-5: Kinetic parameter of [pyridyl-2,6-^{14}C]fluopyram in irradiated samples

Kinetic model	DT_{50} actual	DT_{90} actual	DT_{50} fast / slow	VA	χ^2err / SWARC	k_1	k_2	g	t-test k_1 / k_2	95th CI of k_1	95th CI of k_2
	(d)	(d)	(d)		(% / -)	(1/d)	(1/d)	(-)	(-)	(1/d)	(1/d)
SFO	25.0	83.2	-	+	2.0 / -	0.0277	-	-	<0.001 / -		-

VA = visual assessment, + = good, o = acceptable, - = poor
SWARC = Scaled Weighted Area under Residue Curve
CI = confidence interval

Trigger Endpoints: SFO fit is statistically (χ^2err <15%, t-test <0.05) good and visually acceptable. Consequently, **SFO** degradation model is appropriate for trigger endpoints.

SFO

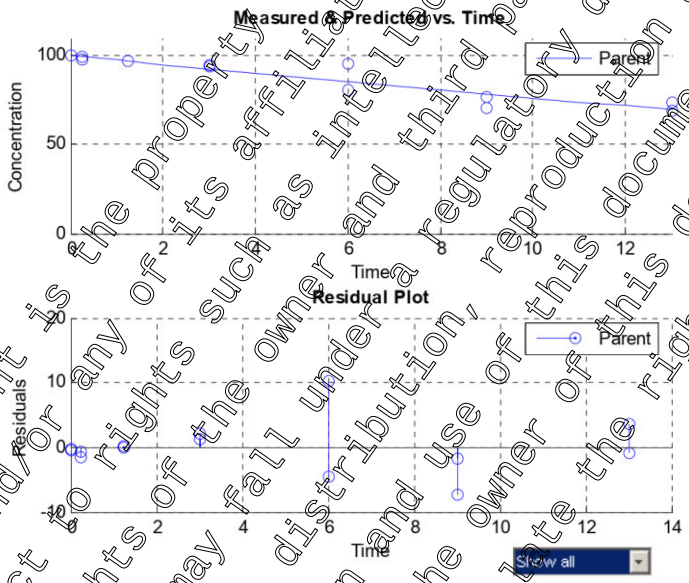


Table 7.2.1.2-6: Environmental half-lives of fluopyram

Irradiated test system	Single First Order Model			Equivalent days natural light in Phoenix, AZ		Equivalent days natural light in Athens, Greece	
	Experimental DT_{50} (d)	Experimental DT_{90} (d)	Chi^2Err	DT_{50} (d)	DT_{90} (d)	DT_{50} (d)	DT_{90} (d)
phenyl (label A)	21.0	69.7	1.1	52.1	172.9	81.0	268.0
pyridyl (label B)	25.0	83.2	2.0	62.5	208.0	97.0	323.0

III. CONCLUSIONS

Fluopyram was slowly but steadily degraded in aqueous buffer solution of pH 7 at 25 °C under exposure to simulated sunlight under aerobic conditions in the laboratory, while fluopyram was stable in dark control samples. One photo-degradation product in aqueous buffer solution of pH 7 was formed and identified as fluopyram-lactam.

3. Assessment and conclusion

Assessment and conclusion by applicant:
The study is considered to be valid and reliable.

Assessment and conclusion by RMS:
Outcome and conclusion of the study: RMS should indicate if they agree to the results and conclusions of the APPL.

1. Information on the study

Data Point:	KCA 7.2.1.2/02
Report Author:	[redacted]
Report Year:	2006
Report Title:	AE C656948: Determination of the quantum yield and assessment of the environmental half-life of the direct photodegradation in water
Report No:	MEF-06/218
Document No:	M-279154-01-1
Guideline(s) followed in study:	Germany UBA (1992) Phototransformation of Chemicals in Water, Part A; Test Method: ECETOC; U.S. EPA OPPTS Guideline No. N/A equivalent to U.S. EPA OPPTS Guideline No. 835.SUPP
Deviations from current test guideline:	Current Guideline: OECD 316 (2008) None
Previous evaluation:	yes, evaluated and accepted in DAR (2011)
GLP/Officially recognised testing facilities:	Yes, conducted under GLP/Officially recognised testing facilities
Acceptability/Reliability:	Yes

2. Full summary of KCA 7.2.1.2/02

Executive Summary
The quantum yield of direct phototransformation in water of fluopyram was determined using polychromatic light according to the ECETOC method.

The UV-VIS absorption spectrum of a solution of 10.02 mg/L fluopyram in water showed one maximum at 270 nm (abs 0.1149) and a shoulder at 216 nm (abs 0.3623). The UV-VIS absorption spectra of fluopyram in buffered aqueous solutions at pH 4, pH 7, and pH 9 showed comparable absorption properties. The absorption of light by fluopyram terminates at above 292 nm and does not extend into the range of wavelengths relevant for the environment. No quantum yield of direct phototransformation in water could be determined. In general, the absorption properties indicate that direct interactions of fluopyram in aqueous solution with the sunlight in the troposphere is unlikely.

Direct phototransformation in aqueous solution does not contribute to the overall elimination of fluopyram in the environment. Even if a maximum quantum yield of $\Phi = 1$ is assumed, the prediction of the so-called environmental phototransformation half-life by means of arithmetic computer models would result in values of more than one year.

Thus, direct phototransformation in aqueous solution does not contribute to the overall elimination of fluopyram in the environment. This assessment does not consider other potential mechanisms which may enhance the degradation in natural water, e.g. by indirect photolytic processes. Since such processes

cannot be avoided entirely, i.e. in buffer solutions, any fluopyram degradation observed (compare the two studies summarized before) might have been caused by indirect phototransformation reactions.

I. MATERIALS AND METHODS

A. MATERIALS

1. Test Item

Unlabelled fluopyram (AE C656948)

ID:	AZ 12954
Batch no.:	NLL7687-2
Chemical Purity:	99.4%

2. Test Solutions

Millipore water and 0.01 mol/L aqueous buffer solutions were used (acetate pH 4, phosphate pH 7 and borate pH 9).

B. STUDY DESIGN

1. Experimental Conditions

The method for the determination of the quantum yield developed by the EC/TOC Task Force "Photo degradation" is based on the partition of the polychromatic light into sectors of wavelengths. Sectors of 5 nm were formed within the range of wavelengths from 295 to 400 nm and sectors of 10 nm from 401 nm on. The quantum yield of a photochemical reaction is defined by the proportion of light quanta absorbed by a substance resulting to a reaction.

The test was performed using an initial concentration of 10.02 mg fluopyram/L. The solutions were added into a quartz cell (optical path length (d) = 1 cm, height (h) = 4.4 cm) with Teflon® plug and measured using a UV-VIS-spectrophotometer. No other tests, phototransformation experiments and actinometry were conducted.

2. Analytical Procedures

The UV-VIS absorption properties of the test item were characterised by the number and position of the absorption maxima as well as for each maximum by the molar extinction coefficient ε [L ∗ mol^{-1} cm^{-1}]. Moreover, the bandwidth was determined for each maximum. This corresponds to the range between the two wavelengths as follows:

$$\lambda_1 (Abs_{\lambda max}/2) \text{ to } \lambda_2 (Abs_{\lambda max}/2)$$

The extinction E and (in case of the spectrum in pure water above 290 nm) the ε-values were determined in steps of 1 nm. According to the recent instrument baseline test performed in accordance with the manufacturer's manual, an extinction value of 0.0003 was the background noise level of the instrument.

In case of the respective UV spectrum the extinction value 0.0003 was reached at a wavelength of approximately > 292 nm. 292.5 nm is the lowest possible input wavelength needed for the assessment of the so-called environmental half-life by means of arithmetic models Thus, no calculation can be made.

II. RESULT AND DISCUSSION

A. UV-VIS Absorption Properties of Fluopyram

The UV-VIS absorption spectrum of a solution of 10.02 mg/L fluopyram in water showed one maximum at 270 nm (abs 0.1149) and a shoulder at 216 nm (abs 0.3623). The UV-VIS absorption spectra of report name in buffered aqueous solutions containing 10.02 mg report name/L showed similar absorption properties. The absorption of light by fluopyram terminates at above 292 nm and does not extend into the range of wavelengths relevant for the environment. In general, the absorption properties indicate that

direct interactions of fluopyram in aqueous solution with the sunlight is unlikely. This assessment does not consider any indirect mechanisms, which may enhance the photodegradation in natural water.

B. Phototransformation in the Merry-Go-Round Irradiation Apparatus
No photodegradation was investigated because fluopyram did not absorb light above 292 nm.

C. Quantum Yield of the Direct Phototransformation
No quantum yield of direct phototransformation of fluopyram in water could be determined according to the ECETOC method.

D. Assessment of the Environmental Half-life of Direct Phototransformation
Besides compound specific factors like the quantum yield Φ, the extent of absorption of a compound in the relevant range of the tropospheric sunlight spectrum, the degradation by sunlight is influenced by geographic, climatic, seasonal and matrix-specific conditions.

The environmental half-life for different conditions can be assessed by means of arithmetic models. A prerequisite for the assessments made in the following is the presence of the substance in aqueous solution, i.e. surface water, rain, fog or aerosols water so that exposure to sunlight is given and it is taken for granted that water constituents do not reduce the intensity of sunlight. Moreover, fluopyram must have absorption properties in the range of the tropospheric sunlight spectrum, which is not the case.

Even if a maximum yield of Φ = 1 would apply for fluopyram, environmental half-lives of greater than one year would result, since molar extinction coefficients ε above 292 nm were found to be zero.

III. CONCLUSIONS

Direct phototransformation in aqueous solution does not contribute to the overall elimination of fluopyram in the environment. Even if a maximum quantum yield of Φ = 1 is assumed, the prediction of the so-called environmental phototransformation half-life by means of arithmetic computer models would result in values of more than one year. However, this assessment does not consider any indirect mechanisms, which may enhance the photodegradation in natural water. Since such processes cannot be avoided entirely, i.e. in buffer solutions, any fluopyram degradation observed (compare the two studies summarized before) might have been caused by indirect phototransformation reactions.

3. Assessment and conclusion

Assessment and conclusion by applicant: The study is considered to be valid and reliable.

Assessment and conclusion by RMS: Outcome and conclusion of the study: RMS should indicate if they agree to the results and conclusions of the APPL.

1. Information on the study

Data Point:	KCA 7.2.1.2/03
Report Author:	[redacted]
Report Year:	2012
Report Title:	Reply to EFSA request concerning the consideration of the contribution of photolytic degradation processes to the overall transformation rate in natural aquatic systems
Report No:	EnSa-12-0205
Document No:	M-428270-01-1
Guideline(s) followed in study:	not specified
Deviations from current test guideline:	Current Guideline: not applicable (notifier request)
Previous evaluation:	No, not previously submitted
GLP/Officially recognised testing facilities:	No, not conducted under GLP/Officially recognised testing facilities
Acceptability/Reliability:	Yes

2. Full Summary of KCA 7.2.1.2/03

Introduction

On 24th January 2012 Bayer CropScience received a request for additional information from EFSA within the Peer Review of the Draft Assessment Report (DAR, ref. 1) on the active substance fluopyram. The purpose of this statement is to reply to Request 5:

"Applicant to consider and provide their assessment / view of the contribution that photolysis will make to overall transformation rate in natural sediment water systems, relative to the much slower biotransformation rate apparent in the available dark laboratory sediment water incubations."

Reply

In the DAR, it is stated that "results indicate that aquatic photolysis is not an important route of transformation for AE C656948 (fluopyram) in the aquatic environment and no transformation products are expected to be formed in the natural sediment /water systems."

The understanding of the request is therefore to compare the results of tests in natural water, i.e. of abiotic, sterile photolysis and of biotic water/sediment tests in the dark, in order to conclude on the potential contribution of photo-transformation to the dissipation of fluopyram from the aquatic environment.

Phototransformation study in sterile natural water (please refer to KCA 7.2.1.3/01, M-296408-01-1):
Irradiation was performed at 25 °C equivalent to more than 30 environmental days and to a light intensity of Phoenix, AZ (US) at summer solstice.

The DAR concludes that "Based on the experimental SFO DT_{50} of 21 days (equivalent to 42.0 days, assuming 12 hour days of continuous sunlight), the predicted environmental DT_{50} was calculated to be e.g. 87 (86.6 rounded) solar summer days at Phoenix, AZ, USA. Under dark conditions the half-life under experimental conditions is 387 (386.9 rounded) days."

The results in terms of half-lives of fluopyram from indirect photolysis show their variability dependent on light intensity at the various locations in the world. Even under the intense, US-related light conditions of Arizona, overall transformation was slow as indicated by an environmental DT_{50} of 87

days. A prolonged environmental DT_{50} of 135 days has been extrapolated for Athens light conditions representing the worst case, i.e. the Southern EU.

The results thus indicate well that photolytic transformation processes play a minor role for the dissipation of fluopyram from a natural water environment. This conclusion is supported by the fact that under realistic actual weather conditions including rainfall, clouds and other factors these cause diffuse conditions of light thus attenuating the potential influence of photolytic transformation in the environment in comparison to the idealised, but artificial conditions of the laboratory test.

Water/Sediment Study (please refer to KCA 7.2.2.3/01, M-290531-01-2):
The study followed OECD Guideline 308 requiring incubation in the dark. Incubation was performed in two differing water/sediment systems at 20°C for 120 days in maximum.

Following 120 days of incubation, recovery of ^{14}C-fluopyram was about 89% AR in total systems of both sediment types after 120 days. The results thus indicate slow microbial conversion under the conditions of water/sediment testing.

Conclusion
The investigations performed in natural water therefore showed slow photolytic or microbial conversion of fluopyram under the conditions of testing. For total system degradation in sediment/water tests, the resulting values of degradation half-lives are higher than those derived from phototransformation. The surface water risk assessment has been based on half-lives from the sediment/water tests thus to include significant conservative elements when being compared with those from photo-transformation.

Conclusively, phototransformation is considered to contribute neither to a better understanding of the primary routes and rates, nor to a significant extent to the dissipation of fluopyram from the aquatic environment in the field.

3. Assessment and conclusion

Assessment and conclusion by applicant: Phototransformation is considered to contribute neither to a better understanding of the primary routes and rates, nor to a significant extent to the dissipation of fluopyram from the aquatic environment in the field. Please consider the results of Quantum Yield assessment as well.

Assessment and conclusion by RMS: Outcome and conclusion of the study. RMS should indicate if they agree to the results and conclusions of the APPL.

CA 7.2.1.3 Indirect photochemical degradation

Under sterile conditions in natural water a photo-degradation half-life of 21.2 days was determined for fluopyram. The predicted environmental DT_{50} is calculated to be 86.6 solar summer days in Phoenix, AZ, USA or 135 solar summer days in Athens, Greece. Photolytic degradation of fluopyram in natural water was relatively slow under environmental conditions, and no degradation product at > 5% AR was detected. The maximum amount of lactam was 1.0 to 1.2% of AR, only. Since this study is regarded as highest tier of information, it can be concluded that photolytic transformation will only be a minor contributor to the overall fate of fluopyram under natural outdoor conditions, and no photolytic metabolite has to be included in residue definition for aquatic risk assessments.

1. Information on the study

Data Point:	KCA 7.2.1.3/01
Report Author:	[redacted]
Report Year:	2007
Report Title:	[Phenyl-UL-14C)AE C656948 and [pyridyl-2,6-14C]AE C656948: Phototransformation in natural water
Report No:	MEF-07/227
Document No:	M-296408-01-1
Guideline(s) followed in study:	EU 95/36/EC and 94/37/EC amending 91/414/EEC; SETAC, March 1995; US-EPA, Subdivision N, 162-1; Canada PMRA, DACO No. 8.2.3.2; Equivalent to US EPA OPPTS Guideline No. 835.2240 SUPP
Deviations from current test guideline:	Current Guideline: OECD 316 (2008) the test was performed in natural water instead of buffer solution
Previous evaluation:	yes, evaluated and accepted DAR (2011)
GLP/Officially recognised testing facilities:	Yes, conducted under GLP/Officially recognised testing facilities
Acceptability/Reliability:	Yes

2. Full summary of KCA 7.2.1.3/01

Executive Summary

The photolytic route and rate of degradation of [phenyl-UL-^{14}C]fluopyram and [pyridyl-2,6-^{14}C]fluopyram were studied in natural river water under exposure to simulated sunlight and aerobic conditions in the laboratory at 25 ± 1 °C for 8 days.

The test was performed in static systems consisting of quartz glass vessels each containing 10 mL of test solution equipped with traps for the collection of carbon dioxide and volatile organic compounds.

The actual application rate of the test item was 0.680 mg/L ([phenyl-UL-^{14}C]fluopyram) and 0.669 mg/L ([pyridyl-2,6-^{14}C]fluopyram).
8 days of incubation under exposure to simulated sunlight were equivalent to e.g. 32.8 solar summer days in Phoenix (Arizona, USA). For comparison, additional samples were incubated in the dark.

Duplicate samples were processed and analysed at 1, 2, 3, 6, 7 and 8 days after treatment (DAT) for both irradiated and dark samples. Samples of DAT-0 were processed and analysed immediately after application and were identical for irradiated and dark samples. The volatile traps were assayed at the last sampling interval to determine the amount of carbon dioxide and volatile organic compounds.

Mean material balance ranged from 103.9 to 106.3% of the applied radioactivity (% AR) for irradiated test systems and from 103.3 to 107.2% AR for dark test systems.

For irradiated test systems, only minor $^{14}CO_2$ formation of 0.6% AR ([phenyl-UL-^{14}C]fluopyram) and 0.1% AR ([pyridyl-2,6-^{14}C]fluopyram) was detected at DAT-8. No $^{14}CO_2$ was formed in the dark samples. Organic volatiles were not detected.

The mean occurrence of fluopyram and its metabolite fluopyram-lactam was calculated using the means of both labels. In the irradiated test system, fluopyram decreased from an average of 105.8% AR at DAT-0 to 84.0% AR after DAT-8. In the dark test systems, fluopyram was stable with 104.8% AR at DAT-8.

No degradation products were observed at >10% AR for both labels. For [phenyl-UL-^{14}C]fluopyram up to 12 minor photolytes were observed. One individual very polar region (6.7 min) reached a maximum of 5.5% AR at DAT-7 and decreased to 5.0% at DAT-8. For [pyridyl-2,6-^{14}C]fluopyram up to 13 minor metabolites were observed, each representing not more than 4.5% AR. Using [phenyl-UL-^{14}C]fluopyram, fluopyram-lactam was detected at maximum 1.0 to 1.2% in the samples of day 6 to day 8, only. Using [pyridyl-2,6-^{14}C]fluopyram, fluopyram-lactam was detected up to 0.8 to 1.2% in the samples of day 3 to day 8, only.

The experimental DT_{50} and DT_{90} values of fluopyram in irradiated and dark samples were calculated using single first order (SFO) kinetics. Based on the experimental DT_{50} of 21.2 days for fluopyram, the predicted environmental DT_{50} was calculated to be e.g. 86.6 solar summer days at Phoenix, AZ, USA or 134.5 summer days at Athens, Greece. Under dark conditions the half-life under experimental conditions is 386.9 days.

In conclusion, phototransformation in natural water is of minor importance for degradation of fluopyram in environmental surface waters, and no photoproduct is to be expected.

I. MATERIALS AND METHODS

A. MATERIALS

1. Test Item

[phenyl-^{14}C]AE C656948 ([phenyl-UL-^{14}C]fluopyram)
Sample ID: BECH 2159
Specific Activity: 3.85 MBq/mg
Radiochemical Purity: >99% (HPLC/radio-detection and radio-TLC),
Chemical Purity: >99% (HPLC UV 210 nm)

[pyridyl-^{14}C]AE C656948 ([pyridyl-2,6-^{14}C]fluopyram)
Sample ID: BECH 2160
Specific Activity: 3.85 MBq/mg
Radiochemical Purity: >99% (HPLC/radio-detection and radio-TLC)
Chemical Purity: >99% (HPLC UV 210 nm)

2. Test Water

Test water was sampled from the Rhine River (location km 705). The pH was measured to be 8.1, the conductivity 374 µS/cm and the oxygen saturation 101.9% at a temperature of 19.6 °C. Water from the Rhine River represents typical natural water in agricultural areas. The UV/VIS-spectrum of the Rhine River water was measured in the range of 290 to 800 nm and the UV absorption was < 0.05 (1 cm layer). The amount of organic material is in a range that does not influence the irradiation due to UV absorption in the relevant UV-range > 290 nm. The water was used without further filtration. Before application the water was sterilized by steam pressure to avoid biotic degradation of the test item.

B. STUDY DESIGN

1. Experimental Conditions

The static test system for photolytic degradation in natural water consisted of quartz glass vessels (50 mm x 26 mm x 16 mm) each containing 10 mL of the test solution (natural water + test item). Before, each test vessel was sterilized in an autoclave. The flasks were closed with a solid trap attachment permeable for oxygen, containing soda lime for absorption of carbon dioxide and a polyurethane (PU) foam plug for adsorption of volatile organic compounds (VOC).

The test solutions were prepared under sterile conditions under a clean bench in order to prevent biodegradation of the test item during the study.

For both test solutions, 2-mL aliquots of the application solutions were dosed by an Eppendorf pipette into two Erlenmeyer flasks containing sterile natural water (each 198 mL) to obtain test solution concentrations of about 1 mg/L. The Erlenmeyer flasks were covered (not air-tight) with aluminum foil to protect them from light. The solutions were stirred (magnetic stirrer) under sterile conditions (clean bench) for about one hour to saturate them with oxygen.

The actual application rate of the test item was 0.680 mg/L ([phenyl-^{14}C]fluopyram) and 0.669 mg/L ([pyridyl-^{14}C]fluopyram). Aliquots of 10 mL of the test solutions were distributed into the test vessels by a sterile Eppendorf pipette. The vessels were fitted with traps and kept in a Suntest® chamber (irradiated samples) or climatic chamber (dark samples). The content of acetonitrile in the test solutions was <0.1%.

The irradiated test systems were continuously irradiated under artificial sunlight for 8 days at 25 ± 1°C in a Suntest® irradiation unit containing a xenon lamp simulating natural sunlight. The temperature was maintained by using a cooling plate connected to a refrigerated circulating chiller. The light emission was filtered with a 290 nm cut-off UV-filter, which eliminated all wavelengths < 290 nm. The intensity of the xenon lamp was monitored at the beginning and the end of the overall test period using an irradiance sensor. The global light intensity was calculated as 1469 W/m^2 for 300 to 3000 nm. The radiation intensity and exposure time under experimental conditions can be related to natural solar radiation at e.g. Phoenix (Arizona, USA), representing extraordinary conditions. At this light intensity, it takes 5.9 h in the Suntest unit to equal one solar summer day, e.g. at Phoenix. Therefore, the equivalent of 30 solar days is achieved by this design using continuous irradiation for approximately 7.4 days at Phoenix.

The dark test systems were incubated in a climatic cabinet in the dark for 8 days at 25 ± 1°C.

2. Sampling

Duplicates of the test vessels were processed for analysis immediately after the application of the treatment solutions on day 0. Subsequently, samples of both irradiated and dark test systems were taken and processed at 1, 2, 3, 6, 7 and 8 days after treatment (DAT).

3. Analytical Procedures

At each sampling interval, test solutions were analysed by liquid scintillation counting (LSC) and HPLC/radio-detection as primary method to determine the degradation of fluopyram (both labels) as well as the formation and decline of degradation products. The results of the primary method were confirmed for representative test solutions by a LC confirmatory method. The amounts of volatiles were determined by LSC after extraction of the solid traps.

The limit of quantification (LOQ) for the LSC method was defined as the double average instrument background count rate, i.e. 0.22 Bq. The limit of detection (LOD) for the HPLC/radio-detection method was 0.3% AR.

Test item identity was confirmed by HPLC-MS(/MS) including accurate mass determination. No metabolites were further identified by spectroscopically methods. The metabolite fluopyram-lactam was identified by co-chromatography.
The sterility was checked at several sampling intervals throughout the test. Aliquots of the test solutions were applied onto a culture medium and incubated at 30 °C for at least two weeks.

The degradation kinetics of the test item was determined according to FOCUS guidance document using the software KinGUI 1.1 using a single first order kinetic model. Model input datasets were the residual amounts found in each replicate test system at each sampling interval. The amount of fluopyram at DAT-0 was included in the parameter optimization procedure, but for optimal goodness of fit, the value was

allowed to be estimated by the model. DT_{50} and DT_{90} values were calculated from the resulting kinetic parameters.

II. RESULTS AND DISCUSSION

A. DATA

Radioactive mass balance and distribution of [phenyl-UL-^{14}C]-, [pyridyl-2,6-^{14}C]fluopyram and metabolites in soil extracts are summarized in Table 7.2.1.3-1 and Table 7.2.1.3-2 for irradiated and dark samples. Sterility checks showed that sterility was maintained throughout the study. The pH value of the test solution increased slightly from 8.2 to 9.5 during incubation.

Table 7.2.1.3-1: Photodegradation of [^{14}C]fluopyram in natural water (mean values expressed as % AR) – irradiated samples

Compound	Source	Label [3]	DAT						
			0 [1]	1	2	3	6	7	8
Fluopyram	Irradiated	A	106.2	106.6	101.6	98.6	86.4	84.7	84.4
		B	105.4	103.8	97.6	92.5	84.4	84.4	83.6
		Mean	**105.8**	**105.2**	**99.6**	**95.5**	**85.4**	**85.4**	**84.0**
6.7 min	Irradiated	A	n.d.	n.d.	1.2	2.0	5.1	5.5	5.0
		B	n.d.	n.d.	0.7	1.2	1.9	1.9	2.0
		Mean	**n.d.**	**n.d.**	**1.0**	**1.6**	**3.5**	**3.7**	**3.5**
8.9 min	Irradiated	A	n.d.	n.d.	0.7	1.3	2.5	3.6	3.0
		B	n.d.	n.d.	n.d.	n.d.	0.6	n.d.	0.6
		Mean	**n.d.**	**n.d.**	**0.7**	**1.3**	**1.6**	**3.6**	**1.8**
22.9 min	Irradiated	A	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
		B	n.d.	0.3	1.8	2.2	3.2	3.6	4.5
		Mean	**n.d.**	**0.3**	**1.8**	**2.2**	**3.2**	**3.6**	**4.5**
24.1 min	Irradiated	A	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
		B	n.d.	0.3	0.7	1.3	1.8	2.4	2.0
		Mean	**n.d.**	**0.3**	**0.7**	**1.3**	**1.8**	**2.4**	**2.0**
24.6 min	Irradiated	A	0.5	1.1	2.2	3.0	4.4	5.1	4.4
		B	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
		Mean	**0.5**	**1.1**	**2.2**	**3.0**	**4.4**	**5.1**	**4.4**
26.3 min	Irradiated	A	n.d.	n.d.	n.d.	n.d.	0.6	0.9	0.7
		B	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d
		Mean	**n.d.**	**n.d.**	**n.d.**	**n.d.**	**0.6**	**0.9**	**0.7**
29.9 min	Irradiated	A	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
		B	n.d.	0.4	0.9	1.0	1.6	1.2	1.6
		Mean	**n.d.**	**0.4**	**0.9**	**1.0**	**1.6**	**1.2**	**1.6**
32.4 min	Irradiated	A	n.d.	n.d.	n.d.	n.d.	1.0	0.9	2.4
		B	n.d.	n.d.	n.d.	n.d.	1.0	1.6	1.2
		Mean	**n.d.**	**n.d.**	**n.d.**	**n.d.**	**1.0**	**1.3**	**1.8**
34.5 min	Irradiated	A	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
		B	n.d.	n.d.	n.d.	n.d.	0.8	1.4	0.8
		Mean	**n.d.**	**n.d.**	**n.d.**	**n.d.**	**0.8**	**1.4**	**0.8**
36.2 min	Irradiated	A	n.d.	n.d.	n.d.	n.d.	0.8	0.9	0.8
		B	n.d.	n.d.	1.1	1.6	2.4	2.9	2.0
		Mean	**99.5**	**99.6**	**1.1**	**1.6**	**1.6**	**1.9**	**1.4**
37.5 min	Irradiated	A	n.d.	n.d.	n.d.	n.d.	0.8	0.8	1.5
		B	n.d.	n.d.	1.0	1.1	1.7	1.7	2.1
		Mean	**n.d.**	**n.d.**	**1.0**	**1.1**	**1.3**	**1.3**	**1.8**

Compound	Source	Label [3]	DAT						
			0 [1]	1	2	3	6	7	8
40.3 min	Irradiated	A	n.d.	n.d.	0.6	0.8	1.1	1.1	1.0
		B	n.d.	0.4	0.9	1.3	1.1	1.0	1.1
		Mean	**n.d.**	**0.4**	**0.8**	**1.1**	**1.1**	**1.1**	**1.1**
45.8 min (fluopyram-lactam)	Irradiated	A	n.d.	n.d.	n.d.	n.d.	1.0	1.2	1.1
		B	n.d.	n.d.	n.d.	0.8	1.0	1.2	0.9
		Mean	**n.d.**	**n.d.**	**n.d.**	**0.8**	**1.0**	**1.2**	**1.0**
49.2 min	Irradiated	A	n.d.	n.d.	n.d.	n.d.	0.5	0.5	0.7
		B	n.d.	n.d.	n.d.	0.5	0.5	0.6	0.8
		Mean	**n.d.**	**n.d.**	**n.d.**	**0.5**	**0.5**	**0.6**	**0.8**
51.2 min	Irradiated	A	n.d.	n.d.	n.d.	n.d.	0.9	0.9	0.8
		B	n.d.	n.d.	n.d.	0.6	0.7	0.7	0.7
		Mean	**n.d.**	**n.d.**	**n.d.**	**0.6**	**0.8**	**0.8**	**0.8**
Total extractable residues	Irradiated	A	106.7	107.7	106.3	105.7	105.1	106.0	105.9
		B	105.4	105.2	104.7	104.0	102.6	104.7	103.9
		Mean	**106.0**	**106.5**	**105.5**	**104.9**	**103.9**	**105.3**	**104.9**
$^{14}CO_2$	Irradiated	A	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	0.6
		B	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	0.1
		Mean	**n.a.**	**n.a.**	**n.a.**	**n.a.**	**n.a.**	**n.a.**	**0.3**
Volatile organics	Irradiated	A	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.d.
		B	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.d.
		Mean	**n.a.**	**n.a.**	**n.a.**	**n.a.**	**n.a.**	**n.a.**	**n.d.**
Total % recovery[2]	Irradiated	A	106.7	107.7	106.3	105.7	105.1	106.0	106.5
		B	105.4	105.2	104.7	104.0	102.6	104.7	104.0
		Mean	**106.0**	**106.5**	**105.5**	**104.9**	**103.9**	**105.3**	**105.2**

n.d.: not detected, DAT: days after treatment, n.a.: not analysed

[1] DAT-0 samples were identical for irradiated and dark samples.

[2] Values taken from Material Balance

[3] Values for [phenyl-UL-^{14}C]fluopyram (A) and [pyridyl-2,6-^{14}C]fluopyram (B) presented are mean values of each experiment as no single values of the replicates were given in the report. Mean values in this table is the mean value of both labels.

Table 7.2.1.3-2: Photodegradation of [^{14}C]fluopyram in natural water (mean values expressed as % AR) – dark samples

Compound	Source	Label [3]	DAT						
			0 [1]	1	2	3	6	7	8
Fluopyram	Irradiated	A	106.2	106.4	107.6	101.2	108.0	102.4	104.1
		B	105.4	107.1	105.7	104.5	104.3	105.3	105.6
		Mean	**105.8**	**106.8**	**106.7**	**102.9**	**106.2**	**103.9**	**104.8**
24.6 min	Irradiated	A	0.5	0.9	0.9	0.8	0.9	0.8	0.9
		B	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
		Mean	**0.5**	**0.9**	**0.9**	**0.8**	**0.9**	**0.8**	**0.9**
Total extractable residues	Irradiated	A	106.7	107.3	108.5	102.0	108.9	103.2	105.0
		B	105.4	107.1	105.7	104.5	104.3	105.3	105.6
		Mean	**106.0**	**107.2**	**107.1**	**103.3**	**106.6**	**104.3**	**105.3**
$^{14}CO_2$	Irradiated	A	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.d.
		B	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.d.
		Mean	**n.a.**	**n.a.**	**n.a.**	**n.a.**	**n.a.**	**n.a.**	**n.d.**
Volatile organics	Irradiated	A	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.d.
		B	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.d.
		Mean	**n.a.**	**n.a.**	**n.a.**	**n.a.**	**n.a.**	**n.a.**	**n.d.**
Total % recovery [2]	Irradiated	A	106.7	107.3	108.5	102.0	108.9	103.2	105.0
		B	105.4	107.1	105.7	104.5	104.3	105.3	105.6
		Mean	**106.0**	**107.2**	**107.1**	**103.3**	**106.6**	**104.3**	**105.3**

n.d.: not detected, n.a.: not analyzed, DAT: days after treatment

[1] DAT-0 samples were identical for irradiated and dark samples.

[2] Values taken from Material Balance

[3] Values for [phenyl-UL-^{14}C]fluopyram (A) and [pyridyl-2,6-^{14}C]fluopyram (B) presented are mean values of each experiment as no single values of the replicates were given in the report. Mean values in this table is the mean value of both labels.

B. MATERIAL BALANCE

For the material balance, a mean was calculated using the single mean material balances for both radiolabels. Mean material balance ranged from 103.9 to 106.8% of the applied radioactivity (% AR) for irradiated test systems and from 103.3 to 107.2% AR for dark test systems. The complete material balances found at all sampling intervals for both irradiated and dark samples demonstrated that there was no significant loss of radioactivity from the test systems or during sample processing.

C. VOLATILES

For irradiated test systems, only minor $^{14}CO_2$ formation of 0.6% AR ([phenyl-UL-^{14}C]fluopyram) and 0.1% AR ([pyridyl-2,6-^{14}C]fluopyram) was detected at DAT-8. No $^{14}CO_2$ was formed in the dark samples. Organic volatiles were not detected.

D. DEGRADATION OF TEST ITEM

The mean occurrence of fluopyram and its metabolite fluopyram-lactam was calculated using the single mean occurrences for [phenyl-UL-^{14}C]fluopyram and [pyridyl-2,6-^{14}C]fluopyram. In the irradiated test system, fluopyram decreased from an average of 105.8% AR at DAT-0 to 84.0% AR after DAT-8. In the dark test systems, fluopyram was stable with 104.8% AR at DAT-8.

No degradation products were observed at >10% AR f or both labels. For [phenyl-UL-^{14}C]fluopyram up to 12 minor photolytes were observed. One individual very polar region (6.7 min) reached a maximum of 5.5% AR at DAT-7 and decreased to 5.0% at DAT-8. For [pyridyl-2,6-^{14}C]fluopyram up to 13 minor metabolites were observed, each representing not more than 4.5% AR.

Using [phenyl-UL-^{14}C]fluopyram, fluopyram-lactam was detected at maximum 1.0 to 1.2% in the samples of day 6 to day 8, only. Using [pyridyl-2,6-^{14}C]fluopyram, fluopyram-lactam was detected up to 0.8 to 1.2% in the samples of day 3 to day 8, only.

F. Kinetics

The first-order experimental DT_{50} values of fluopyram in irradiated and in dark samples were calculated as first order kinetics. Based on the experimental DT_{50} of 21.2 days for fluopyram, the predicted environmental DT_{50} was calculated to be e.g. 86.6 solar summer days at Phoenix, AZ, USA or e.g. 134.5 summer days at Athens, Greece. Under dark conditions the half-life under experimental conditions is 386.9 days.

Table 7.2.1.3-3: Photodegradation kinetics of fluopyram in irradiated and dark samples

Test System	first order half-life		DT_{50} (d)	DT_{50} (d)
	Experimental Half-life (d)	Chi^2Err%	under natural conditions in Phoenix, USA	under natural conditions in Athens, Greece
Irradiated	21.2	1.2194	86.6	134.5
Dark	386.9	0.9516	n.a.	n.a.

n.a.: not applicable

III. CONCLUSIONS

Photolytic degradation of fluopyram in natural water is relatively slow under environmental conditions. No degradation product was detected. Carbon dioxide was formed in very low amounts. Photolytic transformation will only be a minor contributor to the overall fate of fluopyram under natural outdoor conditions.

3. Assessment and conclusion

Assessment and conclusion by applicant:
The study is considered to be valid and reliable.

Assessment and conclusion by RMS:
Outcome and conclusion of the study: RMS should indicate if they agree to the results and conclusions of the APPL.

CA 7.2.2 Route and rate of biological degradation in aquatic systems

CA 7.2.2.1 "Ready biodegradability"

Fluopyram is considered not readily biodegradable. Therefore, no ready biodegradability study was conducted.

CA 7.2.2.2 Aerobic mineralisation in surface water

Biodegradation of [phenyl-UL-^{14}C]fluopyram was studied in surface water under aerobic conditions at two different concentrations (low and high dose) and, additionally, in a sterilised test system. At the end of the study, the concentration of fluopyram was found to be constant in all systems. Mineralisation of fluopyram was low and accounted for <0.3 and <0.1% AR, in the low and high dose, respectively. One minor degradation product was measures twice and never exceeded 1.8% AR. Stability was also shown in the sterile system, with 103% AR fluopyram at the end of the study. As degradation in all treated test systems was negligible, no degradation rate could be calculated. Consequently, aerobic mineralisation in surface water is not a relevant degradation pathway of fluopyram.

1. Information on the study

Data Point:	KCA 7.2.2.2/01
Report Author:	[redacted]
Report Year:	2013
Report Title:	Aerobic mineralisation of 14C-fluopyram in surface water
Report No:	20120189
Document No:	M-482603-01-1
Guideline(s) followed in study:	OECD Guidelines for the Testing of Chemicals, Guideline 309: Aerobic Mineralisation in Surface Water - Simulation Biodegradation Test; April 2004 Draft Commission Regulation SANCO 11802/2010/Rev.7 Setting Out the Data Requirements for Active Substances in Accordance with Regulation (EC) No 1107/2009 of the European Parliament and of the Council Concerning the Placing of Plant Protection Products on the Market
Deviations from current test guideline:	Current Guideline: OECD 309 (2004) Water was stored for 2 days and storage conditions were not reported (temperature/aeration) No solvent control, however, solvent concentration is very low in the test system No information is given how sterility of samples was achieved
Previous evaluation:	No, not previously submitted
GLP/Officially recognised testing facilities:	Yes, conducted under GLP/Officially recognised testing facilities
Acceptability/Reliability:	Yes

2. Full summary of KCA 7.2.2.2/01

Executive Summary

The route and rate of degradation of [phenyl-UL-^{14}C]fluopyram were studied in surface water under aerobic conditions in the laboratory for 60 days in the dark at 20.8 ± 0.2 °C.

The radiolabelled test item was applied to the natural surface water samples at concentrations of 9.36 µg/L (low dose) and 96.01 µg/L (high dose), respectively. Additionally, the high dose was appield to sterilised surface water samples in order to obtain information of abiotic degradation. To ascertain microbial activity of the test water additional sampes were treated with ^{14}C-benzoic acid as reference item.

Mean material balances ranged from 102.1 to 106.5 % AR and from 98.9 to 101.1 % AR for the low dose and high dose, respectively. For sterile samples, the overall material balance was 101.8 % AR.
Mineralisation of the [phenyl-UL-^{14}C]fluopyram accounted for <0.3 and <0.1 % AR, in the low and high dose, respectively. Formation of organic volatiles was not significant as demonstrated by values

≤0.1 % AR in all samples. Extrensive mineralisation of ^{14}C benzoic acid showed good microbial activity of the test water.

The concentration of [phenyl-UL-^{14}C]fluopyram was constant in all systems, accounting for 104.6 and 99.1 % AR at the end of the study, in the low and high dose, respectively. Stability was also demonstrated in the sterile system, with 102.6 % AR at the end of the study. Degradation in all treated test systems was negligible, therefore no degradation rate was to be calculated.

I. MATERIALS AND METHODS

A. MATERIALS

1. Test Item

[phenyl-UL-^{14}C]fluopyram

Sample-ID:	KML 9393
Specific Activity:	5.15 MBq/mg
Radiochemical Purity:	>99 % (HPLC and TLC)
Chemical Purity:	Not reported

2. Test Water

Natural water from a pond was used. The water was sampled freshly from the pond and sieved through a 0.2 mm screen prior to use.

Table 7.2.2.2-1: Physico-chemical properties of test water

Parameter/ Units	Results
Reference (Batch-ID)	Biederthal 01/13
Geographic Location	
City	Biederthal
State	Haut-Rhin
Country	France
Temperature below water surface (°C)	4.2
Oxygen below water surface (mg/L)	15.1
pH at sampling depth	7.9
Turbidity	Visibility through water layer down to about 50 cm
Total Organic Carbon (mg/L)	4.37
Dissolved Organic Carbon (mg/L)	4.19
Total nitrogen (mg/L)	1.10
Nitrate- Nitrogen (mg/L)	2.58
Nitrite- Nitrogen (mg/L)	0.82
Total Phosphorus (mg/L)	0.18
Ammonium (NH^{4+}; mg/L	0.24

B. STUDY DESIGN

1. Experimental Conditions

The test water (100 mL/flask) was quantitatively added to 300 mL Erlenmeyer flasks. The water was stirred continuously through the duration of the study (60 days). Samples were treated at two different concentrations (high and low dose) and in addition sterile samples were set up at one concentration (high dose) in order to obtain information of abiotic degradation. Flasks were each treated with 1000 µL of a 9.852 µg/mL (high dose and sterile) or 1100 µL of a 0.878 µg/mL [phenyl-UL-^{14}C]fluopyram treatment solution. The solution was applied drop-wise to the water surface using a Hamilton syringe. Actual concentrations in the samples were determined as 96.01 and 9.36 µg/L.

After treatment, samples were connected to a trapping system. Each flask was connected to two traps, one containing ethylene glycol to trap organic volatiles and the other one containing 2N NaOH to trap $^{14}CO_2$. The test systems were incubated in the dark at 20.8 ± 0.2 °C under aerobic conditions. Aerobic conditions in the water phase were maintained by constant aeration with moistened air and by stirring of the water to facilitate mass transfer across the air/water interface. Positive controls were also used during the study. Therefore, ^{14}C-benzoic acid was used to verify that the test water showed a good level of microbial activity. Two positive control flasks were treated with ^{14}C-benzoic acid solution, each at a test concentration of 9.117 µg/L. Additionally, two untreated samples were incubated as well, to determine water parameters during the study duration.

2. Sampling

Seven sampling intervals were distributed over the entire incubation period of 60 days. For each of the test concentrations (9.36 and 96.01 µg/L), duplicate flasks were taken at each sampling interval (0, 7, 14, 21, 32, 40 and 60 days). Associated traps were removed and analysed after each sampling interval with exception of time zero samples. At each sampling interval, single sterile samples were taken. Single positive control samples were taken and analysed after 7 and 14 days.

3. Analytical Procedures

At the time of sampling, test item-treated flasks and their associated traps were removed from the system. The volume of the water phase was recorded, pH and oxygen concentration in the water was determined and aliquots were directly submitted to Liquid Scintillation Counting (LSC). The limit of detection (LOD) of the LSC for water samples was 0.115 % AR and the limit of quantification (LOQ) was 0.172 % AR. Aliquots of the water were analysed by High-Performance Liquid Chromatography (HPLC) to quatify the amount of test item and eventual degradation products present in the water. LOD and LOQ of the HPLC was 0.058 % AR and 0.087 % AR, respectively. Selected samples were additionally analysed by one-dimensional Thin-Layer Chromatography (TLC). Samples were either mixed with unlabelled test item or unlabelled reference test item. Furthermore, the corresponding reference item was spotted near the radioactive band in order to check for possible interference with dissolved particles present in the water.

Volume of liquid in the ethylene glycol and sodium hydroxide trap was recored and radioactivity in the trapping solutions was monitored by LSC. LOD and LOQ of the LSC for volation was 0.788 and 1.576 % AR, repectively.

Positive controles containing ^{14}C-benzoic acid were treated in the same way as described above.

II. RESULTS AND DISCUSSION

Results indicated that the anticipated standardised conditions were maintained and that the water was microbially active. The pH of the water in the test flasks averaged 7.86 (range 7.32 to 8.35) for high dose, 7.13 (range 7.68 to 8.36) for sterile high dose and 8.14 (7.60 to 8.35) for low dose. The oxygen concentration of the water in the test flasks averaged 8.26 mg/L (range 7.93 to 9.01 mg/L) for high dose, 8.44 mg/L (range 7.64 to 9.83 mg/L) for sterile high dose and 8.11 mg/L (6.94 to 9.33 mg/L) for low

dose. The range of pH and oxygen concentration of the untreated control samples was similar (pH: 7.52 to 8.32; oxygen concentration: 7.80 to 10.41 mg/L).

Microbial activity of the test water was shown by extensive mineralisation (95.7% ± 4.4 % after 14 days) of the reference test item ^{14}C-benzoic acid.

A. DATA

The distribution of radioactivity in the samples is summarised in Table 7.2.2.2-2 to Table 7.2.2.2-4. The amount of fluoyram and its degradation products is summarised in Table 7.2.2.2-5 to Table 7.2.2.2-7.

Table 7.2.2.2-2: Distribution and recovery of radioactivity in samples treated with [phenyl-UL-^{14}C]fluopyram (high dose – 96.01 µg/L - % AR)

Compound	Replicate	DAT 0	7	14	21	32	40	60
% AR in water	A	99.8	99.7	101.9	97.6	100.2	99.1	99.9
	B	100.7	98.4	100.3	100.0	101.4	99.9	100.2
	Mean	**100.2**	**99.0**	**101.1**	**98.8**	**100.8**	**99.5**	**100.0**
% AR in 2N NaOH trap	A	n.p.	<0.1	<0.1	0.1	0.1	0.1	0.1
	B	n.p.	<0.1	<0.1	0.2	0.1	<0.1	0.1
	Mean	**n.p.**	**<0.1**	**<0.1**	**0.2**	**0.1**	**0.1**	**0.1**
% AR in Ethylene Glycol Trap	A	n.p.	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
	B	n.p.	<0.1	<0.1	<0.1	<0.1	<0.1	0.1
	Mean	**n.p.**	**<0.1**	**<0.1**	**<0.1**	**<0.1**	**<0.1**	**<0.1**
Total Recovery	A	99.8	99.7	102.0	97.7	100.3	99.2	99.9
	B	100.7	98.4	100.3	100.2	101.5	100.0	100.5
	Mean	**100.2**	**99.1**	**101.1**	**98.9**	**100.9**	**99.6**	**100.2**

n.p.: not performed; SD: Standard deviation; DAT: days after treatment

Table 7.2.2.2-3: Distribution and recovery of radioactivity in samples treated with [phenyl-UL-^{14}C]fluopyram (high dose, sterile – 96.01 µg/L - % AR)

Compound	DAT 0	7	14	21	32	40	60
% AR in water	101.2	98.8	102.1	101.6	102.0	102.8	104.3
% AR in 2N NaOH trap	n.p.	<0.1	<0.1	<0.1	<0.1	0.1	<0.1
% AR in Ethylene Glycol Trap	n.p.	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Total Recovery	101.2	98.8	102.1	101.7	102.0	102.9	104.3

n.p.: not performed; SD: Standard deviation; DAT: days after treatment

Table 7.2.2.2-4: Distribution and recovery of radioactivity in samples treated with [phenyl-UL-^{14}C]fluopyram (low dose – 9.36 µg/L - % AR)

Compound	Replicate	DAT 0	7	14	21	32	40	60
% AR in water	A	101.3	101.8	104.3	108.9	107.7	109.8	107.2
	B	102.9	102.8	100.9	100.9	101.5	102.8	102.1
	Mean	**102.1**	**102.3**	**102.6**	**104.9**	**104.6**	**106.3**	**104.6**
% AR in 2N NaOH trap	A	n.p.	<0.1	0.1	<0.1	0.3	0.2	<0.1
	B	n.p.	0.1	<0.1	0.1	<0.1	0.1	0.3
	Mean	**n.p.**	**<0.1**	**0.1**	**<0.1**	**0.2**	**0.1**	**0.1**
% AR in Ethylene Glycol Trap	A	n.p.	<0.1	0.1	<0.1	0.1	0.1	<0.1
	B	n.p.	<0.1	0.1	<0.1	0.1	<0.1	<0.1
	Mean	**n.p.**	**<0.1**	**0.1**	**<0.1**	**0.1**	**0.1**	**<0.1**
Total Recovery	A	101.3	101.8	104.5	108.9	108.0	110.1	107.2
	B	102.9	102.9	101.0	101.0	101.6	102.8	102.3
	Mean	**102.1**	**102.3**	**102.8**	**104.9**	**104.8**	**106.5**	**104.7**

n.p.: not performed; SD: Standard deviation; DAT: days after treatment

Table 7.2.2.2-5: Composition of radioactivity in samples treated with [phenyl-UL-^{14}C]fluopyram (high dose – 96.01 µg/L - % AR)

Compound	Replicate	DAT 0	7	14	21	32	40	60
Parent	A	99.8	99.7	101.9	97.6	100.2	99.1	98.1
	B	100.7	98.4	100.3	100.0	101.4	99.9	100.2
	Mean	**100.2**	**99.0**	**101.1**	**98.8**	**100.8**	**99.5**	**99.1**
M1	A	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	1.8
	B	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	Mean	**n.d.**	**n.d.**	**n.d.**	**n.d.**	**n.d.**	**n.d.**	**0.9**
$^{14}CO_2$	A	n.p.	0.1	<0.1	0.1	0.1	0.1	0.1
	B	n.p.	<0.1	<0.1	0.2	0.1	<0.1	0.1
	Mean	**n.p.**	**<0.1**	**<0.1**	**0.2**	**0.1**	**0.1**	**0.1**
Total	A	99.8	99.7	101.9	97.6	100.3	99.2	99.9
	B	100.7	98.4	100.3	100.2	101.4	100.0	100.4
	Mean	***100.3***	***99.1***	***101.1***	***98.9***	***100.9***	***99.6***	***100.2***

n.d. : not detected; n.p. : not performed
Values calculated in the summary are given in *italics*

Table 7.2.2.2-6: Composition of radioactivity in samples treated with [phenyl-UL-^{14}C]fluopyram (high dose, sterile – 96.01 µg/L - % AR)

Compound	DAT 0	7	14	21	32	40	60
Parent	101.2	98.8	102.1	101.6	102.0	102.8	102.6
M1	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	1.7
$^{14}CO_2$	n.p.	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Total	101.2	98.8	102.1	101.7	102.0	102.9	104.3

n.d. : not detected; n.p. : not performed

Table 7.2.2.2-7: Composition of radioactivity in samples treated with [phenyl-UL-^{14}C]fluopyram (low dose – 9.36 µg/L - % AR)

Compound	Replicate	DAT 0	7	14	21	32	40	60
Parent	A	101.3	101.8	104.3	108.9	107.7	109.8	107.2
	B	102.9	102.8	100.9	100.9	101.5	102.8	102.1
	Mean	**102.1**	**102.3**	**102.6**	**104.9**	**104.6**	**106.3**	**104.6**
M1	A	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	B	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	Mean	**n.d.**	**n.d.**	**n.d.**	**n.d.**	**n.d.**	**n.d.**	**n.d.**
$^{14}CO_2$	A	n.p.	<0.1	0.1	<0.1	0.3	0.2	<0.1
	B	n.p.	0.1	<0.1	0.1	<0.1	0.1	0.3
	Mean	**n.p.**	**0.1**	**0.1**	**0.1**	**0.2**	**0.1**	**0.1**
Total	A	101.3	101.8	104.4	108.9	108.0	110.0	107.2
	B	102.9	102.8	100.9	101.0	101.5	102.8	102.3
	Mean	***102.1***	***102.3***	***102.7***	***105.0***	***104.8***	***106.4***	***104.8***

n.d. : not detected; n.p. : not performed
Values calculated in the summary are given in *italics*

B. MATERIAL BALANCE

Mean material balances ranged from 102.1 to 106.5 % AR and from 98.9 to 101.1 % AR for the low dose and high dose, respectively. Total mean recovery was calculated to be 100.0 ± 1.1 % AR for high dosed samples and 101.8 ± 1.7 % AR for low dosed samples.

For sterile samples, the overall material balance was 101.8 % AR and the range was calculated to be between 98.8 % AR and 104.3 % AR.

C. VOLATILES

Total mineralisation of [phenyl-UL-^{14}C] fluopyram samples accounted for <0.1% AR in both the low and high dose and mineralisation never exceeded 0.3 % AR in a single sample. Formation of organic volatiles was not significant as demonstrated by values <0.1 % AR in all samples.

D. DEGRADATION OF PARENT COMPOUND

The concentration of [phenyl-UL-^{14}C]fluopyram was constant in all systems, accounting for 104.6 and 99.1 % AR at the end of the study, in the low and high dose, respectively. Stability was also demonstrated in the sterile system, with 102.6 % AR at the end of the study. No degradation of the test substance in any system was detected, therefore no degradation rate was to be calculated.

Metabolite "M1" was only detected twice, and never exceeded 1.8 % AR.

III. CONCLUSIONS

In natural surface water at 20.8 ± 0.2 °C in the dark under aerobic conditions [phenyl-UL-^{14}C]fluopyram was stable in all systems tested. Mineralisation to CO_2 was negligible, and just one metabolite was to be detected twice <1.8 % AR.

3. Assessment and conclusion

Assessment and conclusion by applicant:
The study is considered to be valid and reliable.

Assessment and conclusion by RMS:
Outcome and conclusion of the study: RMS should indicate if they agree to the results and conclusions of the APPL.

CA 7.2.2.3 Water/sediment study

The aerobic biodegradation of [phenyl-UL-^{14}C]fluopyram and [pyridyl-2,6-^{14}C]fluopyram was studied in 2 contrasting water-sediment systems (sand and clay). The compound dissipated from the water by a combination of degradation and partitioning to sediment. Formation ofegradation products was insignificant for the water or sediment phases. Five minor transformation products were detected for both systems. No single metabolite exceeded 2.5% of the applied radioactivity. NER were formed to a maximum of 4.4 and 8.4% AR for the phenyl- and the pyridyl-label, respectively. Mineralisation of fluopyram was low to account for ≤0.4% AR in the sandy systems and ≤1.8% AR in the clayey systems.

Half-lives for trigger purposes ($DisT_{50}$), considering double first order in parallel kinetics (DFOP), of fluopyram in aerobic water were 21.1 and 14.2 days for the sand and clay sediment systems, respectively. Half-life values ($DegT_{50}$) of fluopyram in the entire system were calculated to be in the range of 826 to >1000 days. For modelling purposes, the geometric mean $DisT_{50}$ of fluopyram in water was calculated to be 99.5 days (DFOP slow), and the geometric mean $DegT_{50}$ in the whole system amounts to 909 days at level P-I. Considering level P-II results were not fully reliable, mathematically not significantly different from 0, and therefore not usable.

Table 7.2.2.3-1: Dissipation times of fluopyram in water/sediment systems – modelling purpose P-I

Parent	Distribution: Max. in sediment 62.9 % after 120 d (Lawrence, phenyl-label)									
Water / sediment system	pH water phase	pH sed [1]	t. °C	$DegT_{50}$ /DT_{90} whole sys.b(d)	St. (χ^2)	$DisT_{50}$ /DT_{90} Water (d)	St. (χ^2)	$DisT_{50}$ /DT_{90} Sed (d)	St. (χ^2)	Method of calculation
Anglerweiher (sand)	7.9[3]	7.4[3]	20	>1000 / >1000 (SFO)	1.11	$DisT_{50\,fast}$ = 4.298 **$DisT_{50\,slow}$ = 109.74** g = 0.4441 / 271.6 (DFOP)	2.46	na		SFO / DFOP slow
Lawrence (clay)	7.0[3]	6.6[3]	20	826.2 / >1000 (SFO)	1.28	$DisT_{50\,fast}$ = 3.950 **$DisT_{50\,slow}$ = 90.3** g = 0.4875 / 242.9 (DFOP)	4.21	na		SFO / DFOP slow
Geometric mean at 20°C[2]				909.0		99.5 (DFOP slow)		na		

[1] Measured in calcium chloride solution
[2] Normalised using a Q10 of 2.58
[3] Mean of measurements during study duration
na = not applicable

Table 7.2.2.3-2: Dissipation times of fluopyram in water/sediment systems – trigger purpose PI

Parent	Distribution: Max. in sediment 69.9 % after 120 d (Lawrence, phenyl-label)									
Water / sediment system	pH water phase	pH sed (H_2O)	t. °C	$DegT_{50}$ /DT_{90} whole sys. (d)	St. (χ^2)	$DisT_{50}$ /DT_{90} Water (d)	St. (χ^2)	$DisT_{50}$ /DT_{90} Sed (d)	St. (χ^2)	Method of calculation
Anglerweiher (sand)	7.9[1]	7.4[1]	20	>1000 / >1000 (SFO)	1.11	21.13 / 71.6 (DFOP)	2.11	na		SFO / DFOP
Lawrence (clay)	7.0[1]	6.67[1]	20	826.2 / >1000 (SFO)	1.28	14.20 / 212.9 (DFOP)	4.21	na		SFO / DFOP
Geometric mean at 20°C				-		-				

[1] Mean of measurements during study duration
na = not applicable

1. Information on the study

Data Point:	KCA 7.2.2.3/01
Report Author:	[redacted]
Report Year:	2007
Report Title:	[pyridyl-ring-UL-14C]-AE C656948 and [trifluorobenzamide ring-UL-14C]-AE C656948 - aerobic aquatic metabolism
Report No:	MEGMP004
Document No:	M-290653-01-2
Guideline(s) followed in study:	US EPA Subdivision N, Section 162-4; Canada PMRA DACO Number 8.2.3.5.4; OECD Guideline for Testing of Chemicals Number 308; US EPA OPPTS Guideline No. 835.4300
Deviations from current test guideline:	Current Guideline: OECD 308 (2002) None
Previous evaluation:	yes, evaluated and accepted DAR (2004)
GLP/Officially recognised testing facilities:	Yes, conducted under GLP/Officially recognised testing facilities
Acceptability/Reliability:	Yes

2. Full summary of KCA 7.2.2.3/01

Executive Summary

The route and rate of degradation of [phenyl-UL-^{14}C] and [pyridyl-2,6-^{14}C] fluopyram were investigated in two natural water/sediment systems incubated under aerobic conditions at 19.7 ± 0.3°C in the laboratory in the dark for up to 120 days.

Water/Sediment System	Source	Texture [1] (USDA)	pH	TOC [g/kg] / [mg/L]
Anglerweiher	Leverkusen, Germany	sand	5.6 [2] / 6.8 [3]	11 [4] / 13.6 [5]
Lawrence	Jefferson County, USA	clay	5.3 [2] / 7.3 [3]	37 [4] / 13.2 [5]

TOC: total organic carbon
[1] sediment textural class
[2] sediment pH value derived from aqueous 0.01 M $CaCl_2$ suspensions
[3] water pH value determined on site during sampling
[4] sediment TOC determined after sediment collection
[5] water TOC determined at start of study

The test was performed in flow-through systems consisting of flasks containing a water-to-sediment volume ratio of 3/1 (*v/v*) connected to traps for the collection of carbon dioxide (ethanolamine) and, for system Lawrence, volatile organic compounds (ethylene glycol).

The nominal application rate was 28.1 µg per flask, corresponding to a 5-fold maximum single field application rate of 250 g of fluopyram/ha to a water body of 100 cm in depth due to analytical reasons.

For both labels, duplicate samples from each system were processed and analysed 0, 2, 7, 12, 16, 22, 30, 47, 62, 91 and 120 days after treatment (DAT) in the Anglerweiher system and at 0, 4, 7, 11, 15, 21, 33, 47, 62, 90 and 120 days after treatment (DAT) in the Lawrence system.

At each sampling interval, the water was separated from the sediment by decanting and filtering (200 µm). The sediment was extracted on the day of collection three times with ACN/water (9/1, *v/v*) by shaking at 20 °C followed by an accelerated solvent extraction (ASE) using ACN/water (9/1, *v/v*) at 80 °C.

For the phenyl label, mean material balances range from 95.4 to 97.4% of applied radioactivity (AR) for system Anglerweiher and from 95.6 to 98.3% AR for system Lawrence. For the pyridyl label, mean material balances range from 94.1 to 97.6% AR for system Anglerweiher and from 97.9 to 98.7% AR for system Lawrence.

Maximum amounts of carbon dioxide in system Anglerweiher were observed at DAT-62 with 0.4% AR for the phenyl label and 0.1% AR for the pyridyl label. In system Lawrence, maximum occurrence of $^{14}CO_2$ was 1.8% AR at DAT-90 for the phenyl label and 0.2% AR at DAT-120 for the pyridyl label. Organic volatiles were not detected.

Residues in water decreased from DAT-0 to DAT-120 from 91.8 to 28.7% AR in system Anglerweiher for the phenyl label and from 89.6 to 28.1% AR for the pyridyl label. In the Lawrence system, residues in water decreased from DAT-0 to DAT-120 from 94.4 to 19.8% AR for the phenyl label and from 94.0 to 21.6% AR for the pyridyl label.

The amount of radioactivity extractable from the sediment increased from 4.5% AR at DAT-0 to 63.8% AR at DAT-120 for the phenyl label and from 6.8% AR at DAT-0 to 64.2% AR at DAT-120 for the pyridyl label in system Anglerweiher. The amount of radioactivity extractable from the sediment increased from 3.8% AR at DAT-0 to 71.1% AR at DAT-120 for the phenyl label and from 3.9% AR at DAT-0 to 67.8% AR at DAT-120 for the pyridyl label in system Lawrence.

The amount of radioactivity extractable from the total system decreased in system Anglerweiher from DAT-0 to DAT-120 from 96.3 to 92.5% AR for the phenyl label and from 96.4 to 92.2% AR for the pyridyl label. The amount of radioactivity extractable from the total system decreased in system Lawrence from DAT-0 to DAT-120 from 98.2 to 90.8% AR for the phenyl label and from 97.9 to 89.5% AR for the pyridyl label.

The amount of non-extractable residues (NER) increased from DAT-0 to DAT-120 from 0.0 to 2.9% AR for phenyl label and from 0.0 to 3.7% AR in system Anglerweiher. In system Lawrence, NER increased from DAT-0 to DAT-120 from 0.0 to 4.4% AR for the phenyl label and 0.0 to 8.4% AR for the pyridyl label.

In system Anglerweiher, the amount of phenyl-labelled fluopyram in the water phase decreased from DAT-0 to DAT-120 from 91.3% AR to 26.3% AR and for the pyridyl-labelled fluopyram from 89.6% AR to 25.5% AR. In system Lawrence, the amount of phenyl-labelled fluopyram in the water phase decreased from DAT-0 to DAT-120 from 94.0% AR to 18.8% AR and for pyridyl-labelled fluopyram from 94.0% AR to 19.8% AR.

The amount of phenyl-labelled fluopyram in the sediment extracts increased in system Anglerweiher from DAT-0 to DAT-120 from 4.4 to 62.8% AR and for pyridyl-labelled fluopyram from 6.7% AR to 63.3% AR. The amount of phenyl-labelled fluopyram in the sediment extracts increased in system Lawrence from DAT-0 to DAT-120 from 3.8 to 69.9% AR and for pyridyl-labelled fluopyram from 3.9% AR to 67.2% AR.

The amount of phenyl-labelled fluopyram in the total system decreased slightly from DAT-0 to DAT-120 from 95.7 to 89.1% AR and for pyridyl-labelled fluopyram from 96.3 to 88.9% AR in system Anglerweiher. The amount of phenyl-labelled fluopyram in the total system decreased slightly from DAT-0 to DAT-120 from 97.8 to 88.7% AR and for pyridyl-labelled fluopyram from 97.9 to 86.9% AR in system Lawrence.

Degradation of fluopyram was accompanied by the formation of five minor degradation products. None of these products was identified due to their maximum occurrence of 2.5% AR.

In conclusion fluopyram dissipated from supernatant water to the sediment phase, however, it was slowly degraded in water/sediment systems under aerobic conditions in the dark in the laboratory.

I. MATERIALS AND METHODS

A. MATERIALS

1. Test Items

[phenyl-UL-^{14}C]AE C656948 (fluopyram)	
Sample ID	C-1077A
Specific activity	3.85 MBq/mg
Radiochemical purity	98%
[pyridyl-2,6-^{14}C]AE C656948 (fluopyram)	
Sample ID	C-1078A
Specific activity	3.85 MBq/mg
Radiochemical purity	99%

2. Water/sediment systems

The test matrices used in this study were water and sediment collected from Germany (Anglerweiher, Leverkusen) and the United States (Lawrence, Jefferson County, Kansas). No pesticide was applied to or around either area within 5 years prior to collection. Water and sediment of each system were collected from the same area. Sediment and water were collected from a depth of 0–20 cm (Anglerweiher) and 0-15cm (Lawrence), respectively. The samples were stored in a walk-in refrigerator at about 4°C for a maximum of 35 days. The sediment was sieved through a 2-mm sieve, water remained unfiltered. The characteristics of the test systems are provided in the table below.

Table 7.2.2.3-3: Physico-chemical characteristics of the water/sediment test systems

System		Anglerweiher	Lawrence	Anglerweiher	Lawrence
Textural Class (USDA)		N/A	N/A	sand	clay
Sand (%)	**[50 µm – 2 mm]**	N/A	N/A	89.2	7.8
Silt (%)	**[2 µm – 50 µmm]**	N/A	N/A	10.7	27.5
Clay (%)	**[< 2 µm]**	N/A	N/A	0.1	66.7
pH		6.8 [1] / 8.1 [4] / 8.0 [5]	7.3 [1] / 7.4 [4] / 5.7 [5]	5.6 [2] / 5.9 [3]	5.3 [2] / 5.7 [3]
pH during the study (mean value of 11 measurements)		7.89	6.96	7.40	6.53
OC (%)		N/A	N/A	0.1	3.7
TOC (mg/L; study start / study end)		13.6 / 6.0	13.2 / 6.7	N/A	N/A
Cation exchange capacity (meq/100 g)		N/A	N/A	5.1	34.8
Redox Potential (mV) [1]		303	375	N/A	N/A
Oxygen Saturation (mg/L) [4]		4.63	5.1	N/A	N/A
Field moisture capacity at 0.33 bar (%)		N/A	N/A	6.2	41.1
Microbial biomass (cells/g sediment or mL water)					
Beginning of study		24.6×10^6	11.6×10^6	320×10^6	369×10^6
End of study		9.12×10^6	10.1×10^6	103×10^6	307×10^6

DAT = days after treatment, USDA: United States Department for Agriculture, N/A = not applicable, TOC = total organic carbon
[1] determined on-site during sampling
[2] sediment / 0.01 M $CaCl_2$ (1/2)
[3] sediment / water (1/1)
[4] determined at start of the study
[5] determined at end of the study

B. STUDY DESIGN

1. Experimental conditions

The test systems consisted of 500 mL glass flasks (21 cm long, 7.2 cm width) with an impinging tube for aeration. The test systems were continuously flushed with humidified air (flow-through system). The air exiting each flask then passed sequentially through an ethylene glycol trap (Lawrence sediment system only) used for trapping volatile organic compounds (VOC), followed by an ethanolamine trap (Anglerweiher and Lawrence sediment systems) used for trapping $^{14}CO_2$. The ethylene glycol trap was not used with the Anglerweiher sediment system, since no VOC were detected with the Lawrence sediment system.

For each sediment system, the target ratio of sediment to water used in the test system was 1:3 (v:v), which corresponded to 86 mL and 90 mL of sediment and 250 mL and 270 mL of unfiltered pond water for the Anglerweiher and Lawrence sediment systems, respectively. Duplicates per interval were prepared for each radiolabel. Then the test systems were pre-incubated 15 and 9 days for the Anglerweiher and Lawrence sediment systems, respectively, under the projected test conditions in order to equilibrate and to allow the micro-flora to acclimatize.

The nominal study application rate of 125 µg/L (initial water phase concentration) was based on an 5-fold single field treatment use rate of fluopyram (250 g a.i./ha) to facilitate analytical methodology. The actual application rates ranged from 122 to 126 µg/L. Methanol was used in the application solution, which was applied to the water using a microliter pipette. After application, the test vessels (except DAT-0) were connected to the flow-through system and placed into an incubation chamber.

Samples were incubated under aerobic conditions at 19.7 ± 0.3 °C in the dark for a maximum period of 120 days.

Untreated samples were prepared in parallel for each sediment system for the determination of microbial biomass and total organic carbon (TOC).

2. Sampling

Phenyl labelled samples were processed and analysed at 0, 2, 12, 22, 47, 62, 91 and 120 days after treatment (DAT) and pyridyl labelled samples at 0. 7, 16, 30, 62, 91 and 120 DAT for the Anglerweiher system. For the Lawrence system, phenyl labelled samples were processed and analysed at 0, 4, 11, 21, 47, 62 ,90 and 120 DAT and pyridyl labelled samples at 0, 7, 15, 33, 62, 90 and 120 DAT. Volatile traps were analysed for radioactivity on the days that flasks were taken for extraction. For the Lawrence sediment system, ethylene glycol traps were discontinued after two months post-treatment. For each sediment system, ethanolamine traps were replenished at two months post-treatment. The biomass determinations of the untreated samples were carried out at application and at study termination (DAT-0 and DAT-125 for Anglerweiher and DAT-0 and DAT-138 for Lawrence system).

3. Analytical procedures

At each sampling interval, the pH and redox potential were determined in both the water and sediment phases. In addition, the dissolved oxygen content was measured in the water phase. The amount of radioactivity in the volatile traps was determined directly from the liquid traps by liquid scintillation counting (LSC).

Afterwards, the water was separated from the sediment by decanting and filtering (200 µm). The sediment was extracted on the day of collection three times with ACN/water (9:1, *v/v*) by shaking at 20 °C followed by an accelerated solvent extraction (ASE) using ACN/water (9:1, *v/v*) at 80 °C. After each extraction, extract and sediment were separated by centrifugation, decantation and filtration. The first three extracts (ambient temperature) were combined while the ASE extract was kept separate. The volume of each extract was measured and the radioactivity in the sediment extracts and the water was determined by LSC. Water and sediment extracts were frozen (< -15 °C) up to 28 days prior to analysis. The radioactivity of extracted sediments was determined by combustion and LSC to determine the amount on non-extractable residues (NER).

Water samples were analysed by HPLC/radiodetection without concentration. Ambient and ASE sediment extracts were concentrated by rotary evaporation and analysed separately by reverse phase HPLC/radiodetection. The limit of detection (LOD) for the HPLC was determined to be 500 dpm, which corresponded to 2.2 ng based a specific activity of 231,000 dpm/µg. At this level, a single peak above noise could be evaluated. The HPLC system was optimized to quantify peak concentrations representing a minimum of 1% AR (LOQ).

The parent compound was identified by LC-ESI/MS as well HPLC co-chromatography.

II. RESULTS AND DISCUSSION

A. DATA

The pH value of the water remained relatively constant during the study between 7.26 and 8.23 for system Anglerweiher and decreased from 7.39 to 5.66 for system Lawrence. The oxygen content in the water phase ranged between 2.71 and 6.25 mg/L in system Anglerweiher and between 2.82 and 7.23 mg/L in system Lawrence. The redox potential in the water phase ranged between 195 and 248 mV in system Anglerweiher and between 225 and 344 mV in system Lawrence. The pH value of the sediment remained relatively constant during the study between 6.83 and 7.68 for system Anglerweiher and decreased from 6.79 to 5.76 for system Lawrence. The redox potential in the sediment ranged between 102 and 254 mV in system Anglerweiher and between 179 and 316 mV in system Lawrence.

Radioactive mass balance and distribution of [phenyl-UL-^{14}C] and [pyridyl-2,6-^{14}C]fluopyram and metabolites in water and sediment extracts are summarised in Table 7.2.2.3-4 to Table 7.2.2.3-7 for the two water/sediment systems.

Table 7.2.2.3-4: Degradation of [phenyl-UL-^{14}C]fluopyram in water/sediment system Anglerweiher under aerobic incubation at 20 °C (mean of two replicates, expressed as percent of applied radioactivity)

Compound	Source	DAT							
		0	2	12	22	47	62	91	120
Fluopyram	water	91.3 ±2.2	79.0 ±0.6	54.4 ±0.3	48.4 ±1.3	37.8 ±0.5	33.9 ±1.4	29.3 ±1.0	26.3 ±0.1
	sediment [1]	4.4 ±0.5	17.4 ±0.7	38.4 ±1.2	44.4 ±0.9	54.3 ±1.4	57.9 ±0.6	60.6 ±0.8	62.8 ±0.7
	system [2]	95.7 ±1.6	96.4 ±1.3	92.8 ±0.9	92.8 ±2.2	92.1 ±0.9	91.8 ±0.8	89.8 ±1.7	89.1 ±0.8
Unknown A	water	0.5 ±0.8	0.9 ±0.1	0.7 ±0.0	1.0 ±0.1	1.2 ±0.0	1.2 ±0.2	1.6 ±0.7	1.4 ±0.4
	sediment [1]	0.0 ±0.0	0.1 ±0.1	0.2 ±0.3	0.2 ±0.3	0.3 ±0.0	0.2 ±0.2	0.4 ±0.1	0.3 ±0.1
	system [2]	0.5 ±0.8	1.0 ±0.1	0.9 ±0.3	1.2 ±0.2	1.5 ±0.0	1.4 ±0.1	2.1 ±0.8	1.7 ±0.4
Unknown C	water	0.0 ±0.0	0.0 ±0.0	0.0 ±0.0	0.2 ±0.3	0.3 ±0.5	0.0 ±0.0	0.3 ±0.4	0.0 ±0.0
	sediment [1]	0.0 ±0.0	0.0 ±0.0	0.0 ±0.0	0.0 ±0.0	0.2 ±0.2	0.0 ±0.0	0.0 ±0.0	0.0 ±0.0
	system [2]	0.0 ±0.0	0.0 ±0.0	0.0 ±0.0	0.2 ±0.3	0.5 ±0.7	0.0 ±0.0	0.3 ±0.4	0.0 ±0.0
Unknown D	water	0.0 ±0.0	0.0 ±0.0	0.0 ±0.0	0.0 ±0.0	0.0 ±0.0	0.0 ±0.0	0.3 ±0.5	0.6 ±0.2
	sediment [1]	0.0 ±0.0	0.0 ±0.0	0.0 ±0.0	0.0 ±0.0	0.3 ±0.1	0.0 ±0.0	0.6 ±0.3	0.7 ±0.3
	system [2]	0.0 ±0.0	0.0 ±0.0	0.0 ±0.0	0.0 ±0.0	0.3 ±0.0	0.0 ±0.0	0.9 ±0.8	1.3 ±0.5
Unidentified	water	0.5 ±0.8	0.9 ±0.1	0.7 ±0.0	1.2 ±0.2	1.5 ±0.4	1.2 ±0.2	2.3 ±0.8	1.9 ±0.6
	sediment [1]	0.0 ±0.0	0.1 ±0.1	0.2 ±0.3	0.2 ±0.3	0.8 ±0.1	0.2 ±0.2	1.0 ±0.4	1.0 ±0.4
	system [2]	0.5 ±0.8	1.0 ±0.1	0.9 ±0.3	1.4 ±0.5	2.3 ±0.6	1.4 ±0.1	3.3 ±1.2	2.9 ±0.9
Total extractable radioactivity	water	91.8 ±0.4	79.9 ±0.7	55.1 ±0.3	49.6 ±1.5	39.3 ±0.1	35.1 ±1.3	31.4 ±0.2	28.7 ±0.4
	sediment [1]	4.5 ±0.6	17.7 ±0.6	40.9 ±1.0	47.1 ±0.9	55.1 ±1.5	58.0 ±0.4	61.6 ±0.4	63.8 ±0.3
	system [2]	96.3 ±0.8	97.4 ±1.3	96.0 ±0.7	96.7 ±2.5	94.4 ±1.5	93.1 ±0.9	93.0 ±0.6	92.5 ±0.1
Carbon Dioxide		0.0 ±0.0	0.0 ±0.0	0.0 ±0.0	0.0 ±0.0	0.2 ±0.1	0.4 ±0.2	0.3 ±0.0	0.0 ±0.0
Total Volatile Organics		NA	ND	ND	ND	ND	ND	ND	ND
Non-extractable residues		0.0 ±0.0	0.1 ±0.0	0.4 ±0.0	0.7 ±0.1	1.7 ±0.3	2.0 ±0.3	2.4 ±0.4	2.9 ±0.6
Material balance		96.3 ±0.8	97.4 ±1.3	96.4 ±0.7	97.4 ±2.3	96.3 ±1.9	95.5 ±0.4	95.7 ±0.1	95.4 ±0.7

DAT = days after treatment; NA = Not Analysed; ND = Not Detected
[1] Sum of ambient and ASE extract
[2] Entire system: water + sediment

Table 7.2.2.3-5: Degradation of [pyridyl-2,6-^{14}C]fluopyram in water/sediment system Anglerweiher under aerobic incubation at 20 °C (mean of two replicates, expressed as percent of applied radioactivity)

Compound	Source	DAT						
		0	7	16	30	62	91	120
Fluopyram	water	89.6 ±1.4	65.3 ±1.1	50.0 ±1.0	44.9 ±0.3	34.9 ±1.1	29.4 ±0.5	25.5 ±0.8
	sediment [1]	6.7 ±0.9	29.2 ±1.3	40.5 ±0.6	46.7 ±0.2	57.7 ±1.0	61.4 ±1.0	63.3 ±0.5
	system [2]	96.3 ±0.6	94.4 ±2.4	90.5 ±1.5	91.6 ±0.0	91.7 ±2.1	90.7 ±1.6	88.9 ±1.3
Unknown A	water	0.0 ±0.0	0.6 ±0.0	0.4 ±0.6	0.2 ±0.0	0.7 ±0.0	0.6 ±0.2	0.7 ±0.2
	sediment [1]	0.0 ±0.0	0.0 ±0.0	0.0 ±0.0	0.1 ±0.2	0.2 ±0.2	0.0 ±0.0	0.0 ±0.0
	system [2]	0.0 ±0.0	0.6 ±0.0	0.4 ±0.6	0.3 ±0.2	0.9 ±0.2	0.6 ±0.2	0.7 ±0.2
Unknown B	water	0.0 ±0.0	0.5 ±0.0	0.5 ±0.1	0.5 ±0.0	1.0 ±0.0	1.6 ±0.2	1.2 ±0.4
	sediment [1]	0.0 ±0.0	0.0 ±0.0	0.0 ±0.0	0.0 ±0.0	0.0 ±0.0	0.0 ±0.0	0.1 ±0.2
	system [2]	0.0 ±0.0	0.5 ±0.0	0.5 ±0.1	0.5 ±0.0	1.0 ±0.0	1.6 ±0.2	1.3 ±0.2
Unknown C	water	0.0 ±0.0	0.0 ±0.0	0.5 ±0.0	0.0 ±0.0	0.2 ±0.3	0.0 ±0.0	0.6 ±0.2
	sediment [1]	0.0 ±0.0	0.0 ±0.0	0.0 ±0.0	0.0 ±0.0	0.2 ±0.3	0.3 ±0.4	0.7 ±0.0
	system [2]	0.0 ±0.0	0.0 ±0.0	0.0 ±0.0	0.0 ±0.0	0.5 ±0.7	0.3 ±0.4	1.3 ±0.1
Unidentified	water	0.0 ±0.0	1.1 ±0.0	1.0 ±0.7	1.4 ±0.0	1.9 ±0.3	2.2 ±0.0	2.5 ±0.4
	sediment [1]	0.0 ±0.0	0.0 ±0.0	0.0 ±0.0	0.1 ±0.2	0.4 ±0.6	0.3 ±0.4	0.8 ±0.1
	system [2]	0.0 ±0.0	1.1 ±0.0	1.0 ±0.7	1.4 ±0.2	2.3 ±0.9	2.5 ±0.5	3.3 ±0.2
Total extractable radioactivity	water	89.6 ±1.4	66.4 ±1.4	51.0 ±0.2	46.2 ±0.3	36.0 ±0.8	31.6 ±0.5	28.1 ±1.2
	sediment [1]	6.8 ±0.9	30.8 ±1.5	42.4 ±0.7	49.5 ±0.4	58.1 ±0.4	61.7 ±0.6	64.2 ±0.3
	system [2]	96.4 ±0.6	97.3 ±2.5	93.3 ±0.8	95.8 ±0.1	94.1 ±1.3	93.3 ±1.1	92.2 ±1.6
Carbon Dioxide		0.0 ±0.0	0.0 ±0.0	0.0 ±0.0	0.0 ±0.1	0.1 ±0.0	0.0 ±0.0	0.0 ±0.0
Total Volatile Organics		NA	ND	ND	ND	ND	ND	ND
Non-extractable residues		0.0 ±0.0	0.3 ±0.0	0.7 ±0.0	1.0 ±0.0	2.0 ±0.2	3.0 ±0.6	3.7 ±0.1
Material balance		96.4 ±0.6	97.6 ±2.5	94.1 ±1.0	96.8 ±0.1	96.1 ±1.1	96.3 ±0.5	95.9 ±1.5

DAT = days after treatment; NA = Not Analysed; ND = Not Detected
[1] Sum of ambient and ASE extract
[2] Entire system: water + sediment

Table 7.2.2.3-6: Degradation of [phenyl-UL-^{14}C]fluopyram in water/sediment system Lawrence under aerobic incubation at 20 °C (mean of two replicates, expressed as percent of applied radioactivity)

Compound	Source	DAT							
		0	4	11	21	47	62	90	120
Fluopyram	water	94.0 ±1.4	68.7 ±2.0	52.1 ±0.6	41.9 ±2.4	32.6 ±2.1	30.9 ±1.1	25.0 ±1.7	18.8 ±0.7
	sediment [1]	3.8 ±0.8	26.6 ±0.6	43.3 ±1.5	50.8 ±1.5	60.2 ±0.6	62.2 ±0.7	64.7 ±0.7	69.9 ±1.6
	system [2]	97.8 ±2.3	95.3 ±1.3	95.4 ±0.9	92.7 ±0.9	92.8 ±2.7	93.2 ±1.8	89.7 ±2.4	88.7 ±0.9
Unknown A	water	0.4 ±0.6	0.7 ±0.0	0.4 ±0.0	1.2 ±0.4	1.1 ±1.1	0.8 ±0.2	0.5 ±0.2	0.3 ±0.4
	sediment [1]	0.0 ±0.0	0.0 ±0.0	0.2 ±0.2	0.1 ±0.2	0.3 ±0.4	0.0 ±0.0	0.0 ±0.0	0.0 ±0.0
	system [2]	0.4 ±0.6	0.7 ±0.0	0.6 ±0.2	1.3 ±0.6	1.4 ±1.4	0.8 ±0.2	0.5 ±0.2	0.3 ±0.4
Unknown B	water	0.0 ±0.0	0.0 ±0.0	0.0 ±0.0	0.0 ±0.0	1.1 ±0.6	0.3 ±0.4	0.2 ±0.3	0.5 ±0.2
	sediment [1]	0.0 ±0.0	0.0 ±0.0	0.0 ±0.0	0.1 ±0.2	0.3 ±0.4	0.0 ±0.0	0.2 ±0.2	0.0 ±0.0
	system [2]	0.0 ±0.0	0.0 ±0.0	0.0 ±0.0	0.1 ±0.2	1.4 ±1.0	0.3 ±0.4	0.4 ±0.5	0.5 ±0.2
Unidentified	water	0.4 ±0.6	0.7 ±0.0	0.4 ±0.6	1.2 ±0.4	2.2 ±1.7	1.1 ±0.7	1.3 ±0.3	0.9 ±0.5
	sediment [1]	0.0 ±0.0	0.0 ±0.0	0.2 ±0.3	0.3 ±0.4	0.5 ±0.7	0.0 ±0.0	0.8 ±0.3	1.2 ±0.2
	system [2]	0.4 ±0.6	0.7 ±0.0	0.6 ±0.4	1.5 ±0.8	2.8 ±2.4	1.1 ±0.7	2.1 ±0.6	2.1 ±0.8
Total extractable radioactivity	water	94.4 ±0.9	69.3 ±2.0	52.5 ±1.2	43.1 ±2.0	34.8 ±0.5	32.0 ±0.5	26.3 ±1.4	19.8 ±1.2
	sediment [1]	3.8 ±0.8	27.4 ±0.6	45.2 ±1.8	51.1 ±1.9	60.7 ±0.2	62.2 ±0.7	65.6 ±0.4	71.1 ±1.4
	system [2]	98.3 ±1.8	96.7 ±1.4	97.7 ±0.6	94.2 ±0.1	95.6 ±0.4	94.3 ±1.2	91.9 ±1.8	90.9 ±0.1
Carbon Dioxide		0.0 ±0.0	0.0 ±0.0	0.0 ±0.0	0.0 ±0.0	0.1 ±0.0	0.7 ±0.2	1.8 ±0.4	1.6 ±0.1
Total Volatile Organics		NA	ND	ND	ND	ND	ND	ND	ND
Non-extractable residues		0.0 ±0.0	0.3 ±0.0	0.6 ±0.0	1.4 ±0.2	2.3 ±0.0	3.0 ±0.3	4.1 ±1.0	4.4 ±0.1
Material balance		98.3 ±1.7	97.0 ±1.4	98.3 ±0.6	95.6 ±0.3	98.0 ±0.3	97.9 ±1.0	96.9 ±0.3	96.8 ±0.2

DAT = days after treatment; NA = Not Analysed; ND = Not Detected
[1] Sum of ambient and ASE extract
[2] Entire system: water + sediment

Table 7.2.2.3-7: Degradation of [pyridyl-2,6-^{14}C]fluopyram in water/sediment system Lawrence under aerobic incubation at 20 °C (mean of two replicates, expressed as percent of applied radioactivity)

Compound	Source	DAT 0	7	15	33	62	90	120
Fluopyram	water	94.0 ±1.6	64.9 ±2.4	44.9 ±1.5	42.8 ±0.6	30.0 ±0.0	25.9 ±1.5	19.8 ±4.5
	sediment [1]	3.9 ±1.3	31.8 ±1.1	47.8 ±0.9	53.6 ±0.4	61.8 ±0.8	59.3 ±5.7	67.2 ±3.9
	system [2]	97.9 ±0.2	96.7 ±1.3	92.6 ±0.6	96.4 ±1.0	91.8 ±0.8	85.2 ±4.2	86.9 ±0.6
Unknown E	water	0.0 ±0.0	0.0 ±0.0	0.5 ±0.1	0.0 ±0.0	1.2 ±0.2	2.2 ±1.2	1.3 ±0.2
	sediment [1]	0.0 ±0.0	0.0 ±0.0	0.0 ±0.0	0.0 ±0.0	0.0 ±0.0	0.2 ±0.3	0.0 ±0.0
	system [2]	0.0 ±0.0	0.0 ±0.0	0.5 ±0.1	0.0 ±0.0	1.2 ±0.2	2.5 ±1.5	1.3 ±0.2
Unknown B	water	0.0 ±0.0	0.0 ±0.0	0.6 ±0.1	1.9 ±1.1	0.0 ±0.0	0.5 ±0.6	0.0 ±0.0
	sediment [1]	0.0 ±0.0	0.0 ±0.0	0.1 ±0.2	0.0 ±0.0	0.3 ±0.4	0.0 ±0.0	0.0 ±0.0
	system [2]	0.0 ±0.0	0.0 ±0.0	0.8 ±0.1	1.9 ±1.1	0.3 ±0.4	0.5 ±0.6	0.0 ±0.0
Unknown D	water	0.0 ±0.0	0.0 ±0.0	0.0 ±0.0	0.0 ±0.0	0.4 ±0.5	0.3 ±0.4	0.3 ±0.4
	sediment [1]	0.0 ±0.0	0.0 ±0.0	0.1 ±0.2	0.0 ±0.0	0.0 ±0.0	0.8 ±0.1	0.7 ±0.0
	system [2]	0.0 ±0.0	0.0 ±0.0	0.1 ±0.2	0.0 ±0.0	0.4 ±0.5	1.1 ±0.5	0.9 ±0.4
Unidentified	water	0.0 ±0.0	0.0 ±0.0	1.2 ±0.0	0.0 ±0.0	3.5 ±0.8	3.0 ±1.5	1.8 ±1.0
	sediment [1]	0.0 ±0.0	0.0 ±0.0	0.3 ±0.4	0.0 ±0.0	0.3 ±0.4	1.0 ±0.2	0.7 ±0.0
	system [2]	0.0 ±0.0	0.0 ±0.0	1.4 ±0.4	0.0 ±0.0	3.8 ±1.2	4.0 ±1.7	2.5 ±1.0
Total extractable radioactivity	water	94.0 ±1.6	64.9 ±2.4	46.0 ±1.4	42.8 ±0.6	33.5 ±0.8	28.9 ±0.0	21.6 ±5.5
	sediment [1]	3.9 ±1.3	32.7 ±1.3	50.8 ±0.6	53.6 ±0.4	62.1 ±0.4	64.6 ±0.2	67.8 ±3.8
	system [2]	97.9 ±0.3	97.7 ±1.1	96.9 ±0.9	96.5 ±1.1	95.6 ±0.4	93.6 ±0.2	89.5 ±1.6
Carbon Dioxide		0.0 ±0.0	0.0 ±0.0	0.0 ±0.0	0.0 ±0.0	0.0 ±0.0	0.1 ±0.0	0.2 ±0.0
Total Volatile Organics		NA	ND	ND	ND	ND	ND	ND
Non-extractable residue		0.0 ±0.0	0.5 ±0.1	1.1 ±0.1	2.2 ±0.4	2.8 ±0.4	4.7 ±0.1	8.4 ±1.5
Material balance		97.9 ±0.2	98.2 ±1.0	98.0 ±0.8	98.7 ±0.6	98.4 ±0.1	98.4 ±0.1	98.1 ±0.1

DAT = days after treatment; NA = Not Analysed; ND = Not Detected
[1] Sum of ambient and ASE extract
[2] Entire system, water + sediment

B. MASS BALANCE

For the phenyl label, mean material balances range from 95.4 to 97.4% of applied radioactivity (AR) for system Anglerweiher and from 95.6 to 98.3% AR for system Lawrence. For the pyridyl label, mean

material balances range from 94.1 to 97.6% of applied radioactivity (AR) for system Anglerweiher and from 97.9 to 98.7% AR for system Lawrence.

C. EXTRACTABLE AND NON-EXTRACTABLE RESIDUES

Residues in water decreased from DAT-0 to DAT-120 from 91.8 to 28.7% AR in system Anglerweiher for the phenyl label and from 89.6 to 28.1% AR for the pyridyl label. In the Lawrence system, residues in water decreased from DAT-0 to DAT-120 from 94.4 to 19.8% AR for the phenyl label and from 94.0 to 21.6% AR for the pyridyl label.

The amount of radioactivity extractable from the sediment increased in system Anglerweiher from 4.5% AR at DAT-0 to 63.8% AR at DAT-120 for the phenyl label and from 6.8% AR at DAT-0 to 64.2% AR at DAT-120 for the pyridyl label. The amount of radioactivity extractable from the sediment increased in system Lawrence from 3.8% AR at DAT-0 to 71.1% AR at DAT-120 for the phenyl label and from 3.9% AR at DAT-0 to 67.8% AR at DAT-120 for the pyridyl label.

The amount of radioactivity extractable from the total system decreased in system Anglerweiher from DAT-0 to DAT-120 from 96.3 to 92.5% AR for the phenyl label and from 96.4 to 92.2% AR for the pyridyl label. The amount of radioactivity extractable from the total system decreased in system Lawrence from DAT-0 to DAT-120 from 98.2 to 90.8% AR for the phenyl label and from 97.9 to 89.5% AR for the pyridyl label.

The amount of non-extractable residues (NER) increased from DAT-0 to DAT-120 from 0.0 to 2.9% AR for phenyl label and from 0.0 to 3.7% AR in system Anglerweiher. In system Lawrence, NER increased from DAT-0 to DAT-120 from 0.0 to 4.4% AR for the phenyl label and 0.0 to 8.4% AR for the pyridyl label.

D. VOLATILE RADIOACTIVITY

Maximum amounts of carbon dioxide in system Anglerweiher were observed at DAT-62 with 0.4% AR for the phenyl label and 0.1% AR for the pyridyl label. In system Lawrence, maximum occurrence of $^{14}CO_2$ was 1.8% AR at DAT-90 for the phenyl label and 0.2% AR at DAT-120 for the pyridyl label. Organic volatiles determined were not detected.

E. TRANSFORMATION OF THE TEST ITEM

In system Anglerweiher, the amount of phenyl-labelled fluopyram in the water phase decreased from DAT-0 to DAT-120 from 91.3% AR to 26.3% AR and for the pyridyl-labelled fluopyram from 89.6% AR to 25.3% AR. In system Lawrence, the amount of phenyl-labelled fluopyram in the water phase decreased from DAT-0 to DAT-120 from 94.0% AR to 18.8% AR and for pyridyl-labelled fluopyram from 94.0% AR to 19.8% AR.

The amount of phenyl-labelled fluopyram in the sediment extracts increased in system Anglerweiher from DAT-0 to DAT-120 from 4.4 to 62.8% AR and for pyridyl-labelled fluopyram from 6.7% AR to 63.3% AR. The amount of phenyl-labelled fluopyram in the sediment extracts increased in system Lawrence from DAT-0 to DAT-120 from 3.8 to 69.9% AR and for pyridyl-labelled fluopyram from 3.9% AR to 67.2%AR.

The amount of phenyl-labelled fluopyram in the total system decreased from DAT-0 to DAT-120 from 95.7 to 89.1% AR and for pyridyl-labelled fluopyram from 96.3 to 88.9% AR in system Anglerweiher. The amount of phenyl-labelled fluopyram in the total system decreased from DAT-0 to DAT-120 from 97.8 to 88.7% AR and for pyridyl-labelled fluopyram from 97.9 to 86.9% AR in system Lawrence.

Degradation of fluopyram was accompanied by the formation of five minor degradation products. None of these products exceeded a maximum occurrence in any compartment of 2.5% AR.

F. KINETICS

New kinetic calculations based on more recent guidance are necessary, therefore the information included in this study is not considered relevant. Evaluation of the rate of degradation is reported under KCA 7.2.2.3/06.

III. CONCLUSIONS

Fluopyram dissipated from supernatant water to the sediment phase, however, it was slowly degraded in water/sediment systems under aerobic conditions in the dark in the laboratory.

Formation of carbon dioxide was up to a maximum of 1.8% AR and non-extractable residues were up to 8.4% AR at the study end.

Degradation of fluopyram was accompanied by the formation of five minor degradation products. None of these products exceeded a maximum occurrence in any compartment of 2.5% AR.

3. Assessment and conclusion

Assessment and conclusion by applicant: The study and its data are considered to be valid and reliable for use in risk assessment.

Assessment and conclusion by RMS: Outcome and conclusion of the study: RMS should indicate if they agree to the results and conclusions of the APPI.

Data Point:	KCA 7.2.2.3/02
Report Author:	[redacted]
Report Year:	2008
Report Title:	Kinetic evaluation of the aerobic aquatic metabolism of fluopyram (AE C656948) in water/sediment systems using MatLab
Report No:	MEF-07/317
Document No:	M-296730-01-1
Guideline(s) followed in study:	not specified
Deviations from current test guideline:	Current guideline not applicable (see justification)
Previous evaluation:	yes, evaluated and accepted DAR (2011)
GLP/Officially recognised testing facilities:	No, not conducted under GLP/Officially recognised testing facilities
Acceptability/Reliability:	No

The kinetic evaluation of the aquatic metabolism study was performed according to FOCUS kinetics (2006): Guidance Document on Estimating Persistence and Degradation Kinetics from Environmental Fate Studies on Pesticides in EU Registration, EC Document Reference Sanco/10058/2005 version 1.0. To address most recent guideline updates a new kinetic evaluation was preformed and therefore this evaluation is not considered in the current dossier. The new evaluation can be found under KCA 7.2.2.3/06 (M-761916-01-1).

Data Point:	KCA 7.2.2.3/03
Report Author:	[redacted]
Report Year:	2007
Report Title:	[14C-pheny-UL]AE C656948: Anaerobic aquatic metabolism
Report No:	MEGMP063
Document No:	M-293275-01-2
Guideline(s) followed in study:	US EPA Subdivision N, Section 162-3; US EPA OPPTS Guideline No. 835.4400
Deviations from current test guideline:	Current Guideline: not applicable (see justification)
Previous evaluation:	yes, evaluated and accepted DAR (2011)
GLP/Officially recognised testing facilities:	Yes, conducted under GLP/Officially recognised testing facilities
Acceptability/Reliability:	No

Anaerobic aquatic metabolism studies are not a data requirement in the EU. Therefore, this study is not submitted in the current dossi

Data Point:	KCA 7.2.2.3/04
Report Author:	[redacted]
Report Year:	2007
Report Title:	[pyridyl-2,6-14C]AE C656948: Anaerobic aquatic metabolism
Report No:	MEGMP066
Document No:	M-293276-01-2
Guideline(s) followed in study:	US EPA Subdivision N, Section 162-3; US EPA OPPTS Guideline No. 835.4400
Deviations from current test guideline:	Current Guideline: not applicable (see justification)
Previous evaluation:	yes, evaluated and accepted DAR (2011)
GLP/Officially recognised testing facilities:	Yes, conducted under GLP/Officially recognised testing facilities
Acceptability/Reliability:	No

Anaerobic aquatic metabolism studies are not a data requirement in the EU. Therefore, this study is not submitted in the current dossi

Data Point:	KCA 7.2.2.3/05
Report Author:	[redacted]
Report Year:	2009
Report Title:	Fluopyram - Bayer CropScience response to PMRA comments regarding redox potential (Eh) in anaerobic soil and aquatic studies
Report No:	M-354014-01-1
Document No:	M-354014-01-1
Guideline(s) followed in study:	not applicable
Deviations from current test guideline:	Current Guideline: not applicable (notifier response)
Previous evaluation:	No, not previously submitted
GLP/Officially recognised testing facilities:	not applicable
Acceptability/Reliability:	Yes

This position paper clarified the situation regarding anaerobic conditions, under consideration of the "redox potential (Eh)" measurements, reported in two anaerobic aquatic metabolism studies (M-293275-01-2 and M-293276-01-2), was conducted to address a request from PMRA (June 22, 2009). As anaerobic aquatic metabolism studies are no data requirement for EU, both studies will be not submitted anymore. Therefore, this statement regarding the anaerobic conditions in the water/sediment systems is regarded as redundant and is not part of this dossier. The part of the position paper covering anaerobic soil is summarised under KCA 7.1.1.2/02.

1. Information on the study

Data Point:	KCA 7.2.2.3/06
Report Author:	[redacted]
Report Year:	2020
Report Title:	Fluopyram (FLU): Kinetic evaluation of aerobic aquatic metabolism in water/sediment systems according to FOCUS kinetics using KinGUI 2.1
Report No:	EnSa-19-0513
Document No:	M-761916-01-1
Guideline(s) followed in study:	not applicable
Deviations from current test guideline:	Current Guideline: not applicable (kinetic evaluation)
Previous evaluation:	No, not previously submitted
GLP/Officially recognised testing facilities:	No, not conducted under GLP/Officially recognised testing facilities
Acceptability/Reliability:	Yes

2. Full summary of KCA 7.2.2.3/06

Executive Summary

To derive kinetic parameters for modelling and trigger purposes, a kinetic analysis was conducted using the software tool KinGUI 2.1 and following the recommendations given by FOCUS Kinetics. The analysis is based on residue data from an aerobic aquatic laboratory metabolism study in two water-sediment systems (see KCA 7.2.2.3/01, M-290531-01-2).

The $DegT_{50}$ values for fluopyram (modelling endpoints) at level P-I were between 826.2 and 1000 days and the $DisT_{50}$ between 90.3 and 109.74 days (slow phase). At level P-II, no reliable corresponding degradation rate pairs could be derived for modelling or trigger purpose. The $DegT_{50}$ values for fluopyram (trigger endpoints) at level P-I were between 826.2 and 1000 days and the $DisT_{50}$ between 14.20 and 21.13 days.

I. METHODS

A kinetic modelling analysis of aerobic aquatic laboratory residue data of fluopyram (FLU) was conducted in order to derive kinetic parameters suitable for modelling and for trigger purpose, using the software tool KinGUI 2.1. The identification of the appropriate kinetic model followed the recommendations given by FOCUS Kinetics (FOCUS, 2006, 2014) based on a detailed statistical analysis including visual assessment, χ^2 statistic, significance t-test and correlation analysis. Additionally, the Scaled Weighted Area under Residue Curve (SWARC) was used as a further indicator for the visual assessment and to choose the appropriate model.

The modelling analysis is based on residue data from an aerobic aquatic laboratory metabolism study in two water-sediment systems in the dark. A sandy system (Angelerweiher) from Leverkusen, Germany and one clayey system (Lawrence) from Jefferson County, Kansas, USA were chosen in the study. Residues of the 2 labels were considered as replicates in the kinetic analysis.

The FOCUS kinetics report distinguishes between two levels of kinetics: At Level I a single compartment is used to derive (i) degradation endpoints from the total system or (ii) dissipation or decline endpoints from each compartment separately, in water, sediment or total system from maximum onwards. Level II considers two-compartmental approaches to estimate the real degradation in water and sediment, in parallel, considering exchange rates between water and sediment.

Kinetic parameters were derived for trigger and modelling purpose, based on parent only fit. Since no metabolites were identified in both systems, no pathway fit was performed. And since the amount of applied radioactivity in sediment is rising until study end, in both systems, a decline from maximum onwards could not be evaluated.

II. RESULTS

Results of the kinetic evaluation for trigger and modelling purpose, based on parent only data from an aerobic aquatic laboratory metabolism study in two water-sediment systems are summarised in the tables below.

Dissipation from water, fluopyram - level P-I

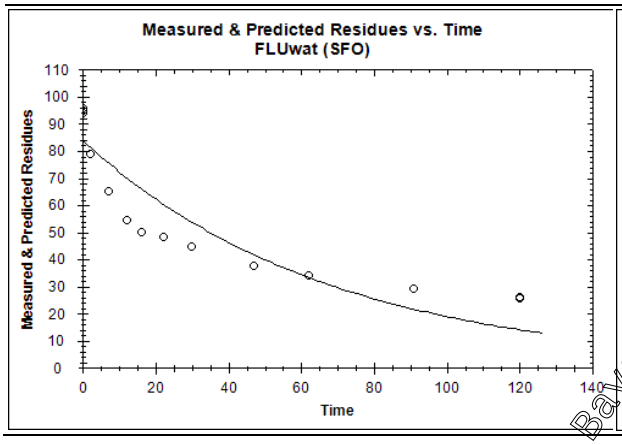
Table 7.2.2.3-8: Fluopyram: kinetic and statistical results of dissipation from water in the Anglerweiher system

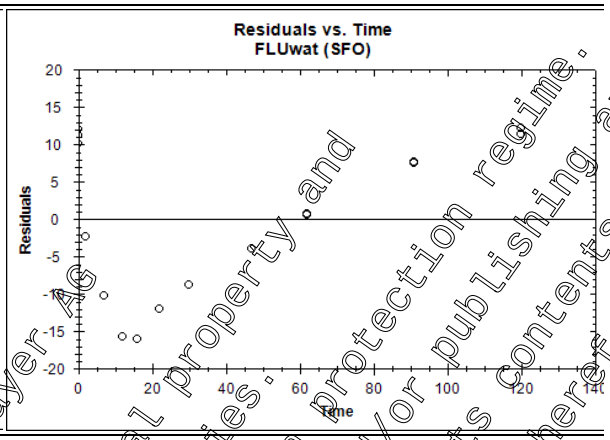
Kinetic model	$DisT_{50}$ actual	$DisT_{90}$ actual	$DisT_{50}$ fast / slow	VA	χ^2err / SWARC	k_1 / α	k_2 / β	g / t_b	t-test k_1 / k_2	95th CI of k_1 / α	95th CI of k_2 / β
	(d)	(d)	(d)		(% / -)	(1/d / -)	(1/d / d)	(- / d)	(-)	(d / -)	(d / -)
SFO	46.57	154.7	-	-	16.2 / 373	0.014884	-	-	< 0.001	0.01059 - 0.019	-
DFOP	**21.13**	**271.6**	4.198 / **109.74**	+	2.46 / 3.71	0.16510	0.006316	**0.4441**	< 0.001 / < 0.001	0.13000 - 0.200	0.00538 - 0.007
FOMC	21.25	2487	749 [P]	+	2.01 / 6.33	0.34861	3.37135	-	-	0.32097 - 0.376	2.63047 - 4.112
HS	29.17	226.5	7.549 / 84.97	o	5.57 / 24.0	0.09182	0.008158	5.441	< 0.001 / < 0.001	0.04876 - 0.135	0.00676 - 0.010

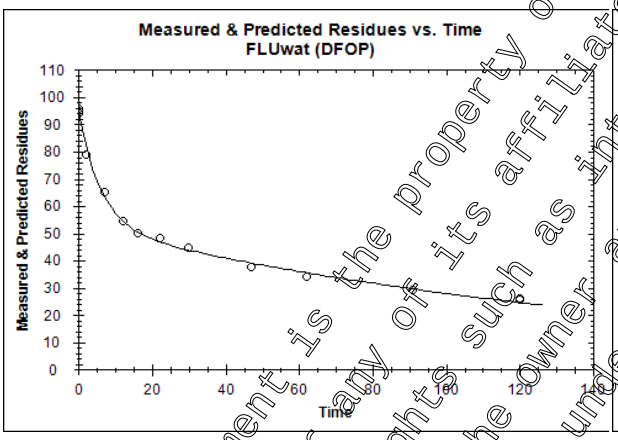
VA = visual assessment, + = good, o = acceptable, - = poor
SWARC = Scaled Weighted Area under Residue Curve
CI = confidence intervall
[P] = pseudo DT_{50} = DT_{90} / 3.32

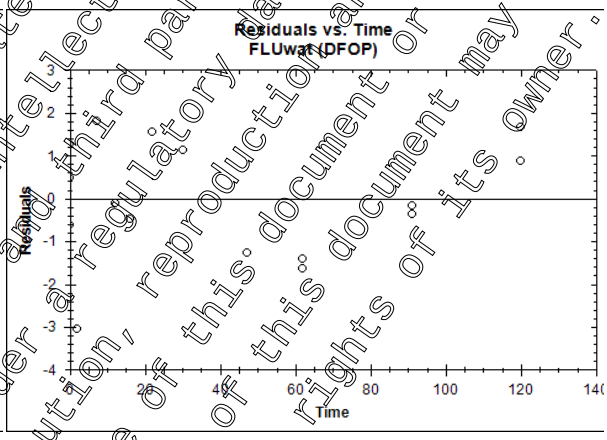
Modelling Endpoint: SFO fit is statistically (χ^2err ~15%) and visually poor. SWARC value is > 40, indicating a biphasic decline. DFOP, FOMC and HS fits were alternatively tested. The residues do not fall < 10 % during study period, therefore FOMC fit is not suitable.
DFOP and HS fits are statistically (χ^2err, t-test) and visually acceptable. Consequently, **DFOP** model is considered appropriate for modelling endpoints, as it shows lowest χ^2err of all suitable models (SFO, DFOP, HS) and best visual fit. Conservatively, the slow DT_{50} can be used for modelling, as residues did not fall < 10 %.

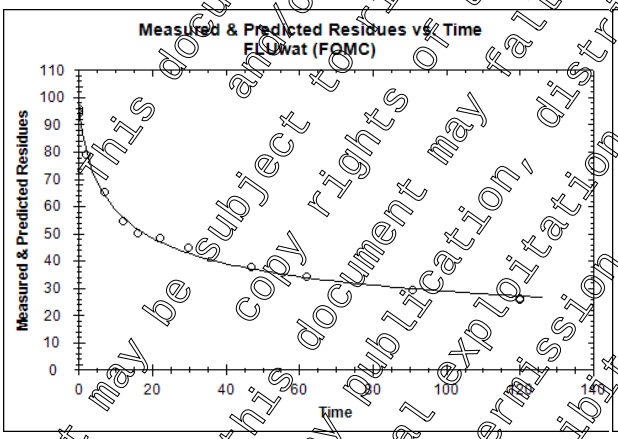
Trigger Endpoint: SFO fit is statistically (χ^2err ~15%) and visually poor. DFOP, FOMC and HS fits were alternatively tested. For FOMC, DT_{90} is extrapolated far beyond study end. FOMC is therefore not suitable, especially for accumulation assessments.
DFOP and HS fits are statistically (χ^2err, t-test) and visually acceptable. Consequently, **DFOP** model is considered appropriate for trigger endpoints, as it shows lowest χ^2err of all suitable models (SFO, DFOP, HS) and best visual fit.

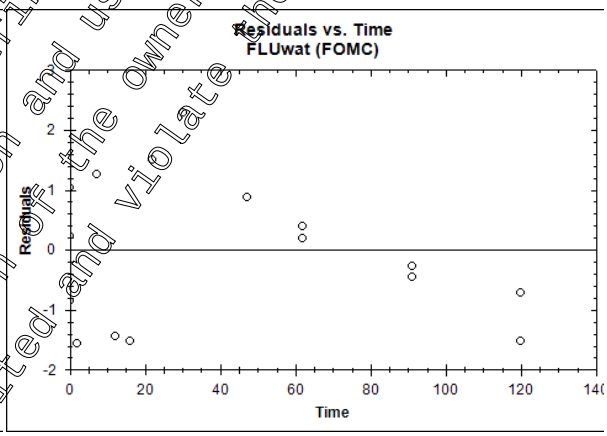












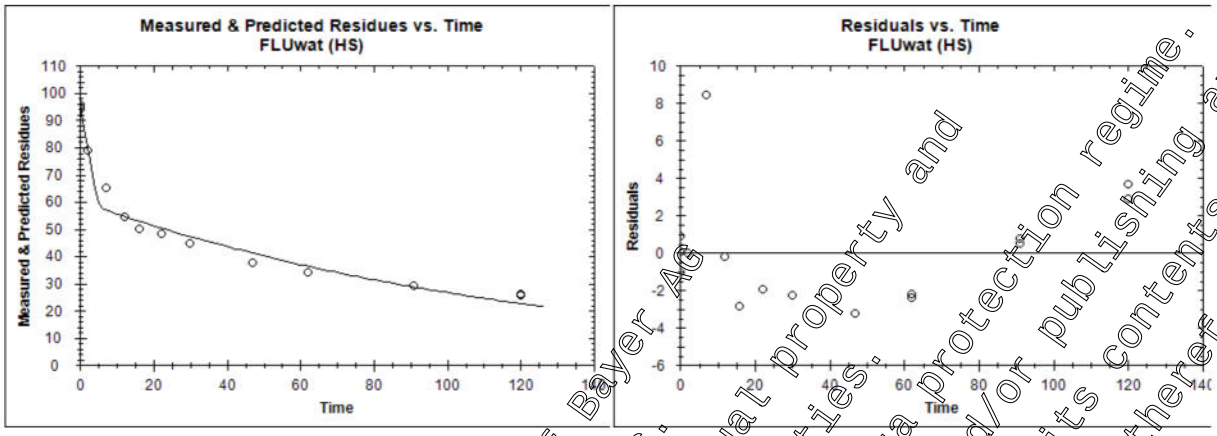


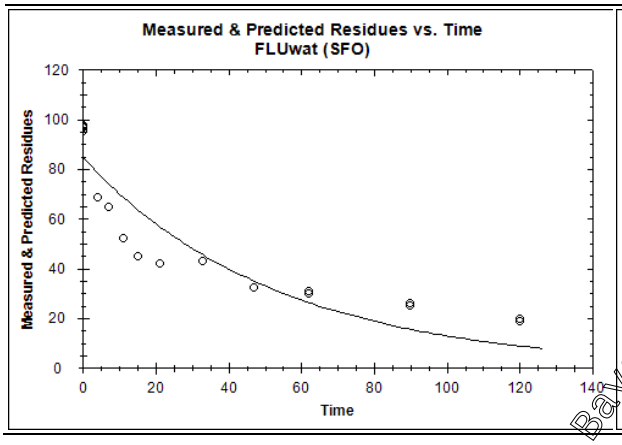
Table 7.2.2.3-9: Fluopyram: kinetic and statistical results of dissipation from water in the Lawrence system

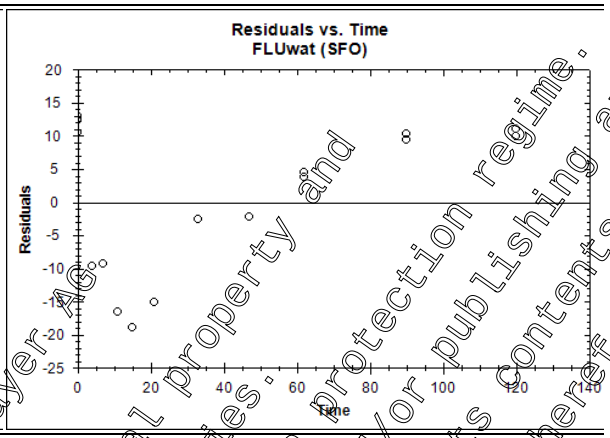
Kinetic model	$DisT_{50}$ actual	$DisT_{90}$ actual	$DisT_{50}$ fast / slow	VA	χ^2err / SWARC	k_1 / α	k_2 / β	g / t_b	t-test k_1 / k_2	95th CI of k_1 / α	95th CI of k_2 / β
	(d)	(d)	(d)		(%)	(1/d / -)	(1/d / d)	(- / d)	(-)	(d / -)	(d / -)
SFO	36.77	122.1	-	-	9.4 / 314	0.018851	-	-	< 0.05	0.01288 - 0.025	-
DFOP	**14.20**	**212.9**	3.950 / **30.3**	+	4.24 / 1.78	0.17550	0.007676	**0.4875**	< 0.001 / < 0.001	0.13020 - 0.221	0.00609 - 0.009
FOMC	15.29	956.7	288.2 [P]	+	4.87 / 10.7	0.40381	2.43723	-	-	0.34490 - 0.473	2.03257 - 4.842
HS	19.08	176.4	8.129 / 69.1	+	7.78 / 6.10	0.085232	0.010036	6.675	< 0.001 / < 0.001	0.05546 - 0.115	0.00802 - 0.012

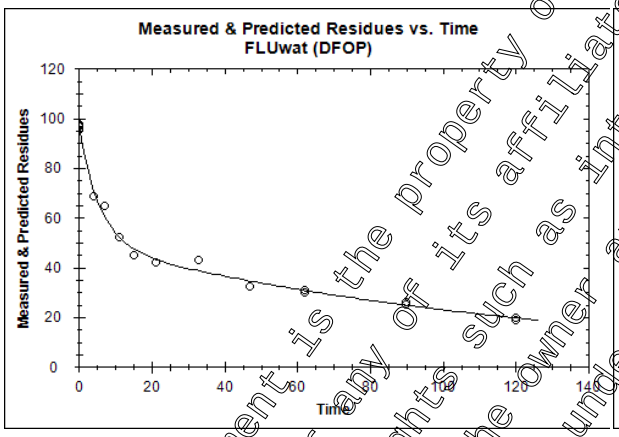
VA = visual assessment, + = good, o = acceptable, - = poor
SWARC = Scaled Weighted Area under Residue Curve
CI = confidence interval
[P] = FOMC: pseudo DT_{50} > DT_{90} / 3.32

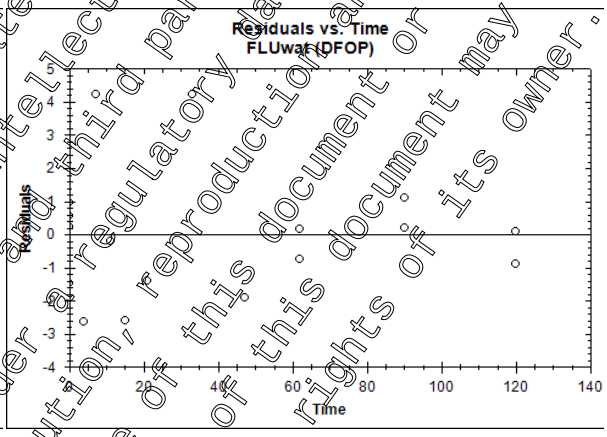
Modelling Endpoint: SFO fit is statistically (χ^2err > 15%) and visually poor. SWARC value is > 40, indicating a biphasic decline. DFOP, FOMC and HS fits were alternatively tested. The residues do not fall < 10 % during study period, therefore FOMC fit is not suitable.
DFOP and HS fits are statistically (χ^2err, t-test) and visually acceptable. Consequently, **DFOP** model is considered appropriate for modelling endpoints, as it shows lowest χ^2err of all suitable models (SFO, DFOP, HS) and best visual fit. Conservatively, the slow DT_{50} can be used for modeling, as residues did not fall < 10 %.

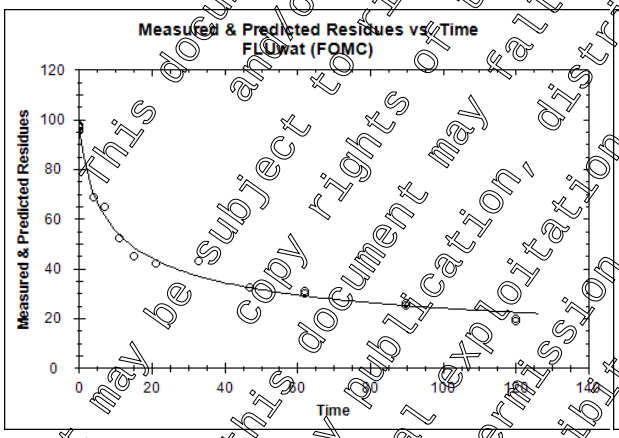
Trigger Endpoint: SFO fit is statistically (χ^2err ~15%) and visually poor. DFOP, FOMC and HS fits were alternatively tested. For FOMC, DT_{90} is extrapolated far beyond study end. FOMC is therefore not suitable, especially for accumulation assessments.
DFOP and HS fits are statistically (χ^2err, t-test) and visually acceptable. Consequently, **DFOP** model is considered appropriate for trigger endpoints, as it shows lowest χ^2err of all suitable models (SFO, DFOP, HS) and best visual fit.

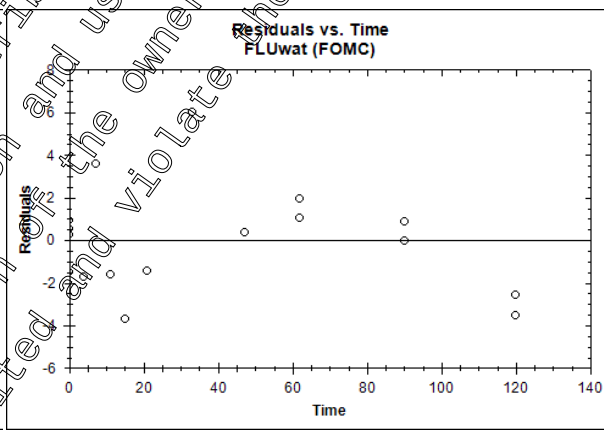


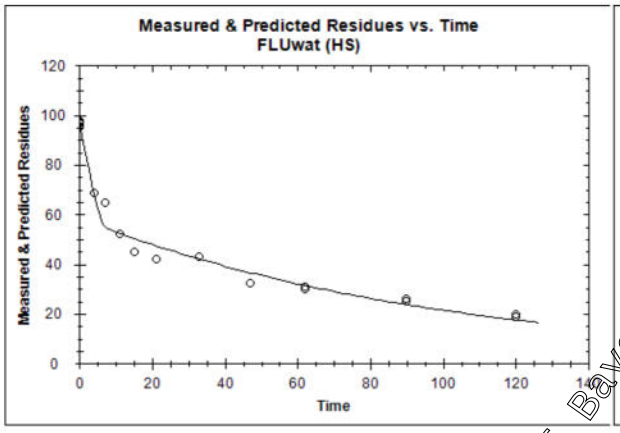


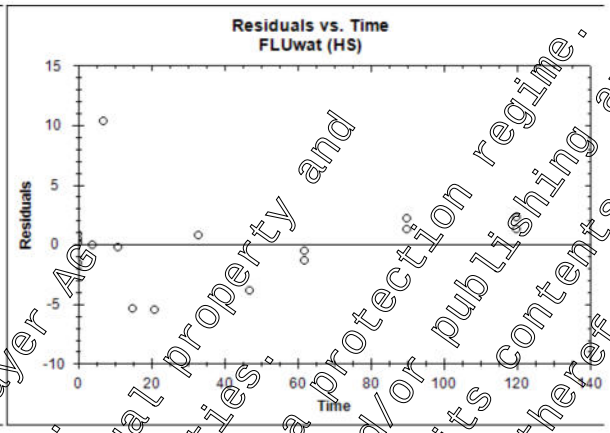












Degradation in total system, fluopyram - level B.1

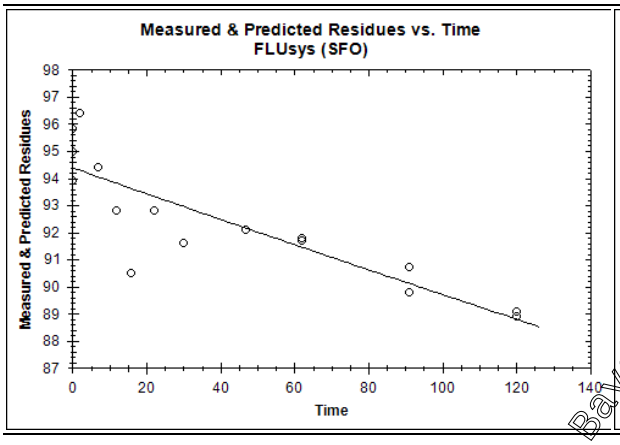
Table 7.2.2.3-10: Fluopyram: kinetic and statistical results of degradation in total system in the Anglerweiher system

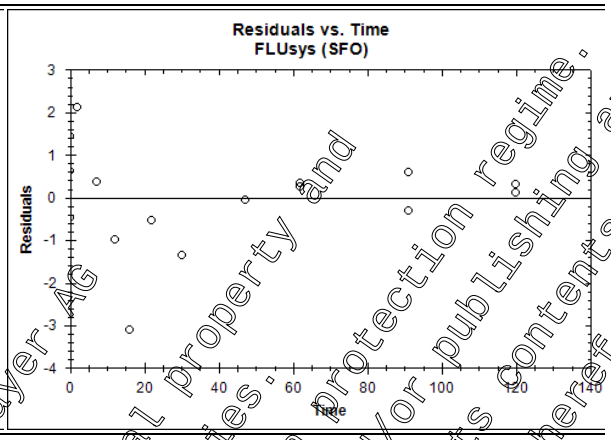
Kinetic model	$DegT_{50}$ actual	$DegT_{90}$ actual	$DegT_{50}$ fast / slow	VA	χ^2err / SWARC	k_1 / α	k_2 / β	g / t_b	t-test k_1 / k_2	95th CI of k_1 / α	95th CI of k_2 / β
	(d)	(d)	(d)		(%)	(1/d / -)	(1/d / d)	(- / d)	(-)	(d / -)	(d / -)
SFO	**>1000**	**>1000**	-	o	1.11 / 6.7	0.00051	-	-	< 0.001	0.00036 – 0.001	-
DFOP	>1000	>1000	5419 / > 1000	o	0.91 / 1.79	0.12790	0.000322	0.0249	0.2 / 0.013	-0.16 – 0.416	0.00007 – 0.001
FOMC	>1000	>1000		o	0.93 / 2.35	0.02053	7.02150	-	-	0.00477 – 0.036	-8.256 – 22.3
HS	>1000	>1000	348.5 / >1000	o	0.79 / 1.7	0.00099	0.00030	16.0	0.010 / 0.004	0.00052 – 0.003	0.00011 – <0.0005

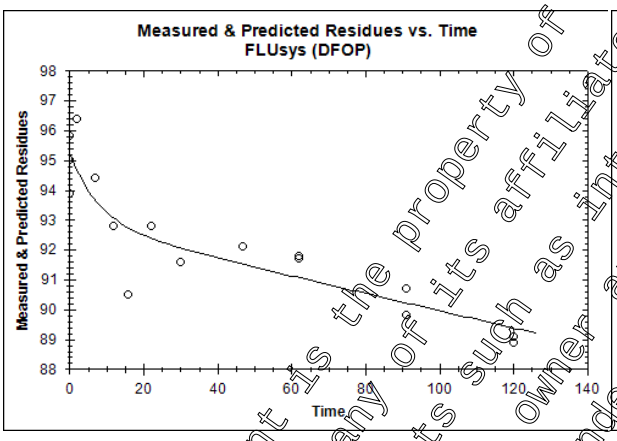
VA = visual assessment: + = good, o = acceptable, - = poor
SWARC = Scaled Weighted Area under Residue Curve
CI = confidence interval
F = FOMC: pseudo $DT_{50} = DT_{90} / 3.32$

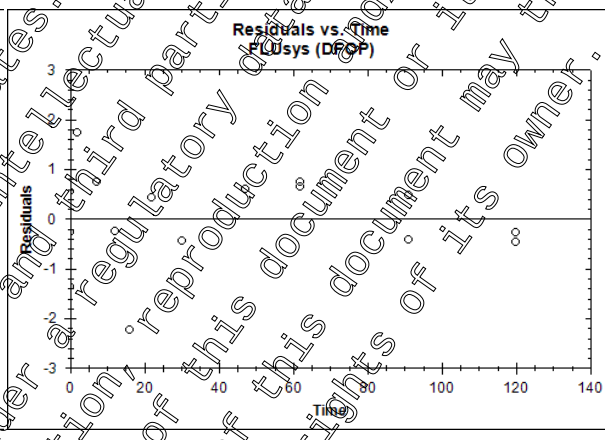
Modeling Endpoint: SFO fit is statistically (χ^2err <15%, t-test <0.05) excellent and visually acceptable. SWARC value is < 40, not indicating a biphasic decline. Consequently, **SFO** degradation model is appropriate for modelling endpoints.

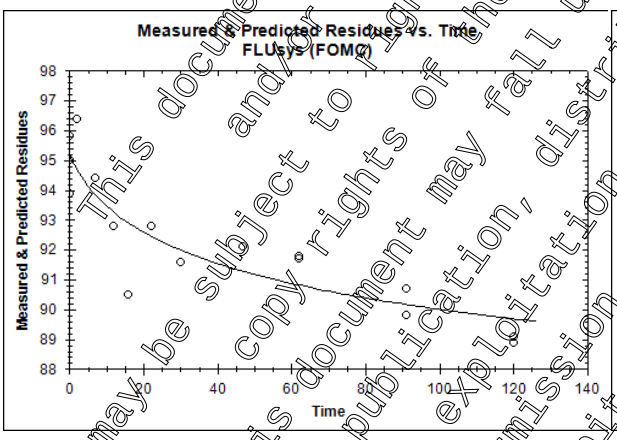
Trigger Endpoint: SFO fit is statistically (χ^2err <15%, t-test <0.05) excellent and visually acceptable. The FOMC fit does not result in a very significant improved fit and its DT_{50} and DT_{90} is extrapolated far beyond study end. For all fits the scattering residue data reduce the visual goodness. Consequently, **SFO** model with a lower amount of parameters is considered appropriate for trigger endpoints.

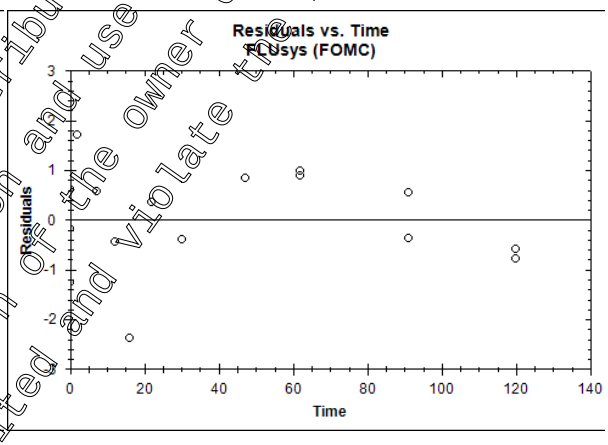


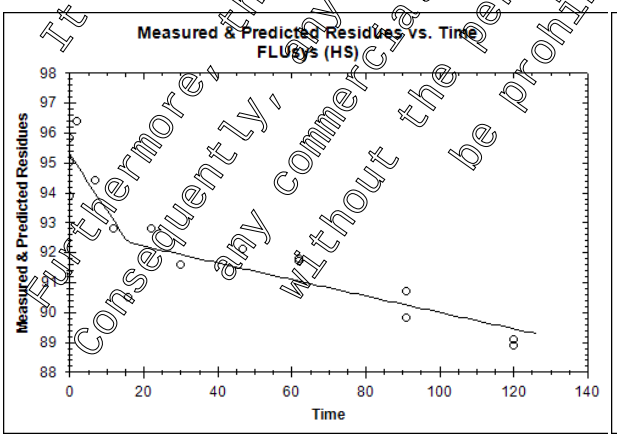












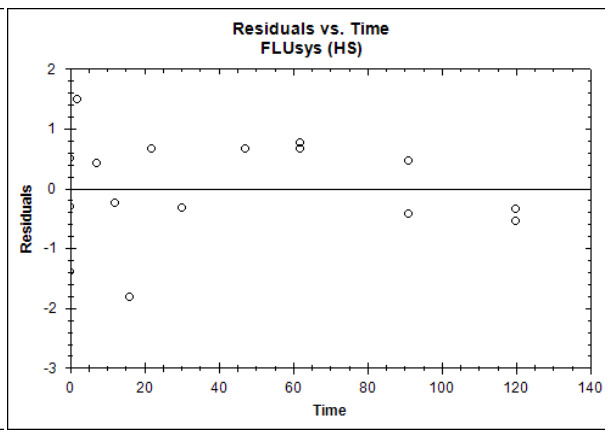


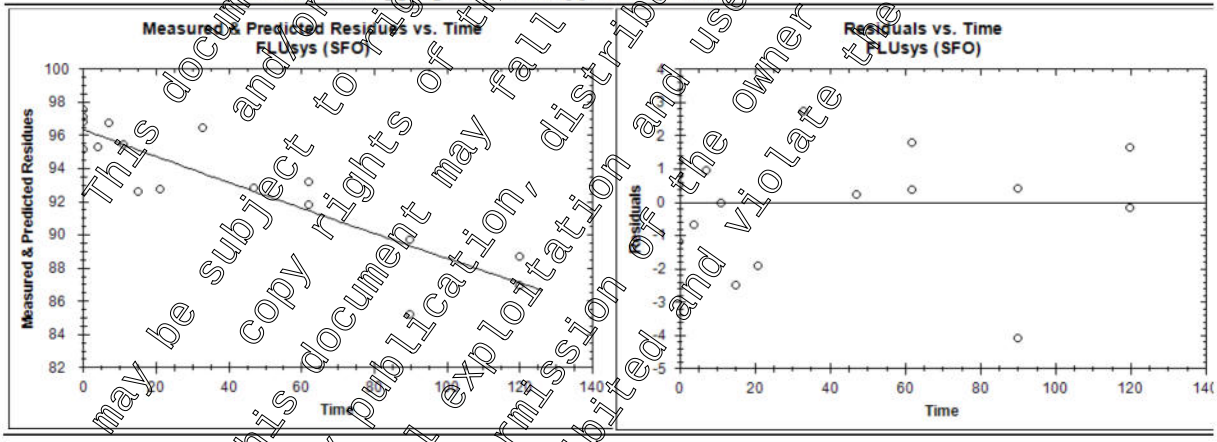
Table 7.2.2.3-11: Fluopyram: kinetic and statistical results of degradation in total system in the Lawrence system

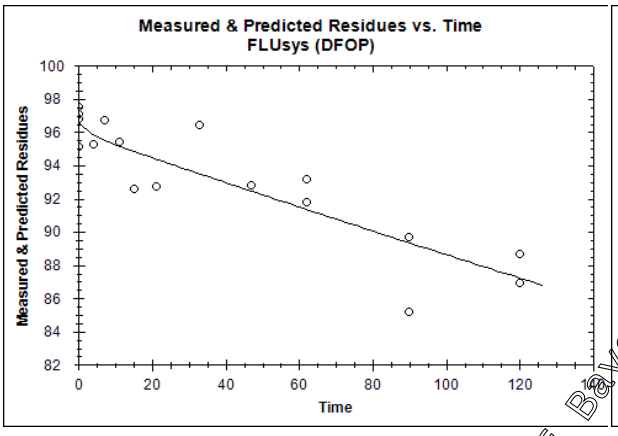
Kinetic model	$DegT_{50}$ actual	$DegT_{90}$ actual	$DegT_{50}$ fast / slow	VA	χ^2err / SWARC	k_1 / α	k_2 / β	g / t_b	t-test k_1 / k_2	95th CI of k_1 / α	95th CI of k_2 / β
	(d)	(d)	(d)		(%)	(1/d / -)	(1/d / d)	(- / d)	(-)	(d / -)	(d / -)
SFO	**826.2**	**>1000**	-	+	1.28 / 3.36	0.000839	-		<0.001	0.00062 - 0.00	
DFOP	861.5	>1000	2.340 / 869.9	+	1.38 / 2.87	0.09627	0.0008	0.007	0.452 / <0.001	-4.057 – 5.03	0.00045 - 0.001
FOMC	1079	>1000		+	1.34 / 3.45	1.191	1.366	-	-	-27.52 - 29.9	-32840 - 35568
HS	826.2	>1000	826.3 / >1000	+	1.40 / 3.36	0.00083	2.22E-14	1232	<0.001 / <0.001	0.0006 - 0.001	2.2E-14 - <0.0005

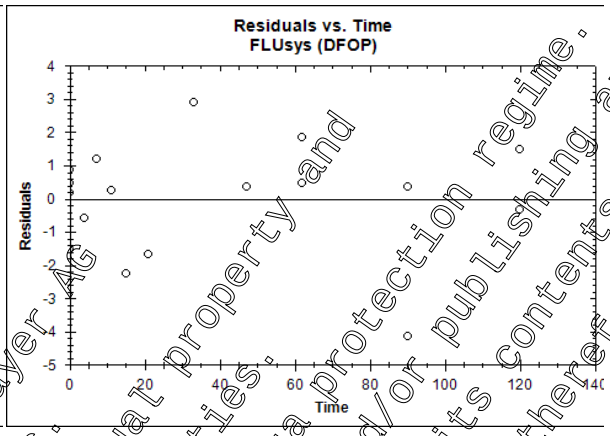
VA = visual assessment, + = good, o = acceptable, - = poor
SWARC = Scaled Weighted Area under Residue Curve
CI = confidence intervall
[F] = FOMC: pseudo DT_{50} = DT_{90} / 3.32

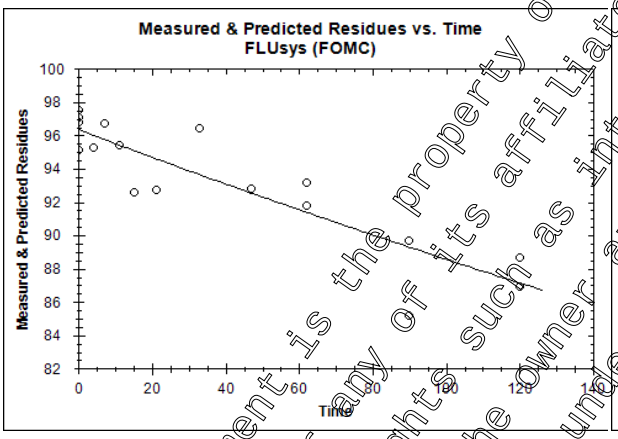
Modeling Endpoint: SFO fit is statistically (χ^2err <15%, t-test <0.05) good and visually acceptable. SWARC value is <40, not indicating a biphasic decline. Consequently, **SFO** degradation model is appropriate for modelling endpoints.

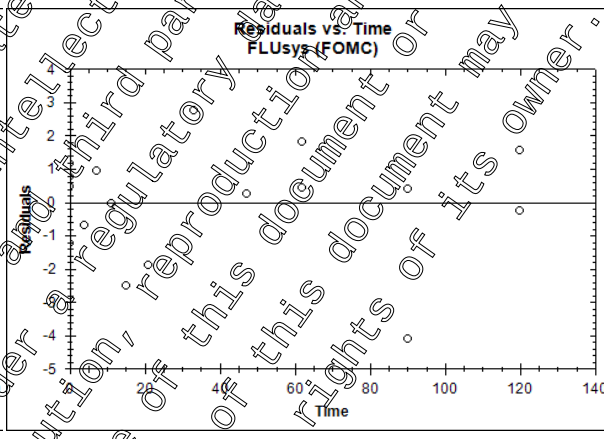
Trigger Endpoint: SFO fit is statistically (χ^2err <15%, t-test <0.05) good and visually acceptable.
The FOMC fit does not result in an improved fit and its DT_{50} and DT_{90} is extrapolated far beyond study end. Consequently, **SFO** model with a lower amount of parameters is considered appropriate for trigger endpoints.

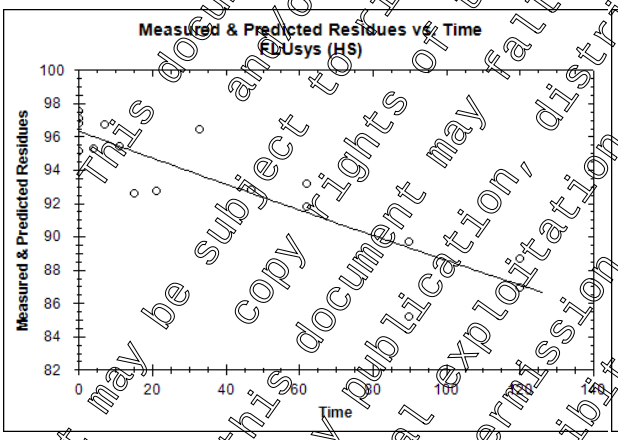


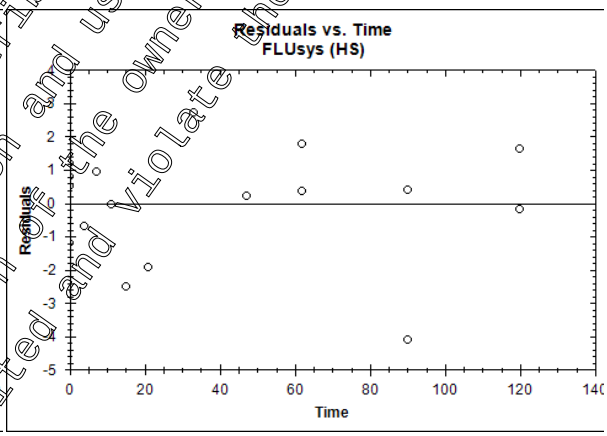












Degradation in water and sediment, separately, fluopyram - level P-II

Table 7.2.2.3-12: Fluopyram: kinetic and statistical results of degradation (SFO) and partitioning in water and sediment, separately (level P-II) in Anglerweiher system

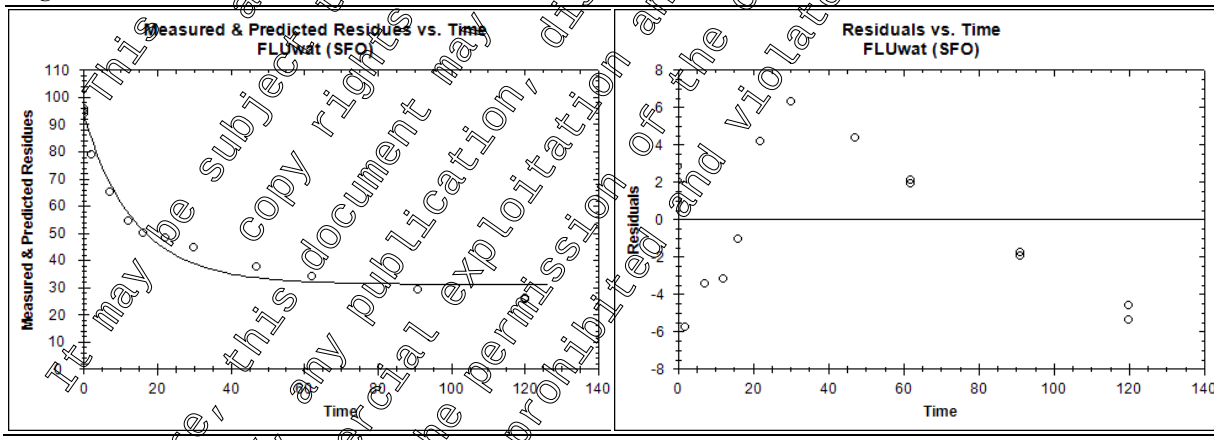
Test system	compart-ment	M_0	$DegT_{50}$	$DegT_{90}$	χ^2err	k_{deg}	t-test k_{deg}	VA
		(% AR)	(d)	(d)	(%)	(1/d)	(-)	
Anglerweiher	Water	92.9	1215	>1000	6.43	0.000571	0.433	o
	Sediment	0 fix	>1000	>1000	8.27	2.35E-14	0.5	-

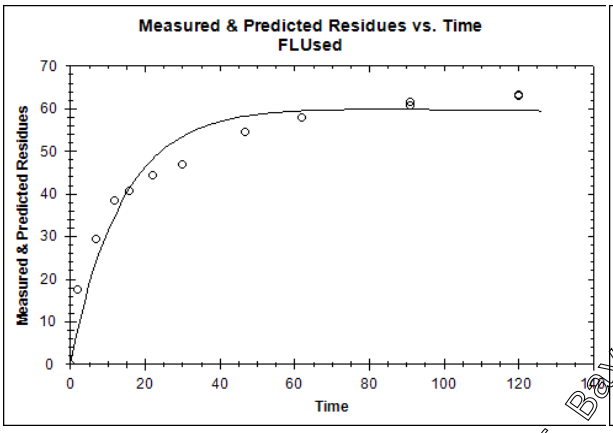
Test system	partitioning from compart-ment …	$k_{wat-sed}$	$k_{sed-wat}$	t-test of k	$F_{sed\ modelling}$	$F_{sed\ theoretical}$
		(1/d)	(1/d)	(-)	(-)	(-)
Anglerweiher	Water	0.04668		< 0.001	0.656	0.548
	Sediment		0.02444	< 0.001		

VA = visual assessment, + = good, o = acceptable, - = poor

Endpoints: The SFO degradation rates k_{deg} from water and from sediment separately, at P-II level are statistically not reliable (t-test). The visual fits are acceptable in the water phase, but poor in the sediment phase. The backtransfer rate from sediment to water is > 0. Consequently, **no reliable corresponding degradation rate pairs** could be derived by fitting at level P-II for modelling or trigger purpose.
Additionally, the F_{sed} test according to FOCUS[4] kinetics is carried out to assess the reliability of the modelled partitioning rates ($k_{wat-sed}$, $k_{sed-wat}$). The fraction of parent compound that transfers into the sediment at equilibrium (F_{sed}) is calculated using: 1. fitted P-II partitioning rates ($F_{sed,\ modelling}$) and 2. conditions of the study or tabled values ($F_{sed,\ theoretical}$). The modelled and theoretical F_{sed} values show no high conformity, which shows only a moderate reliability of the estimated partitioning rates.

Anglerweiher





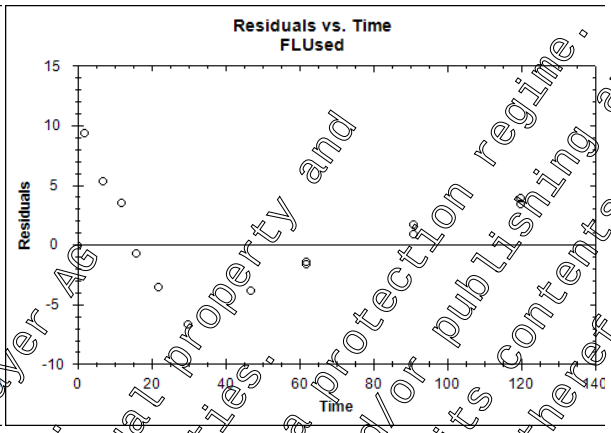


Table 7.2.2.3-13: Fluopyram: kinetic and statistical results of degradation (SFO) and partitioning in water and sediment, separately (level P-II) in Lawrence system

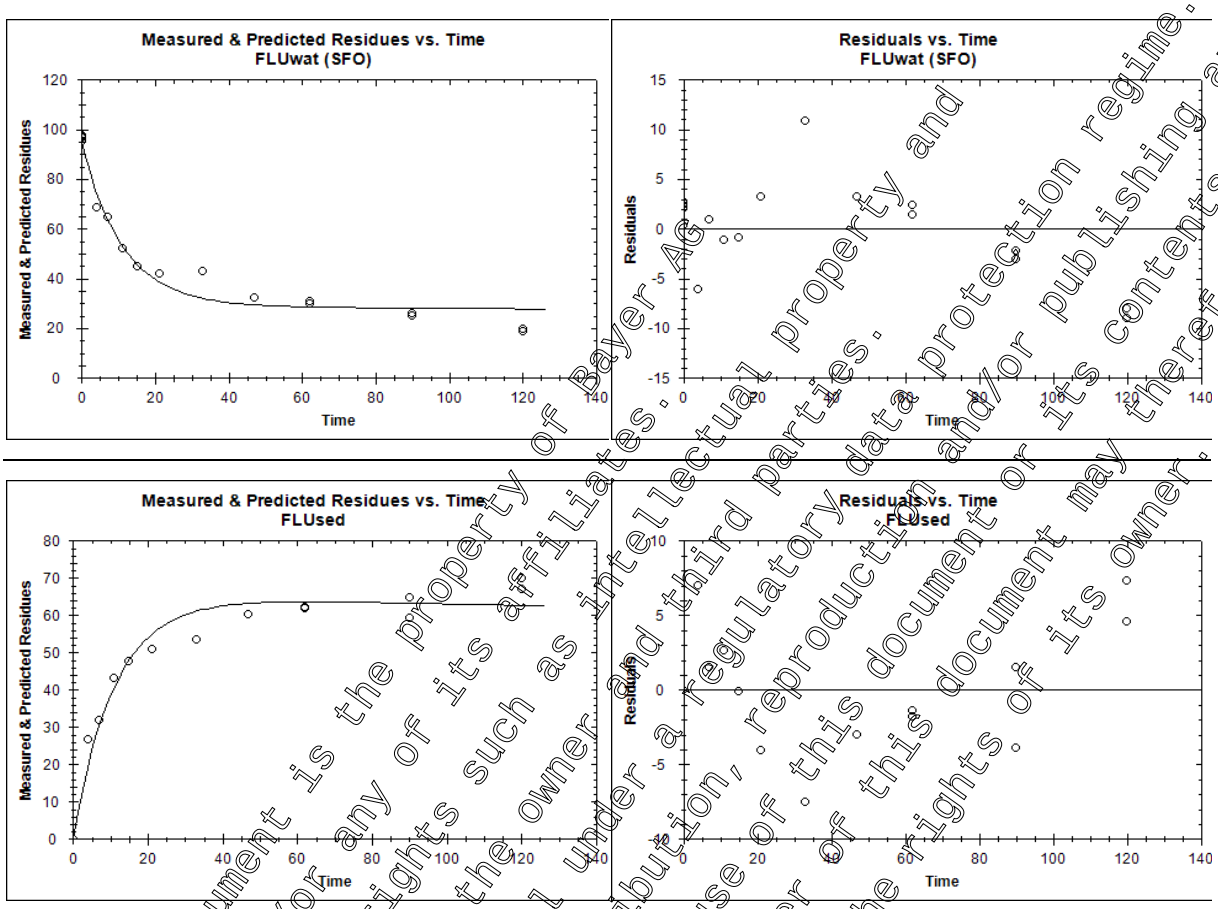
Test system	compart-ment	M_0	$DegT_{50}$	$DegT_{90}$	χ^2err	k_{deg}	t-test k_{deg}	VA
		(% AR)	(d)	(d)	(%)	(1/d)	(-)	
Lawrence	Water	94.8	648.1	>1000	8.75	0.00107	0.409	-
	Sediment	0 fix	>1000	>1000	6.69	2.34E-14	0.5	-

Test system	partitioning from compart-ment …	$k_{wat-sed}$	$k_{sed-wat}$	t-test of k	$F_{sed\ modelling}$	$F_{sed\ theoretical}$
		(1/d)	(1/d)	(-)	(-)	(-)
Lawrence	Water	0.06162		0.001	0.690	0.649
	Sediment		0.02764	< 0.001		

VA = visual assessment, + = good, o = acceptable, - = poor

Endpoints: The SFO degradation rates k_{deg} from water and from sediment, separately, at P-II level are statistically not reliable (t-test). The visual fits are poor in the water and in the sediment phase. The backtransfer rate from sediment to water is > 0. Consequently, **no reliable corresponding degradation rate pairs** could be derived by fitting at level P-II for modelling or trigger purpose.
Additionally the F_{sed} test according to FOCUS kinetics is carried out to assess the reliability of the modelled partitioning rates $k_{wat-sed}$, $k_{sed-wat}$. The fraction of parent compound that transfers into the sediment at equilibrium (F_{sed}) is calculated using: 1. fitted P-II partitioning rates ($F_{sed,\ modelling}$) and 2. conditions of the study or tabled values ($F_{sed,\ theoretical}$). The modelled and theoretical F_{sed} values show a moderate conformity, which might confirm the reliability of estimated partitioning rates.

Lawrence



III. CONCLUSIONS

Results of the kinetic evaluation for trigger and modelling purpose, based on parent only data from an aerobic aquatic laboratory metabolism study in two water-sediment systems are summarised in the tables below.

Table 7.2.2.3-14: Degradation and dissipation in water/sediment systems: modelling endpoints of fluopyram, Level P-I

Fluopyram (FLU)	**Distribution: Max. in sediment 69.9 % after 120 d (Lawrence, phenyl)**									
Water / sediment system	**pH[1] water phase**	**pH sed[1] (water)**	**t. (°C)**	**DegT$_{50}$ / DT$_{90}$ whole sys. (d)**	**St. (χ^2) (%)**	**DisT$_{50}$ / DT$_{90}$ water (d)**	**St. (χ^2) (%)**	**DisT$_{50}$ / DT$_{90}$ sed (d)**	**St. (χ^2) (%)**	**Method of calculation whole sys. / water / sed**
Anglerweiher, sand, D	7.89	7.40	20	>1000 / >1000 (SFO)	1.11	DisT$_{50\ fast}$ = 4.198 **DisT$_{50\ slow}$ = 109.74** g = 0.4441 / 271.6 (DFOP)	2.30	na		SFO / DFOP slow
Lawrence, clay, USA	6.96	6.57	20	826.2 / >1000 (SFO)	1.28	DisT$_{50\ fast}$ = 3.950 **DisT$_{50\ slow}$ = 90.3** g = 0.4875 / 212.9 (DFOP)	4.21	na		SFO / DFOP slow
Geometric mean at 20°C				909.0		99.5 (DFOP slow)	-	-		-

[1] mean value measured at each sampling interval during the study

Table 7.2.2.3-15: Degradation and dissipation in water/sediment systems: modelling endpoints of fluopyram, Level P-II

Fluopyram (FLU)	**Distribution: Max. in sediment 69.9 % after 120 d (Lawrence, phenyl)**									
Water / sediment system	**pH[1] water phase**	**pH sed[1] (water)**	**t. (°C)**	**DT$_{50}$ / DT$_{90}$ whole sys. (d)**	**St. (χ^2) (%)**	**DegT$_{50}$ / DT$_{90}$ water (d)**	**St. (χ^2) (%)**	**DegT$_{50}$ / DT$_{90}$ sed (d)**	**St. (χ^2) (%)**	**Method of calculation whole sys. / water / sed**
Anglerweiher, sand, D	7.89	7.40	20	-	-	n.r.	-	n.r.	-	-
Lawrence, clay, USA [A]	6.96	6.57	20	-	-	n.r.	-	n.r.	-	-

[1] mean value measured at each sampling interval during the study
n.r. not fully reliable, mathematically not significantly different from 0; not usable

Table 7.2.2.3-16: Degradation and dissipation in water/sediment systems: trigger endpoints of fluopyram, Level P-I

Fluopyram (FLU)	**Distribution: Max. in sediment 69.9 % after 120 d (Lawrence, phenyl)**									
Water / sediment system	**pH[1] water phase**	**pH sed[1] (water)**	**t. (ºC)**	**$DegT_{50}$ / DT_{90} whole sys. (d)**	**St. (χ^2) (%)**	**$DisT_{50}$ / DT_{90} water (d)**	**St. (χ^2) (%)**	**$DisT_{50}$ / DT_{90} sed (d)**	**St. (χ^2) (%)**	**Method of calculation whole sys. / water / sed**
Anglerweiher, sand, D [A]	7.89	7.40	20	>1000 / >1000 (SFO)	1.11	21.13 / 271.6 (DFOP)	2.11	na		SFO / DFOP
Lawrence, clay, USA [A]	6.96	6.57	20	826.2 / >1000 (SFO)	1.28	14.20 / 212.9 (DFOP)	4.21	na		SFO / DFOP

[1] mean value measured at each sampling interval during the study

3. Assessment and conclusion

<u>Assessment and conclusion by applicant:</u>
The kinetic evaluation followed FOCUS guidances and is considered to be valid and reliable.

<u>Assessment and conclusion by RMS:</u>
Outcome and conclusion of the study: RMS should indicate if they agree to the results and conclusions of the APPL.

CA 7.2.2.4 Irradiated water/sediment study

The route and rate of degradation of fluopyram in water and sediment were comprehensively studied in sections CA 7.2.1 to CA 7.2.2.3. Therefore, an irradiated water/sediment study is not required and was not conducted.

CA 7.2.3 Degradation in the saturated zone

No studies have been conducted to investigate degradation of fluopyram in the saturated zone.

CA 7.3 Fate and behaviour in air

The vapour pressure of fluopyram (1.2×10^{-6} Pa at 20 °C, CA 2.2) is below the trigger values of 10^{-5} Pa (plant) and 10^{-4} (soil) indicating potential for volatilisation as a significant pathway of entry of residues into the air. Additionally, the calculated Henry's constant (2.98×10^{-5} Pa m^3 mol^{-1} in distilled water and buffer pH 7 at 20°C, CA 2.2) serves as indication that fluopyram is non-volatile and therefore will not reach the atmosphere via volatilisation.

For the sake of completeness the half-life of fluopyram in air can be assessed by the computer program AOPWIN™ (v 1.91), based on structure-activity relationships developed by Atkinson *et al*. The half-life is estimated to be 1.7 days based on a mean concentration of hydroxyl radicals present in the troposphere of 1.5×10^6 OH radicals/cm^3. Due to the low vapour pressure of fluopyram in connection with its degradability in air it is expected that fluopyram cannot be transported in gaseous phase over large distances and cannot accumulate in the atmosphere.

Trifluoroacetate (TFA), arises from many different sources (see KCA 7.5/**12**, M-603942-01-1, Solomon 2016), and is a terminal degradation product of fluopyram in soil; therein it is the dissociated anion of trifluoroacetic acid. Triflouroacetic acid has a dissociation constant (pKa-value) of 1.3, and hence, is deprotonated under environmental and physiological conditions and due to the high buffering capacities of environmental and physiological matrices shows no acidic properties. This clearly indicates that trifluoroacetate, being entirely dissociated when formed from fluopyram in soil, would display very limited volatility (< 1.0 x 10^{-6} Pa, 20°C, M-420190-01-1) and hence no risk to the atmosphere. Therefore, no relevant applicant studies are submitted on trifluoroacetate, and no public literature articles were regarded as relevant for the air compartment. In case that liquid media in air (clouds, etc.) are concerned for estimating local and global effects of TFA, contributions solely referring to the rather non-volatile fluopyram can hardly be done, since there are ubiquitous other sources of volatile TFA precursors in air and aqueous phases.

The vapour pressure of fluopyram-7-hydroxy (1.55 x 10^{-9} Pa, see CA 2.14) is below the trigger values of 10^{-5} Pa (plant) and 10^{-4} (soil) indicating potential for volatilisation. Therefore, it will not reach the atmosphere via volatilisation, and a risk for the air can be excluded.

CA 7.3.1 Route and rate of degradation in air

1. Information on the study

Data Point:	KCA 7.3.1/01
Report Author:	[redacted]
Report Year:	2006
Report Title:	AE C456948: Calculation of the chemical lifetime in the troposphere
Report No:	MEF-06/50/
Document No:	M-284597-01-1
Guideline(s) followed in study:	EU 91/414/EEC amending 91/414/EEC Annex I, 2.10.2; EU 95/36/EC amending 91/414/EEC Annex I, 7.2.1; Equivalent to US EPA OPPTS Guideline No. 835.SUPP
Deviations from current test guideline:	Current Guideline: not applicable (calculation)
Previous valuation:	yes, evaluated and accepted RMS (2011)
GLP/Officially recognised testing facilities:	No, not conducted under GLP/officially recognised testing facilities
Acceptability/Reliability:	Yes

2. Full summary of KCA 7.3.1/01

Executive Summary

The half-life in air of fluopyram was estimated according to structure-activity relationship (SAR) methods developed by Atkinson.

The half-life of fluopyram in air was estimated with 1.73 to 2.60 days, depending on the model input parameter of the mean concentration of hydroxyl radicals present in the troposphere ("short-term" scenario: typical OH radical concentration during daylight hours / "long-term" scenario: typical OH radical concentration averaged over day and night-times).

I. METHODS

The half-life of fluopyram in air was estimated according to structure-activity relationship (SAR) methods developed by Atkinson *et al.* The approach of Atkinson *et al.* was based on a comprehensive

set of experimental data to result in a quantitative structure-activity relationship (QSAR) mathematic model that allows an estimation by calculation, starting from the molecular structure of a compound. The calculation procedure has been transferred into the personal computer program "Atmospheric Oxidation Program" (AOP) by Meylan & Howard. The version AOPWIN™ 1.91 (U.S. EPA, 2000) was used for the calculations being part of the EPI Suite™ set of programs.

Considering the chemical structure of fluopyram, it can be concluded that reactions with photochemically produced hydroxyl radicals will mainly determine its degradation rate in air. Reactions with ozone have no relevant impact on the overall assessment. A value of 1.5 x 10^6 OH radicals/cm³ is generally regarded a typical concentration for daylight hours, which may be used in "short-term" calculations as a 12-hours-day-time concentration (12 hours period is an average daylight time for a whole year, excluding the night). Alternatively, 0.5 x 10^6 OH radicals/cm³ is regarded as a 24-hours-mean (constant) OH radical concentration in the troposphere, representing a "long-term" average value that includes night-time (when OH radical concentration is zero).

II. RESULTS AND DISCUSSION

The overall reaction rate of fluopyram with hydroxyl radicals is estimated to be 6.1759 x 10^{-12} cm³ x molecule^{-1} x s^{-1}. This rate is derived mainly from incremental reactions like hydrogen abstraction (5.8590 cm³ x molecule^{-1} x s^{-1}) and an addition reaction to aromatic rings (assumed value of 0.3170 cm³ x molecule^{-1} x s^{-1}, value estimated).

Based on the overall hydroxyl radical reaction rate constant, in combination with the "long term" concentration of these radicals in the atmosphere (i.e. 24 h day, 0.5 x 10^6 OH radicals/cm³, 12 h day, 1.5 x 10^6 OH radicals/cm³), the half-life of fluopyram in air is derived to be 2.60 days (24 h day) and 1.73 days (12 h day). This estimate should be regarded as worst-case assumption as the approach does not consider the contribution of any other reactive species than hydroxyl radicals to the overall atmospheric degradation of fluopyram in air.

III. CONCLUSIONS

Fluopyram is considered to be susceptible to reactions with hydroxyl radicals which contribute to the overall degradation of the substance in the atmosphere. Various moieties of the molecule were identified as possible targets for radical reactions. Attack by hydroxyl radicals should result in the formation of multiple primary radicals. These may lead to secondary oxidation products, which can be eliminated from the air by wet and/or dry deposition.

The half-life of fluopyram in air was estimated with 1.73 to 2.60 days. Concluded from the short half-life time of in air, it is expected that fluopyram cannot be transported in gaseous phase over large distances and cannot accumulate in the atmosphere. Furthermore, only limited quantities of fluopyram will enter the atmosphere, due to the low vapour pressure of the substance.

3. Assessment and conclusion

Assessment and conclusion by applicant:
The study is acceptable to cover this data point. The results are considered to be valid and reliable.

Assessment and conclusion by RMS:
Outcome and conclusion of the study: RMS should indicate if they agree to the results and conclusions of the APPL.

CA 7.3.2 Transport via air

The transport via air of fluopyram was not studied since its vapour pressure is below the trigger value of 10^{-5} Pa.

CA 7.3.3 Local and global effects

Due to the negligible volatilisation potential and the fast degradation of fluopyram in air, no significant local and global effects from atmospheric transport of fluopyram are expected.

CA 7.4 Definition of the residue

CA 7.4.1 Definition of the residue for risk assessment

The residue definition for risk assessment includes fluopyram and its degradation products fluopyram-7-hydroxy and TFA. As both degradation products can be formed during the degradation of fluopyram in soil, they were regarded as relevant for risk assessments in soil, and due to potential entry routes like run-off or leaching also considered in groundwater and surface water. An overview is given in the following:

Compartment	Residues for risk assessment
Soil:	Fluopyram, fluopyram-7-hydroxy, TFA
Groundwater:	Fluopyram, fluopyram-7-hydroxy, TFA
Surface water:	Fluopyram, fluopyram-7-hydroxy, TFA
Sediment:	Fluopyram
Air:	Fluopyram

CA 7.4.2 Definition of the residue for monitoring

The residue definition for monitoring for compartments soil, water and air is fluopyram only.

CA 7.5 Monitoring data

Monitoring data for Fluopyram from databases in the EU

For the previous evaluation of fluopyram, no applicant studies or articles reporting monitoring activities were submitted.

For the current fluopyram approval renewal, there is one new applicant monitoring report referring to soil, groundwater, surface water, drinking water, sediment and air monitoring (KCA 7.5/01, M-759463-02-1). It describes the collection process of public monitoring data (from regional/national environment agencies) for European countries for fluopyram. Public monitoring data was not found for drinking water and soil. The available monitoring data was analysed for exceedance of regulatory thresholds appropriate for the compartment and the results were summarised.

There are three published peer-reviewed papers. KCA 7.5/02 (M-755508-01-1) reports monitoring results for fluopyram in groundwater and raw surface water used for drinking water extraction in The Netherlands. KCA 7.5/03 (M-681600-01-1) reports monitoring results for fluopyram using Empore™ disk-based passive samplers in groundwater wells near Lyon and KCA 7.5/04 (M-760205-01-1) reports monitoring results for fluopyram residues in clay loam soil from the Canary Islands, Spain. These articles are considered to contain supportive information.

Headline Monitoring Results

In the new applicant review study (KCA 7.5/01, M-759463-02-1), fluopyram was quantified in a small proportion of groundwater (0.49% of the 18855 analyses were above LOQ) and surface water (29.9% of the 9178 analyses were above LOQ) analyses retrievable from readily available public monitoring databases spanning 2014 – November 2020 for 6 countries (Austria, France, Germany, Italy, The Netherlands and Sweden). In the cases where residue levels were above LOQ, there were rarely findings above the applied regulatory thresholds, resulting in compliance rates >99.9%. For the sediment compartment (Sweden only) there were no reported residue concentrations above the Tier 1-RAC-Sed (2.6 mg/kg d.w.) within the 12 samples, indicating 100% compliance. A small number of records relating to concentrations in air were also found in France and Sweden where fluopyram was quantified (16.4% of the 1399 analyses showed residue levels above LOQ (0.002 - 0.0188 ng/m^3)). For all compartments, it cannot be discounted that some of the detections identified are erroneous given they arise from non-GLP monitoring networks and programmes of unknown quality.

In the published peer reviewed paper (KCA 7.5/02, M-755508-01-1) monitoring results (samples taken in 2016) for fluopyram in groundwater and surface water used for drinking water extraction in The Netherlands were reported. There were no fluopyram detections in groundwater samples and only 6 of the 38 surface water detections were ≥ 0.1 µg/L (exact concentrations not quoted). However, these represent concentrations in raw surface water while the threshold of 0.1 µg/L applies to treated drinking water at the tap of consumers. Following the drinking water production process, after flocculation and dune filtration, concentrations were below 0.05 µg/L. In the published peer reviewed paper (KCA 7.5/03, M-681600-01-1) fluopyram was detected above the minimum quantification level (0.5 ng/L) in 67% of the samples acquired via passive sampling from 12 groundwater wells. The maximum detected was 24 ng/L. In the published peer reviewed paper (KCA 7.5/04, M-760205-01-1), fluopyram was not detected in any of the 18 analysed soil samples taken from agricultural lands in the Canary Islands, Spain. The LOQ of fluopyram was determined to be 0.5 ng/g soil. These articles are considered to contain supportive information only.

The RACs and maximum reported concentrations in each compartment are summarised in the table below.

Table 7.5- 1: Summary of reported maximum concentrations of fluopyram with regulatory acceptable concentrations (RAC) in each environmental compartment

Compartment	Regulatory acceptable concentration	Compliance (%)	Maximum Concentration
Soil	7.56 mg a.s./kg soil	100	No detections (M-760205-01-1)
Groundwater	0.1 µg/L	99.95	0.25 µg/L (M-759463-02-1)
Surface water	5.0 µg/L	99.90	12.0 µg/L (M-759463-02-1)
Drinking water	0.1 µg/L	NA	Not documented
Sediment	2.6 mg/kg d.w.	100	1.5 µg/kg d.w. (M-759463-02-1)
Air	NA	NA	4.459 ng/m^3 (M-759463-02-1)

NA: Not applicable

For all compartments, it cannot be discounted that some of the detections identified are erroneous given they arise from non-GLP monitoring networks and programmes of unknown quality.

Headline Conclusions

It can be concluded from the assessment of the readily available public monitoring datasets that fluopyram does not pose a concern for the environment where data were available for the investigated environmental compartments.

The new applicant study and published peer-reviewed paper considered in this monitoring chapter are listed in Table 7.5- 2. In addition, this table shows the relevant compartment that each study/literature article addresses.

Table 7.5- 2: Monitoring study and literature article covering fluopyram monitoring

Annex point	Study (Author, year, DART no.)	Study type	Source (CRO/sponsor/ journal)	Status	Monitoring activities					
					SOIL	GW	SW	DW	SED	AIR
APPLICANT STUDY										
New study/assessment										
KCA 7.5/01	M-759463-02-1	Public environmental monitoring data (groundwater, surface water, drinking water, soil, air and sediment)	Knoell Germany Bayer AG	Valid						
Existing study/assessment										
There are no existing applicant studies										
RELEVANT LITERATURE ARTICLE										
KCA 7.5/02	Sjerps R.M.A. *et al.*, 2019. M-759508-01-1	Occurrence of pesticides in Dutch drinking water sources	Chemosphere (235) 510 - 518	Supportive information						
KCA 7.5/03	Pinasseau, L. *et al.*, 2020. M-681600-01-1	Calibration and field application of an innovative passive sampler for monitoring groundwater quality	Talanta 208 (2020) 120307	Supportive information						
KCA 7.5/04	Acosta-Dacal, A. *et al*, 2021. M-760205-01-1	Optimization and validation of a QuEChERS-based method for the simultaneous environmental monitoring of 218 pesticide residues in clay loam soil	Science of the Total Environment (753) 142015	Supportive information						

GW: Groundwater; SW: Surface water; DW: Drinking water; SED: Sediment

: Study contained information

: Study did not contained information

1. Information on the study

Data Point:	KCA 7.5/01
Report Author:	[redacted]
Report Year:	2021
Report Title:	Fluopyram (FLU) and metabolites: Public environmental monitoring data (groundwater, surface water, drinking water, soil, air and sediment)
Report No:	EnSa-20-0868
Document No:	M-759463-02-1
Guideline(s) followed in study:	None
Deviations from current test guideline:	Current Guideline: not applicable
Previous evaluation:	No, not previously submitted
GLP/Officially recognised testing facilities:	No, not conducted under GLP/Officially recognised testing facilities
Acceptability/Reliability:	Yes

2. Full summary of KCA 7.5/01

Executive Summary

Searches for public monitoring data were performed to provide an overview of residue concentrations of fluopyram and its metabolites fluopyram-benzamide, fluopyram-7-hydroxy, and fluopyram-pyridyl-carboxylic acid (PCA) in the environmental compartments of groundwater, surface water, sediment, soil and air in the framework of the EU approval renewal of fluopyram according to 1107/2009 and 844/2012. The search was predominantly based on internet sources identifying databases and reports which are publicly accessible e.g. from the Environmental Agencies of European countries. The data search was conducted with "fluopyram", "fluopyram-benzamide", "fluopyram-7-hydroxy" and "fluopyram-pyridyl-carboxylic acid" as key words. If applicable, the time period for which monitoring results were searched was from 1995 to November 2020. Available monitoring data were analysed for exceedance of regulatory thresholds appropriate for the compartment and the results were summarised. The search revealed that monitoring information is not generally publicly available in all European countries and not necessarily available at a national level, in some cases only being available for some states/regions/provinces.

In terms of concentration thresholds, this report facilitates analysis within the context of the Water Framework Directive (2000/60/EC) and associated Groundwater Directive (2006/118/EC), the Drinking Water Directive (1998/83/EC) and the Plant Protection Products Directive (1107/2009/EC). Regulatory Acceptable Concentrations (RACs) for fluopyram are considered for surface water (5.0 µg/L) and for sediment (2.6 mg/kg d.w.); for groundwater a value of 0.1 µg/L applies.

As part of the EFSA conclusion (2013) for fluopyram; fluopyram-benzamide, fluopyram-7-hydroxy, and PCA were classified as non-relevant metabolites. This conclusion was derived from applying the guidance document for the assessment of the relevance of metabolites in groundwater within the EU (Sanco/221/2000 rev. 10 Feb 2003), which remains the currently valid guidance document today. However as no monitoring of these metabolites was documented in any database/report under consideration, these metabolites will not be discussed further.

The groundwater monitoring data search indicated that fluopyram concentrations above the regulatory trigger of 0.1 µg/L are rare (9 analyses; 0.048% of 18855 analyses) with a maximum concentration of 0.25 µg/L.

The surface water monitoring data search indicated that fluopyram concentrations above the Tier 1-RAC-SW (5.0 µg/L) are rare (8 analyses, 0.098% of 9187 analyses), with a maximum concentration of 12 µg/L.

The sediment monitoring data search indicated no residue concentrations above Tier 1 RAC-Sed (2.6 mg/kg), with a maximum concentration of 1.5 µg/kg d.w..

The air monitoring data search indicated fluopyram concentrations above the LOQ (0.002 - 0.0188 ng/m^3) were found (230 analyses, 16.4% of 1399 analyses). The reported median and maximum concentrations are 0.163 ng/m^3 and 4.459 ng/m^3, respectively.

For all compartments, it cannot be discounted that some of the detections identified are erroneous given they arise from non-GLP monitoring networks and programmes of unknown quality.

For drinking water and soil, fluopyram monitoring data was not found.

Overall, it can be concluded from the assessment of readily available public monitoring datasets that fluopyram does not pose a concern for the investigated environmental compartments where data was available.

I. MATERIALS AND METHODS

Material
Fluopyram and its metabolites were the subject of this overview of monitoring results.

Analytical method
The search was based predominantly on internet searches identifying databases and reports which are publicly accessible e.g. from the Environmental Agencies of European countries.

Searches were performed in databases or national information portals (Table 7.5- 3). Fluopyram and its metabolites were the subject of this overview of monitoring results. The search was conducted with "fluopyram", "fluopyram-benzamide", "fluopyram-7-hydroxy" and "fluopyram-pyridyl-carboxylic acid" as key words, including national spellings. As monitoring of fluopyram-benzamide, fluopyram-7-hydroxy, and PCA was not documented in any database/report under consideration, these metabolites will not be discussed further.

If applicable, the time period for which monitoring results were searched, was from 1995 to November 2020. Where monitoring data was found, this was analysed for exceedance of regulatory thresholds appropriate for the compartment and the results were summarised.

The search revealed that monitoring information is not generally publicly available for each European country and not necessarily available at a national level, in some cases only being available for some states/regions/provinces. This applies, for example, for Germany and its Federal States.

Public monitoring databases and associated monitoring reports were investigated for several countries covering groundwater and/or surface water and to a lesser extent sediment, soil and air. The information in the databases and/or reports was collated and/or evaluated for each European country's agency/organisation. An overview of the monitoring situation is presented in Table 7.5- 3. Several more countries were examined regarding monitoring data. However, as they either did not report any relevant public monitoring data or no monitoring program was established, they are not discussed further.

The German database regarding the river "Elbe" includes monitoring data from 9 federal states: Berlin, Brandenburg, Hamburg, Lower Saxony, Schleswig-Holstein, Mecklenburg-Vorpommern, Saxony,

Saxony-Anhalt and Thuringia. Measurements refer to different water bodies (e.g. rivers, lakes, ditches, ports, seashores, ponds) located all around the "Elbe" in Germany. The entire area is split up in 7 sub-areas formed by rivers Havel, Elbe, Elde, Mulde, Schwarze Elster, Saale, Tideelbe as coordinating spaces (Koordinierungsräume). Each coordinating space includes several sub-waterbodies that can be used for search of monitoring data. It is also possible to do specific searches with user's own parameters (monitoring period and relevant substances can be chosen).

For the river "Danube", a database in German is available. It is possible to do a specific search with several selecting options to get information on the coordinating spaces (Koordinierungsräume) of the river "Danube".

Table 7.5- 3: Searching results for Austria, Czech Republic, Denmark, France, Germany, Greece, Ireland, Italy, the Netherlands, Portugal, Romania, Slovenia, Spain, Sweden, Switzerland, United Kingdom and also includes 'supra national' i.e. EU or river basin data sources

Country	Data Source/Organisation	Monitoring Data available [Yes/No]
Europe	NORMAN - EMPODAT Database	No monitoring data reported[3]
	Danube River Basin Water Quality Database	No monitoring data reported[3]
	European Environment Agency – Status and quality of Europe's water database (Waterbase)	Please see comment below[4]
Austria	Austrian Federal Ministry for Sustainability and Tourism – H2O Water Database	Yes
	Austrian Federal Environment Agency and Ministry for Sustainability and Tourism – Several reports	No monitoring data reported[3]
Czech Republic	IS Arrow – Assessment and Reference of water monitoring	No monitoring data reported[3]
Denmark	Geological Survey of Denmark and Greenland – Groundwater database (Jupiter)	No monitoring data reported[3]
	"Danish Pesticide Leaching Assessment Programme"	No monitoring data reported[3]
France	ADES – National Groundwater Quality Portal	Yes
	Naiades – National Surface Water Quality Data Portal	Yes
	ATMO – National network of associations for the air quality[1]	Yes
	CNEP – National pesticide monitoring plan in air	Yes
Germany	Sachsen Environment Agency – Surface water/Groundwater Quality Portal (IDA)	Yes
	Rheinland Pfalz - GeoPortal	No monitoring data reported[3]
	Rheinland-Pfalz Environmental Agency – Annual reports on water quality monitoring	Yes
	Rheinland Pfalz Environmental Agency – Annual reports of stations for water investigation	No monitoring data reported[3]
	Baden-Württemberg State Institute for the Environment – Interactive data and map service (UDO)	No monitoring data reported[3]
	German Federal agency for hydrology – Rhine river basin community	No monitoring data reported[3]

	Elbe River Basin - Data information system	No monitoring data reported[3]
	LAWA - Working Group on water issues of the Federal States and the Federal Government	No monitoring data reported[3]
	Bavarian Environmental Agency – Environment atlas	Yes
	Schleswig-Holstein – Agency for Agriculture, Environment and Rural Areas	No monitoring data reported[3]
Greece	Greek Ministry of Energy and climate Change – Report on quality of surface and groundwater of the country	No monitoring data reported[3]
Ireland	Irish Environmental Protection Agency – Annual reports on Water Quality in Ireland	No monitoring data reported[3]
Italy	Italian National Institute for Environmental Protection and Research (ISPRA) – Pesticide Portal and national and regional annual reports	Yes
Netherlands	Dutch Institute of Environmental Sciences - Atlas for pesticides in surface water	Yes
	Water Quality Data portal of the Netherlands	Yes
	Ground Water Quality Reports	Yes
	"Research on exposure of residents to pesticides in the Netherlands"	No monitoring data reported[3]
	Groundwater Atlas for Pesticides – pesticide model[2]	No monitoring data reported[3]
Portugal	Portuguese Environment Agency – Report on state of environment	No monitoring data reported[3]
Romania	Romanian National Administration "Apele Române" – Several reports	No monitoring data reported[3]
Slovenia	Slovenia Environment Agency – Several reports and raw data	No monitoring data reported[3]
Spain	Ríos hormonados Amplia presencia de plaguicidas disruptores endocrinos en los ríos españoles"	No monitoring data reported[3]
	Spanish Water framework Junta de Andalucía	No monitoring data reported[3]
	Hydrographic confederation of Ebro	No monitoring data reported[3]
	Hydrographic confederation of Guadalquivir	No monitoring data reported[3]
	Hydrographic confederation of Jucar	No monitoring data reported[3]
	Hydrographic confederation of Segura	No monitoring data reported[3]
	Basque Water agency	No monitoring data reported[3]
Sweden	Swedish University of Agricultural Sciences –Pesticide Database	Yes
	"Long-term Data from the Swedish National Environmental Monitoring Program of Pesticides in Surface Waters"	No monitoring data reported[3]
Switzerland	Swiss National Environment Agency – Several reports	No monitoring data reported[3]
	Regional Environment Agency of Canton Solothurn – Several raw data	No monitoring data reported[3]
United Kingdom	England Environment Agency - Water quality archive	No monitoring data reported[3]
	UK Water Quality Sampling Harmonised Monitoring	No monitoring data reported[3]

	Drinking Water Inspectorate of England and Wales – Chief Inspector Annual Reports and regional overviews	No monitoring data reported[3]
	Pesticide Monitoring Bulletin	No monitoring data reported[3]

[1]:The data from this database was not used since some discrepancies were found in the dataset.
[2]:The data from this database is used only as indicative information since the quality check from authorities is still on-going. The database will be "ready" for use in 2021.
[3]: A preliminary assessment of the EEA Waterbase database suggests it to be a very spatially and temporally limited subset of that collected directly from the regional/national environmental agencies in this study. In order to compare data sources and supplying organisations as an additional cross-check, the underlying reports describing the data contained in the EEA dataset were requested from the EEA. Unfortunately, this was not possible since "Details of the reports are not public available". Given these data collated by the EEA would replicate large parts of the dataset compiled in this study, thereby introducing spatial and temporal bias, they were not included in this assessment.
[4]: A search was conducted in the monitoring dataset but no reference to fluopyram could be found in monitoring databases or reports.

II. RESULTS AND DISCUSSION

Fluopyram was quantified in a small proportion of groundwater (0.49% of the 18855 analyses were above LOQ) and surface water (29.92% of the 9178 analyses were above LOQ) analyses from public monitoring databases (2014 – 2020) for 6 countries (Austria, France, Germany, Italy, The Netherlands and Sweden). Where fluopyram was quantified with residue levels > LOQ, there were rarely findings above the applied regulatory thresholds, resulting in compliance rates > 99.9%. For the sediment compartment (Sweden only) there were no reported residue concentrations above the Tier 1-RAC-Sed (2.6 mg/kg d.w.) within the 12 samples, indicating 100% compliance. A small number of records relating to concentrations in air were also found in France and Sweden where fluopyram was occasionally quantified (16.4% of the 1399 analyses showed residue levels > LOQ (0.002 - 0.0188 ng/m^3)).

Soil

Monitoring data for fluopyram was not found for soil.

Groundwater

A total of 18855 groundwater analyses were investigated (Table 7.5- 4), of which 93 analyses quantified fluopyram (with residue levels ≥ LOQ), including 9 analyses exceeding the regulatory threshold of 0.1 µg/L (0.048% of analyses; 99.95% compliance). These exceedances were found in analyses from Austria and France where they represented 0.08% and 0.06% of all analyses in those countries, respectively. The maximum reported groundwater concentration was 0.25 µg/L (Austria).

Table 7.5- 4: Summary of public monitoring results for fluopyram in groundwater

Country	Data Source/Organisation	Monitoring Period	Analyses	Quantifications[1] (≥ LOQ)	≥ 0.1 µg/L	≥ 0.1 µg/L (%)
Austria	Federal Ministry for Sustainability and Tourism – H$_2$O Water Database	2019 - 2020	3883[2]	5	3	0.08
France	ADES – National Groundwater Quality Portal	2017 - 2020	9601	30	6	0.06
Germany	Sachsen Environmental Agency (IDA)	2018 - 2019	415	4	0	0.0
	Bavarian Environmental Agency – Environment atlas	2017 - 2020	2206	0	0	0.0

Italy	Italian National Institute for Environmental Protection and Research (ISPRA)	2015 - 2016	146	0	0	0.0
Netherlands	Water Quality Data portal of the Netherlands	2014 - 2019	1614	52	0	0.0
	Groundwater Quality Reports	2015 - 2016	876	2	0	0.0
Sweden	Swedish University of Agricultural Sciences – Pesticide Database	2017 - 2018	114	0	0	0.0

[1]: Quantifications represent the number of analyses with residue levels that are neither "zero" nor "< LOQ". The value of the LOQ is dependent on the analytical method and therefore variable (LOQ values ranged from 0.002 to 1.0 µg/L and in some databases the LOQ value was not specified).

[2]: Analyses including 28 analyses of deep groundwater.

Surface water

A total of 9187 analyses of surface water were investigated (excluding Germany - Rheinland-Pfalz reports, Table 7.5- 5), of which 2749 analyses quantified fluopyram (with residue levels ≥ LOQ), including 8 analyses (all from The Netherlands) which exceeded the regulatory acceptable concentration (Tier 1-RAC-SW) of 5.0 µg/L (0.088% of analyses; 99.90% compliance). The maximum reported surface water concentration was 12 µg/L (The Netherlands).

Table 7.5- 5: Summary of public monitoring results for fluopyram in surface water

Country	Data Source/Organisation	Monitoring Period	Analyses	Quantifications[1] (≥ LOQ)	≥ 0.1 µg/L[2]	≥ 0.1 µg/L[2] (%)
France	Naïades – National Surface Water Quality Data Portal	2016 - 2018	1509	37	6	0.06
Germany	Sachsen Environmental Agency (IDA)	2017 - 2020	1079	287	0	0.0
	Rheinland Pfalz Environment Agency- reports	2014	360	-[3]	-[3]	-[3]
Italy	Italian National Institute for Environmental Protection and Research (ISPRA)	2014 - 2016	1023	0	0	0.0
Netherlands	Dutch Institute of Environmental Sciences - Atlas for pesticides in surface water	2015 - 2019	698	-[4]	0	0.0
	Water Quality Data portal of the Netherlands	2015 - 2019	4643	8	0	0.17
Sweden	Swedish University of Agricultural Sciences – Pesticide Database	2017 - 2018	235	48	0	0.0

[1]: Quantifications represent the number of analyses with residue levels that are neither "zero" nor "< LOQ". The value of the LOQ is dependent on the analytical method and therefore variable (LOQ values ranged from 0.001 to 0.1 µg/L and in some databases the LOQ value was not specified.
[2]: RAC value for fluopyram: 5.0 µg/L
[3]: In the Rheinland Pfalz Environment Agency- reports, surface water data were only compared to 0.1 µg/L, therefore no complete statistics were possible.
[4]: In the database from the Dutch Institute of Environmental Sciences - Atlas for pesticides in surface water, surface water data were only presented as "average per year", "maximum per year" and "90th percentile per year", however the maximum value reported (0.906 µg/L) was always below 5.0 µg/L.

Drinking water
Monitoring data for fluopyram was not found for drinking water.

Sediment
Sweden reported 12 analyses of sediments (Table 7.5- 6) of which 2 analyses quantified fluopyram (with residue levels ≥ LOQ). No analysis exceeded the regulatory acceptable concentration (Tier 1-RAC-Sed) of 2.6 mg/kg d.w.. The maximum reported sediment concentration was 1.5 µg/kg d.w..

Table 7.5- 6: Summary of public monitoring results for fluopyram in sediment

Country	Data Source/Organisation	Monitoring Period	Analyses	Quantifications[1] (≥ LOQ)	≥ RAC[2]	≥ RAC[2] (%)
Sweden	Swedish University of Agricultural Sciences – Pesticide Database	2017 - 2018	12	2	0	0.0

[1]: Quantifications represent the number of analyses with residue levels that are neither "zero" nor "< LOQ". The value of the LOQ is dependent on the analytical method and therefore variable (LOQ values ranged from 0.3 to 1.0 µg/kg d.w.).
[2]: RAC value for FLU: 2.6 mg/kg d.w.

Air

A total of 1399 analyses of air were investigated (Table 7.5- 7), of which 230 analyses quantified fluopyram (with residue levels ≥ LOQ, LOQ ranging from 0.002- 0.188 ng/m^3). The median and maximum reported residue concentrations were 0.163 ng/m^3 and 4.459 ng/m^3, respectively.

Table 7.5- 7: Summary of public monitoring results for fluopyram in air

Country	Data Source/Organisation	Monitoring Period	Analyses	Quantifications[1] (≥ LOQ)	Quantifications[1] (≥ LOQ, %)
France	CNEP - National pesticide monitoring plan in air	2018 - 2019	1348	206	15.3
Sweden	Swedish University of Agricultural Sciences – Pesticide Database	2017 - 2018	51	24	47.1

[1]: Quantifications represent the number of analyses with residue levels that are neither "zero" nor "< LOQ". The value of the LOQ is dependent on the analytical method and therefore variable (LOQ values ranged from 0 to 0.188 ng/m^3).

III. CONCLUSION

The groundwater monitoring data search indicated that fluopyram concentrations above the regulatory trigger of 0.1 µg/L were rare (9 analyses, 0.048% of 18855 analyses) with a maximum concentration of 0.25 µg/L.

The surface water monitoring data search indicated that fluopyram concentrations above the Tier 1-RAC-SW (5.0 µg/L) were rare (8 analyses, 0.098% of 9187 analyses), with a maximum concentration of 12 µg/L.

The sediment monitoring data search indicated no residue concentrations above Tier 1-RAC-Sed (2.6 mg/kg) for the 12 samples, with a maximum concentration of 1.5 µg/kg d.w..

The air monitoring data search indicated fluopyram concentrations above the LOQ (0.002 - 0.0188 ng/m^3) were found (230 analyses, 16.4% of 1399 analyses). The reported median and maximum concentrations reported are 0.163 ng/m^3 and 4.459 ng/m^3, respectively.

For all compartments, it cannot be discounted that some of the detections identified are erroneous given they arise from non-GLP monitoring networks and programmes of unknown quality.

For drinking water and soil, fluopyram monitoring data was not found.

Overall, it can be concluded from the assessment of readily available public monitoring datasets that fluopyram does not pose a concern for the investigated environmental compartments where data were available.

3. Assessment and conclusion

Assessment and conclusion by applicant:

Assessment:

This is a comprehensive overview of publicly available fluopyram monitoring data across the EU, covering an extended period of time (from 1995 to November 2020). However, it cannot be discounted that some of the detections identified are erroneous given they arise from non-GLP monitoring networks and programmes of unknown quality; and that there are currently no guidelines for the conduct of monitoring studies.

Conclusion:

Fluopyram concentrations above the regulatory trigger for groundwater and surface water were rare, indicating very high rates of compliance. For the sediment compartment, no residue concentrations above Tier 1-RAC-Sed were found, indicating full compliance. Air monitoring concentrations above the LOQ (0.002 - 0.0188 ng/m^3) were also found. Overall, it can be concluded from the assessment of readily available public monitoring datasets that fluopyram does not pose a concern for the investigated environmental compartments where data was available.
This review study is considered valid and reliable.

Assessment and conclusion by RMS:

Outcome and conclusion of the study: RMS should indicate if they agree to the results and conclusions of the APPL.

1. Information on the published literature article

Data Point:	KCA 7.5/02
Report Author:	Sjerps, R. M. A.; Kooij, P. J. F.; Van Loon, A.; Van Wezel, A. P.
Report Year:	2019
Report Title:	Occurrence of pesticides in dutch drinking water sources
Report No:	M-755508-01-1
Document No:	M-755508-01-1
Guideline(s) followed in study:	not applicable
Deviations from current test guideline:	Current Guideline; not applicable
Previous evaluation:	No, not previously submitted
GLP/Officially recognised testing facilities:	No, not conducted under GLP/Officially recognised testing facilities
Acceptability/Reliability:	Yes

2. Full summary of KCA 7.5/02

Executive Summary

The occurrence of pesticides in groundwater and surface water sources used for drinking water production in The Netherlands was determined using both routine monitoring data from Dutch drinking water companies and by studying the presence of newly authorised pesticides (including fluopyram) in drinking water sources. The routine monitoring data were collected from 2010 - 2014 in The Netherlands, covering 408 pesticides and 52 metabolites (this monitoring did not include fluopyram).

A LC-MS/MS method was developed for 24 recently authorised pesticides, selected based on their mobility and persistence, and applied in a Dutch/Belgian ground- and surface water monitoring campaign. Fifteen of these pesticides were detected (≥ LOD), including fluopyram, at concentrations above the water quality standard from the Water Framework Directive. Fluopyram was detected (≥ LOD of 0.002 µg/L) in a total of 41 out of the 150 samples, with 38 detections in surface water and 3 in dune filtrates. In 6 of the 38 fluopyram surface water detections the concentration was > 0.1 µg/L (exact concentrations not quoted). However, these represent concentrations in raw surface water while the threshold of 0.1 µg/L applies to treated drinking water at the tap of consumers. Following the drinking water production process, after flocculation and dune filtration, concentrations were below 0.05 µg/L. There were no detections in riverbank filtrates and groundwater samples.

I. MATERIALS AND METHODS

Material

The presence of fluopyram in groundwater and surface water sources was determined.

Sampling method

Monitoring campaign for recently (after 2005 to 2015) authorised pesticides

Water samples were taken at 127 locations in The Netherlands and Flanders (Belgium). The samples included 23 surface waters used for drinking water production, 4 dune filtrates, 10 riverbank filtrates, and 90 groundwaters used as drinking water source. The surface water samples included 5 large river systems such as the Rhine and Meuse, 10 small river systems, 4 reservoir systems, 2 infiltration ponds and 2 seepage waters. The samples from dune- and riverbank filtrates and groundwater originate from mixed raw waters, pumping wells and observation wells. All locations were sampled in May and June 2016. Due to potential seasonal differences surface waters were sampled a second time at the end of August 2016. The developed analytical method (as described below) for the recently authorised pesticides, was applied in these samples.

Analytical method

Monitoring campaign for recently (after 2005 to 2015) authorised pesticides

From 2005 to 2015, 66 active substances were newly authorised on the Dutch market. Eight of these were not further evaluated, as they were either only applied in closed systems without possible emissions to water or had low inherent toxicity. Twenty-eight of the evaluated newly authorised pesticides were classified as relevant as they are both persistent (DT_{50} > 7d) and mobile (log K_{ow} < 4), 26 pesticides are either mobile or persistent and therefore classified as potentially relevant. These 54 relevant and potentially relevant pesticides were candidates for implementation in a measurement method.

For several of the selected recently authorised pesticides, no routine analytical method used by drinking water laboratories was available. For 24 compounds (including fluopyram), a LC-MS/MS method was developed and validated.

For sample treatment, 50 µL of an internal standard solution at a concentration of 0.50 mg/L was added to 45 mL of the water sample and homogenised. The samples were filtered through a 0.20 µm filter and transferred into an auto sampler vial. A UHPLC system equipped with a Hypersil GOLD C18 column was used for the chromatographic separation. Mobile phase A was composed of 0.05% (v/v) acetic acid in water and mobile phase B was composed of 0.05% (v/v) acetic acid in acetonitrile. The gradient conditions were as follows: initial time 5% B; 1.0 min 5% B; 15 min 100% B; 17 min 100% B; 17.5 min 5% B and re-equilibration at 5% B till 20 min. The column temperature was kept at 25°C and the flow rate was 300 µl/min. The auto sampler temperature was kept at 15°C, and 100 µL was injected into the LC-MS/MS system.

Each pesticide was identified and quantified using two transitions in selected reaction monitoring mode. Calibration standards in drinking water were used to obtain external calibration curves for the pesticides ranging from 0.01 µg/L to 10.0 µg/L. All pesticides, except flubendiamide, were detected in positive

heated electrospray ionization mode (HESI+). The capillary and vaporizer temperature were 275°C and 350°C, respectively. The pressure for the sheath gas was 30 psi and for the ion sweep 5 psi. The auxiliary gas flow was set to 10 L/min. The individual pesticide standards in acetonitrile were infused in the mass spectrometer to determine the S-lens voltage and the collision energy needed to obtain products ions from the precursor ion, and to determine retention time and peak shape. For validation, the pesticides were spiked at concentrations of 0.01, 0.10 and 1.0 µg/L to drinking- and surface water to determine relative standard deviation and recovery and the limit of quantification.

LOD: The limit of detection for fluopyram was 0.001 µg/L (drinking water) and 0.002 µg/L (surface water).

Recovery rates: for fluopyram, the recoveries in drinking- and surface water at a concentration of 1.0 µg/L were 99.9 and 99.3%, respectively.

Repeatability: for fluopyram, was below 5% in both compartments.

Reporting limit: 0.01 µg/L in both drinking water and surface water.

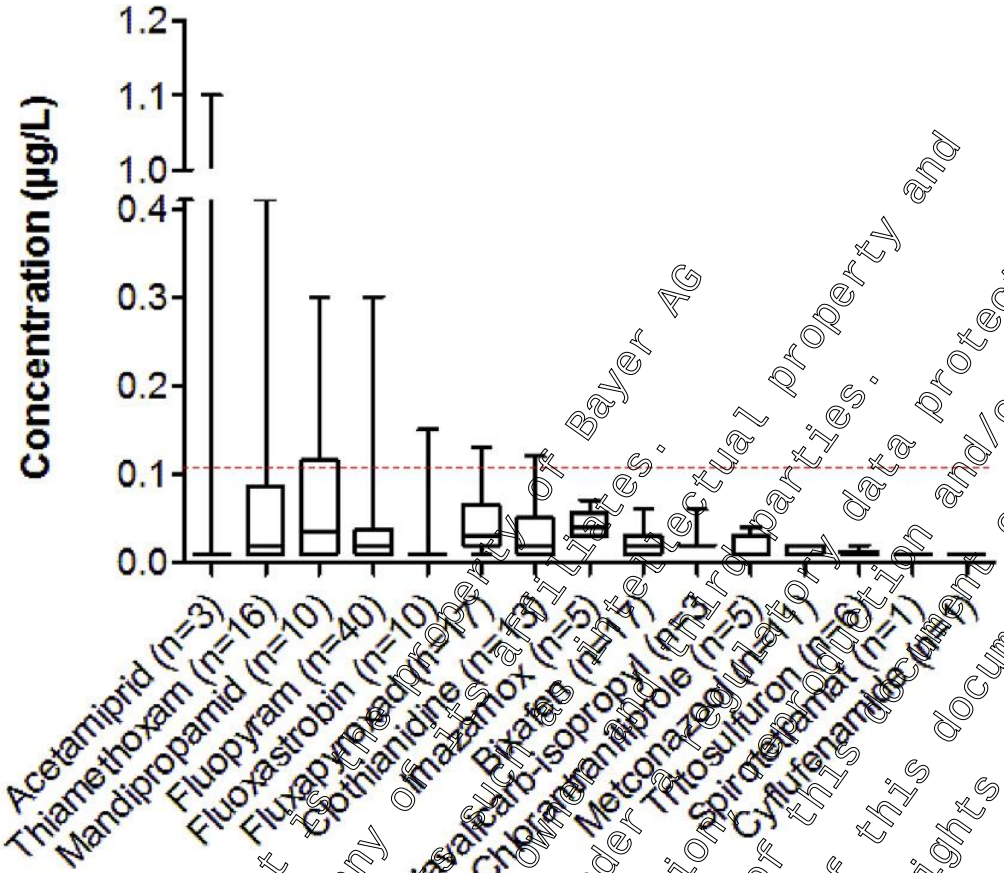
Linearity: not reported.

Evaluating routine monitoring data 2010 - 2014
All ten water companies in The Netherlands provided their routine monitoring data over the years 2010 - 2014, the composite dataset includes 408 pesticides and 52 metabolites in 29,766 individual records (not including fluopyram).

II. RESULTS AND DISCUSSION

Monitoring campaign for relevant recently authorised pesticides
15 out of the 24 recently authorised pesticides included in the novel LC-MS/MS method were detected in the monitored drinking water relevant surface waters, including seven pesticides at concentrations above the water quality standard (Figure 7.5- 1; Table 7.5- 8). More than half of the measured pesticides were detected, independent of their mobility and persistent properties. The pesticides that were not detected often had low sales data.

Fluopyram was detected (≥ LOD of 0.002 µg/L) in a total of 41 out of the 150 samples, with 38 detections in surface water and 3 in dune filtrates. Six of the surface water samples had fluopyram concentrations > 0.1 µg/L (exact concentrations not quoted). However, these represent concentrations in raw surface water while the threshold of 0.1 µg/L applies to treated drinking water at the tap of consumers. Following the drinking water production process, after flocculation and dune filtration, concentrations were below 0.05 µg/L. There were no detections in riverbank filtrates and groundwater samples.



The box represents the 25th, 50th and 75th percentiles, the edges the minimum and maximum values. The number between brackets after the pesticide names on the x-axis represents the number of detections above the reporting limit summarised by the statistics. The dotted line represents the water quality standard of 0.1 µg/L for individual pesticides in drinking and ground water according to the Water Framework Directive.

Figure 7.5- 1: Concentration range of 15 recently authorised pesticides detected in surface waters (n = 19) and ground waters (n = 2) [note: all values < LOD have been excluded]

Table 7.5- 8: Fluopyram occurrences in drinking-water related surface waters (SW), dune filtrates (DF), riverbank filtrates (RBF) and groundwater

	Number of samples with detected pesticides					Number of samples with pesticides > 0.1 µg/L				
Pesticide	**Total (n=150)**	**SW (n=46)[a]**	**DF (n=4)**	**RBF (n=10)**	**GW (n=90)**	**Total (n=150)**	**SW (n=46)**	**DF (n=4)**	**RBF (n=10)**	**GW (n=90)**
Fluopyram	41	38	3	0	0	6	6	0	0	0

SW: Surface water; DF: Dune filtrates; RBF: Riverbank filtrates; GW: Ground water

All locations were sampled in May and June 2016. Due to potential seasonal differences surface waters were sampled a second time at the end of August 2016 i.e. surface water samples represent only 23 sites and fluopyram was not necessarily found at all 23 locations.

Evaluating existing routine monitoring data 2010 - 2014 for pesticides

In 67% of the 226 ground- and surface water sources for drinking water production, pesticides that have been on the market for a longer time and/or their metabolites were detected. No results relating to fluopyram are reported in this section.

III. CONCLUSION

The occurrence of pesticides in ground- and surface water used as drinking water sources in The Netherlands was assessed in a total of 150 samples collected in 2016. Fluopyram occurred in a total of 41 out of the 150 samples (≥ LOD of 0.002 µg/L), with 38 detections in surface water and 3 in dune filtrates. In 6 of the 38 surface water detections the concentration was > 0.1 µg/L (exact concentrations not quoted). However, these represent concentrations in raw surface water while the threshold of 0.1 µg/L applies to treated drinking water at the tap of consumers. Following the drinking water production process, after flocculation and dune filtration, concentrations were below 0.05 µg/L. There were no detections in riverbank filtrates and groundwater samples.

3. Assessment and conclusion

Assessment and conclusion by applicant:

Assessment:

This article reports monitoring results for fluopyram in groundwater and surface water used for drinking water extraction in The Netherlands, sampled in 2016. However, this article has major restrictions; for example, no details on description of sampling sites or sampling methodology reported, nor storage conditions, and results cannot be related to definite times and locations. In addition, the work wasn't carried out according to GLP, and there are currently no guidelines for the conduct of monitoring studies.

Conclusion:

Fluopyram concentrations were > 0.1 µg/L in 6 of 38 surface water samples where it was detected. However, following the drinking water production process, after flocculation and dune filtration, concentrations were below 0.05 µg/L. There were no detections in riverbank filtrates and groundwater samples.

The information of this publication is regarded as supportive information.

Assessment and conclusion by RMS:

Outcome and conclusion of the study. RMS should indicate if they agree to the results and conclusions of the APPL.

1. Information on the published literature article

Data Point:	KCA 7.5/03
Report Author:	Pinasseau, L.; Wiest, L.; Volatier, L.; Fones, G. R.; Mills, G. A.; Mermillod-Blondin, F.; Vulliet, E.
Report Year:	2019
Report Title:	Calibration and field application of an innovative passive sampler for monitoring groundwater quality
Report No:	M-681600-01-1
Document No:	M-681600-01-1
Guideline(s) followed in study:	--
Deviations from current test guideline:	Not applicable
Previous evaluation:	No, not previously submitted
GLP/Officially recognised testing facilities:	not applicable
Acceptability/Reliability:	Yes

2. Full summary of of KCA 7.5/03

Executive Summary

This study describes the development of a novel Empore™ disk-based passive sampler specially adapted to groundwater monitoring. The sampler was calibrated in the laboratory using conditions that corresponded to groundwater. The retention and elution performance for sixteen pesticides (including fluopyram) and pharmaceuticals on the Empore™ disk was evaluated.

In the field phase of the study, passive samplers were deployed in twelve characterised groundwater wells in the eastern metropolitan area of Lyon (France) between 26th October and 5th November 2018 (ten days). The detection frequency for fluopyram was 83% (based on a chromatography system detection limit), and 67% of calculated time-weighted average concentrations (C_W) were greater than the Method Quantitation Limit (i.e. when the signal to noise ratio was greater than 10). In summary, fluopyram was frequently detected, but at very low concentrations. C_W ranged from 0.5 to 24 ng/L, with a median concentration of 8.5 ng/L.

I. MATERIAL AND METHODS

Materials

Initially, a laboratory calibration experiment was performed using four substances (atrazine, hexazinone, metolachlor and sulfamethoxazole, taken to be representative of the 16 target substances) to determine sampler uptake rates. A field study was then undertaken in twelve groundwater wells, presenting contrasting physico-chemical conditions, which allowed for the estimation of the concentrations of 16 pesticides and pharmaceuticals, including fluopyram.

Analytical methods

SDB-XC Empore™ disks (ED) were cleaned and conditioned. Nine EDs were placed per rig. After deployment, EDs were extracted individually on a tube rotator using 10 mL of acetone/MeOH (50/50; v/v). Triplicate extracts from three EDs were pooled and then evaporated to dryness using nitrogen and stored at -20°C until analysis. Samples were reconstituted in 500 µL of water/MeOH (95/5; *v/v*) and diluted 30 times prior to instrumental analysis.

All samples were analysed using an HPLC system equipped with a binary pump coupled to a triple quadrupole mass spectrometer with an electrospray ion (ESI) source working in positive ionization mode. Chromatographic separation was carried out using a Poroshell 120 EC-C18 column maintained at 30°C. The mobile phases consisted of: (A) water and (B) MeOH with 0.1% formic acid in both phases. The flow rate was 0.5 mL/min with an elution gradient. MS detection was carried out in the multiple reaction monitoring (MRM) mode. Two MRM transitions (*m/z*) were monitored (quantification and confirmation) for fluopyram 397.0 → 208 and 397.0 → 145.0, respectively. No pharmaceuticals or pesticides were detected in solvent and procedural blanks.

IDL: Instrument detection limit (IDL) for fluopyram was 1.8 ng/L.

IQL: Instrument quantification limit (IQD) for fluopyram was 6.1 ng/L.

MQL: Method quantification limit (MQL) was established using metolachlor as a surrogate for fluopyram, with a concentration of 0.17 ng/L. (However, C_W values for fluopyram were apparently calculated when the signal to noise ratio was greater than 10 – it is not clear what MQL this corresponded to).

HPLC-MS/MS RSD: Relative standard deviation (RSD, n=3) was 13%.

Analytical recoveries from the EDs were performed for all 16 targeted compounds.

The accumulation of analytes in the ED follows a first-order kinetic model between the start of exposure and the half-time to equilibrium. During the calibration experiment, sampling rate, R_S, was determined from the slope of the regression between the mass of analyte accumulated against the time of exposure. Once R_S is known, C_W, which corresponds to the time-weighted average (TWA) concentration during a field deployment, can be calculated. R_S values were determined only for the four representative substances.

Field trials were undertaken in the eastern metropolitan area of Lyon (France) using twelve groundwater wells located in sites monitored in the framework of the field observatory in urban hydrology. The selected wells had water chemistry which did not differ from that of groundwater in the aquifer. A total of twelve ED rigs were used (one rig per well) and deployed for ten days between 26th of October - 5th of November, 2018. Water conductance and temperature, dissolved oxygen and pH were measured during the deployment period.

II. RESULTS AND DISCUSSION

Uptake of compounds on a SDB-XC disk

The totality of each of the 16 analytes was retained on the ED for which the retention was about 98% with one exception (sulfamethoxazole). The overall recovery for fluopyram was 51.2% (Table 7.5- 9). No trend with polarity (i.e. log D_{ow}) was observed, except for the most hydrophilic and hydrophobic compounds that exhibited lower recoveries, which included fluopyram.

Table 7.5- 9: Log D_{ow} and mean percentage recovery of the fluopyram from the SDB-XC disk at three concentrations (10, 100 and 500 ng/L, n=3)

Log D_{ow}	Mean recoveries (%)			Overall mean recoveries (%)
pH = 7.4[1]	10 ng/L	100 ng/L	500 ng/L	
4.23	42.8 ± 2.2	46.8 ± 1.6	54.1 ± 2.8	51.2 ± 7.4

[1]As calculated on chemicalize

To determine TWA concentrations (C_W), the extrapolation of the metolachlor R_S values to fluopyram was made on the basis of retention times, log D_{ow}, and chemical structures. It was assumed that compounds with similar physico-chemical properties, and in particular with similar behaviour on a reversed-phase chromatographic columns (i.e. retention time) would exhibit similar uptake behaviour on the ED during the field trial. Consequently, R_S of metolachlor was applied to fluopyram.

Semi-quantitative determination of emerging pollutants in groundwater
To minimise matrix effects, samples were diluted 30 times before analysis. In addition, six internal standards were also added to correct for any matrix effects and to help increase the robustness of the method. After such a dilution, matrix suppressions in the ED blank and GW extracts were all below 30% for the six internal standards.

After retrieval of the twelve deployment rigs (six sites, with two GW sampling points per site) and analysis of the groundwater extracts, C_W were determined and average and maximum values are given in Table 7.5- 10.

The detection frequency for fluopyram was 83%. Frequency of detection of fluopyram with C_W >MQL (taken to be when the signal to noise ratio was greater than 10) was 67%. The authors state that, therefore, fluopyram was frequently detected, but at very low concentrations. C_W ranged from 0.5 to 24 ng/L, with a median concentration of 8.5 ng/L.

Table 7.5- 10: Detection frequency (%), median, minimum and maximum concentrations (ng/L) of fluopyram in groundwater from 12 wells

Detection frequency (%)		Median Cw (ng/L)	Minimum Cw (ng/L)	Maximum Cw (ng/L)	MQL (ng/L)
Global	>MQL				
83	67	8.5	0.5	24	[1]

[1] Cw values calculated when signal - to - noise ratio >10 based on an MQL of 0.17 for metolachlor

III. CONCLUSION

This work used a novel ED-based passive sampler. The detection frequency for fluopyram was 83%. Frequency of detection of fluopyram with C_W >MQL was 67%. Hence, fluopyram was frequently detected, but at very low concentrations. C_W ranged from 0.5 to 24 ng/L, with a median concentration of 8.5 ng/L. These concentrations were calculated based on previously determined sampling rates and represent time weighted average concentrations over 10 days.

3. Assessment and conclusion

Assessment and conclusion by applicant:
Assessment:
This article reports a novel ED-based passive sampler for the groundwater monitoring of 16 semi-polar and polar pollutants in 12 characterised groundwater wells near Lyon, France. Details on the analytical work are well reported. However, this article has major restrictions (e.g. key specific system behaviour characteristics for fluopyram were not determined, no details on description of sampling sites). In addition, the work wasn't carried out according to GLP, and there are currently no guidelines for the conduct of monitoring studies, nor for the interpretation of passive sampler results.

Conclusion:
During the course of the calibration and field application of an innovative passive sampler for monitoring groundwater quality, C_W estimates for fluopyram (in 12 urban groundwater wells sampled in Lyon, France) ranged from 0.5 to 24 ng/L, with a median concentration of 8.5 ng/L.
The information of this publication is regarded as supportive information.

Assessment and conclusion by RMS: Outcome and conclusion of the study: RMS should indicate if they agree to the results and conclusions of the APPL.

1. Information on the published literature article

Data Point:	KCA 7.5/04
Report Author:	Acosta-Dacal, A.; Rial-Berriel, C.; Diaz-Diaz, R.; Bernal-Suarez, M. D. M.; Luzardo, O. P.
Report Year:	2021
Report Title:	Optimization and validation of a quechers-based method for the simultaneous environmental monitoring of 218 pesticide residues in clay loam soil
Report No:	M-760205-01-1
Document No:	M-760205-01-1
Guideline(s) followed in study:	not applicable
Deviations from current test guideline:	Current Guideline: not applicable
Previous evaluation:	No, not previously submitted
GLP/Officially recognised testing facilities:	No, not conducted under GLP/Officially recognised testing facilities
Acceptability/Reliability:	Yes

2. Full summary of KCA 7.5/04

Executive Summary

A modified QuEChERS method was optimised, validated and verified for the extraction of 218 pesticide residues in agricultural soil samples. The 218 analytes are extracted using a single step, without clean-up, with matrix matched calibration, and two complementary techniques: liquid and gas chromatography tandem triple quad mass spectrometry (LC-MS/MS and GC-MS/MS). The procedures were optimised to improve the overall performance for the target compounds and the soil matrix. The method was fully validated on a representative agricultural soil sample of the Canary Islands (clay loam soil) in terms of linearity, accuracy and precision. The limit of quantification (LOQ) for fluopyram was 0.5 ng/g.

The validated method was applied to a series of actual samples of agricultural soil (n = 18). The samples came from 3 farm vineyards, 3 mixed vegetable farms, 3 fruit tree farms, 3 banana farms, 3 farms with crop in transition to organic production, 1 avocado farm, and 2 abandoned farmlands. Fluopyram was not detected in any of the 18 soil samples (all with the characteristics of the soil used for the method validation) taken from farmlands or in the 2 soil samples from the investigation on a wildlife poisoning case.

I. MATERIALS AND METHODS

Material

The aim of this work was to optimise and validate a modified QuEChERS-based extraction method for the quantitative determination of multiple pesticide residues (including fluopyram) in clay loam soils by means of 2 complementary analyses by LC-MS/MS and GC–MS/MS.

Sample method
For the method development, soil samples classified as clay loam from two farms dedicated to organic production were chosen. In order to verify the applicability of the method after the validation process, the method was applied to a series of 18 clay loam agricultural soil samples from the Canary Islands, Spain. The samples came from 3 farm vineyards, 3 mixed vegetable farms, 3 fruit tree farms, 3 banana farms, 3 farms with crop in transition to organic production, 1 avocado farm, and 2 abandoned farmlands. In addition, two soil samples from the investigation on a wildlife poisoning case were also analysed. In each sampling plot, a composite sample was prepared from at least four subsamples collected at depths between 20 and 30 cm. The soil was then homogenized, air-dried at room temperature and sieved (2 mm mesh).

For the classification of soil samples, electrical conductivity, pH, moisture, particle distribution and oxidizable organic carbon (to calculate the organic matter content) were determined.

Analytical methods
10 ± 0.05 g of dried/sieved soil plus 10 mL of ACN-2.5% Formic acid (FA) were added into a 50 mL centrifuge tube and shaken vigorously. $MgSO_4$ and CH_3COONa were added, shaken vigorously for 1 min and sonicated for 15 min. Samples were then placed in a rotatory shaker for 25 min and then centrifuged for 10 min at 4200 rpm (3175.16 × g). An aliquot of supernatant extract was filtered and directly analysed by GC–MS/MS or diluted with H_2O (1:1, v/v) and analysed by LC-MS/MS.

The samples for recovery experiments and quality controls (QCs) were spiked to achieve the desired concentration and were left to stand for 1 h prior to extraction. 100 µL of procedural internal standards (P-IS) mix solution was added to all samples, including the blanks.

LC-MS/MS analysis of 167 compounds (including fluopyram) was conducted using a LC system coupled to a mass spectrometer using a Poroshell 120 EC-C18 column equipped with a guard pre-filter and pre-column at 50°C. The mobile phases consisted of 2 mM ammonium acetate 0.1% FA in ultrapure water (A) and 2 mM 0.1% FA ammonium acetate in MeOH (B) and used a binary gradient. MS/MS analyses were performed using a Jet Stream Electrospray Ionization Source in both positive and negative ionization mode, with dynamic multiple reaction monitoring. The optimisation of MS/MS conditions for each compound, including the search for the precursor and product ions and the collision energy, was performed. Most of the analytes were determined in positive mode (including fluopyram). Two MRM transitions (*m/z*) were monitored for fluopyram 397.0 → 173.0 (quantification) and 397.0 → 145.0 (confirmation).

The optimised QuEChERS-based method was validated in terms of linearity, accuracy and precision. In order to assess possible interferences in the chromatographic response, a matrix effect study was performed. The calibration curves, either in the matrix extract or in the solvent (both diluted with water (1:1, v/v) for LC-MS/MS) were prepared in the range of 6.25 – 50 ng/mL in triplicate. The matrix effect (ME) was evaluated comparing the response obtained for each analyte in the soil extract with that given in the solvent at the same concentration in both equipment, extracting the blank to the soil matrix signal. No significant matrix effects were considered when ME was between 80 and 120%. The main trend observed for ME in LC-MS/MS was towards signal suppression although this was not significant for most of them.

To improve the accuracy of the quantification, as well as to simplify the procedure, it was decided to use matrix matched calibration.

Linearity: Obtained from a triplicate range of 9 levels (from 0.39 to 100 ng/g). The response was satisfactory for all the compounds, with a deviation of back-calculated concentration from true concentration < 20%, for LC-MS/MS, either in matrix extract or in matrix-extract diluted with water (1:1, v/v), respectively. R^2 values were above 0.99 for all analytes.

Accuracy and the precision: Were tested with recovery experiments at 7 concentration levels in quintuplicate: 0.5, 1.0, 2.5, 5, 10, 20 and 50 ng/g. The method presented satisfactory accuracy (recoveries in the range 70 – 120%) and precision (RSD < 20%) for 198 analytes (90.8% of the compounds) for all the fortification levels.

LOQ: The limit of quantification (LOQ) for fluopyram was 0.5 ng/g.

LOD: Limit of Detection (LOD; values not reported) was determined as the lowest point of the calibration curve having a signal to-noise ratio above 3 (Peak-to-Peak algorithm) and having acceptable accuracy (80–120%).

The GC-MS/MS analysis was not relevant for fluopyram

II. RESULTS AND DISCUSSION

Application of the method to real samples
Fluopyram was not detected in any of the 18 soil samples (all with the characteristics of the soil used for the method validation) taken from farmlands or in the 2 soil samples from the investigation on a wildlife poisoning case.

III. CONCLUSION

Fluopyram was not detected in any of the 18 agricultural clay loam soil samples from the Canary Islands, Spain. The LOQ for fluopyram was 0.5 ng/g.

3. Assessment and conclusion

Assessment and conclusion by applicant:
Assessment:
This article reports optimisation and validation of a QuEChERS based method for the simultaneous monitoring of 218 pesticide residues (including fluopyram) in clay loam soil from the Canary Islands, Spain. Details on the analytical work and sampling methodology including recovery and QC samples are well reported. However, this article has major restrictions (e.g. no details on description of sampling sites, nor storage conditions, and results cannot be related to definite times and locations). In addition, the work wasn't carried out according to GLP, and there are currently no guidelines for the conduct of monitoring studies.

Conclusion:
Fluopyram was not detected in any of the 18 agricultural clay loam soil samples from the Canary Islands, Spain. The LOQ for fluopyram was 0.5 ng/g.
The information of this publication is regarded as supportive information.

Assessment and conclusion by RMS:
Outcome and conclusion of the study: RMS should indicate if they agree to the results and conclusions of the APPL

Monitoring data for TFA from databases in the EU

For the previous evaluation of fluopyram, no applicant studies or articles reporting trifluoroacetate (TFA) monitoring activities were submitted.

TFA is a terminal degradation product of fluopyram in soil; it is the dissociated anion of trifluoroacetic acid. Trifluoracetic acid has a dissociation constant (pKa-value) of 1.3, and hence, is deprotonated under environmental and physiological conditions and due to the high buffering capacities of environmental and physiological matrices shows no acidic properties. This clearly indicates that trifluoroacetate, being entirely dissociated when formed from fluopyram in soil, would display very limited volatility and hence would not transfer to the atmosphere. There are, however, many other environmentally relevant sources of both TFA and trifluoroacetic acid. Analytical detection methodology doesn't discriminate between TFA and trifluoroacetic acid, but the differences between these two species with respect to exposure routes are important.

TFA is likely to be naturally produced in the deep oceans. For example, it has been demonstrated that TFA concentrations are uniform to at least 4000 m in the Southern Ocean and to 2000 m in the mid-Atlantic, indicating that TFA in the oceans is still largely from pre-industrial times. It is thought that the source may be deep ocean volcanic vents. The ocean TFA can be transferred to land via sea-salt spray.

However, most of the TFA detected in the non-marine environment is believed to be anthropogenic in nature. TFA can be generated from many organic molecules that contain the trifluoroethyl moiety (e.g. refrigerant gases, pharmaceuticals, pesticides and polymers), and trifluoracetic acid is also used in their manufacture on an industrial scale (emissions of trifluoroacetic acid can take place from the manufacturing plants). Although trifluoroacetic acid can be emitted directly into the environment, the major source of trifluoroacetic acid in the atmosphere is volatile substances containing the trifluoroethyl moiety that photolytically degrade in the atmosphere to generate trifluoroacetic acid. These include hydrochlorofluorocarbons (HCFCs), hydrofluorocarbons (HFCs) and hydrofluoroolefins (HCFOs), which are produced in very large amounts and used as refrigerants, propellants and solvents. Trifluoroacetic acid produced in the atmosphere is believed to be relatively quickly removed and deposited to land by wet deposition (as fog, rain and snow) or by dry deposition. This process occurs throughout the world (even in relatively remote places), such that TFA is to be found in most water samples analysed (including in rainwater); this atmospheric generation of trifluoroacetic acid is the major source of TFA generally detected in environmental compartments, and this is reflected in the literature articles presented and summarised here.

Presence and sources of TFA in environmental compartments

The two applicant studies (KCA 7.5/05, M-760366-01-1 and KCA 7.5/06, M-761706-02-1) demonstrated that TFA was detected in different water sources across Germany and in a small sample size set of analyses from Austria. No concentrations breached relevant regulatory threshold values. The maximum concentration in groundwater samples was 4.4 µg/L, and 17 µg/L in surface water.

The determination of TFA in ocean waters was conducted (KCA 7.5/10, M-455778-01-1) in order to estimate its global abundance and to assess whether today's levels are mainly of anthropogenic origin or whether biological and/or geological sources should also be considered. Ocean water samples were collected in the Southern Ocean in 1998 and 1999, and in the Mid-Atlantic Ocean in 1998. TFA levels of around 200 ng/L were determined in all water samples from the Mid-Atlantic Ocean (down to 4000 m) and the Southern Ocean (down to 2000 m), independent of depth. Investigations included the concentrations of chlorofluorocarbons (CFCs), the detected gradient with depth of which strongly implied significant pre-industrial TFA sources and slow in-situ removal processes on decadal or longer time scales. The present evidence of homogeneous TFA levels in the Atlantic Ocean water samples taken together with previous analyses from other locations of the Atlantic and one of the Pacific, suggests that oceanic TFA levels worldwide could be at about 200 ng/L. Hence, it can be estimated that the world's oceans contain about 268 million tonnes of TFA. Similar concentrations were also reported

in another publication (KCA 7.5/18, M-585141-01-1). Thus, TFA is likely to be a natural ionic solute in ocean water, suggesting that continuous low-level releases from geological or biological sources over a long period of time may have resulted in present day oceanic levels.

Samples of snow, ice and rain were collected in several remote areas (East Antarctica, northern Canada, northern Sweden, western Ireland and central Poland) to investigate the presence of TFA (KCA 7.5/08, M-604966-01-1). Samples of firn (ice that is at an intermediate stage between snow and glacial ice) were collected from East Antarctica, derived from 40 cm lengths of a 20 m core that was drilled during 1996 - 1997. The deepest part of the firn core was estimated to represent snow that accumulated about 190 years ago. TFA was present in all of the firn samples from Antarctica; concentrations ranged from 6 to 56 ng/L, with an average of 25 ng/L. There was no obvious relationship between concentration and depth in the firn core. Therefore, pre-industrial presence of significant background concentrations of TFA was confirmed. The snow samples collected in the Northern and Southern Hemispheres varied markedly with respect to TFA levels. The mean concentration of TFA in snow from Sweden and Canada was 10 ng/L and the corresponding value for Antarctica was 40 ng/L. In addition, TFA was detected at a concentration of 5 ng/L in glacier ice from a semipolar glacier in northern Sweden. The concentrations of TFA in individual rainfalls varied markedly; at Mace Head, on the west coast of Ireland, TFA levels ranged from 2 to 92 ng/L, while rain collected in the city of Gdansk, Poland, contained up to 1100 ng/L of TFA.

An investigation of the presence of TFA in precipitation (rain and snow) across Germany was reported in M-754282-01-1 (KCA 7.5/13). Precipitation is considered to be the most important diffuse source of TFA to the nonmarine environment. This study provided a comprehensive overview of the occurrence of TFA in precipitation by a systematic and nation-wide field monitoring campaign. In total, 1187 precipitation samples, which were collected over the course of 12 consecutive months at eight locations across Germany, were analysed. The median, the estimated average, and the precipitation-weighted average TFA concentration of all analysed wet deposition samples were 0.210, 0.703, and 0.335 µg/L, respectively. A maximum concentration of 38 µg/L was determined. For Germany, an annual wet deposition flux of 190 µg/m^2 or approximately 68 t was calculated for the sampling period from February 2018 to January 2019, but in a more typical year the annual wet deposition flux of TFA in Germany is likely to be 274 µg/m^2 or approximately 98 t. Residues were also determined in major German rivers between 1995 and 1996 (KCA 7.5/18, M-585141-01-1) where the concentrations of TFA varied from 10 to 630 ng/L.

In M-604969-01-1 (KCA 7.5/09), the presence of haloacetates (including TFA) and major inorganic ions in fog and rain was investigated at one site in Germany. Fogwater (96 samples) and rainwater samples (over 100 samples) were collected from July 1998 to March 1999 at an ecological research site in northeastern Bavaria, Germany. TFA was found in all samples, at concentrations of up to 2 µg/L. TFA was found in fogwater associated with westerly winds and showed higher average concentrations in fog than in rain (a similar finding was reported for samples taken in Nevada and California in 1996 - 1997; KCA 7.5/19, M-585142-01-1). Taking into account the results of a trajectory study and the associated correlation analysis, the air masses that had been influenced by marine sources showed a pattern different to that of nonmarine air masses. The high concentrations of TFA in the nonmarine air masses as well as its significant correlation to nitrate and sulphate (which are closely associated with power plants, industrial facilities and motor vehicles) suggested that TFA or its atmospheric precursors were of industrial origin (similar findings were reported for lake and rain samples collected in 1997 in Canada, where urban centres were considered to be the source of elevated trifluoroacetic acid residues; KCA 7.5/21, M-585144-01-1, and in streams in Northern California in 1998 where elevated levels of TFA were reported at sites downwind of urban areas; KCA 7.5/20, M-604967-01-1).

The kinetic reaction rate of trifluoroacetic acid with hydroxyl radicals was experimentally investigated (KCA 7.5/11, M-455782-01-1) using relative rate techniques. The relevant rate constant was determined to be 9.35 × 10^{-14} cm^3 molecule^{-1} s^{-1} (± 2.08). The authors estimated that this corresponds to an

atmospheric lifetime (due to reaction with hydroxyl radicals) of about 230 days. However, they also asserted that the removal of trifluoroacetic acid from the atmosphere would be at a similar rate to HNO_3, which has a lifetime of 9 days with respect to wet deposition and 10 - 30 days with respect to dry deposition. The atmospheric fate of isoflurane (an anaesthetic used in the 1990s) was also investigated in the laboratory (KCA 7.5/23, M-605021-01-1) where it was estimated that at the end of the 1990s, isoflurane was emitted at a rate of 750 tonnes/year, yielding 440 tonnes of trifluoroacetic acid.

In the study described in M-585148-01-1 (KCA 7.5/07) the occurrence, the fate, and the mass fluxes of trifluoroacetic acid have been assessed in the aquatic environment in Switzerland (samples collected in 1996/7), based on more than 1000 concentration measurements in rain and snow, surface water, groundwater, and wastewater. No statistically different average concentrations among six precipitation sampling sites located in various areas in Switzerland were observed (range of average trifluoroacetic acid concentrations: 33 - 220 ng/L). This, together with similar average concentrations in precipitation at a remote site close to the free troposphere at an elevation of 3580 m above sea level and at an urban site that receives precipitation which scavenged the Earth's boundary layer suggests that trifluoroacetic acid was derived from well-mixed precursor(s) in the atmosphere. This was further corroborated through very similar trifluoroacetic acid concentrations measured in a small number of samples in precipitation and seawater from Norway and Vietnam, and in precipitation and surface waters in Siberia. The concentrations of trifluoroacetic acid in surface waters (average of rivers and lakes) were 1.6 times lower than in precipitation, and mass flux calculations showed that precipitation is the dominant source of trifluoroacetic acid (> 95%). These results confirm that the atmosphere is an important source of trifluoroacetic acid in aquatic compartments, and that precipitation is most likely the major transfer mechanism to the biosphere.

A comprehensive survey of the sources and fate in the environment of trifluoroacetic acid and its salts has recently been published (KCA 7.5/12, M-603942-01-1). In many ways, trifluoroacetic acid is chemically similar to nitric or hydrochloric acid because of its low pKa, it rapidly forms salts when released to the terrestrial environment and surface waters. The salts display different properties from the acid. For example, the sodium salt is highly soluble in water (625 g/L) but is neutral, not corrosive, and has negligible volatility. It is this salt form of trifluoroacetic acid that is relevant to exposures in the environment. There are number of sources of trifluoroacetic acid and trifluoroacetic acid salts in the environment. Some of these are natural and others are anthropogenic. For oceans, the data strongly implies that a large amount of the trifluoroacetic acid salts in the ocean is from natural rather than human-made sources. However, salts of trifluoroacetic acid in surface fresh waters are more likely of anthropogenic origins. Trifluoroacetic acid is widely used in industry and production in the United States, and in 2002, was estimated at between 450 and 4500 tonnes (t) acid equivalents (a.e.). Whether and in what quantities trifluoroacetic acid and its salts are released into the environment from industrial uses is highly uncertain.

In KCA 7.5/12, M-603942-01-1, it is also reported that several of the hydrochlorofluorocarbons (HCFC) and hydrofluorocarbons (HFC) used as refrigerants, propellants and solvents degrade in the atmosphere to give trifluoroacetic acid. These include halothane, isoflurane, HCFC-123, HCFC-124, HFC-134a, HFC-143a, hydrofluoroolefin (HFO)-1234yf, and HFO-1234ze. Once formed in the atmosphere, trifluoroacetic acid partitions almost entirely into fog and cloud water and is carried to the surface in precipitation. Data on global production of HFO-1234yf for 2015 were not available, but projected production for North America was estimated to be from 50,000 to 100,000 tonnes/yr in the next 50 – 100 yr. HFO-1234yf is a replacement for HFC-134a, global production of which (without a ban) is projected to be 600,000 tonnes/yr in 2050. Thus, global production of HFO-1234yf might be expected to be of similar magnitude by 2050 if replacement is complete. Therefore, production of HFO-1234yf could begin in 2016 and increase to 100,000 tonnes/yr by 2050 for a total of about 3,255,000 tonnes (the atmospheric lifetime of HFO-1234yf is estimated at approximately 6 d and conversion to trifluoroacetic acid is 1:1 on a molar basis). Assuming that the total yield of trifluoroacetic acid just described formed in the atmosphere from 1990 to 2050 is transported to oceans as a terminal sink and then uniformly

mixed, the added concentration in the ocean would be 15.3 ng a.e./L (currently concentration is about 200 ng/L). An analysis of rainwater monitoring was undertaken in 2007 – 2008 in Guagzhou, China (KCA 7.5/27, M-754605-01-1). Simulation modelling strongly suggested that the trifluoroacetic acid levels measured could be mostly accounted for by the levels of HCFCs/HFCs used in the region (with them being responsible for 83 – 97% of trifluoroacetic acid measured levels). It has also been recently reported (KCA 7.5/30, M-758268-01-1) that landfill sites in China can be a significant source of trifluoroacetic acid in the surrounding area, and recent investigations in Sweden supported these observations (KCA 7.5/32, M-758273-01-1), and also suggested that firefighting training sites and hazardous waste management facilities can be point sources for environmental trifluoroacetic acid contamination. Additionally, it has been reported (KCA 7.5/36, M-765262-01-1) that products in fire extinguishers, and thermolysis of fluoroploymers can also be sources of trifluoroacetic acid in the environment.

Various model simulations on the likely generation of trifluoroacetic acid from the mobile air conditioning unit refrigerant HFO-1234yf have been reported for Europe, USA and China (KCA 7.5/31, M-757883-01-1; KCA 7.5/25, M-599310-01-1; KCA 7.5/26, M-464526-01-1); the relatively short atmospheric lifetime of HFO-1234yf (2 - 11 days) resulted in the prediction of a more localised trifluoroacetic acid precipitation centered on likely HFO-1234yf emission patterns (i.e. closely associated with urban/industrial locations and correlated with population densities); with annual average TFA levels of 480 ng/L (USA), 620 ng/L (EU) and 638 ng/L (China) predicted in rainfall based on vehicle numbers in 2016. Analysis of the presence of HFO-1234yf at two sites in Switzerland in 2011 - 2014 showed a steadily increasing atmospheric concentration, and calculations indicated that the source of the residues was Belgium and The Netherlands (KCA 7.5/28, M-757135-01-1). A very recent publication (KCA 7.5/37, M-765301-01-1) compared the simulated global effect of substituting HFO-1234y for HFC-134a, and predicted a 33-fold increase (based on 2015 emissions) in the atmospheric formation of trifluoroacetic acid, equivalent to 2150 tonnes at the global scale, translating into a 250-fold increase of surface level trifluoroacetic acid levels over Europe.

Whatever the source of trifluoroacetic acid in the atmosphere or other compartments in the environment, the ultimate sink is in surface waters (KCA 7.5/12, M-603942-01-1). Trifluoroacetic acid is soluble in water and dissolves or partitions into water (droplets in the atmosphere in the case of the atmospheric degradation of HCFCs, HFCs and HFOs). Upon contact with soil or surface waters, trifluoroacetic acid forms salts with ions such as sodium, potassium, magnesium, and calcium, which are present in soils and most surface waters. These salts of trifluoroacetic acid behave in a manner exactly the equivalent of salts of other minerals. Where mineral salts have accumulated in salt lakes, playas, and oceans, trifluoroacetic acid salts from natural and anthropogenic sources also accumulate. Playas and salt lakes are terminal sinks for salts, including trifluoroacetic acid. These water bodies contain more than the 3.5 g/L of salt found in the oceans. For example, the Great Salt Lake in Utah has concentrations of salts that vary from 50 to 270 g/L. Expressed in the same units as used for the measured environmental concentrations of trifluoroacetic acid (ng salt/L), this is 270,000,000,000 ng salts/L.

NOTE: TFA refers to trifluoroacetate in M-455778-01-1, M-585141-01-1, M-603993-01-1, M-604966-01-1, M-604967-01-1, M-604971-01-1, M-754282-01-1, M-757131-01-1, M-758267-01-1 and M-604969-01-1; but refers to trifluoroacetic acid in M-455782-01-1, M-457426-01-1, M-464526-01-1, M-585142-01-1, M-585144-01-1, M-585148-01-1, M-599310-01-1, M-603942-01-1, M-605021-01-1, M-754605-01-1, M-757128-01-1, M-757134-01-1, M-757135-01-1, M-757883-01-1, M-758268-01-1, M-758271-01-1, M-758273-01-1, M-761706-02-1, M-765262-01-1, M-765301-01-1 and M-760366-01-1.

Summary

Trifluoroacetate (TFA) is a terminal degradation product of fluopyram in soil; TFA, being entirely dissociated when formed from fluopyram in soil, would display very limited volatility and hence would not transfer to the atmosphere.

TFA is likely to be naturally produced in the deep oceans. Most of the TFA detected in the non-marine environment, however, is believed to be anthropogenic in nature. TFA can be generated from many organic molecules that contain the trifluoroethyl moiety (e.g. refrigerant gases, pharmaceuticals, pesticides and polymers), and trifluoracetic acid is also used in their manufacture on an industrial scale (emissions of trifluoroacetic acid can take place from the manufacturing plants). Although trifluoroacetic acid can be emitted directly into the environment, the major source of trifluoroacetic acid in the atmosphere is volatile substances containing the trifluoroethyl moiety that photolytically degrade in the atmosphere to generate trifluoroacetic acid. These include HCFCs, HFCs and HCFOs, which are produced in very large amounts and used as refrigerants, propellants and solvents. Trifluoroacetic acid produced in the atmosphere is relatively quickly removed and deposited to land by wet deposition (as fog, rain and snow) or by dry deposition. This process occurs throughout the world (even in relatively remote places), such that TFA is to be found in most water samples analysed (including in rainwater); the atmospheric generation of trifluoroacetic acid is the major source of TFA generally detected in environmental compartments, and fluopyram does not contribute to this.

Headline Monitoring Results

In the new applicant review study (KCA 7.5/06, M-761706-02-1), TFA was found in databases (and reports) from Austria and Germany. The groundwater monitoring data search (32 analyses in total) resulted in a compliance rate of 100% with the selected arbitrary threshold applied (10 µg/L), with a maximum concentration of 4.4 µg/L. The surface water monitoring data search (417 analyses in total) resulted in a compliance rate of 100% with the Tier 1-RAC-SW of 120 µg/L, with a maximum concentration of 17 µg/L. In the new applicant review study (KCA 7.5/05, M-760366-01-1), TFA could be detected in almost all drinking water samples, the concentration seldom exceeded 2.0 µg/L and only once 3.0 µg/L. For all compartments, it cannot be discounted that some of the detections identified are erroneous given they arise from non-GLP monitoring networks and programmes of unknown quality.

Several peer reviewed published papers report TFA monitoring data. Of particular note is the monitoring results of TFA in soil from Canada, Malawi, UK and Chile reported in KCA 7.5/12, M-603942-01-1.

The RACs and maximum reported concentrations in each compartment are summarised in the table below.

Table 7.5- 11: Summary of reported maximum concentrations of TFA with regulatory acceptable concentrations (RAC) in each environmental compartment

Compartment	Regulatory acceptable concentration	Compliance (%)	Maximum Concentration
Soil	20 mg/kg dws	NA	9400 ng acid equivalents/kg d.w. (M-603942-01-1)
Groundwater	10 µg/L	100	4.4 µg/L (M-761706-02-1)
Surface water	120 µg/L	100	17.0 µg/L (M-761706-02-1)
Drinking water	10 µg/L*	NA	3.8 µg/L (M-760366-01-1)
Marine water	NA	NA	ca. 200 ng/L (M-455778-01-1)
Sediment	NA	NA	Not documented
Air	NA	NA	Not documented

NA: Not applicable; dws: Dry weight of soil; *: Selected arbitrary threshold.
For all compartments, it cannot be discounted that some of the detections identified are erroneous given they arise from non-GLP monitoring networks and programmes of unknown quality.

Headline Conclusions

It can be concluded from the assessment of the readily available public monitoring datasets that TFA does not pose a concern for the environment where data were available for the investigated environmental compartments.

The new applicant studies and published peer-reviewed papers considered in this monitoring chapter are listed in the table below. In addition, this table shows the relevant compartment that each study/literature article addresses.

Table 7.5- 12: Monitoring study and literature article covering TFA monitoring

Annex point	Study (Author, year, DART no.)	Study type	Source (CRO/sponsor / journal)	Status	Monitoring activities						
					SOIL	GW	SW	DW	MW	SED	AIR
APPLICANT STUDIES											
New studies/assessments											
KCA 7.5 /05	M-760366-01-1	Assessment of TFA concentrations in water	Tier 3 Bayer	Valid							
KCA 7.5 /06	M-761706-02-1	Public environmental TFA monitoring data (groundwater and surface water)	Knoell Bayer	Valid							
Existing studies/assessments											
There are no existing applicant studies											
RELEVANT LITERATURE ARTICLES											
KCA 7.5 /07	Berg, M. *et al.* 2000 M-585148-01-1	Concentrations and mass fluxes of chloroacetic acids and trifluoroacetic acid in rain and natural waters	Environmental Science and Technology 34(13) 2675 - 2683	Reliable							
KCA 7.5 /08	Von Sydow L.M. *et al.* 2000 M-604966-01-1	Natural background levels of trifluoroacetate in rain and snow	Environmental Science and Technology 34(15) 3115 - 3118	Reliable							
KCA 7.5 /09	Römpp, A. *et al.*, 2001 M-604969-01-1	Haloacetates in fog and rain	Environmental Science and Technology 35(7) 1294 - 1298	Reliable							
KCA 7.5 /10	Frank, H. *et al.*, 2002 M-455778-01-1	Trifluoroacetate in ocean waters	Environmental Science and Technology 36(1) 12 - 15	Reliable							

Annex point	Study (Author, year, DART no.)	Study type	Source (CRO/sponsor / journal)	Status	Monitoring activities						
					SOIL	GW	SW	DW	MW	SED	AIR
KCA 7.5 /11	Hurley, M.D. *et al.*, 2004 M-455782-01-1	Reaction rates of TFA with OH radicals and atmospheric loss of TFA	Journal of Physical Chemistry 108(4) 615 - 620	Reliable							
KCA 7.5 /12	Solomon, K.R. *et al.*, 2016 M-603942-01-1	Monitoring of TFA in environmental compartments	Journal of Toxicology and Environmental Health, Part B, Critical reviews (19(7) 289 - 304	Reliable							
KCA 7.5 /13	Freeling, F *et al.* 2020 M-754282-01-1	TFA in precipitation	Environmental Science and Technology 54(18) 11210 - 11219	Reliable							
KCA 7.5 /15	Ball, J. C., Wallington, T. J., 1993 M-757129-01-1	Formation of trifluoroacetic acid from the atmospheric degradation of hydrofluorocarbon 134a: A human health concern?	Journal of the Air and Waste Management Association 43(9) 1260 - 1262	Supportive information							
KCA 7.5 /16	James, F., 1993 M-757131-01-1	The atmospheric degradation and impact of 1,1,1,2-tetrafluoroethane (hydrofluorocarbon 134a)	Chemosphere 27(8) 1565 - 601	Supportive information							
KCA 7.5 /17	Wujcik, C. E., Zehavi, D., Seiber, J. N., 1998 M-757434-01-1	Trifluoroacetic acid levels in 1994 - 1996 fog, rain, snow and surface waters from California and Nevada	Chemosphere 36(6) 1233 - 1245	Reliable							
KCA 7.5 /18	Frank, H., Jordan, A., 1999 M-385148-01-1	Trifluoroacetate in the environment. Evidence for sources other than HFC/HCFCs	Environmental Science and Technology 33(4) 522 - 527	Reliable							
KCA 7.5 /19	Wujcik, C. E, Cahill, T. M.,	Determination of trifluoroacetic acid in 1996 -	Environmental Science and Technology	Reliable							

Annex point	Study (Author, year, DART no.)	Study type	Source (CRO/sponsor / journal)	Status	Monitoring activities						
					SOIL	GW	SW	DW	MW	SED	AIR
	Seiber, J. N., 1999 M-585142-01-1	1997 precipitation and surface waters in California and Nevada	33(10) 1747 - 1751								
KCA 7.5 /20	Cahill, T. M., Seiber, J. N., 2000 M-604967-01-1	Regional distribution of trifluoroacetate in surface waters downwind of urban areas in Northern California, U.S.A.	Environmental Science and Technology 34(14) 2905 - 2912	Reliable							
KCA 7.5 /21	Scott, B. *et al.*, 2000 M-585144-01-1	Haloacetic acids in Canadian lake waters and precipitation	Environmental Science and Technology 34(20) 4266 - 4272	Reliable							
KCA 7.5 /22	Römpp, A., Klemm O., Frank, H. 2001 M-604971-01-1	Haloacetates and nitrophenols in fog and rain	Transport and Chemical Transformation in the Troposphere, Proceedings of EUROTRAC Symposium, March 27 - 31, 2000	Supportive information							
KCA 7.5 /23	Wallington, T.J. *et al.*, 2002 M-605021-01-1	Atmospheric chemistry of $CF_3CH_2OCHF_2$ and $CF_3CHClOCHF_2$: Kinetics and mechanisms of reaction with Cl atoms and OH radicals and atmospheric fate of $CF_3C(O•)HOCHF_2$ and $(CF_3C(O•)ClOCHF_2$ radicals	Journal of Physical Chemistry 106(36) 8391 - 8398	Supportive information							
KCA 7.5 /24	Wilson, S.R. Solomon, K. R., Tang, X.,	Changes in tropospheric composition and	Photochemical and Photobiologica	Supportive information							

Annex point	Study (Author, year, DART no.)	Study type	Source (CRO/sponsor / journal)	Status	Monitoring activities						
					SOIL	GW	SW	DW	MW	SED	AIR
	2007 M-457426-01-1	air quality due to stratospheric ozone depletion and climate change	l Sciences 6(3) 301-310								
KCA 7.5 /25	Luecken, D. *et al.*, 2010 M-599310-01-1	Ozone and TFA impacts in North America from degradation of 2,3,3,3-tetrafluoropropene (HFO-1234yf): a potential greenhouse gas replacement	Environmental Science and Technology 44(1) 343-348	Supportive information							
KCA 7.5 /26	Henne *et al.*, 2012 M-464526-01-1	Environmental impacts of HFO-1234y and other HFOs	ASHRAE/NIST Refrigerants Conference	Reliable							
KCA 7.5 /27	Wang, Q., Wang, X., Ding, X. 2014 M-754605-01-1	Rainwater trifluoroacetic acid (TFA) in Guangzhou, South China: Levels, wet deposition fluxes, and source implication	Science of the Total Environment, (468 - 469) 272 - 279	Reliable							
KCA 7.5 /28	Vollmer, M.K. *et al.*, 2015 M-757135-01-1	First Observations of the Fourth-Generation Synthetic Halocarbons HFC-1234yf, HFO-1234ze(E), and HCFC-1233zd(E) in the Atmosphere	Environmental Science and Technology 49(5) 2703-2708	Supportive information							
KCA 7.5 /29	Scheurer, M. *et al.*, 2017 M-603993-01-1	Small, mobile, persistent: Trifluoroacetate in the water cycle Overlooked sources, pathways, and consequences for drinking water supply	Water Research (126) 460 - 471	Reliable							

Annex point	Study (Author, year, DART no.)	Study type	Source (CRO/sponsor / journal)	Status	Monitoring activities						
					SOIL	GW	SW	DW	MW	SED	AIR
KCA 7.5 /30	Tian, Y. *et al.*, 2018 M-758268-01-1	Occurrence and phase distribution of neutral and ionizable per- and polyfluoroalkyl substances (PFASs) in the atmosphere and plant leaves around landfills: A case study in Tianjin, China	Environmental Science and Technology 52(3) 1301 - 1310	Reliable							
KCA 7.5 /31	Wang, Z. *et al.*, 2018 M-757883-01-1	Impacts of the degradation of 2,3,3,3-tetrafluoropropene into trifluoroacetic acid from its application in automobile air conditioners in China, the United States, and Europe	Environmental Science and Technology 52(5) 2815 - 2826	Supportive information							
KCA 7.5 /32	Björnsdotter, M.K. *et al.*, 2019 M-758273-01-1	Ultra-short-chain perfluoroalkyl acids including trifluoromethane sulfonic acid in water connected to known and suspected point sources in Sweden	Environmental Science and Technology 53(19) 11093 - 11101	Supportive information							
KCA 7.5 /33	Chen, H. *et al.*, 2019 M-758267-01-1	Per-and polyfluoroalkyl substances (PFASs) in precipitation from mainland China: Contributions of unknown precursors and short-chain (C2-C3) perfluoroalkyl carboxylic acids	Water Research (U53) 169 - 177	Reliable							
KCA 7.5 /34	Dörgerloh, U., Becker, R., Kaiser, M., 2019	Evidence for the formation of difluoroacetic acid in	Molecules (24) 1039	Supportive information							

Annex point	Study (Author, year, DART no.)	Study type	Source (CRO/sponsor / journal)	Status	Monitoring activities						
					SOIL	GW	SW	DW	MW	SED	AIR
	M-758271-01-1	chlorofluorocarbon-contaminated groundwater									
KCA 7.5 /35	Janda, J. *et al.*, 2019 M-765202-01-1	Robust trace analysis of polar (C2-C8) perfluorinated carboxylic acids by liquid chromatography-tandem mass spectrometry: method development and application to surface water, groundwater and drinking water	Springer-Verlag GmbH Germany	Reliable							
KCA 7.5 /36	Björnsdotter, M. K. *et al.* 2020 M-765262-01-1	Challenges in the analytical determination of ultra-short-chain perfluoroalkyl acids and implications for environmental and human health	Analytical and Bioanalytical Chemistry 412(20) 4785 - 4796	Reliable							
KCA 7.5 /37	Holland R. *et al.*, 2021 M-765301-01-1	Investigation of the production of trifluoroacetic acid from two halocarbons, HFC-134a and HFO-1234yf and its fates using a global three-dimensional chemical transport model	ACS Earth and Space Chemistry (2021) ahead of print	Reliable							

GW: Groundwater; SW: Surface water; DW: Drinking water; MW: Marine water; SED: Sediment

: Study contained information

: Study did not contain information

1. Information on the study

Data Point:	KCA 7.5/05
Report Author:	[redacted]
Report Year:	2021
Report Title:	Trifluoroacetic acid in water: Drinking water screening in Germany and supplementary samples of additional water sources and countries
Report No:	B16059
Document No:	M-760366-01-1
Guideline(s) followed in study:	None
Deviations from current test guideline:	Current Guideline: not applicable
Previous evaluation:	No, not previously submitted
GLP/Officially recognised testing facilities:	No, not conducted under GLP/Officially recognised testing facilities
Acceptability/Reliability:	Yes

2. Full summary of KCA 7.5/05

Executive Summary

To assess the concentrations of trifluoroacetic acid (TFA) in drinking water, 477 drinking water samples were taken across Germany in December 2016 and January 2017. In parallel, an additional sampling phase was started in December 2016 and was completed in December 2017. This included further random drinking water samples, drinking water samples regularly taken at the same locations, surface water, rainwater, groundwater, spring water, and snow. All water samples were analysed for their TFA concentrations.

During the first phase 338 out of 477 samples (71%) collected in Germany had TFA concentrations above the LOQ (0.05 µg/L) and 139 samples (29%) were below. The majority of samples (n = 272, 57%) had TFA concentrations between 0.1 and 1.0 µg/L, 34 (7%) of samples had TFA concentrations between 1.0 and 3.0 µg/L and only one sample had a TFA concentration above 3.0 µg/L. Samples taken during the second phase showed that for all additional water sources, TFA concentrations above LOQ were detected (except for snow samples). Nevertheless, concentrations never exceeded 3.0 µg/L.

I. MATERIAL AND METHODS

Materials

The samples were analysed for TFA concentrations by liquid chromatography–mass spectrometry (HPLC-MS/MS).

Sampling method

Drinking water screening Germany (first phase)

In the first phase, drinking water samples were collected in Germany from 12th of December 2016 to 3rd of January 2017 (Table 7.5- 13).

Table 7.5- 13: Number of drinking water samples taken for the screening in Germany (first phase, December 2016 – January 2017)

State	Number of samples
Baden-Wuerttemberg	31
Bavaria	90
Brandenburg	33
Bremen	2
Hamburg	5
Hesse	28
Mecklenburg-Hither-Pomerania	16
Lower Saxony	66
North Rhine-Westphalia	106
Rhineland-Palatinate	23
Saarland	4
Saxony	18
Saxony-Anhalt	24
Schleswig-Holstein	24
Thuringia	8
Germany (total)	**477**

In order to access the TFA concentrations in drinking water in Germany, a sufficient number of randomly distributed location points was generated. These points were adjusted to be closer to major thoroughfares. During the sampling the locations were approximated, and the samples were taken in locations as near to the originally selected locations as possible. The water samples were taken from drinking water sources by filling tap water into glass bottles; additionally, the exact locations were noted.

In Figure 7.5- 2 the original random sampling points are displayed as white circles, the adjusted sampling points as black crosses and the actual noted sampling points as red squares

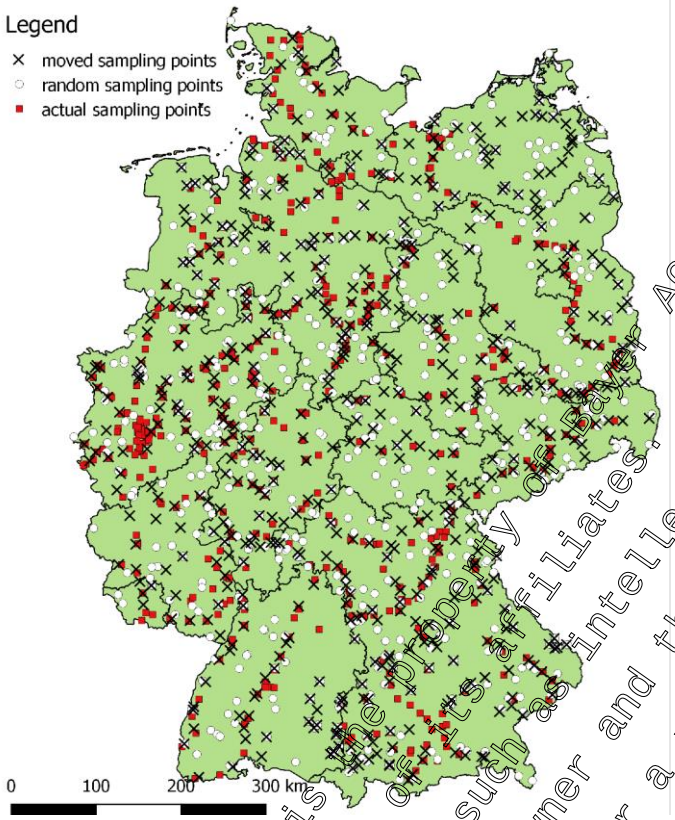


Figure 7.5- 2: Sampling points across Germany for the first phase (December 2016 - January 2017)

All samples were then stored at room temperature, until 16th of December 2016 when all drinking water screening samples were sent to the analytical test facility of the sponsor.

Additional sampling (second phase)
The second phase started in December 2016 and was completed in December 2017.

In the second phase, further sampling of drinking water, but also of other water sources (i.e. surface water, rainwater, groundwater, spring water, and snow) was conducted. Sampling was not restricted to Germany; a small number of samples were also taken in other European countries and in the USA. Additionally, drinking water samples from selected locations in Germany were collected on a monthly basis in order to monitor the contents of TFA over a complete 12-month period (Table 7.5- 14).

Table 7.5- 14: Number of additional samples (second phase, December 2016 – December 2017) for each country and source

Country	Number of samples					
	Drinking water	Surface water	Rainwater	Spring water	Groundwater	Snow
Croatia	2	0	0	0	0	0
Denmark	1	0	0	0	0	0
France	6	1	0	0	0	0
Germany	128[1]	2	50	14	5	2
Italy	3	0	0	0	0	0
Norway	2	6	0	0	0	1
Switzerland	1	0	0	0	0	0
USA	3	0	0	0	0	0

[1]: three samples taken during the first phase were included in this dataset as they served as starting points for some of the locations of the one-year drinking water monitoring

In Europe, sampling locations were not pre-determined as in the first phase, but randomly chosen. In some of the locations repeated measurements were conducted. This was the case for some of the drinking water samples, where consecutive measurements over a 12-month period were conducted. Samples in the USA (drinking water only) were taken in November 2017 at three locations: Orlando, Miami Beach and Key West, in the State of Florida. Samples taken in the second phase were collected continuously and analysed in batches depending on the capacity of the analytical test facility.

Analytical method
TFA determinations in water was performed by HPLC-MS/MS.

For validation, deionized water was used, as all other tested water samples showed significant blank values. Water samples were diluted with acetonitrile, internal standard solution added (200 µL sample + 790 µL acetonitrile + 10 µL internal standard) and analysed by direct injection into an HPLC-MS/MS instrument using electrospray in the negative mode. The linearity of HPLC-MS/MS detection was demonstrated for TFA in standard solutions in water / acetonitrile (containing internal standard) in the concentration range from 0.01 µg/L to 1.0 µg/L (corresponding to 0.05 µg/L to 5.0 µg/L in water samples). The repeatability of HPLC-MS/MS detection for TFA was determined based on 10 injections of a standard solution of 0.01 µg/L and 10 injections of a standard solution of 0.10 µg/L (corresponding to 0.05 µg/L and 0.5 µg/L in a water sample). (note: analytical method drinking water was applied M-583581-01-1).

LOQ: The limit of quantification was 0.05 µg/L.

Linearity: between 0.01 µg/L and 1.0 µg/L (corresponding to 0.05 µg/L and 5.0 µg/L in water samples), the correlation coefficient was 0.9999 (1/x-weighted).

Peak ratios of TFA: relative standard deviation ranged between 2.6% at 0.01 µg/L and 2.1% at 0.10 µg/L.

Retention time: relative standard deviation was 0.3% at both 0.01 µg/L and 0.10 µg/L.

For the screening of German drinking water (first phase) the percentages of samples below and above the LOQ of TFA were calculated, as well as the percentages of samples in the intervals from 0.05 µg/L to 0.1 µg/L, 0.1 µg/L to 1.0 µg/L, 1.0 µg/L to 3.0 µg/L, and above 3.0 µg/L. Additionally, the percentages of samples with TFA concentrations per state were calculated. Minimum, maximum, mean, median, 25th, and 75th quantile were calculated with the differentiation for the different water origins. The results of the samples of the second phase were graphically displayed as boxplots, barplots or line plots without any further calculations.

All calculations were conducted with the software "R", plotting was conducted using the packages *ggmap* and *ggplot2*. A geographic assessment about the distribution of sampled TFA concentrations was made using QGIS version 2.18.3.

II. RESULTS AND DISCUSSION

Drinking water screening Germany (first phase)

338 out of 447 (71%) of the drinking water samples contained TFA concentrations above the LOQ (0.05 µg/L) and 139 samples (29%) were below.

Figure 7.5- 3 depicts the percentages of TFA concentrations of the total sampling size. 31 (6%) of the samples contained TFA concentrations between the LOQ and 0.1 µg/L. The majority of samples (n = 272, 57%) had TFA concentrations between 0.1 and 1.0 µg/L; 34 (7%) of samples had TFA concentrations between 1.0 and 3.0 µg/L and only one sample had a TFA concentration above 3.0 µg/L (3.8 µg/L). Thus, 36% of all samples (n = 170) showed TFA concentrations below 0.1 µg/L and 7% (35 samples) concentrations above 1.0 µg/L.

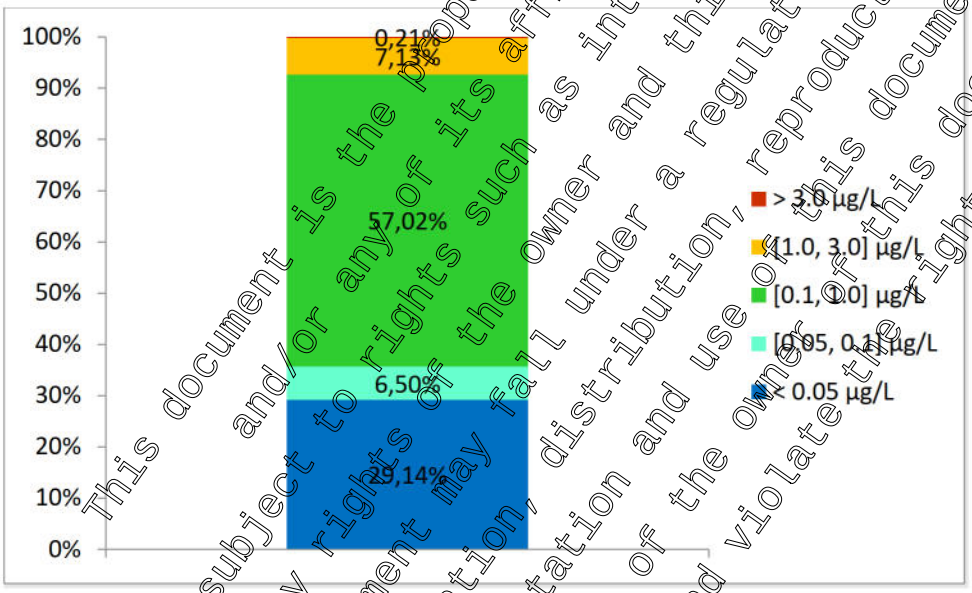


Figure 7.5- 3: Percentage of TFA concentrations in the sample in the intervals < 0.05 µg/L, 0.05 µg/L to 0.1 µg/L, 0.1 µg/L to 1.0 µg/L, 1.0 µg/L to 3.0 µg/L and > 3.0 µg/L

Table 7.5- 15 shows the number of drinking water samples per state, the number of samples that contained a TFA concentration above 1.0 µg/L, the percentage of these samples of the respective state, and the percentage of these samples of the whole of Germany. Most samples were taken in North Rhine-Westphalia, Bavaria, and Lower Saxony. In Berlin no samples were taken. In North Rhine-Westphalia, Baden Wuerttemberg, Lower Saxony, Rhineland-Palatinate and Bavaria the percentages of the samples with TFA concentrations above 1.0 µg/L were 19.81% (21 out of 106 samples), 12.90% (4 out of 31 samples), 10.77% (5 out of 65 samples), 8.70% (2 out of 23) and 3.33% (3 out of 33 samples) in relation to states respectively. For the other states no TFA concentrations above 1 µg/L were found in the samples.

Table 7.5- 15: Number of samples per state, number of samples per state with TFA concentrations above 1.0 µg/L, and percentage of the samples with TFA concentrations above 1.0 µg/L in relation to the state sampling size, and in relation to the sampling size of the whole of Germany

State	Number of samples	Number of samples with TFA > 1.0 µg/L	% of samples with TFA > 1.0 µg/L in relation to the state	% of samples with TFA > 1.0 µg/L in relation to the whole of Germany
Baden-Wuerttemberg	31	4	12.90	0.84
Bavaria	90	3	3.33	0.63
Brandenburg	33	0	0.00	0.00
Bremen	2	0	0.00	0.00
Hamburg	5	0	0.00	0.00
Hesse	28	0	0.00	0.00
Mecklenburg-Hither-Pomerania	16	0	0.00	0.00
Lower Saxony	65	5	10.77	1.47
North Rhine-Westphalia	106	21	19.81	4.40
Rhineland-Palatinate	23	2	8.70	0.42
Saarland	4	0	0.00	0.00
Saxony	18	0	0.00	0.00
Saxony-Anhalt	24	0	0.00	0.00
Schleswig-Holstein	24	0	0.00	0.00
Thuringia	8	0	0.00	0.00
Germany (total)	**477**	**35**	**7.34**	**7.34**

Additional sampling (second phase)

Drinking water, USA

In November 2017, in the state of Florida, TFA concentrations ranged from < 0.05 µg/L for a sample from Orlando to 2.241 µg/L in a sample from Key West. While this is a relatively high value, it is still within the range of TFA concentrations found in drinking water in Germany. Also, due to the limited number of samples (3), it is hard to make a comparison between the concentrations found in Europe and in the USA.

Drinking water, Europe

For the drinking water samples taken in Germany during the second phase, the maximum concentration of TFA was 2.800 µg/L found in a location in Düsseldorf. Three samples were below the LOQ (from Bavaria, Lower Saxony and North Rhine-Westphalia). The median value was 0.723 µg/L. However, this dataset is less representative than the drinking water screen done in the whole of Germany during the first phase, the number of samples taken was smaller and mainly originate from North Rhine-Westphalia (96 samples, 75%), while other states are completely missing and repeated samplings were taken in certain locations.

All drinking water samples (n = 6) taken in France, contained TFA concentrations above LOQ. The range was 0.643 µg/L to 1.750 µg/L with a median of 1.143 µg/L. Concentrations are within the range found in German drinking water; however, as sampling was limited to 6 samples and one region of France, any comparison to other countries has to be considered with caution.

Drinking water, one-year monitoring – Germany

Water samples from Burscheid and 51375 Leverkusen showed the lowest concentrations of TFA in comparison to the other sampling sites and low amplitudes during the course of measuring period. The range of TFA concentrations was 0.258 µg/L – 0.387 µg/L for Burscheid and 0.211 µg/L – 0.531 µg/L

for 51375 Leverkusen. The similarity of these findings is due to the same reservoir origin of the water for both households (Große Dhünntalsperre). However, most other water providers, with the exceptions of the samples taken in Monheim where the origin of water is solely groundwater, use state mixed sources for their water. This mix, however, is not constantly of the same composition, but determined by the availability of each of the different sources and the need to control the level of certain substances (e.g. nitrate) in the drinking water. Therefore, it is not possible to reliably state the origin of these water samples. For some of the sampling points high amplitudes were recorded during the course of measuring period. This was the case for Düsseldorf and Bonn, with ranges of 1.364 µg/L – 2.800 µg/L and 0.475 µg/L - 1.233 µg/L, respectively. Other sampling locations, e.g. Aachen, show a rather flat curve and concentrations similar to those found in Burscheid or Leverkusen.

Differences in the concentrations of TFA as well as the development over time could be detected for the different sampling locations. Nevertheless, the fact that the majority of drinking water samples originated from mixed sources, made it impossible to conclude how different entry ways (e.g. agriculture, effluent from industry) could have influenced the TFA concentrations in drinking water.

Surface water, Europe

A total of 9 surface water samples were taken; 6 in Norway, 2 in Germany and 1 in France. TFA concentrations ranged from < 0.05 µg/L to 1.134 µg/L. While the samples taken in Norway generally showed lower concentrations than the samples taken in Germany and France, the database was too small to make a meaningful comparison between the countries.

Rainwater, Germany

TFA was present in almost all rainwater samples (92%, 46 out of 50), with only 4 samples below the LOQ. TFA concentrations ranged from < 0.05 µg/L to 1.678 µg/L. No pattern was perceivable from the location where samples were taken. As TFA is formed in the atmosphere, the location of the sampling is probably less indicative than are climatic factors or weather events.

Spring water, Germany

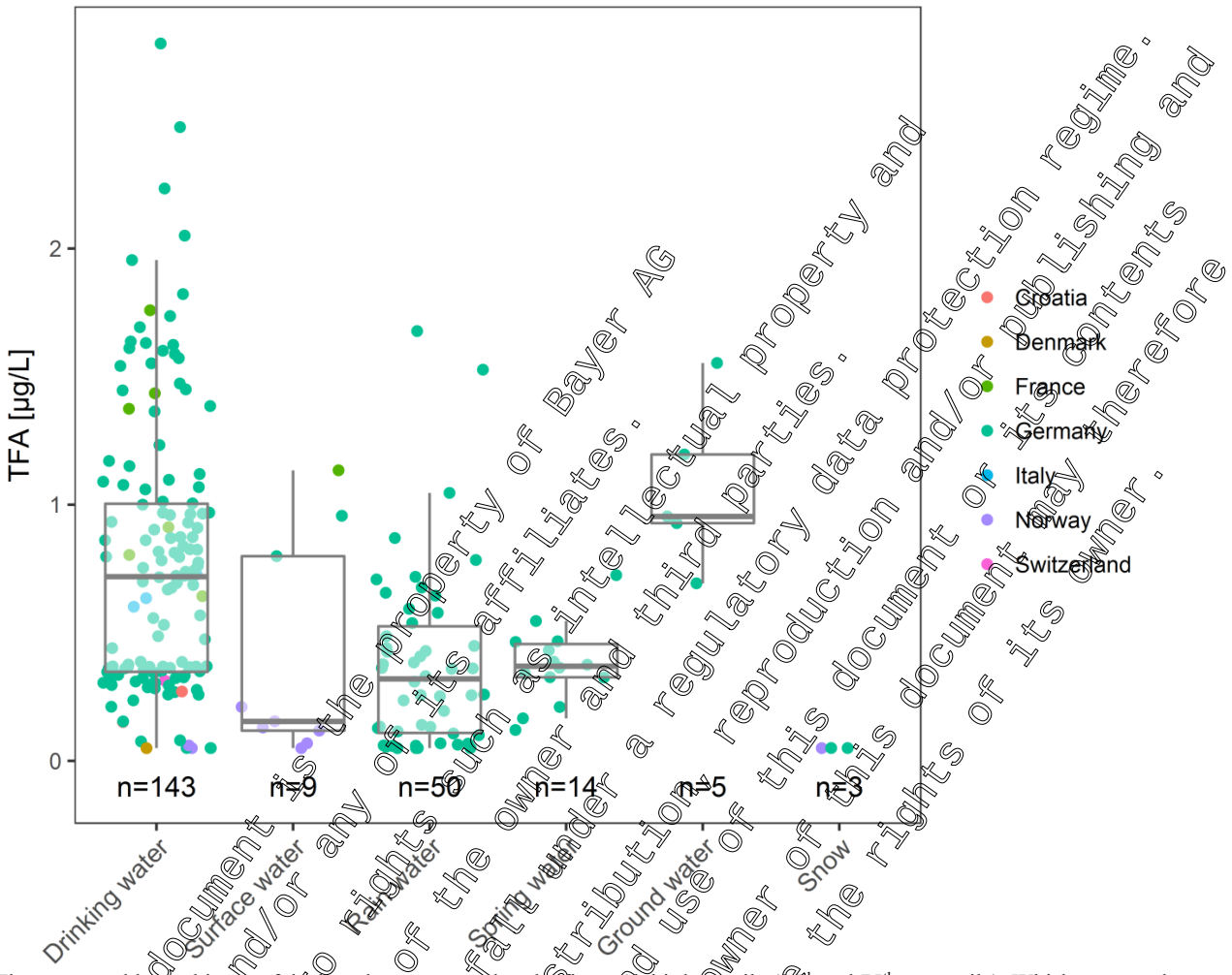
Spring water samples (n = 14) from the Black Forest, the Palatine Forest and the Taunus were collected from springs in remote places without influence of agricultural activities. The sampled spring "Rhumequelle" near Rhumspringe located in the south-eastern part of Lower Saxony is a karst spring, which consists of a ca. 7 m to 8 m deep bowl (approximate area 500 m^2), receiving most of its water from seepage of the rivers Sieber and Oder, two rivers draining part of the Harz mountains and accompanying regions.

TFA was present in all samples. The highest concentration was 0.725 µg/L from a location in the Taunus and the lowest concentration was 0.121 µg/L from a spring in the Black Forest. The concentrations of TFA from Rhumspringe are well within the range of the other samples.

Groundwater, Germany

Five samples were taken between May 2017 and October 2017 from a private well in Steinheim (Lower Saxony). TFA was present in all 5 samples with a range between 0.693 µg/L to 1.553 µg/L.

Figure 7.5-4 illustrates the overview of TFA concentrations in Europe for samples taken in the second phase (2016 – 2017).



The upper and lower hinges of the boxplot correspond to the first and third quartile (25th and 75th percentile). Whiskers extend from the highest value to the lowest value within 1.5 times the interquartile range. Additionally, each data point is shown according to the country the sample was taken in. Contents < LOQ (0.05 µg/L) are displayed as 0.05 µg/L.

Figure 7.5- 4: Overview of TFA concentrations in Europe for samples taken in the second phase (2016-2017)

III. CONCLUSIONS

TFA was detectable in almost all sampled water sources. However, while TFA could be detected in almost all drinking water samples, the concentration seldom exceeded 2.0 µg/L and only once 3.0 µg/L.

3. Assessment and conclusion

Assessment and conclusion by applicant:

Assessment:

The study was not conducted to GLP, and although sampling locations are given, the sampling methodology was not reported (however, TFA is known to be very stable in the aqueous phase, non-adsorptive and not influenced by temperature); therefore, sample contamination cannot be entirely excluded. These issues notwithstanding, the reported data appears representative and informative. There are currently no guidelines for the conduct of monitoring studies.

Conclusion

The data presented strongly suggest that TFA is ubiquitous in water, as it was detectable in almost all sampled water sources. Further, no conclusions could be reached concerning the source of the detected TFA. However, whilst TFA could be detected in almost all drinking water samples, the concentrations never exceeded 4.0 µg/L, which is below the scientifically arbitrary threshold of concern of 10 µg/L for non-relevant pesticide metabolites. This study is considered valid and reliable.

Assessment and conclusion by RMS: Outcome and conclusion of the study: RMS should indicate if they agree to the results and conclusions of the APPL.

1. Information on the study

Data Point:	KCA 7.5/06
Report Author:	[redacted]
Report Year:	2021
Report Title:	Trifluoroacetic acid (TFA): Public environmental monitoring data (groundwater, surface water, drinking water, soil, air and sediment)
Report No:	EnSa-21-0002
Document No:	M-760706-02-1
Guideline(s) followed in study:	None
Deviations from current test guideline:	Current Guideline: not applicable
Previous evaluation:	No, not previously submitted
GLP/Officially recognised testing facilities:	No, not conducted under GLP/Officially recognised testing facilities
Acceptability/Reliability:	Yes

2. Full summary of KCA 7.5/06

Executive Summary

Searches for public monitoring data were performed to provide an overview of residue concentrations of trifluoroacetic acid (TFA) in the environmental compartments of groundwater, surface water, drinking water, soil, air and sediment. The search was predominantly based on internet sources identifying databases and reports which are publicly accessible e.g. from the Environmental Agencies of European Countries. The data search was conducted with “trifluoroacetic acid” and “TFA” as key words. This also covered national spellings or translations of the analyte. If applicable, the time period for which monitoring results were searched for was from 1995 to November 2020. Where monitoring data was found, this was analysed for exceedance of key thresholds appropriate for the compartment and the results summarised. The search revealed that monitoring information is not generally publicly available in all European countries and not necessarily available at a national level, while in some cases being available at federal state/region/province level.

In terms of concentration thresholds, this report facilitates analysis within the context of the Water Framework Directive (2000/60/EC) and the associated Groundwater Directive (2006/118/EC), the Drinking Water Directive (1998/83/EC) and the Plant Protection Products Directive (1107/2009/EC). Key Regulatory Acceptable Concentrations (RACs) for TFA are considered for surface water. In the framework of the guidance document for the assessment of the relevance of metabolites in groundwater within the EU (Sanco/221/2000 rev. 10 Feb 2003), which remains the currently valid guidance document

today, TFA was classified as a non-relevant metabolite. For the purposes of this report, although there is no scientific basis behind it, the 10 µg/L value has been chosen as an arbitrary threshold value to categorise groundwater monitoring findings of TFA.

A small amount of monitoring data for TFA was found in databases (and reports) from Austria and Germany. The groundwater monitoring data search (32 analyses in total) resulted in a compliance rate of 100% with the selected arbitrary threshold applied (10 µg/L), with a maximum concentration of 4.4 µg/L. The surface water monitoring data search (417 analyses in total) resulted in a compliance rate of 100% with the Tier 1-RAC-SW of 120 µg/L, with a maximum concentration of 17 µg/L. It cannot be discounted that some of the detections identified in groundwater and surface water are erroneous given they arise from non-GLP monitoring networks and programmes of unknown quality. It should also be noted that TFA is a common metabolite that may originate from other parent pesticides, but also originates from other chemicals/uses. It is thus impossible to determine the source of the TFA detected in public monitoring programmes.

TFA monitoring data was not found for drinking water, soil, air and sediment.

Overall, it can be concluded from the assessment of readily available public monitoring datasets that TFA does not pose a concern for the investigated environmental compartments where data was available.

I. MATERIAL AND METHODS

Material

Trifluoroacetic acid (TFA) is a common metabolite of a range of chemicals including hydrofluorocarbons used as refrigerants, pharmaceuticals, pesticides and polymers. Therefore, it would be difficult, if not impossible, to determine the source of the TFA detected in public monitoring programmes.

Analytical Method

The search was based predominantly on internet searches identifying databases and reports which are publicly accessible e.g. from the Environmental Agencies of European countries. In the guidance document for the assessment of the relevance of metabolites in groundwater within the EU (Sanco/221/2000 rev. 10 Feb 2003), a limit value and as such a concentration threshold of 10 µg/L was selected for pragmatic reasons. For the purposes of this report, although there is no scientific basis behind it, the 10 µg/L value has been chosen as a threshold value to categorise groundwater monitoring findings of TFA.

Searches were performed using a list of databases or national information portals. TFA was the subject of this overview of monitoring results. The search was conducted with “trifluoroacetic acid” and “TFA” as key words. This also covered national spellings or translations of the analyte.

If applicable, the time period for which monitoring results were searched for was from 1995 to November 2020. Where monitoring data was found, this was analysed for exceedance of key thresholds appropriate for the compartment and the results were summarised.

The search revealed that monitoring information is not generally publicly available and not necessarily available at a national level, in some cases only being available for some states/regions/provinces. This applies, for example, to Germany and its Federal States.

Public monitoring databases and associated monitoring reports were investigated for several countries covering groundwater and/or surface water and to a lesser extent drinking water, soil, sediment and air. The information in the databases and/or reports was collated and/or evaluated for the European country’s agency/organisation on the search list. An overview of the monitoring situation is presented in Table 7.5-

16. Several more countries were examined regarding monitoring data, however as they either did not report any relevant public monitoring data or no monitoring program was established, they are not discussed further.

Table 7.5- 16: Searching results for Austria, Czech Republic, Denmark, France, Germany, Greece, Ireland, Italy, the Netherlands, Portugal, Romania, Slovenia, Spain, Sweden, Switzerland, United Kingdom and also including 'supra national' i.e. EU or river basin data sources

Country	Data Source/Organisation	Monitoring Data available [Yes/No]
Europe	NORMAN - EMPODAT Database	No monitoring data reported[1]
	Danube River Basin Water Quality Database	No monitoring data reported[1]
	European Environment Agency – Status and quality of Europe's water database (Waterbase)	Please see comment below[2]
Austria	Austrian Federal Ministry for Sustainability and Tourism – H_2O Water Database	Yes
	Austrian Federal Environment Agency and Ministry for Sustainability and Tourism – Several reports	No monitoring data reported[1]
Czech Republic	IS Arrow – Assessment and Reference of water monitoring	No monitoring data reported[1]
Denmark	Geological Survey of Denmark and Greenland – Groundwater database (Jupiter)	No monitoring data reported[1]
	"Danish Pesticide Leaching Assessment Programme"	No monitoring data reported[1]
France	ADES – National Groundwater Quality Portal	No monitoring data reported[1]
	Naiades – National Surface Water Quality Data Portal	No monitoring data reported[1]
	ATMO – National network of associations for the air quality	No monitoring data reported[1]
	CNEP –National pesticide monitoring plan in air	No monitoring data reported[1]
Germany	Sachsen Environment Agency – Surface water/Groundwater Quality Portal (IDA)	Yes
	Rheinland Pfalz - GeoPortal	No monitoring data reported[1]
	Rheinland Pfalz Environmental Agency – Annual reports on water quality monitoring	No monitoring data reported[1]
	Rheinland Pfalz Environmental Agency – Annual reports of stations for water investigation	No monitoring data reported[1]
	Baden-Württemberg State Institute for the Environment – Interactive data and map service (UDO)	No monitoring data reported[1]
	German Federal agency for hydrology – Rhine river basin community	No monitoring data reported[1]
	Elbe River Basin - Data information system	Yes
	LAWA - Working Group on water issues of the Federal States and the Federal Government	No monitoring data reported[1]
	Bavarian Environmental Agency – Environment atlas	Yes
	Schleswig-Holstein – Agency for Agriculture, Environment and Rural Areas	No monitoring data reported[1]

	Niedersachsen Water Management, Coastal Defence and Nature Conservation Agency – Report on TFA	Yes
	NRW Agency for Nature, Environment and Consumer Protection – ECHO report on TFA	Yes
Greece	Greek Ministry of Energy and climate Change – Report on quality of surface and groundwater of the country	No monitoring data reported[1]
Ireland	Irish Environmental Protection Agency – Annual reports on Water Quality in Ireland	No monitoring data reported[1]
Italy	Italian National Institute for Environmental Protection and Research (ISPRA) – Pesticide Portal and national and regional annual reports	No monitoring data reported[1]
Netherlands	Dutch Institute of Environmental Sciences - Atlas for pesticides in surface water	No monitoring data reported[1]
	Water Quality Data portal of the Netherlands	No monitoring data reported[1]
	Ground Water Quality Reports	No monitoring data reported[1]
	"Research on exposure of residents to pesticides in the Netherlands"	No monitoring data reported[1]
	Groundwater Atlas for Pesticides – pesticide model[3]	No monitoring data reported[1]
Portugal	Portuguese Environment Agency – Report on state of environment	No monitoring data reported[1]
Romania	Romanian National Administration "Apele Romane" Several reports	No monitoring data reported[1]
Slovenia	Slovenia Environment Agency – Several reports and raw data	No monitoring data reported[1]
Spain	Ríos hormonados Amplia presencia de plaguicidas disruptores endocrinos en los ríos españoles"	No monitoring data reported[1]
	Spanish Water framework Junta de Andalucía	No monitoring data reported[1]
	Hydrographic confederation of Ebro	No monitoring data reported[1]
	Hydrographic confederation of Guadalquivir	No monitoring data reported[1]
	Hydrographic confederation of Júcar	No monitoring data reported[1]
	Hydrographic confederation of Segura	No monitoring data reported[1]
	Basque Water agency	No monitoring data reported[1]
Sweden	Swedish University of Agricultural Sciences –Pesticide Database	No monitoring data reported[1]
	"Long-term Data from the Swedish National Environmental Monitoring Program of Pesticides in Surface Waters"	No monitoring data reported[1]
Switzerland	Swiss National Environment Agency – Several reports	No monitoring data reported[1]
	Regional Environment Agency of Canton Solothurn – Several raw data	No monitoring data reported[1]
United Kingdom	England Environment Agency - Water quality archive	No monitoring data reported[1]
	UK Water Quality Sampling Harmonised Monitoring	No monitoring data reported[1]
	Drinking Water Inspectorate of England and Wales – Chief Inspector Annual Reports and regional overviews	No monitoring data reported[1]

	Pesticide Monitoring Bulletin	No monitoring data reported[1]

[1]: A search was conducted in the monitoring dataset but no reference to TFA could be found in monitoring databases or reports.

[2]: A preliminary assessment of the EEA Waterbase database suggests it to be a very spatially and temporally limited subset of that collected directly from the regional/national environmental agencies in this study. In order to compare data sources and supplying organisations as an additional cross-check, the underlying reports describing the data contained in the EEA dataset were requested from the EEA. Unfortunately, this was not possible since "Details of the reports are not public available". Given these data collated by the EEA would replicate large parts of the dataset compiled in this study, thereby introducing spatial and temporal bias, they were not included in this assessment.

[3]: The data from this database is used only as indicative information here since the quality check from authorities is still on-going. The database will be "ready" for use in 2021.

II. RESULTS AND DISCUSSION

Trifluoroacetic acid (TFA) was quantified in the majority of the analyses (ca. 85.8% of the 449 analyses showed residue levels above the LOQ) in groundwater and surface water analyses retrievable from readily available public monitoring databases spanning 2017 – 2020 for Austria and Germany. Data showed a compliance rate of 100% with the selected threshold applied for groundwater (10 µg/L) and the key threshold applied for surface water (120 µg/L). No analyses in the other compartments were identified.

Soil

Monitoring data for TFA was not found for soil.

Groundwater

For TFA, a total of 32 groundwater analyses were investigated (see Table 7.5-17), of which 19 analyses quantified TFA (with residue levels at or above LOQ (0.2 to 0.5 µg/L, when stated)). A compliance rate of 100% with the selected threshold of 10 µg/L was found. The maximum groundwater concentration was reported as 4.4 µg/L (in Germany).

Table 7.5-17: Summary of public monitoring results for TFA in groundwater

Country	Data source/organisation	Monitoring period	Analyses	Quantification[1] (≥ LOQ)	≥ 10 µg/L	≥ 10 µg/L (%)
Austria	Federal Ministry for Sustainability and Tourism - H2O Water database	2018	6	5	0	0.0
Germany	Sachsen Environment Agency – Surface water/Groundwater Quality Portal (IDA) and report	2018 - 2019	19	7	0	0.0
	NRW Agency for Nature, Environment and Consumer Protection – ECHO report on TFA	2017	7	7	0	0.0

[1]: Quantifications represent the number of analyses with residue levels ≥ LOQ (neither "zero" nor "< LOQ"). The value of the LOQ depends on analytical method utilised and therefore is variable (LOQ values ranged from 0.2 to 0.5 µg/L and in some databases LOQ value was not specified).

Surface water

A total of 417 analyses of surface water were investigated (see Table 7.5- 18), of which 366 analyses quantified TFA (with residue levels at or above LOQ (0.05 to 0.5 µg/L, when stated)). A compliance rate of 100% with the Tier 1-RAC-SW of 120 µg/L was found. The maximum surface water concentration was reported as 17 µg/L (in Germany).

Table 7.5- 18: Summary of public monitoring results for TFA in surface water

Country	Data source/organisation	Monitoring period	Analyses	Quantification[1] (≥ LOQ)	≥ 120 µg/L[2]	≥ 120 µg/L (%)
Germany	Sachsen Enviroment Agency – Surface water/Groundwater Quality Portal (IDA) and report	2018 - 2020	210	160	0	0.0
	Elbe River Basin – Data information system	2017 - 2019	71	71	0	0.0
	Niedersachsen Water Management, Coastal Defence and Nature Conservation Agency – Report on TFA	2018	106	106	0	0.0
	NRW Agency for Nature, Environment adn Consumer Protection – ECHO report on TFA	2017	30	29	0	0.0

[1]: Quantifications represent the number of analyses with residue levels ≥ LOQ (neither "zero" nor "< LOQ"). The value of the LOQ depends on analytical method utilised and therefore is variable (LOQ values ranged from 0.2 to 0.5 µg/L and in some databases LOQ value was not specified).
[2]: RAC value for TFA

Drinking water

Monitoring data for TFA was not found for drinking water.

Air

Monitoring data for TFA was not found for air.

Sediment

Monitoring data for TFA was not found for sediment.

III. CONCLUSIONS

The TFA groundwater monitoring data search (32 analyses in total) resulted in a compliance rate of 100% with the selected threshold applied (10 µg/L), with a maximum concentration of 4.4 µg/L.

The TFA surface water monitoring data search (417 analyses in total) resulted in a compliance rate of 100% with the Tier 1-RAC-SW of 120 µg/L with a maximum concentration of 17 µg/L.

For groundwater and surface water, it cannot be discounted that some of the detections identified are erroneous given they arise from non-GLP monitoring networks and programmes of unknown quality. It should also be noted that TFA is a common metabolite that may originate from other parent pesticides, but also, more significantly, originates from other chemicals/uses. It is thus impossible to determine the source of the TFA detected in public monitoring programmes.

TFA monitoring data was not found for drinking water, soil, air and sediment.

Overall, it can be concluded from the assessment of readily available public monitoring datasets that TFA does not pose a concern for the investigated environmental compartments where data was available.

3. Assessment and conclusion

Assessment and conclusion by applicant:
Assessment:
This is a comprehensive overview of publicly available TFA monitoring data across the EU, covering an extended period of time (from 1995 to November 2020). However, it cannot be discounted that some of the detections identified are erroneous given they arise from non-GLP monitoring networks and programmes of unknown quality; and that there are currently no guidelines for the conduct of monitoring studies.

Conclusion:
TFA concentrations in groundwater and surface water did not reach the regulatory threshold in any reported publicly available monitoring data. Overall, it can be concluded from the assessment of readily available public monitoring datasets that TFA does not pose a concern for the investigated environmental compartments where data was available.
This review study is considered valid and reliable.

Assessment and conclusion by RMS:
Outcome and conclusion of the study: RMS should indicate if they agree to the results and conclusions of the APPL

1. Information on the published literature article

Data Point:	KCA 7.5/07
Report Author:	Berg, M.; Mueller, S. R.; Muehlemann, J.; Wenner, A.; Schwarzenbach, R. P.
Report Year:	2000
Report Title:	Concentrations and mass fluxes of chloroacetic acids and trifluoroacetic acid in rain and natural waters in Switzerland
Report No:	M-585148-01-1
Document No:	M-585148-01-1
Guideline(s) followed in study:	--
Deviations from current test guideline:	Current Guideline: not applicable
Previous evaluation:	No, not previously submitted
GLP/Officially recognised testing facilities:	not applicable
Acceptability/Reliability:	Yes

2. Full summary of KCA 7.5/07

Executive Summary
In this study, the occurrence and mass fluxes of monochloroacetic acid (MCA), dichloroacetic acid (DCA), and trichloroacetic acid (TCA), and trifluoroacetic acid (TFA) were assessed on a regional scale over Switzerland, based on more than 1000 concentration measurements in rain and snow, surface water, groundwater, and wastewater. Among different precipitation events, the measured concentrations of

TFA varied significantly from < 3 to 1550 ng/L. However, no statistically different average concentrations among six precipitation sampling sites located in various areas in Switzerland were observed (range of average TFA concentrations: 33 - 220 ng/L). The similar average concentrations in precipitation at a remote site close to the free troposphere at an elevation of 3580 m above sea level (Jungfraujoch) and at a site that receives precipitation which scavenged the Earth's boundary layer (urban site Dübendorf/Zürich) suggests that TFAs are derived from well-mixed precursor(s) in the atmosphere. Mass flux calculations show that precipitation is the dominant source of TFA (> 95%). The authors concluded that the results further indicate that TFA is quite persistent in the aquatic and terrestrial environment and may thus accumulate in soils and groundwater.

I. MATERIAL AND METHODS

Material

The occurrence, fate, and the mass fluxes of TFA were assessed simultaneously in the aquatic environment in Switzerland. The very diverse topography of Switzerland represented an ideal location to investigate both local point sources and diffuse input routes of TFA. Concentrations in precipitation at alpine sites situated close to the free troposphere could be compared with those determined in highly populated sites located in the Swiss Midland. Additionally, as there is no major input of water except by precipitation, and the export of water occurs predominantly (> 90%) by the two rivers Rhine and Rhone, mass fluxes can be calculated.

Sampling method

The sampling sites and their characteristics are described in Table 7.5- 19. In addition, four swimming pools and five industrial wastewaters were analysed. Entire precipitation events and time-resolved rain events were sampled 2 m above surface with polyethylene funnels of 0.05 m^2 and a large Teflon funnel of 5 m^2, respectively. The rain samplers were cleaned with tap water, dried with unbleached paper cloth, and covered with polyethylene foil until sampling. The samples were collected in borosilicate glass flasks. The Rhine water at Weil, the Rhone water at Chancy and the wastewater effluents were taken with flow-proportional samplers equipped with cooled sampling containers (4°C). Grab samples of river water, lake water, and moor water were collected directly with 100 mL polyethylene flasks 0.5 m below surface. Immediately after collection, all samples were conserved with 0.06% (w/v) NaN_3 and transported within less than 24 h to the laboratory. All samples were stored in 100-mL polyethylene flasks at 20°C until analysis.

Table 7.5- 19: Characteristics of the sampling sites in Switzerland

n			abbrev in Figure 1	altitude (m)	characteristics	av precipitation (mm/yr)
				Rain and Snow (7/96–6/97)		
33	Dübendorf		(a)	430	urban area, vicinity of Zürich	1170
8	Locarno		(b)	210	urban area	1930
6	Glarus		(c)	520	rural area	1500
6	Davos		(d)	1180	rural area, below Weissfluhjoch	1160
5	Weissfluhjoch		(e)	2690	alpine mountain, above Davos	2540
15	Jungfraujoch		(f)	3580	high alpine mountain, permanent snow	4150

n			abbrev in Figure 1	altitude (m)	characteristics	av water discharge (m^3/s)	av altitude of catchmt (m)	inhabitants[a] in catchmt (inh/(m^3/s))
					Rivers (5/96–6/97)			
4	Rhine 1	at Diepoldsau	1	410	alpine catchmt	230	1 800	1 380
8	Rhine 2	at Rekingen	2	320	Lake Konstanz in catchmt	440	1 260	5 570
21	Rhine 3	at Weil	3	240	Lake Konstanz in catchmt	1 000	1 100	6 470
4	Kl. Emme	at Littau	4	430	alpine catchmt	15	1 050	3 110
5	Aare	at Brugg	5	330	several lakes in catchmt	314	1 010	6 180
4	Thur	at Andelfingen	6	360	rural catchmt	9	770	1 140
4	Limmat	at Gebenstorf	7	330	Lake Zürich in catchmt	102	1130	8 260
4	Glatt	at Rheinsfelden	8	340	densely populated catchmt	7	498	39 870
4	Rhone 1	at Porte du Scex	9	380	alpine catchmt	172	2 130	1 600
13	Rhone 2	at Chancy	10	350	Lake Geneva in catchmt	326	1 580	4 360

n			abbrev in Figure 1	altitude (m)	characteristics	av water residence time (yr)	surface area (km^2)	inhabitants[b] in catchmt (inh/km^3)
					Midland Lakes[c] (5/97–6/97)			
6	Greifensee		A	440	eutrophic lake, 32 m deep	1.1	8.5	660 000
8	Murtensee		B	450	eutrophic lake, 46 m deep	1.6	22.8	138 000
6	Sempachersee		C	500	eutrophic lake, 87 m deep	15.0	14.4	19 000
					Mountain Lakes[d] (7/97)			
2	Tambo 1		D	2330	alpine glacier lake, 9 m deep	0.1–0.3[e]	0.01	0
2	Tambo 2		D	2360	alpine meteor water lake, 1 m deep	no outflow	<0.01	0
2	Jöri 1		E	2520	alpine lake, 21 m deep	0.1–0.4[e]	0.05	0
2	Jöri 2		E	2660	alpine lake, 6 m deep	0.05–0.1[e]	0.01	0
					Moor (6/97)			
3	Steinmoos	at Schanghau	F	930	pristine moor, alpine			0

n		abbrev in Figure 1[h]	altitude (m)	characteristics	industrial[g] ratio (%)	av sludge age (d)	inhabitants in catchmt (inh/km^3)
				Communal Wastewaters Effluents[f] (6/97–7/97)			
3	Pfungen		400	small rural district	0	27	10 000
3	Niederglatt		410	rural district	10	12	38 000
4	Uster		450	rural district with industry	40	8	65 000
3	Winterthur		400	urban district	15	15	140 000
4	Zürich		400	large urban district	30	9	415 000

[a] Water discharge proportional number of inhabitants in catchment area. [b] Lake volume proportional number of inhabitants in catchment area. [c] Samples were taken with a Niskin bottle at various depths at the deepest point of the lake. [d] Samples were taken from the shore. [e] Water residence time is strongly dependent on weather conditions. [f] No disinfecting agents are used in Switzerland for wastewater treatment. [g] Fraction of industrial wastewater treated in the plant. [h] Location not shown in Figure 1.

Precipitation and surface water samples from Norway, Russia (Siberia), and Vietnam were taken for comparative purposes. They were sampled in duplicate in 50-mL polyethylene flasks, preserved on-site with NaN_3, and stored at 4°C. Sample contamination during transport was monitored by transporting additional halogenated acetic acid (HAA) -free samples of very old groundwater (see Table 7.5- 20). Sample preparation was carried out in a secluded building where no HAAs were used. To avoid contamination by ambient air, the sample handling was carried out on a clean bench. HAAs present on the glassware surface were destroyed/removed by heating the equipment for at least 2 h to 200°C in an oven that was continuously purged with purified air. All samples were extracted and analysed in duplicate.

Analytical method

Water samples (10 mL aliquots) were added individually to a stoppered glass vial and spiked with 500 ng/L of internal standard 2,2-dichloropropionic acid (2,2-DCPA). The sample was shaken, acidified

and 2.0 mL of methyl *tert*-butyl ether (MTBE) were added. The analytes were extracted into the MTBE phase and the samples cooled until phase separation.

The extracted HAAs were derivatized and the HAA 1-(pentafluorophenyl) ethyl esters analysed by gas chromatograph and a mass spectrometer (GC/MS) system within 24 h or stored at -20°C if a delay of more than 1 day occurred. The GC/MS system, operated in the negative chemical ionization mode (NCI), was equipped with a deactivated fused silica precolumn and a DB capillary column. Helium was used as the carrier gas. For TFA mass trace, 113 (*m*/*z*) was monitored.

Calibration curves were obtained by extracting and analysing very old groundwater spiked with internal standard 2,2-DCPA and varying the TFA concentrations. For each calibration, a blank value was calculated and subtracted from the sample measurements.

LOD: The limit of determination (LOD) was 0.3 ng/L for TFA.

MDL: The method detection limit (MDL) range was 3 - 43 ng/L, average 11 ng/L. Changing the sensitivity and precision of the analysis caused different MDLs for different sample sequences. Therefore, MDLs for every sequence were determined.

Coefficient of determination: The calibrations were linear in the range of 0 - 2000 ng/L for TFA, with coefficient of determination of $r^2 \geq 0.994$.

Despite the tremendous precautions taken, contamination during sample preparation could not be completely avoided. Detailed investigations revealed that HAAs were present in ambient air, in sulfuric acid, and in MTBE. Undistilled MTBE used as received from the manufacturer was less contaminated than freshly distilled MTBE, indicating contamination during the reflux procedure and hence, undistilled MTBE from a new bottle was used for each series of analysis.

Drifting partial pressure of the reactant gas in the MS source caused unstable responses of the HAA ions. Better stability was obtained when the reactant gas valve was adjusted 24 h before analysis and measuring a standard and a blank after every 10th sample to monitor the drift. Additionally, obtained calibration points were used for linear sample to sample interpolation of the calibration curves. This enabled consistent measurements to be obtained for sequences of more than 100 samples.

H. RESULTS AND DISCUSSION

TFA concentrations

The results for the TFA concentration measurements in Switzerland are shown in Table 7.5- 20. Only in the 15,000-years old groundwater was the TFA value below the MDL (< 11 ng/L). In general, the concentrations observed in precipitation were higher than those detected in surface waters (i.e., midland lakes, rivers, and moor water). These results confirm that the atmosphere is an important source of TFA, and that precipitation is most likely the major transfer mechanism to the biosphere.

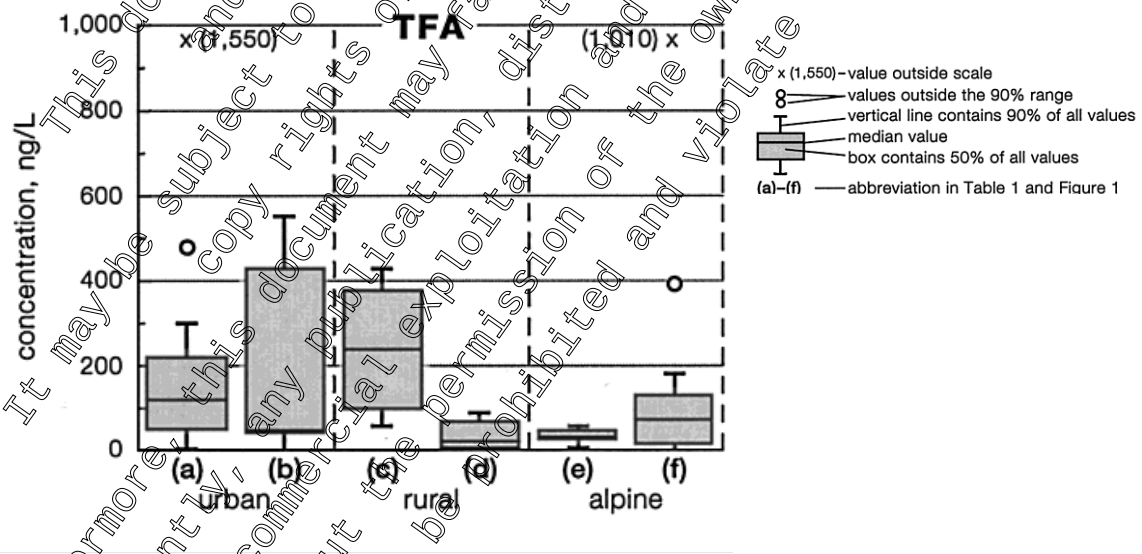
Table 7.5- 20: Average TFA concentrations measured in Switzerland (1996-1997)

Source		TFA concentration (ng/L)	
	n	**average**	**range**
	Natural waters		
Rain and snow	73	151	< 3 - 1550
Rivers	80	87	12 - 328
Midland lakes (Eutrophic; 400-500 m above sea level)	20	119	37 - 204
Mountain lakes (glacier; > 2300 m above sea level)	8	141	46 - 360
Moor water	3	107	59 - 175
Very old groundwater (ca. 15000 years)	3	< 5	
	Other waters		
Drinking water (from unchlorinated groundwater)	6	71	16 - 123
Swimming pools	4	4.8[1]	4.1 - 5.7[1]
Communal wastewater effluent	17	0.23[1]	0.09 - 0.60[1]
Industrial wastewater effluent	5	47.3[1]	< 0.1 - 206[1]

All concentrations are in ng/L unless marked with an ([1]), which indicates that the concentration is in µg/L.

Precipitation

Figure 7.5- 5 shows that, despite the very different geographic characteristics of the precipitation sampling sites and despite the broad concentration range in single precipitation samples, the average TFA concentration and their range in rain and snow did not differ by more than a factor of 2 - 3. No seasonal pattern of TFA concentrations in precipitation was observed during the 16-month study period.



The locations are described in Table 7.5- 19. They represent three categories of anthropogenic influence: urban area, rural area, and alpine region.

Figure 7.5- 5: Box plots of the precipitation concentrations measured in entire precipitation events at different sampling sites.

As shown in Table 7.5- 21, average TFA concentrations in small precipitation events of ≤ 3 mm were about a factor 2 higher than in larger events of > 3 mm, due to the washout dynamics of TFA, where the

initial TFA concentration measured in the first 0.05 mm precipitation of TFA decreased rapidly from 980 ng/L to 10 times lower during the first 2.4 mm precipitation.

Table 7.5- 21: Average TFA concentrations for precipitation events of ≤ 3.0 and > 3.0 mm

Precipitation amount	*n*	TFA (ng/L)
≤ 3.0 mm	29	220
> 3.0 mm	48	105

The similarity of average TFA concentrations and mass fluxes during the 16-month study period found at very different geographic and topographic locations suggest that TFA in precipitation is derived from long-lived and well-mixed precursor(s) in the atmosphere.

Midland Lakes, Rivers, and Wastewater Effluents

The concentrations of TFA surface waters (average of rivers and lakes) were 1.6 times lower than in precipitation. Grab samples from a chemical industry wastewater treatment plant contained 207 µg/L TFA, indicating that industrial wastewater plants can act as point sources.

Retention and/or Degradation of TFA in the Aquatic Environment

A significantly higher TFA concentration (360 ng/L) as compared to precipitation water was measured in the exclusively meteor water receiving mountain lake Tambo 2, which has no outflow. In contrast, only 100 ng/L TFA was found in the glacier lake Tambo 1 at 60 m distance to lake Tambo 2. This finding supports the postulated accumulation of TFA in evaporative aqueous systems with limited degradation and seepage.

TFA Mass Fluxes over Switzerland

The estimated TFA mass balance for Switzerland is based on the measured average concentrations in precipitation, wastewater (see Table 7.5- 20), and river water (Rhine 3 and Rhone 2; Table 7.5- 19). Calculations show that precipitation is the dominant source for TFA (230 g km^2/yr; 96%). The mass balance for TFA suggests an apparent elimination of about 60% in the catchment area. Considering the persistence of TFA in the environment, the author has postulated that this compound can accumulate particularly in the soil and groundwater environment.

Comparison with Other Measurements in the Northern Hemisphere

Table 7.5- 22 summarizes TFA concentrations measured in precipitation and seawater in Norway and Vietnam, and in precipitation and surface waters in Siberia. The similar concentration range in precipitation in Switzerland, Norway, Siberia, and Vietnam supports the hypothesis that the precursors and/or TFA are widely distributed in the atmosphere of the Northern Hemisphere.

Table 7.5- 22: Occurrence of TFA in other regions of the Northern hemisphere and comparison with the average concentrations determined in Switzerland in 1996-1997

Source	Location	Sampling dates	*n*	TFA (ng/L)
Rain and snow	Baikal, Siberia	6/96, 12/96	6	30 - 215
	Hanoi, Vietnam	8/96	4	4 - 150
	Switzerland, average	5/96 - 7/97	73	151
Rivers	Baikal, Siberia	6/96, 7/97	8	19 - 115
	Switzerland, average	5/96-7/97	80	87
Lakes	Baikal, Siberia[1]	6/96	6	12 - 35
	Tometrask, Norway	7/96	1	47
	Switzerland, average	6/96-7/97	20	119
Sea water	Haiphong, Vietnam	7/96,	2	53/66
	Lofotes, Norway	7/96	2	64/65

[1]: Samples were taken from the epilimnion and the hypolimnion in the north, the middle and the south basin of Lake Baikal.

III. CONCLUSIONS

The TFA concentrations observed in precipitation were 1.6 times higher than those detected in surface waters. These results confirm that the atmosphere is an important source of TFA and that precipitation is most likely the major transfer mechanism to the biosphere. The similarity of average concentrations and mass fluxes during the 16-month study period suggest that TFA in precipitation is derived from long-lived and well-mixed precursor(s) in the atmosphere. Grab samples from a chemical industry wastewater treatment plant indicated that industrial wastewater plants can act as point sources.

Mass flux calculations show that precipitation is the dominant source of TFA (> 95%). The results further indicate that TFA is quite persistent in the aquatic and terrestrial environment.

3. Assessment and conclusion

Assessment and conclusion by applicant:

Assessment:

This article from public literature reports monitoring results for TFA in precipitation, snow, rivers, lakes, old groundwater, drinking water, swimming pools and wastewater effluent in Switzerland 1996-1997, including details of the analytical work. Sampling methodology was well reported (including LOD, MDL, coefficient of determination and the precautions taken to avoid TFA contamination). However, the work wasn't carried out according to GLP, and there are currently no guidelines for the conduct of monitoring studies.

Conclusion:

The TFA concentrations in precipitation were 1.6 times higher than those detected in surface waters, confirming that the atmosphere is an important source of TFA and that precipitation is most likely the major transfer mechanism to the biosphere. The similarity of average concentrations and mass fluxes suggest that TFA in precipitation is derived from long-lived and well-mixed precursor(s) in the atmosphere.

The information of this publication is regarded as supportive information.

Assessment and conclusion by RMS:

Outcome and conclusion of the study: RMS should indicate if they agree to the results and conclusions of the APPL.

1. Information on the published literature article

Data Point:	KCA 7.5/08
Report Author:	Von Sydow, L. M.; Grimvall, A. B.; Boren, H. B.; Laniewski, K.; Nielsen, A. T.
Report Year:	2000
Report Title:	Natural background levels of trifluoroacetate in rain and snow
Report No:	M-604966-01-1
Document No:	M-604966-01-1
Guideline(s) followed in study:	--
Deviations from current test guideline:	Current Guideline: not applicable
Previous evaluation:	No, not previously submitted
GLP/Officially recognised testing facilities:	not applicable
Acceptability/Reliability:	Yes

2. Full summary of KCA 7.5/08

Executive Summary

It has been shown that some of the fluorinated ethane derivatives being introduced as CFC-replacements can be transformed to TFA (trifluoroacetate) in the atmosphere. TFA is extremely stable in the environment, and this has raised questions regarding how widespread TFA is in the environment. TFA was found to be ubiquitous in precipitation: samples of rain from Ireland and Poland, snow from Canada, Sweden, New Zealand and East Antarctica contained 1 - 1100 ng/L, and a firn core drilled in Antarctica, contained concentrations of 3 - 56 ng/L, measured in layers formed during the 19th century. The pre-industrial presence of significant background concentrations of TFA were confirmed in historic precipitation samples from the analysis of firn.

1. MATERIAL AND METHODS

Material

The objectives of this study were (i) to investigate the presence of TFA in precipitation collected at remote sites and (ii) to test the hypothesis that natural sources play a significant role in the current background levels. With this end in view, gas chromatography with mass spectrometric detection (GC-MS) was employed to determine TFA levels in rain, snow, and glacier ice and in different segments of a 20 m firn core drilled in East Antarctica.

Sampling method

Samples of snow and rain were collected in several remote areas (East Antarctica, northern Canada, northern Sweden, western Ireland and central Poland). Snow was sampled by pressing 2 L polyethylene bottles horizontally through snowpacks just below the surface layer. Rainwater was collected using a funnel-shaped stainless-steel sampler (surface area 3 m^2) that was emptied within 24 h after each rain event. Glacier ice was taken from the subpolar Mårmaglaciären in northern Sweden. Ice and snow closest to the surface of the glacier (1.5 m snow; 20 cm ice) was removed and large blocks of solid ice (5 - 27 L) were cut out using a chain saw.

Samples of firn were derived from 40 cm lengths of a 20 m core that was drilled during the 1996-1997 Norwegian Antarctic Research Expedition (NARE). The 10- to 40-cm-long core segments were packed in polyethylene bags. Three of the segments were further protected from contamination during transport and storage by putting the plastic bags in stainless steel cylinders made airtight with a copper gasket.

All samples were transported and stored frozen (-20°C) pending analysis. To reduce the risk of sample contamination, a handsaw was used to remove the outer 5 cm of the glacier ice prior to chemical analysis. Likewise, a 50-mm inner core was acquired from the original 75-mm firn core by using a specially designed device made of Teflon and stainless steel.

The age of the sampled firn was calculated from measurements made on a core drilled next to the core analysed in the present study. Information about the depth of the layer dating from 1954 to 1955 was obtained from records of β-activity, and electrical conductivity measurements (ECM) were used to reveal firn layers formed after major volcanic eruptions. The deepest part of the firn core (20.2 m) was estimated to represent snow that accumulated about 190 years ago. Glacier ice was sampled where clearly visible annual growth layers enabled identification of sections of ice that had been formed at least 500 years ago.

Analytical method

The volumes of the analysed samples of rain, melted snow and ice varied from 200 to 1000 mL. The individual samples were treated as follows: an internal standard (2,2-dichloropropionic acid) was added, and the sample evaporated in a rotary evaporator. To avoid loss of TFA during the final phase of evaporation, the concentrated sample was transferred to a smaller flask and phosphate buffer (pH 5.9) added to control the pH. Toluene and the derivatizing agent 1-(2,3,4,5,6-pentafluorophenyl) diazoethane were then added. A final hexane extract was analysed on a GC equipped with a mass spectrometer in the selected ion monitoring (SIM) mode. The 69, 195, 308 TFA related ions were monitored. Gas chromatographic conditions: HP-5 column (30 m x 0.25 mm, phase thickness 0.25 µm); carrier gas helium, flow rate 39 cm/s; pulsed split-less injection (1 min), 1 µL injected manually; injector temperature 250°C; temperature program 30°C (5 min), 5°C /min, 105°C; transfer line temperature 280°C.

Calibration functions were established by analysing a total of twelve 10 mL samples of Milli-Q water spiked with 0, 100, 200, or 300 ng of TFA.

LOD: The limit of detection (LOD) was 1 ng/L for TFA.

Blank levels: were always < 1 ng/L of TFA.

Linearity: The response was found to be almost linear over the concentration range; $R^2 = 0.96$.

II. RESULTS AND DISCUSSION

TFA concentrations

The results of the GC-MS analyses show that the analytical procedure employed was adequate to determine TFA in precipitation collected at remote sites. The low and stable blank level (<1 ng/L) showed that aqueous samples could be handled without being contaminated. Hence, there was no doubt that the analysed samples of rain, snow, and firn did contain TFA upon arrival at the laboratory.

Contamination during conveyance from the sampling site to the laboratory was ruled out for Antarctic firn samples that were transported in airtight metal tubes. Samples moved and stored at low temperature (-20°C) in pretested polyethylene bottles were also well protected against contamination. In addition, the GC analyses did not reveal any significant differences between firn samples stored in airtight tubes and polyethylene bottles.

GC/MS/SIM analysis allowed detection of the 1-(pentafluorophenyl) ethyl ester of TFA at concentrations as low as 1 ng/L.

TFA was present in all of the firn samples from Antarctica; concentrations ranged from 6 to 56 ng/L, with an average of 25 ng/L. There was no obvious relationship between concentration and depth in the firn core.

The snow samples collected in the Northern and Southern Hemispheres varied markedly in regard to TFA levels (Table 7.5- 23). The mean concentration of TFA in snow from Sweden and Canada was 10 ng/L and the corresponding value for Antarctica was 40 ng/L. In addition, TFA was detected at a concentration of 5 ng/L in glacier ice from a semipolar glacier in northern Sweden.

Table 7.5- 23: Concentrations of TFA in 12 samples of snow accumulated during the past winter and in a sample of old glacier ice from Mårmaglaciären in Northern Sweden

Sampling area	Latitude and longitude	Sampling period	TFA (ng/L)
Östergötland, Sweden	58°00'N 15°31'E	Feb 1997	9
			18
			9
Resolute Bay, Canada	74°41'N 95°54'W	Mar 1996	32
			2
			4
			1
Tod Mountain, BC, Canada	49°16'N 123°07'W	Nov 1994	4
Mt. Cook, New Zealand	43°35'N 170°15'E	Oct 1995	2
Dronning Maud Land, Antarctica	72°01'S - 75°30'S 02°40'W - 11°48'W	Nov 1995 – Mar 1996	1
			9
			110
Mårmaglaciären	69°10'N 18°40'E	Jan 1996	5

The concentrations of TFA in individual rainfalls varied markedly (Table 7.5- 24). At Mace Head, on the west coast of Ireland, TFA levels ranged from 2 to 92 ng/L. While rain collected in the city of Gdansk, Poland, contained up to 1100 ng/L of TFA, thus indicating the presence of a local source.

Table 7.5- 24: Concentrations of TFA in rain from individual rainfalls

Sampling area	Latitude and longitude	Sampling period	TFA (ng/L)
Mace Head, Ireland	53°16'N 9°03'W	Feb-Mar 1996	3
			58
			92
			62
			17
			2
			7
			13
Gdansk, Poland	54°22'N 18°35'E	May 1996	50
			26
			96
			1100

III. CONCLUSIONS

TFA is ubiquitous in precipitation even at very remote sites and natural sources play an important role in the global distribution of TFA.

3. Assessment and conclusion

Assessment and conclusion by applicant:
Assessment:
This article from public literature reports monitoring results for TFA in rain, melted snow and ice, including analytical work. Sampling methodology was well reported and included some performance criteria (e.g. LOD, blanks and linearity), but the work wasn't carried out according to GLP. However, generally the methodology appears to be robust. There are currently no guidelines for the conduct of monitoring studies.

Conclusion:
Samples of rain from Ireland and Poland, snow from Canada, Sweden, New Zealand and East Antarctica contained 1 - 1100 ng/L of TFA. The pre-industrial presence of significant background concentrations (3 - 56 ng/L) of TFA were confirmed in historic precipitation samples from the analysis of firn.
The information of this publication is regarded as supportive information.

Assessment and conclusion by RMS:
Outcome and conclusion of the study: RMS should indicate if they agree to the results and conclusions of the APPL.

1. Information on the published literature article

Data Point:	KCA 7.5/09
Report Author:	Roemppp, A.; Klemm, O.; Fricke, W.; Frank, H.
Report Year:	2001
Report Title:	Haloacetates in fog and rain
Report No:	M-604968-01-1
Document No:	M-604969-01-1
Guideline(s) followed in study:	--
Deviations from current test guideline:	Current Guideline; not applicable
Previous evaluation:	No, not previously submitted
GLP/Officially recognised testing facilities:	not applicable
Acceptability/Reliability:	Yes

2. Full summary of KCA 7.5/09

Executive Summary
Atmospheric haloacetates can arise from photochemical degradation of halogenated hydrocarbons and from direct anthropogenic emissions. There is also evidence of natural sources although these are quantitatively uncertain. As haloacetates are highly soluble in water, hydrometeors are most significant for their deposition. Fogwater (96 samples) and rainwater samples (over 100 samples) were collected from July 1998 to March 1999 at an ecological research site in northeastern Bavaria, Germany. They were analysed for monofluoroacetate (MFA), difluoroacetate (DFA), trifluoroacetate (TFA), monochloroacetate (MCA), dichloroacetate (DCA), trichloroacetate (TCA), monobromoacetate (MBA), dibromoacetate (DBA) and major inorganic ions. Concentrations of up to 2 µg/L TFA were

found in fogwater associated with westerly winds and showed higher average concentrations in fog than in rain.

I. MATERIAL AND METHODS

Material

The present study was undertaken (i) to gain insight into the anthropogenic or natural origin of the major haloacetates including TFA and (ii) to estimate the significance of fog and/or rain for the total deposition of these compounds.

Sampling method

Fogwater and rain samples were collected at an ecological research site located in a spruce forest in northeast Bavaria at an elevation of 776 m asl (altitude above sealevel). Fogwater collectors were installed on a meteorological tower 24 m above ground and triggered automatically by means of a visibility detector. At this site, fog most often represented clouds advected from the west crossing France and Western Germany with their highly diverse land-use patterns of agricultural areas, industrial regions, and forest patches. Fogwater samples were collected during each fog event (defined as visibility being less than 500 m) between July 1998 and March 1999, lasting 1270 h in total. Precipitation of 855 mm in the form of rain and snow was registered during this time. Ninety-six fogwater and over 100 rainwater samples were collected and stored frozen (-20°C) prior to analysis.

Analytical method

After addition of internal standards, the haloacetates were extracted with *tert*-butyl methyl ether, derivatized with 1-(pentafluorophenyl)diazoethane and determined by gas chromatography coupled to a mass spectrometer in the negative chemical ionization and selected ion monitoring (SIM) modes. The ion monitored for TFA was *m/z* 113.

The limits of detection and quantification was defined as 3- and 7-fold of the standard deviation above the respective analytical system blank values (deionized water). These were determined for each sample series separately due to high day-to-day variability.

Values of sampling system blanks (rinsing of the fog collectors with deionized water) were in the range of the analytical blank values. There was no TFA contamination from the Teflon parts of the fog collector.

Concentrations of sodium, potassium, magnesium, and calcium were determined by inductively coupled plasma atomic emission spectroscopy; those of ammonium, chloride, nitrate, and sulphate were determined by ion chromatography. Conductivity and pH of the samples were also determined.

The origin of the air masses associated with the fog events in October 1998 were analysed using 72-h backward trajectories for three different pressure levels (1000, 900, and 850 hPa) utilizing the European model of the German Weather Service. As sampling took place at an elevation of 800 m asl, the two lower trajectories (1000 and 900 hPa) were used for characterization of the origin of air masses.

II. RESULTS AND DISCUSSION

TFA concentrations in fogwater

The concentrations of TFA in fogwater are given in Table 7.5- 25. A total of 87 fogwater samples were collected with 76 of these collected during westerly winds. Figure 7.5- 6 shows the dependence of TFA on wind direction. Concentrations were higher in fogwater advectively transported by westerly winds (90th percentile concentration, 0.65 µg/L) compared to easterly winds (90th percentile concentration, 0.43 µg/L).

Table 7.5- 25: TFA concentration in fog

Haloacetate	Median concentration in fog (µg/L)	Min/max concentration (µg/L)	Number of samples detected above blank level
TFA	0.23	0.02/1.9	85

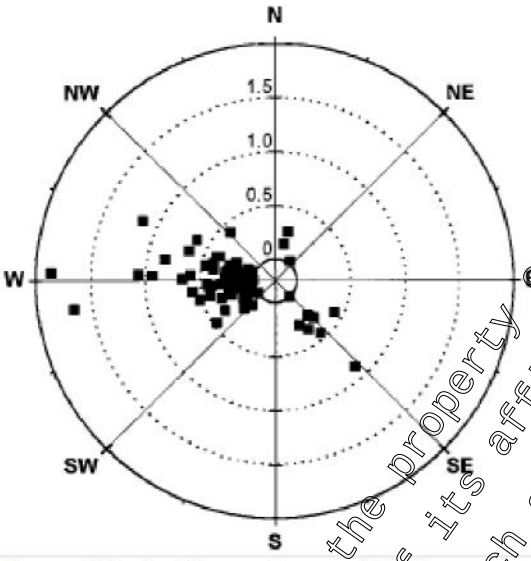


Figure 7.5- 6: Dependence of TFA concentrations (µg/L) on wind direction

The fog events of October 1998 were divided as being of "marine" or "nonmarine" nature according to their backward trajectories. Those which had been over the open sea (North Atlantic or North Sea) for more than one-fourth of the last 72 h before arrival at the research site were regarded as marine, although they had been influenced by different terrestrial sources on their way to the site. Marine tracers sodium and chloride, predominated in fog associated with marine air, while in nonmarine air masses the median concentrations of ammonium, nitrate, sulphate, and TFA were higher (Table 7.5- 26).

The fogwater samples in October 1998 were further analysed for correlation of TFA to inorganic electrolytes, as shown in Table 7.5- 27. Significance levels were calculated using the Spearman Rank Correlation test.

Table 7.5- 26: Concentrations of TFA in fogwater associated with marine and nonmarine air in October 1998

Substance	Marine			Nonmarine		
	Range (µg/L)	Median (µg/L)	Number of samples	Range (µg/L)	Median (µg/L)	Number of samples
TFA	0.02 -0.93	0.10	7	0.02 – 0.42	0.23	7
	Range (mg/L)	Median (mg/L)	Number of samples	Range (mg/L)	Median (mg/L)	Number of samples
Ammonium	0.3 - 33	2.5	7	0.5 - 13	6.5	7
Sodium	0.3 – 3.3	1.1	6	0.3 - 0.9	0.3	3
Chloride	0.7 - 4.8	2.3	6	0.6 -1.7	1.1	5
Nitrate	2.5 - 70	7.5	7	1.1 - 24	14	7
Sulphate	1.4 - 40	4.0	7	3.9-45	10	7

Table 7.5- 27: Results of correlation analysis of TFA and inorganic ions in fog water samples of October 1998

Halo-acetate	Na^+		Cl^-		SO_4^{-2}		NO_3^-		NH_4^+		Conductivity	
	P (%)	(n)	P (%)	(n)	P (%)	(n)	P (%)	(n)	P (%)	(n)	P (%)	(n)
TFA	ns	0	ns	17	99	23	99	23	99	40	99	22

ns: not significant

Concentrations of TFA in fog and rain are presented in Figure 7.5- 7. On average, TFA concentrations in fog were 6.6-fold those of rain (concentration ratios, min 0.6 – max 18). Only on three occasions (August 28, October 2, October 9) out of 14, did rain have similar levels to fog.

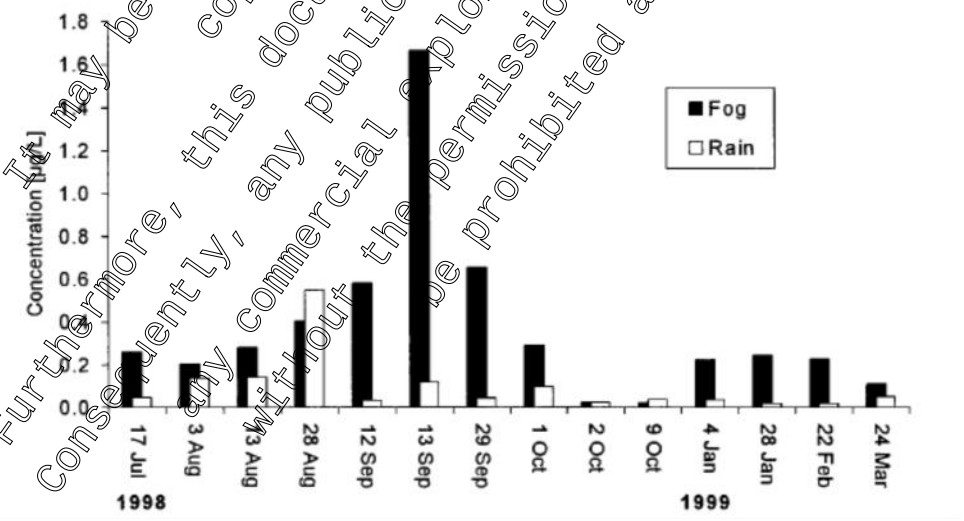


Figure 7.5- 7: TFA concentrations in fogwater and rain samples

TFA was found in all samples. Taking into account the results of the trajectory study and the correlation analysis, the air masses that had been influenced by marine sources show a pattern different to that of nonmarine air masses. The high concentrations of TFA in the nonmarine air masses as well as its significant correlation to nitrate and sulphate (which are closely associated with power plants, industrial facilities and motor vehicles) suggest that TFA or its precursors are of terrestrial and/or anthropogenic origin.

Concentrations of TFA were higher in fog than in rain. Deposition of fogwater has been estimated to account for 25-50% of the total atmospheric water input at the research site. Based upon the average rain and fogwater concentrations, fog is estimated to contribute between 70 - 90% of the total deposition of TFA This indicated that fog may be more important than rain for the input of this acid into forest ecosystems.

III. CONCLUSIONS

The higher concentrations of TFA in the nonmarine air masses as well as its significant correlation to nitrate and sulphate suggest that TFA or its precursors are of terrestrial and/or anthropogenic origin.

Deposition of fogwater has been estimated to account for 25 - 50% of the total atmospheric water input at the research site. Based upon the average rain and fogwater concentrations, fog is estimated to contribute between 70 - 90% of the total deposition of TFA. This indicated that fog may be more important than rain for the input of this acid into forest ecosystems.

3. Assessment and conclusion

Assessment and conclusion by applicant:

Assessment:

This article from public literature reports monitoring results for TFA in rain and fogwater from a spruce forest in northeast Bavaria, Germany at an elevation of 776 m asl, including details of the analytical work. Sampling methodology was well reported, but no performance characteristics of the analytical method (e.g. LOD and LOQ values, recoveries, linearity etc.) were reported, and the work wasn't carried out according to GLP. However generally the methodology appears to be robust. There are currently no guidelines for the conduct of monitoring studies.

Conclusion:

The high concentrations of TFA in the nonmarine air masses as well as its significant correlation to nitrate and sulphate suggest that TFA or its precursors are of terrestrial and/or anthropogenic (possibly industrial) origin. On average, TFA concentrations in fog were 6.6-fold those in rain samples, indicating that fog may be more important than rain for the input of this acid into forest ecosystems.

The information of this publication is regarded as supportive information.

Assessment and conclusion by RMS:

Outcome and conclusion of the study: RMS should indicate if they agree to the results and conclusions of the APPL.

1. Information on the published literature article

Data Point:	KCA 7.5/10
Report Author:	Frank, H.; Christoph, E.; Holm-Hansen, O.; Bullister, J. L.
Report Year:	2002
Report Title:	Trifluoroacetate in ocean waters
Report No:	M-455778-01-1
Document No:	M-455778-01-1
Guideline(s) followed in study:	--
Deviations from current test guideline:	Current Guideline: not applicable
Previous evaluation:	No, not previously submitted
GLP/Officially recognised testing facilities:	not applicable
Acceptability/Reliability:	Yes

2. Full summary of KCA 7.5/10

Executive Summary

Trifluoroacetate (TFA) is presently increasing in concentration in some environmental compartments, especially in the plant biomass of industrialised countries. Direct anthropogenic emissions of TFA are probably low, and the major anthropogenic sources are most likely various TFA precursors. As TFA has been found in ocean waters from remote locations, the question arose whether it is also a naturally occurring environmental chemical. Determination of the depth dependence of TFA in the ocean water column should shed some light on this question. However, in environmental analytical studies, the risk of systematic errors can be high and may lead to wrong conclusions. Therefore, special attention has been paid to the fact that TFA is a common atmospheric pollutant in the urban environment and that contributions from sampling, storage, and transport potentially lead to artificially high TFA values.

The results of the ocean water sampling campaigns indicate that TFA is a naturally occurring chemical, homogeneously distributed in ocean waters of all ages with a concentration of about 200 ng/L.

I. MATERIAL AND METHODS

Material

The aim of this study was the determination of TFA in ocean waters in order to estimate the global abundance of this environmental chemical and to assess whether today's levels are mainly of anthropogenic origin or whether biological and/or geological sources must be considered.

Sampling method

Ocean water samples were collected in the Southern Ocean near Elephant Island on January 19 and 25, 1998, at 60.6° S, 56.5° W; on January 23, 1999, at 60.5° S, 57.5° W; on January 26, 1999, at 60.25° S, 54.5° W; and in the Mid-Atlantic Ocean from Las Palmas de Gran Canaria (Canary Islands, Spain) to Miami (Florida) on January 29 and 30, 1998, at 24° N, 28° W.

During the 1998 sampling campaigns, the water samples were collected by Niskin samplers into new 500 mL brown soda-lime glass bottles previously washed with 1N NaOH, deionized water, $1NH_2SO_4$ and deionized water. The bottles were rinsed once with ocean water of the same sample, filled to leave an air volume of about 10 mL and closed with gastight polypropylene (PP) lined screw caps. Three samples were taken for each depth. During the 1999 sampling campaign, new (prewashed as above) cylindrical 500 mL PP bottles were used. Upon arrival at Bayreuth, all samples were stored at 4°C.

The samples were allowed to warm to room temperature. Three aliquots (10 mL) were transferred into 30 mL PP screw-cap vials, each aliquot was spiked with a heptafluorobutyric acid solution in deionized water leading to an in-sample concentration of 134 ng/L heptafluorobutyrate ($CF_3CF_2CF_2COO^-$). After addition of sodium chloride and acidification to pH 1, each sample was extracted with 1 mL of MTBE under agitation, and the ethereal phases transferred into silanized 1 mL crimp-cap vials and derivatized to their pentafluorophenylethyl esters.

Analytical method
An aliquot (1 µL) of the derivatized ethereal extract was injected onto a fused silica capillary (15 m × 0.25 mm) coated with 0.25 µm of methyl(95%)-phenyl(5%)-silicone installed in a gas chromatograph coupled to a mass spectrometer operated in the negative chemical ionization mode (NCI-MS). The mass spectrometer was tuned daily using perfluorotributylamine, optimizing on the fragment ions *m/z* 127, 195, 245, and 302. The ion selected for quantification of trifluoroacetate was *m/z* 113, relative to the ion *m/z* 213 of the internal standard heptafluorobutyrate. Identification of TFA was done by verification of retention times.

Calibration was performed using artificial seawater (ASW) prepared by dissolving pure salts in deionized water. Calibration was performed by spiking ASW with a solution of sodium trifluoroacetate in deionized water, leading to calibration concentrations ranging from 28 to 339 ng/L TFA, followed by sample preparation and GC/MS analysis.

Blanks obtained by analysing deionized water were different between different sample preparation periods in 1998 and 1999. During the last sample preparation period following the ocean water sampling in 1999, the blanks were between 2 and 13 ng/L. The mean value was 8 ng/L with a standard deviation of 4 ng/L (n = 6). The limit of detection was calculated as the sum of the mean blank and 3-fold of its standard deviation and the limit of quantification was the sum of the mean blank and 6-fold of its standard deviation.

LOD: The limit of determination (LOD) was 20 ng/L TFA.

LOQ: The limit of quantification (LOQ) was 32 ng/L TFA.

For the 1998 sampling period, ca. 400-years old mineral water (Kondrauer Mineralwasser, Kondrau, Germany) was used as the control forwarded together with the empty glass bottles to the sampling sites. At the time and location of sampling, the control water was poured into the Niskin sampling device, the sampler was slowly rotated for 15-20 min, and the water was then poured back into the original shipping bottle. In this fashion, any contamination during sample transfer, transport of the empty or filled bottles to the sampling site, and back to laboratory would have been detected. The TFA values obtained for the forwarded mineral water were 35 ± 4 ng/L (n = 3), for mineral water stored at the University of Bayreuth were 35 ± 5 ng/L (n = 3), for deionized water were 33 ± 3 ng/L (n = 3), and for ASW were 34 ± 1ng/L (n = 3). Thus, the differences between the various control samples were smaller than their standard deviations, indicating that there was no contamination during sampling, transport, and storage.

For the 1999 sampling period, 8 samples of 500 mL of ASW were forwarded (four in PP, four in glass) to the Antarctic in addition to the empty PP bottles. Controls were performed in parallel using PP and glass bottles in order to determine whether different materials gave rise to different TFA values. At each of the two sampling stations, water from 10, 50, 100, 200, and 750 m was drained directly from the Niskin sampler into the rinsed sample bottles. For testing with ASW samples, the Niskin bottles used for the 200 and 750 m samples were removed from the sampling device and rinsed with 250 mL of the ASW for 5 - 10 min, which was then discarded. Two other portions of ASW (500 mL each) were then poured into the two Niskin bottles, which were rotated slowly in a horizontal position, so that the entire inside surface was rinsed for 15-20 min. These control samples were then drained out of the Niskin bottle directly back into the same bottle (either glass or PP), the cap was tightly screwed on, and the

bottles returned with all other sample bottles. Two bottles were also stored and kept sealed in the laboratory. All these controls showed an average TFA level of 25 ± 8 ng/L (n = 24).

Statistical analyses (F-test: error probability α 5%) verified that for opened (forwarded) control samples there were only slight nonsignificant differences between those stored in glass or those stored in PP. Applying the student t-test, one control sample series showed a significant difference (α = 5%) between samples stored in PP and those stored in glass bottles. The slightly smaller control values in glass bottles may have been caused by adsorption of TFA on alkali glass surfaces as it has been found before with radioactively labelled TFA. However, the differences were not consistent and were minor as compared to the spread of actual TFA data.

The TFA contents in the forwarded control samples (both the refilled and the permanently sealed controls) showed insignificant differences to controls stored in the laboratory (student t-test: α = 5%). Also, there was only insignificant difference (α = 5%) between sealed and opened controls.

Determined TFA values (Table 7.5- 28 and Table 7.5- 29) are blank corrected (non-corrected data minus corresponding blank values). Propagated errors were calculated from the standard deviations of the actual analyses plus those of the corresponding blank values.

II. RESULTS AND DISCUSSION

TFA concentrations

TFA levels of ca. 200 ng/L have been determined in all water samples from the Mid-Atlantic Ocean (Table 7.5- 28) and the Southern Ocean (Table 7.5- 29), independent of depth. As there were doubts about the identity of TFA in ocean waters, meticulous assessments of potential sources of contaminations of controls as well as careful comparison of GC retention times and mass spectra under negative-chemical ionization were necessary.

Table 7.5- 28: TFA concentrations and CFC-12 age of Mid-Atlantic seawater samples

Depth (m)	TFA concentration ± SD (ng/L) (n = 6)	CFC-12 apparent age (yr)
0	190 ± 10	<5
40	210 ± 12	<5
120	205 ± 16	<5
380	210 ± 6	12
1000	205 ± 16	46
4000	195 ± 16	>60
4150	200 ± 16	>60

Collected in January 1998 in the Mid-Atlantic Ocean (24°N28° W). CFC-12 apparent ages were calculated using observed CFC-12 concentration in each seawater sample (details not given).

Table 7.5- 29: TFA concentrations in Southern Ocean water samples

Depth (m)	TFA concentration ± SD (ng/L)[1] *(n = 3)*	TFA concentration ± SD (ng/L)[2] *(n = 3)*
10	195 ± 22	210 ± 27
50	185 ± 10	220 ± 26
100	195 ± 8	205 ± 22
200	195 ± 6	170 ± 28
500	205 ± 10	
750	195 ± 12	190 ± 21
10	195 ± 6	165 ± 28
50	200 ± 12	205 ± 24
100	200 ± 6	205 ± 29
200		190 ± 19
500	200 ± 10	
750	200 ± 22	205 ± 18
1000	205 ± 6	
1500	220 ± 13	
2000	210 ± 6	

[1]: Collected at various depths north of Elephant Island at 60.6° S, 56.5° W (January 19 and 22, 1998).
[2]: Collected at various depths north of Elephant Island at 60.5° S, 57.5° W (January 23, 1999) and at 60.25S, 54.5° W (January 26, 1999).

Concentrations of CFC-11 and CFC-12 were also determined for the samples from the Mid-Atlantic. CFC-12 apparent ages (Table 7.5- 29) were calculated and were in good agreement with trends calculated on the basis of CFC-11 data. These provide estimates of the time scales over which subsurface waters have been isolated from contact with the atmosphere. In this region of the North-eastern Atlantic, the upper waters (0 – ca. 200 m) are rapidly ventilated on time scales of a few years or less. Water samples collected at 380 and 1000 m showed increasing apparent ages with depth. Below about 1700 m, the deep waters in this region of the eastern Atlantic are relatively isolated, and the water samples collected at abyssal depths (4000 and 4150 m) in this region of the eastern North Atlantic were essentially CFC-free and indicate minimal contact with the atmosphere for at least the time period during which CFCs have been present in the atmosphere (ca. 60 yr).

The sampling locations in the Southern Ocean were all in pelagic waters south of the Antarctic Polar Front. Water column CFC measurements were not performed at the time when the samples were collected. However, CFCs had been determined in this region during an expedition in 1985; high levels (CFC-11: 550 pg/L) had been found in the upper 200 m of the water column at that time due to exchange with the atmosphere on time scales of a few years. The CFC decreased to low levels (CFC-11, < 7 pg/L) in the deeper layers, indicating isolation from the atmosphere for at least several decades.

While the age tracer's CFC-11 and CFC-12 and the biologically active compounds oxygen, phosphate, silicate and nitrate all show strong vertical gradients, the TFA levels are virtually identical over the whole water column in the Mid-Atlantic and Antarctic waters, which implies significant pre-industrial TFA sources and slow in-situ removal processes on decadal or longer time scales.

The present evidence of homogeneous TFA levels in the Atlantic Ocean water samples taken together with previous analyses from other locations of the Atlantic and one of the Pacific, suggest that oceanic TFA levels could be worldwide at about 200 ng/L. Assuming an average oceanic concentration of TFA of 200 ng/L, the total amount of TFA in the oceans with a volume 1.34 x 10^{21} L would be 268 million ton. Thus, TFA is likely to be a natural ionic solute in ocean water, suggesting that continuous low level releases from geological or biological sources over a long period of time may have resulted in present day levels.

III. CONCLUSIONS

TFA is likely to be a natural ionic solute in ocean water, suggesting that continuous low level releases from geological or biological sources for a long period of time may have resulted in present day levels. The results of the ocean water sampling indicated that TFA is a naturally occurring chemical, homogeneously distributed in ocean waters of all ages with a concentration of about 200 ng/L.

3. Assessment and conclusion

Assessment and conclusion by applicant:

Assessment:

This article from public literature reports monitoring results for TFA in the Southern Ocean and in the Mid-Atlantic Ocean from 1998 to 1999, including details of the analytical work. Sampling methodology was well reported and blanks/controls were employed. However, the work wasn't carried out according to GLP, and there are currently no guidelines for the conduct of monitoring studies.

Conclusion:

The results of the ocean water sampling indicate that TFA is a naturally occurring chemical, homogeneously distributed in ocean waters of all ages with a concentration of about 200 ng/L.

The information of this publication is regarded as supportive information.

Assessment and conclusion by RMS:

Outcome and conclusion of the study: RMS should indicate if they agree to the results and conclusions of the APPL.

1. Information on the published literature article

Data Point:	KCA 7.5/11
Report Author:	Sulbaek Andersen, M.; Martin, J.; Ellis, D.; Wallington, T.; Hurley, M.; Mabury, S.
Report Year:	2004
Report Title:	Atmospheric Chemistry of Perfluorinated Carboxylic Acids: Reaction with OH Radicals and Atmospheric Lifetimes
Report No:	M-455782-01-1
Document No:	M-455782-01-1
Guideline(s) followed in study:	--
Deviations from current test guideline:	Current Guideline: not applicable
Previous evaluation:	No, not previously submitted
GLP/Officially recognised testing facilities:	not applicable
Acceptability/Reliability:	Yes

2. Full summary of KCA 7.5/11

Executive Summary

Relative rate techniques were used to study the kinetics of the reactions of OH radicals with a homologous series of perfluorinated acids, $F(CF_2)_nCOOH$ ($n = 1, 2, 3, 4$), in 700 Torr of air at 296 ± 2 K. For $n > 1$, the length of the $F(CF_2)_n$ group had no discernible impact on the reactivity of the molecule. For $n = 1$, $k(OH + F(CF_2)nCOOH) = (9.35 \pm 2.08) \times 10^{-14}/cm^3$ molecule/s. For $n = 2\text{-}4$, $k(OH + F(CF_2)_nCOOH = (1.69 \pm 0.22) \times 10^{-13}\ cm^3$/molecule/s. Dimerization constants for $2F(CF_2)_nCOOH = (F(CF_2)_nCOOH)_2$ were determined to be $0.32 \pm 0.03\ Torr^{-1}$, $0.30 \pm 0.03\ Torr^{-1}$, $0.41 \pm 0.04\ Torr^{-1}$, and $0.46 \pm 0.05\ Torr^{-1}$ for $n = 1, 2, 3, 4$, respectively. Atmospheric lifetimes of $F(CF_2)_nCOOH$ with respect to reaction with OH radicals are estimated to be approximately 230 days for $n = 1$ and 130 days for $n > 1$. Reaction with OH radicals is a minor atmospheric fate of $F(CF_2)_nCOOH$. The major atmospheric removal mechanism for $F(CF_2)_nCOOH$ is believed to be wet and dry deposition which probably occurs on a time scale of the order of 10 days.

I. MATERIAL AND METHODS

Materials

The environmental fate, disposition, and persistence of trifluoroacetic acid, the smallest of the perfluorinated carboxylic acids (PFCAs), has been the subject of numerous studies. The source of the large amounts of trifluoroacetic acid observed in the environment (particularly the oceans) is unknown. trifluoroacetic acid is a minor product emitted to the atmosphere from thermolysis of fluoropolymers, which is unlikely to make a significant contribution to the observed global burden of PFCAs.

To improve understanding of the atmospheric fate of PFCAs the authors conducted an experimental study of the kinetics of the reaction of OH with the first four members of the homologous series $F(CF_2)_nCOOH$. Atmospheric lifetimes with respect to reaction with OH are estimated and compared to the expected lifetimes with respect to removal via wet and dry deposition.

Analytical method

Experiments were performed in a 140 litre Pyrex reactor interfaced to a Mattson Sirus 100 FTIR spectrometer. The reactor was surrounded by 22 fluorescent blacklamps which were used to photochemically initiate the experiments. OH radicals were produced by the photolysis of CH_3ONO in the presence of NO in air.

Relative rate techniques were used to measure the rate constant relative to a reference reaction whose rate constant has been established previously.

The reference compounds were monitored by FTIR spectroscopy using an infrared path length of 27 m, and a resolution of $0.25\ cm^{-1}$. Infrared spectra were derived from 32 co-added interferograms. The acids are liquids and were introduced into the chamber by transferring the vapor above the liquid into a calibrated volume. The contents of the calibrated volume were swept into the chamber using air. The acid concentrations in the chamber were calculated using the measured pressures of their vapor in the calibrated volumes.

A variation of the relative rate technique was used in which the loss of the reactant was monitored indirectly by observing the formation of an oxidation product. The loss of the PFCA reactant can be calculated from the observed formation of its oxidation product, COF_2.

COF_2 is readily detected by its absorption features at 774 and 1850-2000 cm^{-1}. Reference compounds were monitored using absorption features over the following wave number ranges: C_2H_4, 850-1050 cm^{-1} and C_2H_2, 670-800 cm^{-1}. Initial concentrations of the gas mixtures for the relative rate experiments were 8-363 mTorr of $F(CF_2)_nCOOH$ ($n = 1, 2, 3, 4$), 2-10 mTorr of the reference compounds (C_2H_2 or C_2H_4),

100-232 mTorr of CH_3ONO, and 10-25 mTorr of NO in 700 Torr of air diluent. All experiments were performed at 296 K with reagents purities > 99%.

II. RESULTS AND DISCUSSION

Determination of the Gas-Phase Dimerization Constant for $F(CF2)_nCOOH$.
To correct for dimer formation in the calibrated volume, the dimerization constant was determined for the perfluorinated acids, $F(CF2)_nCOOH$ (n = 1, 2, 3, 4).

The dimerization constants were determined to be 0.32 ± 0.03 $Torr^{-1}$, 0.30 ± 0.03 $Torr^{-1}$, and 0.41 ± 0.04 $Torr^{-1}$ for FCF_2COOH, $F(CF_2)_2COOH$, and $F(CF_2)_3COOH$, respectively. These dimerization constants were used to account for dimer formation in the calibrated volume during the introduction of perfluorinated acids into the chamber. The vapour-phase dimerization constant for CF_3COOH at 298 K has been reported in previous studies to be Kd = 0.27 ± 0.02 $Torr^{-1}$, Kd = 0.30 ± 0.02 $Torr^{-1}$ and 0.45 $Torr^{-1}$.

Relative Rate Study of the Reaction of OH Radicals with CF_3COOH.
The reactivity of OH radicals towards CF_3COOH was studied relative to reactions 2 and 3.

$OH + CF_3COOH$	→ products	(1)
$OH + C_2H_2$	→ products	(2)
$OH + C_2H_4$	→ products	(3)

Linear least-squares fits to the data give values of $k1/k2$ = 0.103 ± 0.017 and $k1/k3$ = 0.0116 ± 0.0012. Using $k2 = 8.45 \times 10^{-13}$ and $k3 = 8.66 \times 10^{-12}$ values for $k1$ = (8.70 ± 1.44) × 10^{-14} and (1.00 ± 0.11) × 10^{-13} cm^3/molecule/s. Within the experimental uncertainties, consistent results were obtained in experiments conducted using two different reference compounds. The final value cited for $k1$ is the average of the two determinations together with error limits which encompass the extremes of the individual determinations. Hence, $k1 = (9.35 \pm 2.08) \times 10^{-14}$ cm^3/molecule/s.

Atmospheric Implications
The values of $k(OH + F(CF_2)_nCOOH)$ measured can be used to provide an estimate of the atmospheric lifetime of $F(CF_2)_nCOOH$ with respect to reaction with OH radicals. Assuming an atmospheric lifetime for CH_3CCl_3 with respect to reaction with OH radicals of 5.99 years and a rate constant for the CH_3CCl_3 + OH reaction of 1.0×10^{-14} cm^3/molecule/s leads to an estimate of the atmospheric lifetime of CF_3-COOH of $(1.0 \times 10^{-14}) / (9.35 \times 10^{-14}) \times 5.99 \times 365 \approx 230$ days. These atmospheric lifetime estimates are approximations.

The average daily concentration of OH radicals in the atmosphere varies significantly with both location and season. The estimates presented here are for the global average lifetime with respect to reaction with OH radicals. The atmospheric lifetime of perfluorinated acids depends not only on gas-phase reactivity, but also on the rate of wet and dry deposition. The key physical property controlling the deposition of perfluorinated acids is the Henry's Law Constant (KH), which has been determined for trifluoroacetic acid. A previous author concluded that trifluoroacetic acid would be removed from the atmosphere at a rate similar to HNO_3, which has a lifetime of 9 days with respect to wet deposition, and 10 - 30 days with respect to dry deposition (760 Torr = 101.3 kPa). Therefore, any gas-phase reactions of trifluoroacetic acid with OH radicals are of minor importance. Recent environmental field measurements of TFA suggest that wet and dry deposition are of approximately equal importance.

III. CONCLUSION

The reaction of trifluoroacetic acid with OH radicals occurs with a rate constant of (9.35 ± 2.08) × 10^{-14} cm^3/molecule/s and the atmospheric lifetime of trifluoroacetic acid with respect to reaction with

OH radicals in the gas phase is approximately 230 days. The major atmospheric loss mechanism is dry and wet (particle mediated) deposition which occur on a time scale which is probably of the order of 10 days. Reaction with OH is a minor atmospheric loss mechanism.

3. Assessment and conclusion

Assessment and conclusion by applicant:
Assessment:
The study does not report being conducted to GLP or other guidelines. However, the experimental methodology was fully reported. Results from this study are presented with reference to other similar studies and are often in line with those results. The reported data appears robust.

Conclusion
The data provide estimates for reaction rates of trifluoroacetic acid with OH radicals, as well as estimates of atmospheric lifetimes of trifluoroacetic acid. The work concludes that the major loss of trifluoroacetic acid from the atmosphere is through wet and dry deposition within ca. 10 days as opposed to reaction with OH radicals.

The information of this publication is regarded as supportive information.

Assessment and conclusion by RMS:
Outcome and conclusion of the study. RMS should indicate if they agree to the results and conclusions of the APPL.

1. Information on the published literature article

Data Point:	KCA 7.5/12
Report Author:	Solomon, K. R.; Velders, G. J. M.; Wilson, S. R.; Madronich, S.; Longstreth, J.; Aucamp, P. J.; Bornman, J. F.
Report Year:	2016
Report Title:	Sources, fates, toxicity , and risks of trifluoroacetic acid and its salts: Relevance to substances regulated under the Montreal and Kyoto Protocols
Report No:	M-603942-01-1
Document No:	M-603942-01-1
Guideline(s) followed in study:	--
Deviations from current test guideline:	Current Guideline: not applicable
Previous evaluation:	No, not previously submitted
GLP/Officially recognised testing facilities:	not applicable
Acceptability/Reliability:	Yes

2. Full summary of KCA 7.5/12

Executive Summary
Trifluoroacetic acid (TFA) is a breakdown product of several hydrochlorofluorocarbons (HCFC), regulated under the Montreal Protocol (MP), and hydrofluorocarbons (HFC) used mainly as refrigerants. TFA is (1) produced naturally and synthetically, (2) used in the chemical industry, and (3) a potential environmental breakdown product of a large number (> 1 million) chemicals, including pharmaceuticals, pesticides, and polymers. The contribution of these chemicals to global amounts of TFA is uncertain, in contrast to that from HCFC and HFC regulated under the MP. TFA salts are stable in the environment and accumulate in terminal sinks such as playas, salt lakes, and oceans, where the only process for loss of water is evaporation. Total contribution to existing amounts of TFA in the oceans as a result of the continued use of HCFCs, HFCs, and hydrofluoroolefines (HFOs) up to 2050 is estimated to be a small fraction (< 7.5%) of the approximately 0.2 µg acid equivalents/L estimated to be present at the start of the millennium.

I. MATERIAL AND METHODS

Material
The study tested a risk null-hypothesis that the total concentration of TFA from all sources in various environmental compartments was not greater than the no-observed-effect-concentration for the most sensitive representative species.

Sampling method
This is a review article. TFA has been addressed in several assessments by the United Nation Environmental Programme (UNEP) panels that advise the parties (countries) to the Montreal Protocol (MP). Scientific Assessment Panel, the Environmental Effects Assessment Panel (UNEP EEAP 1998, 2006, 2009, 2010, 2011, 2014) and the Technical Effects Assessment Panel (UNEP 2011) have included sections on TFA in their reports since 1998. This evaluation was an extension of what was noted in those assessments.

II. RESULTS AND DISCUSSION

Sources of TFA
There are a number of sources of TFA and TFA salts in the environment. Some of these are natural and others are anthropogenic. Concentrations of TFA salts in the ocean were detected and are in the range of 200 ng a.e./L. Even in remote locations, such as the Southern Oceans, the concentrations of TFA do not vary with depth. Sampling in various parts of the Arctic, Atlantic, and Pacific oceans for TFA salts revealed that levels in deep (> 1000 m) waters of the Atlantic were close to 160 ng/L. Based on radiocarbon dating (aging) with ^{14}C, the water at this depth was older than 1000 yr, suggesting significant natural sources of TFA salts in the oceans. Samples in the region of undersea hydrothermal vents revealed greater concentrations than surrounding water, suggesting that hydrothermal vents are one of these natural sources of TFA salts. Annual inputs of 6000 kg a. e. of TFA were estimated from a hydrothermal vent. The concentrations of TFA salts reported from contemporary samples of surface freshwaters, fog, and rain range from 20 ng a.e./L to hundreds of ng/L. This is greater than the levels of TFA salts in pre-industrial (>2000-yr-old) freshwater from Greenland and Denmark, levels that were below the level of detection (LOD) (2 ng a.e./L). What is clear from these data is that a large amount of the TFA salts in the ocean is from natural rather than human-made sources. However, salts of TFA in surface fresh waters are more likely of anthropogenic origins.

TFA is widely used in industry and production in the United States, and in 2002, was estimated at between 450 and 4500 tonnes (t) a.e. Whether and in what quantities TFA and its salts are released into the environment from industrial uses is highly uncertain.

Several of the hydrochlorofluorocarbons (HCFC) and hydrofluorocarbons (HFC) may degrade into TFA. These include halothane, isoflurane, HCFC 123, HCFC-124, HFC-134a, HFC-143a,

hydrofluoroolefin (HFO)-1234yf, and HFO-1234ze. The yield of TFA from each precursor molecule depends upon the specific molecule because of competition between several degradation pathways, of which, only some lead to TFA. Once formed in the atmosphere, TFA partitions almost entirely into fog and cloud water and is carried to the surface in precipitation. Two medical anaesthetics, halothane and isofurane, that degrade or are metabolized to produce TFA were included in the UNEP Review (UNEP EEAP 1998) and were estimated to produce approximately 800 tonnes TFA/yr. However, these two compounds are no longer in use and total historical volumes of production are not known. Data for the production of HFC-134a, HFC-143a, and HFC-227ea were estimated. Data on global production of HFO-1234yf for 2015 were not available, but projected production for North America was estimated to be from 50,000 to 100,000 tonnes/yr in the next 50–100 yr. HFO-1234yf is a replacement for HFC-134a, global production of which (without a ban) is projected to be 600,000 tonnes/yr in 2050. Thus, global production of HFO-1234yf might be expected to be of similar magnitude by 2050 if replacement is complete. For the purposes of this assessment, it was presumed that production of HFO-1234yf would begin in 2016 and increase to 100,000 tonnes/yr by 2050 for a total of about 3,255,000 tonnes. This is probably an underestimate, as HFO-1234yf is currently being introduced as a propellant for aerosol products. The atmospheric lifetime of HFO-1234yf is estimated at approximately 6 d and conversion to TFA is 1:1 on a molar basis. Two modeling studies on potential releases of TFA from HFO-1234yf in the European Union (EU) and United States predicted increased deposition of TFA in precipitation over Europe and North America. After complete conversion of the European vehicle fleet to HFO-1234yf, maximum concentrations in rainwater as large as 2500 ng/L were predicted over the Mediterranean and Northern Africa. The isomer of the refrigerant HFO-1234yf is HFO-1234ze. The oceans contain 1.357 billion km^3 of water. Assuming that the total yield of TFA just described formed in the atmosphere from 1990 to 2050 is transported to oceans as a terminal sink and then uniformly mixed, the added concentration in the ocean would be 15.3 ng a.e./L.

Although some longchain perfluorinated chemicals are not easily degraded, these chemicals do decompose at high temperatures to yield TFA and other compounds. TFA was identified as a product of thermal decomposition of several fluoropolymers. Based upon models, it has been suggested that contributions of approximately 21 ng/L from these sources may be made to rainfall in the airshed of a large metropolitan area. The global input of TFA to the environment from these sources remains uncertain.
Some pesticides might degrade to produce TFA as a terminal residue. However, most pesticides that contain the $-CF_3$ group are not highly volatile and degrade in the terrestrial environment rather than in the atmosphere.

Environmental fate of TFA
Whatever the source of TFA in the atmosphere or other compartments in the environment, the ultimate sink is in surface waters. TFA is soluble in water and dissolves or partitions into water (droplets in the atmosphere in the case of the atmospheric degradation of HFCs and HFOs). Upon contact with soil or surface waters, TFA forms salts with ions such as sodium, potassium, magnesium, and calcium, which are present in soils and most surface waters. TFA salts released from other sources, such as industrial wastes and sewage treatment, also remain in the aqueous phase and eventually move to terminal sinks in the ocean, salt, or playas (endorheic lakes) from which there is no outflow and the only loss of water is via evaporation. TFA salts are extremely stable in the environment and likely have half-lives of centuries. It is important to recognize that in the environment, salts of TFA behave in a manner exactly the equivalent of salts of other minerals. Where mineral salts have accumulated in salt lakes, playas, and oceans, trifluoroacetic acid salts from natural and anthropogenic sources also accumulate. Playas and salt lakes are terminal sinks for salts, including trifluoroacetic acid. These water bodies contain more than the 3.5 g/L of salt found in the oceans. For example, the Great Salt Lake in Utah has concentrations of salts that vary from 50 to 270 g/L. Expressed in the same units as used for the measured environmental concentrations of TFA (ng salt/L), this is 270,000,000,000 ng salts/L.

Precipitation and snow

Several authors reported TFA concentrations in precipitation, which vary with location. Studies in California demonstrated concentrations of TFA in fog and rain ranged from 31 – 3779 ng acid equivalents (a.e.)/L and were generally lower in more remote areas. Further observations confirmed this trend; measurements in rain and snow in Switzerland revealed levels from < LOD (3 ng a.e./L) to 1550 ng/L. Concentrations of TFA in rain were larger at the beginning of a rainfall event, with the greatest concentrations in the first millimetre of rain. This was consistent with the high solubility of TFA in water, and rapid partitioning from air to water. In another study in Chile, Malawi, and Canada, TFA concentrations ranged in rainwater from 6 – 87, 4 – 15, and < 0.5 – 350 ng a.e./L, respectively. Concentrations of TFA in rainwater collected in two cities in Japan ranged from 29 – 76 ng a.e./L. Similarly, in Guangzhou, located in the Pearl River Delta in China, concentrations of TFA in rainwater measured during April 2007 – March 2008 ranged from 46 – 974 ng a.e./L.

Soils

In terrestrial systems, the first points of contact of precipitation (and therefore TFA) are vegetation, soil, and surface water. Once in contact with soil or surface water, TFA reacts with minerals to form salts. A previous author noted that TFA was poorly retained in soils in general, but that retention in soils with more organic matter was greater. The binding constant for TFA and organic carbon in soils (K_{OC}) is small, and as a salt, the anion form of the molecule binds even less to soil and is highly mobile. Measured concentrations of TFA in soils are relatively small. Previous authors have reported, in Canada, TFA values from < 0.0 – 1400 ng a.e./kg dry weight (d.w.) of soil; in Malawi, < 100 – 7500 ng a.e./kg d.w.; In the United Kingdom, 850 – 5000 ng a.e./kg d.w.; and 100 – 9400 ng a.e./kg d.w. in Chile. These low levels suggested that soils were not a repository or terminal sink of TFA salts in the environment. These results were consistent with the known chemical properties of these salts. TFA was infrequently detected in groundwater and then only at low concentrations (≥ 23 ng/L). Given its large mobility in soil, this was unexpected but may be due to slow percolation into the groundwaters tested.

Surface Waters

Previous authors reported that concentrations of TFA measured in surface waters vary widely with location, season, and type of water body (Table 7.5- 30). Data from playas and salt lakes were not included in the table, but environmental measurements in many diverse locations illustrated existing concentrations of 100 to 300 ng a.e./L in water, with one site (Dead Sea) having a concentration of 6,400 ng a.e./L (attributed to collection of TFA salt over thousands of years). This was greater than the levels of TFA salts in pre-industrial (> 2,000-yr-old) freshwater from Greenland and Denmark. Levels that were below the level of detection (LOD = 2 ng a.e./L) indicated that salts of TFA in surface fresh waters were more likely of anthropogenic origins.

In a previous modelling study on the projected use of HFO-1234yf in the United States, the author predicted increased concentrations of TFA salts in terminal water bodies in North America of 1000 – 15,000 ng a.e./L after 50 years of use. In some locations, such as playas in the Sonoran Desert, elevated concentrations of 40,000 to 200,000 ng a.e./L were predicted for the same period of time due to its closeness to major sources of TFA, such as California.

Table 7.5- 30: Concentrations of TFA in surface fresh waters

Location	Type of water body	Range of concentrations in ng a.e./L[1]
Northern California	Surface water	5 – 300
Yukon and Alaska	Surface waters	8 – 27
British Columbia	Surface waters	21 - 63
Switzerland	Rivers	12 - 328
	Midland lakes	37 – 204
	Mountain lakes	46 – 360
	Moor water	59 – 175
	Drinking water	16 - 123
Beijing	Surface waters	380 - 820
	Drinking water	155

[1] a.e. = acid equivalents

Oceans

Previous authors reported TFA concentrations in the Mid-Atlantic and the Southern Ocean off Elephant Island were all close to 200 ng a.e./L at depths ranging from the surface to 4150 m. Sampling in various parts of the Arctic, Atlantic, and Pacific oceans for TFA salts revealed that levels in deep (> 1000 m) waters of the Atlantic were close to 160 ng/L. Overall, a general value of 200 ng a.e./L for the concentration of TFA in the oceans was considered to be representative.

Based on radiocarbon dating (aging) with ^{14}C, the water at this depth was older than 1,000 years, which suggested significant natural sources of TFA salts in the oceans. Samples in the region of undersea hydrothermal vents revealed greater concentrations than surrounding water, suggesting that hydrothermal vents are one of these natural sources of TFA salts.

III. CONCLUSIONS

The data suggests that a large amount of the TFA salts in the ocean is from natural rather than human-made sources, whereas the salts of TFA in surface fresh waters are more likely of anthropogenic origins. The ultimate sink for TFA is in surface waters.

Overall, a general TFA value of 200 ng a.e./L is considered to be representative in the oceans, while concentrations of TFA measured in surface waters vary widely with location, season, and type of water body. Studies in fog and rain showed TFA concentrations were generally lower in more remote areas, with concentrations of TFA greatest in the first millimetre of rain.

The authors concluded that current and estimated concentrations of TFA and its salts in the environment that result from degradation of HCFCs, HFCs and HFOs in the atmosphere do not present a risk to humans and environment.

3. Assessment and conclusion

Assessment and conclusion by applicant:

Assessment:

This article from public literature collates monitoring results for TFA in precipitation, snow, soil, surface water and oceans from several monitoring literature articles which define monitoring time periods/locations and include details of the analytical work/methodology. However, the work wasn't carried out according to GLP, and there are currently no guidelines for the conduct of monitoring studies.

Conclusion:
The data suggests that a large amount of the TFA salts in the ocean is from natural rather than human-made sources, whereas the salts of TFA in surface fresh waters are more likely of anthropogenic origins.
The information of this publication is regarded as supportive information.

Assessment and conclusion by RMS:
Outcome and conclusion of the study: RMS should indicate if they agree to the results and conclusions of the APPL.

1. Information on the published literature article

Data Point:	KCA 7.5/13
Report Author:	Freeling, F.; Behringer, D.; Heydel, F.; Scheurer, M.; Ternes, T.; Noedler, K.
Report Year:	2020
Report Title:	Trifluoroacetate in precipitation: deriving a benchmark data set
Report No:	M-754282-01-1
Document No:	M-754282-01-1
Guideline(s) followed in study:	---
Deviations from current test guideline:	Current Guideline: not applicable
Previous evaluation:	No, not previously submitted
GLP/Officially recognised testing facilities:	not applicable
Acceptability/Reliability:	Yes

2. Full summary of KCA 7.5/13

Executive Summary
Precipitation is considered to be the most important diffuse source of trifluoroacetate (TFA) to the nonmarine environment although information regarding the wet deposition of TFA as well as general data on the spatial and temporal variations in TFA concentration in precipitation is scarce. This study provided a comprehensive overview of the occurrence of TFA in precipitation by a systematic and nation-wide field monitoring campaign. In total, 1187 precipitation samples, which were collected over the course of 12 consecutive months at eight locations across Germany, were analysed. The median, the estimated average, and the precipitation weighted average TFA concentration of all analysed wet deposition samples were 0.210, 0.703, and 0.335 µg/L, respectively. For Germany, an annual wet deposition flux of 190 µg/m² or approximately 68 t was calculated for the sampling period from February 2018 to January 2019. The campaign revealed a pronounced seasonality of the TFA concentration and wet deposition flux of collected samples. Correlation analysis suggested an enhanced transformation of TFA precursors in the troposphere in the summertime due to higher concentrations of photochemically generated oxidants such as hydroxyl radicals, ultimately leading to an enhanced atmospheric deposition of TFA during summer.

I. MATERIAL AND METHODS

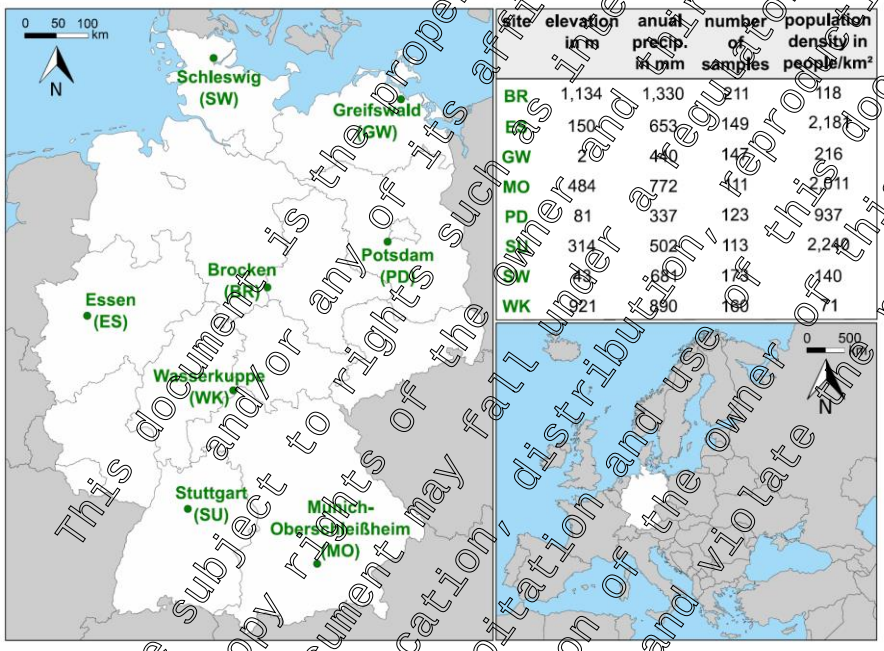
Material

Results from ocean water sampling campaigns indicated that TFA was naturally occurring in ocean waters, albeit from unidentified sources, the predominant quantity of TFA present in the atmosphere in precipitation, freshwaters, soils and terrestrial plants is more likely to originate from anthropogenic sources.

As such, the aim of this study was (i) to determine the present occurrence of TFA in precipitation through a systematic and nation-wide field monitoring campaign in Germany over the duration of an entire year, (ii) to derive annual wet deposition mass fluxes of TFA in Germany and (iii) to elucidate factors that control the spatial and temporal changes in the TFA concentration/flux in precipitation.

Sampling method

Over the course of 12 consecutive months, 1187 precipitation samples were collected from eight German locations (Figure 7.5- 8). All samples were collected by the German Meteorological Service.



site	elevation in m	anual precip. in mm	number of samples	population density in people/km²
BR	1,134	1,330	211	118
ES	150	653	149	2,181
GW	2	440	147	216
MO	484	772	111	2,611
PD	81	337	123	937
SU	314	502	113	2,240
SW	43	688	173	140
WK	921	990	160	71

Annual precipitation refers to the total precipitation at the respective sites over the sampling period (for all sites, except SU: February 2018 – January 2019, for SU: March 2018-February 2019). Population density refers to the population density within a 10 km radius of each site.

Figure 7.5- 8: Geographic location, annual precipitation, number of samples, and populationdensity at studied sites in Germany

An enamelled stainless-steel collection pan (A = 0.64 m²) sat on a cabinet base one meter above ground level. Two infrared heaters were used to melt solid hydrometeors and protect the collection containers (V = 20 L; polyethylene) from freezing. In periods without precipitation, the collection pans and containers were rinsed with deionized water on daily basis to ensure that the concentrations of precipitation samples were not altered by the amount of dry-deposited TFA from periods without precipitation. Precipitation samples from the sites ES, GW, MO, PD, SU, SW, and WK (n = 976) were not substantially influenced by dry-deposited TFA and were therefore representative for the amount of wet-deposited TFA. This subset of samples is hereafter referred to as “wet deposition (WD) samples”.

In contrast to the other sites, BR has extreme weather conditions due to its altitude and exposed location. Samples (n = 211) were collected using a stainless-steel rain gauge (A = 0.05 m^2), designed for precipitation sampling at high-altitude locations affected by strong winds and high annual snowfall. The rain gauge was installed at two meters above ground level and equipped with a windshield. From October to May, an exchangeable collecting container was used, which allowed for melting of solid hydrometeors inside the building of the weather station. The collection pan and the containers were not rinsed with deionized water between precipitation collection periods. The samples contained dry- and wet-deposited TFA and represent the total amount of atmospherically deposited TFA. Therefore, the data from the site BR is displayed and discussed separately from the WD samples.

The following types of samples were collected: A 24-h composite sample (n = 1084) was collected when at least 0.1 mm of precipitation was registered between 09:00 a.m. and 08:59 a.m. of the following day. In some cases, 24-h composite samples could not be obtained due to logistical reasons, and multiday composite samples (n = 103), encompassing time periods between 2 and 15 days, were collected instead. Of each composite sample, a single aliquot (10 – 12 mL) was transferred to a 15 mL polypropylene (PP) centrifugation tube and stored at 4°C for ≤ 2 months until analysis. The corresponding precipitation amounts of composite samples were determined using standardised pluviometers.

Analytical method
An ion exchange liquid chromatography system coupled to an electrospray tandem mass spectrometer operated in the negative ionisation mode was used for analysis. A sample aliquot of 1 mL was transferred to an HPLC vial and spiked with 10 µL of the internal standard (final concentration: 0.1 µg/L).

LOQ: The limit of quantification (LOQ) was 0.025 µg/L for TFA in precipitation, determined in accordance with DIN 32645 by the analysis of equidistant calibration levels.

Method validation: The precision and accuracy of the analytical method for TFA was determined by analysing five replicates of a tap and surface water sample, respectively. Prior to analysis, the tap (background concentration: 0.434 µg/L) and surface water samples (background concentration: 0.543 µg/L) were spiked with a TFA concentration of 0.250 µg/L. Method precision was determined as 1% relative standard deviation (RSD) from the recovery experiments.

Blank values: Field blanks (n = 8) were prepared at each sampling site. A 15 mL PP centrifugation tube was filled with the same type of deionized water used for rinsing the sampling device during periods with no precipitation. Laboratory blanks (n > 50) were used to detect potential contamination during sample preparation by analysing aliquots of ultrapure water that were treated as the environmental samples. No contamination was detected in any of the blank samples and, therefore. no blank correction of the analytical results was required.

Data Reporting
Precipitation concentrations of TFA < 0.1 µg/L and ≥ 0.1 µg/L were reported with two and three significant figures, respectively. Since the concentration data included left-censored observations (i.e. < 0.025 µg/L), regression on order statistics (ROS) was applied for a robust estimate of average (i.e. arithmetic mean) concentrations and to generate censored boxplots.

Precipitation-weighted average concentrations (CP-weighted; µg/L) were calculated to allow comparison of TFA concentration levels between different sites and studies. Daily wet deposition fluxes (F_{wet}; µg/(m^2d)) were calculated for individual WD samples. A fixed value of 0.025 µg/L TFA was used for the calculation of fluxes in the case of concentrations below the LOQ (7% of samples). The annual wet deposition TFA flux ($F_{wet\ (annual)}$; µg/(m^2a)) at a sampling site was obtained by taking the sum of the wet deposition TFA fluxes of all individual samples from the respective site. For the site BR, total deposition fluxes (F_{total}) were determined instead of wet deposition fluxes.

In nine cases, two consecutive sample tubes were incorrectly labelled with an identical sample number and the measured TFA concentration could not be definitively assigned to the correct precipitation amount. Hence, a best-case and worst-case flux scenario were calculated. Due to the negligible differences between the scenarios, only the results of the best-case flux scenario are discussed in the following.

II. RESULTS AND DISCUSSION

Concentrations of TFA in Precipitation

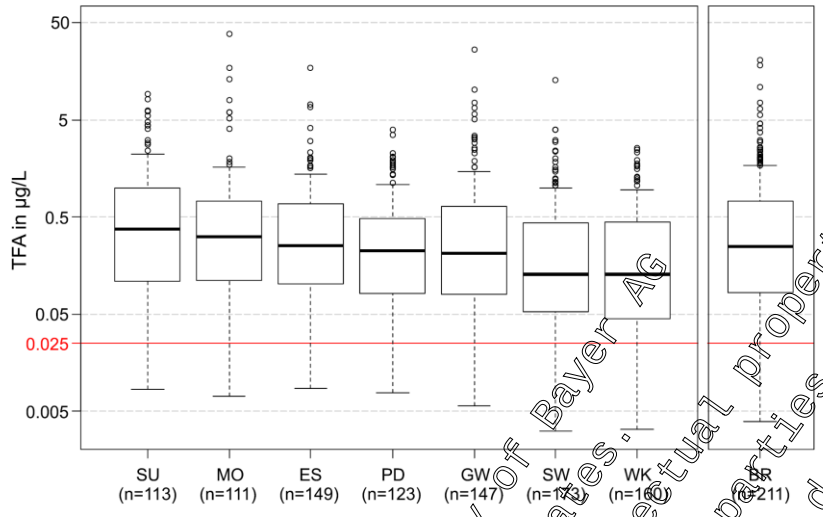
Of the 976 analysed WD samples, 93% showed a TFA concentration above the LOQ (0.025 µg/L). Most TFA concentrations of studied WD samples were in the high ng/L range with *ca.* 16% of analysed WD samples ≥1 µg/L. The maximum TFA concentration observed was 38 µg/L. The median, ROS-estimated average, and precipitation weighted average TFA concentration of all analysed WD samples were 0.210, 0.703, and 0.335 µg/L, respectively (Table 7.5-31). Precipitation-weighted average TFA concentrations ranged from 0.186 µg/L (WK) to 0.520 µg/L (MO). A similar result was obtained for the median TFA concentrations, where values ranged from 0.128 µg/L (WK, SW) to 0.377 µg/L (SU) (Table 7.5-31). The arithmetic mean is not a reliable measure for the comparison of TFA levels of different locations and/or time periods, due to the relationship between TFA concentration and precipitation amount, and the precipitation weighted average concentration should be used instead.

Table 7.5- 31: Statistical parameters of the TFA concentration of studied precipitation samples[1]

Site	Proportion of samples > LOQ (%)	TFA concentration			
		Max, µg/L	Median, µg/L	ROS-estimated avg, µg/L	Precip-weighted avg, µg/L
ES[2]	96.6	17.7	0.255	0.692	0.346
GW[2]	89.8	26.3	0.210	0.883	0.356
MO[2]	96.4	38.0	0.310	1.30	0.520
PD[2]	95.1	3.94	0.227	0.477	0.271
SU[2]	98.2	9.16	0.377	1.02	0.393
SW[2]	91.9	12.8	0.128	0.471	0.284
WK[2]	86.2	2.58	0.128	0.334	0.186
All sites[2]	93.0	38.0	0.210	0.703	0.335
BR[3]	95.3	20.6	0.248	0.895	0.256

[1]: Data is grouped by the sampling site; [2]: Wet deposition sampling; [3]: Total (wet + dry) deposition sampling

Figure 7.5-9 depicts censored boxplots of the TFA concentration (non-precipitation-weighted) grouped by the sampling location and plotted in descending median order for wet deposition. All boxplots are similarly shaped, demonstrating a similar distribution of measured TFA concentration in the precipitation at the studied sites. Site BR (total atmospherically deposited TFA) is included for comparison.



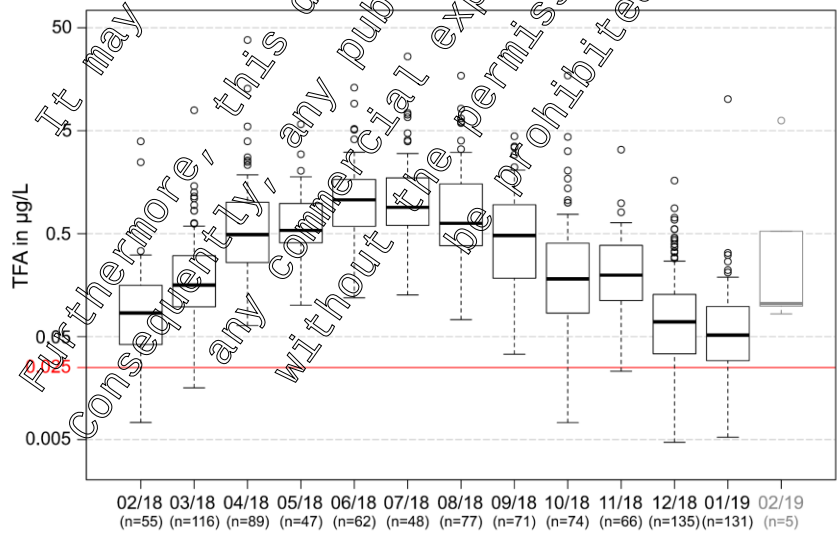
Note that the boxplot of site SU includes data from March 2018 to February 2019, whereas boxplots from other sites include data from February 2018 to January 2019. Sites are plotted in descending median order. The horizontal red line depicts the LOQ.

Figure 7.5- 9: Censored boxplots of TFA concentration (non-precipitation-weighted) present in precipitation samples grouped by the sampling site

Sampling at the site SU was conducted from March 2018 to February 2019 instead of February 2018 to January 2019 due to logistical reasons. Sampling at the site SU was conducted from March 2018- to February 2019 instead of February 2018 to January 2019 due to logistical reasons. When considering only the (congruent) sampling period from March 2018 to January 2019 for all locations, SU was still the site with the highest median concentration (0.381 µg/L). Statistical analysis (Pairwise comparisons; Wilcoxon rank sum tests) within the different months showed few significant differences in the TFA concentration levels between the sites. Statistically significant differences ($p < 0.05$; p-value adjustment method) were found for the sites SU and SW in August 2018 (difference in median: 1.13 µg/L), and for the site pairs GW and WK (0.044 µg/L), and SU and WK (0.058 µg/L) in January 2019.

Seasonal Variation in TFA Precipitation Concentration

Grouping the TFA concentration data of WD samples by the sampling month shows higher variation in interquartile ranges of the formed groups (Figure 7.5- 10). This indicated that for Germany, the TFA concentration in precipitation depends more on the sampling date than on the sampling location, with pronounced seasonality. The lowest median TFA concentration was observed in winter, whereas median concentrations were the highest in summer (Table 7.5- 32).



Note that the boxplot of February 2018 (02/18) does not include data from site SU, whereas the boxplot of February 2019 (02/19) solely represents data from SU and is therefore shown greyed out. Data from the site BR is not included in any of the boxplots. The horizontal red line depicts the LOQ.

Figure 7.5- 10: Censored boxplots of TFA concentration (non-precipitation-weighted) present in precipitation samples grouped by the sampling month

Table 7.5- 32: Statistical parameters of the TFA concentration of studied precipitation samples (WD samples; BR samples not included) grouped by the sampling month

Year	Month	Proportion of samples > LOQ (%)	TFA concentration			
			Max, µg/L	Median, µg/L	ROS-estimated avg, µg/L	Precip-weighted avg, µg/L
2018	February	89.1	3.94	0.085	0.221	0.083
	March	99.1	7.90	0.158	0.326	0.166
	April	100	38.0	0.489	1.33	0.584
	May	100	5.78	0.538	0.846	0.451
	June	100	13.1	1.06	1.57	0.782
	July	100	26.3	0.901	2.12	0.654
	August	100	17.1	0.630	1.49	0.835
	September	100	4.41	0.480	0.764	0.349
	October	94.6	17.2	0.182	0.627	0.128
	November	93.9	3.27	0.198	0.299	0.137
	December	83.7	1.64	0.070	0.130	0.063
2019	January	76.3	10.1	0.052	0.146	0.055
	February	90	6.27	0.105	1.42	0.121

Note that statistical parameters for February 2018 do not include data from site SU, whereas statistical parameters for February 2019 solely represent data from SU.

The substantial temporal variation in the precipitation concentration found in this study indicates that the summary statistics (averages, ranges, etc.) of TFA precipitation concentrations reported by earlier monitoring studies are subject to greater uncertainty, as they were based on rather small numbers of samples or covered only specific periods of the year. The seasonal variation in TFA concentration in precipitation observed in this study is in agreement with other literature which indicated marked seasonality of monthly mean gas-phase concentrations of TFA in Beijing, China. In both studies, the concentration levels of gas-phase TFA were significantly higher in spring and summer than in fall and winter.

The existence of periodic changes of TFA in precipitation suggests that considerable portions of TFA present in the atmosphere and in precipitation result from the atmospheric oxidation of volatile precursors. In turn, direct emissions of TFA to the atmosphere, e.g., from fluoropolymer thermolysis, are presumably of minor importance.

Deposition Fluxes of TFA

Median wet deposition TFA fluxes at the sites ranged from 0.205 µg/(m²d) (PD) to 0.554 µg/(m²d) (MO). Average wet deposition fluxes ranged from 0.743 µg/(m²d) (PD) to 2.96 µg/(m²d) (MO). The median and average TFA flux of all WD samples were 0.357 µg/(m²d) and 1.28 µg/(m²d), respectively (Table 7.5- 33). Wilcoxon rank sum tests within the different months revealed statistically significant differences ($p < 0.05$) for the sampling site pairs MO and PD (difference in median: 0.203 µg/(m²d)), as well as SW and PD (0.147 µg/(m²d)) in February 2018, for MO and all other sites in August 2018 (mean difference in median: 8.05 µg/(m²d)), and for WK and PD (difference in median: 0.141 µg/(m²d)), WK and SU (0.174 µg/(m²d)), and WK and SW (0.173 µg/(m²d)) in January 2019.

In general, the deviations between the monthly medians of the daily TFA deposition of sampling sites were small and below significance ($\alpha = 0.05$). One of the few exceptions was site MO in August 2018 where the median (8.93 µg/(m²d)) was more than ten times higher than the average median over all other sites (0.876 µg/(m²d)).

Table 7.5- 33: Statistical parameters of the wet deposition TFA fluxes of studied precipitation samples[1]

Site	Max, µg/(m²d)	Median, µg/(m²d)	Avg, µg/(m²d)	Annual total µg/(m²a)
ES[2]	14.4	0.452	1.17	226
GW[2]	50.0	0.237	1.07	157
MO[2]	57.0	0.554	2.96	401
PD[2]	7.46	0.205	0.743	91.4
SU[2]	20.7	0.302	1.24	197
SW[2]	22.0	0.290	1.12	193
WK[2]	24.3	0.387	1.04	166
All sites[2]	57.0	0.337	1.28	
BR[3]	35.3	0.774	1.90	340

[1]:Data is grouped by the sampling site [2]: Wet deposition sampling; [3]: Total (wet + dry) deposition sampling.
Statistical parameters of the total deposition flux of site BR are included at the bottom of the table

Seasonal Variation in TFA Deposition Flux

WD flux data grouped by sampling month indicated an annual cycle, with maximum fluxes in summer and minimum fluxes in winter. Pearson correlation analysis between the monthly deposition totals of TFA and the monthly totals of global solar radiation at each of the investigated sites showed positive correlation coefficients ranging from 0.61 to 0.91. The authors suggest that the atmospheric degradation of TFA precursors, and hence the formation of TFA, is controlled by the tropospheric •OH concentration, which ultimately leads to higher atmospheric deposition of TFA in Germany in summer than in winter. However, formation of •OH is much more influenced by UV radiation than what is taken into account by global radiation. Furthermore, the •OH formation by primary sources (mainly through photodissociation of ozone) and secondary sources (through •OH recycling in radical reaction chains) depends on atmospheric conditions and composition (e.g., the NO_x concentration), which means that the variance of •OH cannot solely be explained by variations in the photolysis frequency of ozone. In addition, a potential correlation between the monthly global radiation total and the monthly wet deposition of TFA at a given site depends on whether the photochemically formed TFA is actually deposited in the same month and close to the location of its formation. If there is only little monthly precipitation or if only very few precipitation events occur within a month at a specific site it is more likely that the formed TFA is scavenged from the atmosphere at a later time and therefore transported over greater distances.

Spatial Differences in TFA Deposition Flux.

As precipitation sampling was conducted over 12 consecutive months, accurate estimates of the annual wet deposition flux of TFA at each site could be made. Annual totals of TFA wet deposition ranged from 91.4 µg/m² (PD) to 401 µg/m² (MO) (Table 7.5- 33). The low wet deposition flux at site PD could be explained by the low amount of annual rainfall at the site and therefore a lower potential for TFA scavenging and local TFA deposition. The three sites with the highest annual TFA wet deposition fluxes (MO, ES, SU) are all located in densely populated regions in Germany (>2000 people/km²). This is in accordance with previous findings, which linked the higher TFA concentration in surface waters and air to urbanized regions.

It was concluded that emissions of refrigerants are positively correlated with regions with high degrees of urbanization and high numbers of private vehicles, thus leading to elevated concentrations of TFA in precipitation. However, this is less likely to be the case for HFC refrigerants, as their long atmospheric lifetime of multiple years leads to them being well mixed in the atmosphere. In contrast, for the European Union and the United States, TFA deposition originating from the atmospheric degradation of HFO-1234yf used as the substitute for HFC-134a is likely to be further enhanced. Also, it is expected to be more spatially concentrated due to its low atmospheric lifetime of 10.5 days as well as its higher molar TFA yield compared to HFC-134a.

In the present study, the two coastal sampling sites (GW, SW), did not show elevated TFA fluxes compared to inland sites. The relatively low fluxes of TFA at the two coastal sampling sites and the low fluxes of TFA in winter at all sites indicate that sea spray as a considerable source of TFA in precipitation is unlikely.

It is estimated that about 25% of atmospheric TFA is deposited through dry deposition and this can even be the dominant deposition process in arid and semiarid environments. Low precipitation does not necessarily imply a high contribution of dry to total TFA deposition. It is still conceivable that at sites with low annual precipitation, dry deposition of TFA plays a more important role than that at sites with high annual precipitation. This could be another reason for the low wet deposition flux of TFA at site PD which had very low precipitation (Table 7.5- 33).

On the basis of the assumption that dry deposition contributed 25% to the measured total deposition at the site BR, an annual wet deposition of approximately 255 µg·m^{-2} was derived. Due to the location of the site at the top of Mt Brocken in the sparsely populated region of the Harz Mountains, this value is unexpectedly high. One possible explanation could be the pronounced formation of fog as Mt Brocken is one of the places in Central Europe with the highest average number of days with fog per year (284 days/year). It was estimated that about one-third of the precipitation at site BR collected was fog. On the basis of the Henry constant of TFA, the authors calculated the partitioning between gaseous and condensed water phase during the fog events and found that the latter contained 94% to 99.9% of the total TFA. Therefore, it is conceivable that fog scavenging is highly efficient for TFA, which could ultimately lead to enhanced atmospheric deposition of TFA at sites characterized by a pronounced formation of fog.

III. CONCLUSIONS

An average wet deposition of TFA for Germany for the sampling period from February 2018 to January 2019 of 190 µg/m^2 or approximately 68 t was estimated by multiplying the precipitation-weighted average concentration of all studied WD samples (0.335 µg/L; Table 7.5- 33) with the average precipitation total for Germany for this period (566 mm). It is noted that 2018 was a year with exceptionally low precipitation in Germany. On the basis of the German multiyear average of 819 mm (climatological standard normal 1981−2010) the annual wet deposition flux of TFA in Germany is 274 µg/m^2 or ~98 t. This is substantially higher than the annual wet deposition fluxes of 22 and 30 t calculated for Germany for the periods from April 1995 to March 1996 and October 1995 to September 1996, respectively, and indicates a considerable increase in the atmospheric deposition of TFA in Germany over the last two decades.

The observed seasonal variations in the TFA concentration/ flux suggest that the atmospheric oxidation of volatile precursors is a major source of TFA in the atmosphere and in precipitation. Since some HFCs and HFOs are considered as rising sources of TFA in precipitation, their substitution by halogen-free gases could be an effective measure to reduce the TFA load in precipitation. The author advised that future monitoring efforts determine concentrations and fluxes of TFA in precipitation over an entire year. The presented results indicate that the collection of a small number of samples or the collection of

samples only during selective time periods of the year can lead to a skewed picture of the occurrence of TFA in the precipitation of a specific region.

3. Assessment and conclusion

Assessment and conclusion by applicant:

Assessment:

This article from public literature reports monitoring results for TFA in precipitation at 8 German locations, covering February 2018 to January 2019, including analytical work. Sampling methodology was well reported, and field blanks were employed. However, the work wasn't carried out according to GLP, and there are currently no guidelines for the conduct of monitoring studies.

Conclusion:

Precipitation is considered to be the most important diffuse source of TFA to the non-marine environment. An average TFA wet deposition of 190 µg/m² (ca. 68 t) was estimated for Germany. (Feb 2018 – Jan 2019). The observed seasonal variations in the TFA concentration/ flux suggest that the atmospheric oxidation of volatile precursors is a major source of TFA in the atmosphere and, therefore, in precipitation.

The information of this publication is regarded as supportive information.

Assessment and conclusion by RMS:

Outcome and conclusion of the study. RMS should indicate if they agree to the results and conclusions of the APPL.

1. Information on the published literature article

Data Point:	KCA 7.5/15
Report Author:	Ball, J. C.; Wallington, T. J. (. D.; Ford, D.
Report Year:	1993
Report Title:	Formation of trifluoroacetic acid from the atmospheric degradation of hydrofluorocarbon 134a: a human health concern? bildung von trifluoressigsaeure durch abbau des fluorkohlenwasserstoffs 134a in der atmosphaere: bedeutsam fuer die menschliche gesundheit?
Report No:	M-757129-01-1
Document No:	M-757129-01-1
Guideline(s) followed in study:	not applicable
Deviations from current test guideline:	Current Guideline: not applicable
Previous evaluation:	No, not previously submitted
GLP/Officially recognised testing facilities:	No, not conducted under GLP/Officially recognised testing facilities
Acceptability/Reliability:	Yes

2. Full summary of KCA 7.5/15

Executive Summary

Recognition of the adverse effect of chlorofluorocarbon (CFC) release into the atmosphere has led to an international effort to replace CFCs with environmentally acceptable alternatives. Hydrofluorocarbon 134a (1,1,1,2-tetrafluoroethane; HFC-134a) is a potential substitute for CFC-12 used in automotive air conditioning systems. In March 1992, Ford Motor Company started production of automobiles with HFC-134a refrigerant. Due to the anticipated large-scale industrial use of HFC-134a, concern was raised with regard to the levels of trifluoroacetic acid (TFA) expected in the environment (arising from the degradation of HFC-134a in the atmosphere).

This study indicated that on average, rainwater will contain less than 8×10^{-9} M (0.14 ppb) TFA, the amount of rainfall varies with geographic location and it seems likely that even in the worst case scenario the concentration of TFA in rainwater will not exceed 80×10^{-9} M (1.4 ppb).

I. MATERIAL AND METHODS

Material

Due to the anticipated large-scale industrial use of HFC-134a, concern was raised on the levels of TFA expected in the environment and the impact of this compound on human health.

The aim of this study was to determine (i) What levels of TFA are expected in the environment due to the use of HFC-134a? and (ii) Are these levels of concern for human health?

Analytical method

The only significant atmospheric sink for HFC-134a is reaction with OH radicals. The atmospheric lifetime of HFC-134a (15 years) is approximately an order of magnitude greater than the time taken for air to mix between the northern and southern hemispheres. Hence, following release, HFC-134a will become homogeneously mixed in the atmosphere. The alkyl radical formed in Reaction 1 reacts rapidly (within a microsecond under tropospheric conditions) with molecular oxygen to give the peroxy radical CF_3CFHO_2.

$$CF_3CFH_2 + OH \rightarrow CF_3CFH + H_2O \quad (1)$$

$CF_3CFH + O_2 + M \rightarrow CF_3CFHO_2 + M$ (2)

In the atmosphere, this peroxy radical will react with one or more of the following: NO, NO_2, the hydroperoxy radical (HO_2), or alkyl peroxy radicals (RO_2).

$CF_3CFHO_2 + NO \rightarrow CF_3CFHO + NO_2$ (3)

The reaction of CF_3CFHO_2 with NO is rapid and produces NO_2 and the alkoxy radical CF_3CFHO. In the atmosphere, CF_3CFHO radicals either decompose or react with O_2.

$CF_3CFHO + O_2 \rightarrow CF_3COF + HO_2$ (4)

$CF_3CFHO \rightarrow CF_3 + HC(O)F$ (5)

Reaction with O_2 produces CF_3COF. Decomposition of the alkoxy radical produces a CF_3 radical and HC(O)F. The relative importance of the two possible loss processes for CF_3CFHO radicals was studied as a function of temperature, total pressure, and partial pressure of O_2 by the author. Assuming that Reaction 3 is the sole loss of CF_3CFHO_2 radicals in the atmosphere, then approximately 30% of the HFC-134a will be oxidized to give CF_3COF.

As a result of the inherent strength of C–F bonds, CF_3COF is not expected to react with OH radicals or other trace reactive species in the atmosphere. Photolysis of CF_3COF is of importance only at very short wavelengths which are blocked by the ozone layer. For photolysis to occur, CF_3COF must therefore diffuse above the ozone layer, i.e., above 50 km. This is a very slow process, and physical removal processes in the troposphere such as rain-out are thus expected to dominate its removal. Following inclusion into water droplets, CF_3COF is expected to be hydrolysed to CF_3COOH and hydrofluoric acid (HF). If reaction with NO were the sole atmospheric fate of CF_3CFHO_2 radicals then approximately 30% of the HFC-134a released would be converted into CF_3COOH.

Calculation of the efficiency of conversion of HFC-134a into trifluoroacetic acid is complicated by the fact that RO_2 and HO_2 radicals and NO_2 compete with NO for the available CF_3CFHO_2 radicals in the atmosphere, and the lack of any kinetic or mechanistic information for these reactions.

$CF_3CFHO_2 + RO \rightarrow$ products (6)

$CF_3CFHO_2 + HO_2 \rightarrow CF_3CFHOOH + O_2$ (7)

Reaction with NO_2 forms a thermally unstable peroxynitrate which is expected to rapidly decompose to regenerate the peroxy radical. CF_3CFHO_2 and NO_2 were not considered further by the author. By analogy with other peroxy-peroxy radical reactions the author would expect Reaction 6 to produce a mixture of CF_3CFHO radicals, CF_3COF, and CF_3CFHOH. Each of these products may in turn be further oxidized to CF_3COOH. In the absence of detailed experimental data concerning the kinetics and mechanisms of Reactions 6 and 7 it was not possible for the author to assess accurately their role in the atmospheric chemistry of HFC-134a. Therefore the somewhat unlikely worst case scenario where Reactions 6 and 7 proceed sufficiently rapidly to dominate Reaction 3 was considered by the author and furthermore, that the products of Reactions 6 and 7 are efficiently converted into trifluoroacetic acid.

II. RESULTS AND DISCUSSION

TFA concentrations in rainwater

The global production of CFC-12 in 1986 was 4.0×10^8 kg. In a worst-case scenario i.e. HFC-134a replaced CFC-12 on an equal mass basis and all the HFC-134a was released without recovery, the emission to the atmosphere would be 4.0×10^8 kg or 3.9×10^9 moles per year. At steady state, assuming

all the HFC-134a is converted into TFA, then 3.9×10^9 moles of TFA would be formed in the atmosphere annually. The annual global rainfall is 4.9×10^{17} litres. Thus, on average, rainwater will contain less than 8×10^{-9} M (0.14 ppb) TFA. The amount of rainfall varies with geographic location. In desert areas the rainfall is approximately an order of magnitude less than the global average. The author suggested that it was reasonable to assume that even in the worst case scenario the concentration of TFA in rainwater will not exceed 80×10^{-9} M (1.4 ppb).

TFA is not expected to accumulate in the water supply as the rainwater will be diluted by natural bodies of water and rivers. TFA would also bind to soil as the rainwater percolates through soil or passes over the ground. There could be some uptake of TFA in fish, plankton, or plants but the highest route of exposure would be most likely in rainwater. Therefore, rainwater would contain the highest concentrations of TFA that the human population would be exposed to.

III. CONCLUSIONS

On average, rainwater will contain less than 8×10^{-9} M (0.14 ppb) TFA. The amount of rainfall varies with geographic location. In desert areas the rainfall is approximately an order of magnitude less than the global average. It seems likely that even in the worst-case scenario the concentration of TFA in rainwater will not exceed 80×10^{-9} M (1.4 ppb).

3. Assessment and conclusion

Assessment and conclusion by applicant:

Assessment:

This article from public literature reports estimates for TFA in precipitation due to the atmospheric degradation of HFC-134a, based on theoretical calculations.

Conclusion:

On average, rainwater will contain less than 8×10^{-9} M (0.14 ppb) TFA, the amount of rainfall varies with geographic location and it seems likely that even in the worst case scenario the concentration of TFA in rainwater will not exceed 80×10^{-9} M (1.4 ppb).

The information from this article can be regarded as supportive information.

Assessment and conclusion by RMS:

Outcome and conclusion of the study: RMS should indicate if they agree to the results and conclusions of the APPL.

1. Information on the published literature article

Data Point:	KCA 7.5/16
Report Author:	Franklin, J.
Report Year:	1993
Report Title:	The atmospheric degradation and impact of 1,1,1,2-tetrafluoroethane (hydrofluorocarbon 134a)
Report No:	M-757131-01-1
Document No:	M-757131-01-1
Guideline(s) followed in study:	not applicable
Deviations from current test guideline:	Current Guideline: not applicable
Previous evaluation:	No, not previously submitted
GLP/Officially recognised testing facilities:	No, not conducted under GLP/Officially recognised testing facilities
Acceptability/Reliability:	Yes

2. Full summary of KCA 7.5/16

Executive Summary

This paper reviews existing literature on the atmospheric degradation and impact of the CFC alternative HFC-134a (CF_3CH_2F). Topics covered include: distribution of HFC-134a in the environment; atmospheric lifetime; tropospheric breakdown mechanism, with a discussion of the kinetics of each elementary step; contribution to tropospheric ozone formation; contribution to global warming; removal of the primary degradation products $CF_3C(O)F$, $HC(O)F$ and $C(O)F_2$ from the atmosphere through uptake by cloud, rain and ocean waters, followed by hydrolysis; anticipated environmental concentrations of trifluoroacetate (TFA) and fluoride arising from HFC-134a; contribution of the breakdown products to "acid rain"; ultimate fate of TFA.

I. MATERIAL AND METHODS

Material

TFA ($CF_3C(O)OH$ or CF_3CO_2OH) is a primary oxidation product of HFC-134a. The possible reactions of this compound in condensed aqueous media formed part of a literature review.

II. RESULTS AND DISCUSSION

Deposition of $CF_3C(O)F$ and $CF_3C(O)OH$ (TFA)

Various authors concluded that about 40% of HFC-134a would be degraded to $CF_3C(O)F$, a small proportion of the $CF_3C(O)F$ (0 - 6% relative to the initial HFC-134a) would be dry-deposited to the oceans; most of the $CF_3C(O)F$ would be taken up by cloud water and hydrolysed to TFA. On re-evaporation of cloud droplets, $CF_3C(O)OH$ may be released to the gas phase and some of this (0 - 12% HFC-134a) could be dry-deposited to the oceans. Most of the TFA (22 - 40%/HFC-134a) would be wet-deposited to the ocean and land surfaces. These figures were rough estimates, as Henry's Law coefficient and the hydrolysis rate constant of $CF_3C(O)F$ were not yet known to a sufficient degree of accuracy.

Previous studies calculated the global average concentration of TFA in rainwater and the latitudinal and seasonal distribution of this concentration. For an assumed emission (and degradation) rate of 1000 kt HFC-134a/yr (i.e. about 7 - 10 times the anticipated emissions for the first two decades of the 21st century), the steady-state global average concentration of TFA in rainwater was calculated to be 0.85 - 1.0 ppbw (µg/L), with a maximum concentration of about 1.6 ppbw in the tropics.

If the results were scaled to a more realistic emission rate of 100 kt HFC-134a/yr, this would lead to a global average concentration of TFA in rainwater of about 0.1 ppbw. The calculations assumed an average latitudinally and seasonally dependent precipitation climatology. The local concentration of TFA in rainfall occurring after an exceptionally long dry period would thus be greater than 0.1 ppbw.

Distribution of TFA in the environment

TFA is miscible with water in all proportions. With a pKa value close to zero, it is completely ionized at all environmentally relevant pHs. The TFA anion does not appear to form insoluble salts or complexes with metals likely to be present in the environment. No detectable adsorption of the anion onto any of three standard test soils was observed. Measurements of the n-octanol/water partition coefficient gave $\log_{10}K_{ow}$ = - 4.1, indicating an exceptionally low potential for passive accumulation of TFA in the fatty tissues of animals or plants. These data indicated that TFA is expected to leach away from soil and partition into aqueous compartments of the environment, with most of it ultimately ending up in the oceans. There is a fairly high potential for contamination of groundwater. In a dry local environment, TFA may evaporate and be transported in the atmosphere before being deposited again to the ocean or land surfaces.

Assuming conversion of 40% of HFC-134a to TFA and accumulation of all this TFA in the upper, mixed layer of the oceans (depth 80 m), the author calculated that the sea water concentration of TFA would increase by about 15 pptw (ng/L) per 1000 kt HFC-134a degraded. The latter cumulative amount is unlikely even to have been released to the atmosphere before the year 2005 at the earliest.

The mean steady-state concentrations of TFA in rainwater would be of the order of 0.1 ppbw, for an emission rate of 100 kt HFC-134a per year.

Chemical degradation of TFA in the environment

The UV absorption cross-section of gaseous TFA has been studied. The authors concluded that its tropospheric lifetime with respect to photolysis was > 7 x 10^5 yr. The UV absorption spectrum of TFA was observed to have pressure dependence which was ascribed to the formation of dimers. In the aqueous phase TFA does not absorb at wavelengths greater than 250 nm, so photolysis could not be an environmental sink.

TFA is resistant to defluorination and decarboxylation under all but the most extreme conditions. Defluorination was observed to proceed with a half-life of 150 yr at 80°C in 10% NaOH. In ethylene glycol solution, the sodium salt of TFA underwent decarboxylation with a half-life of 6.5 h at 170°C, with no decomposition of either the Na salt or the free acid observed in the water at temperatures up to 100°C. Another author confirmed that less than 2% decarboxylation occurred in water after 122 h at 97°C. Extrapolation of data to room temperature suggested a lifetime of millions of years.

Authors reported the reaction of the TFA anion with hydrated electrons (rate constant < 2.6 × 10^6 L/mol/s) led to a negligible sink (lifetime > 10^4 yr) considering that the concentration of hydrated electrons in natural surface waters was believed to be < 10^{-18} mol/L.

The rate constant for reaction of the nitrate radical with the TFA anion was reported. This reaction presumably involved transfer of an electron, followed by decarboxylation of the trifluoroacetoxy radical formed. The rate constant of the reaction was found to be 3.9 × 10^3 L/mol/s at ambient temperature. In order to assess the possible significance of decarboxylation induced by nitrate radicals in cloud water, the authors of the study assumed an NO_3 concentration of 10^{-13} mol/L, which led to an aqueous-phase lifetime of 80 yr. Taking into account the total volume of cloud water present in the atmosphere (roughly 5 × 10^{17} m^3), it was shown that this reaction was a negligible sink for TFA.

Other chemical processes which might degrade TFA in the environment include oxidation by photochemically generated valence band holes in metal oxide semiconductor particles, such as TiO_2. (Trichloroacetate is known to undergo such a reaction) and catalytic decarboxylation in the presence of transition metal ions, following literature reports of an analogous reaction for other carboxylic acids. On-going work shows that TFA can be degraded in the presence of ferric ions and UV radiation.

Biodegradation of TFA in the environment

TFA is resistant to biodegradation. Analysis of a TFA-containing industrial waste stream showed that no aerobic or anaerobic microoganisms in the wastewater treatment plant were able to utilize TFA as their sole source of carbon and energy. The same analysis indicated that TFA levels did not drop as the waste stream passed through the treatment plant, suggesting little sequestration or co-metabolism of TFA. No biodegradation of TFA was detected in tests using extended closed-bottle or modified methods, both of which were conducted under aerobic conditions. In various studies, there was no detectable defluorination of TFA by microbes growing on other carbon sources.

Reference to the published literature showed that defluorinating halidohydrolase enzymes, which are widely distributed among aerobic soil microbes and remove fluorine from mono- or di-fluoroacetate, have little or no action on TFA.

Expected tropospheric concentrations

For annual emissions of 100 kt HFC-134a/yr, the steady-state tropospheric concentration of HFC-134a would be about 100 pptv. The contribution from HFC-134a to the gas-phase concentrations of the likely reaction products $CF_3C(O)F$, $HC(O)F$, CF_3OH, $C(O)F_2$, HF, $HC(O)OH$ and $CF_3C(O)OH$, whose lifetimes with respect to wet or dry deposition (or other processes) are expected to be a few months at the very most, would be of the order of 1 pptv or less.

Effects on the composition of seawater

If HFC-134a is assumed to be converted into TFA with a yield of 40 %, and this TFA accumulated in the upper mixed layer of the oceans (depth 80 m), then the concentration of TFA in seawater would increase by about 15 pptw per 1000 kt of HFC-134a degraded. The latter amount is unlikely even to have been released to the atmosphere before the year 2005 at the earliest.

III. CONCLUSIONS

HFC-134a breaks down in the troposphere via a complex series of reactions to give acid fluorides and short-lived compounds such as peroxyalkyl nitrates and hydroperoxides. The principal fate of the acid fluorides will be uptake by cloud water and subsequent hydrolysis, the products of which will be trifluoroacetic acid (TFA), formic acid, CO_2 and HF. Dry deposition of the acid fluorides to ocean or land surfaces may occur to a limited extent, followed by hydrolysis.

TFA is the only significant xenobiotic likely to arise in the environment from the breakdown of HFC-134a. The physical and chemical properties of TFA indicate that it will partition into the aqueous compartments of the environment, where it will be completely ionized, showing no appreciable tendency to adsorb onto soils or to accumulate passively in biota.

Rainwater concentrations of TFA corresponding to the steady-state degradation of 100 kt HFC-134a/yr will be of the order of 10^{-10} parts by weight (0.1 ppbw). If all the TFA produced accumulated in the upper mixed layer of the oceans, there would be a resulting seawater TFA concentration increase of about 1.5×10^{-12} parts by weight (1.5 pptw) per 100 kt HFC-134a degraded.

3. Assessment and conclusion

Assessment and conclusion by applicant:

Assessment:

The article is a review of literature available in the early-1990s regarding the impact of HFC-134a and its degradation/dissipation products, including TFA, on the environment. However, none of the work was carried out according to GLP, and there are currently no guidelines for the conduct of monitoring studies.

Conclusion:

Data presented through modelling and research of TFA production from HFC-134a at the time of review, indicated TFA had no known degradation pathways and exists at very low levels in multiple environmental compartments, with TFA predictions in rainwater of 0.1 ppb and in seawater of 1.5 ppt based on the degradation of 100 kt HFC-134a.

The information from this article can be regarded as supportive information.

Assessment and conclusion by RMS:

Outcome and conclusion of the study. RMS should indicate if they agree to the results and conclusions of the APPL.

1. Information on the published literature article

Data Point:	KCA 7.5/17
Report Author:	Wujcik, C. E.; Zehavi, D.; Seiber, J. N.
Report Year:	1998
Report Title:	Trifluoroacetic acid levels in 1994 - 1996 fog , rain , snow and surface waters from california and nevada
Report No:	M-757134-01-1
Document No:	M-757134-01-1
Guideline(s) followed in study:	not applicable
Deviations from current test guideline:	Current Guideline: not applicable
Previous evaluation:	No, not previously submitted
GLP/Officially recognised testing facilities:	No, not conducted under GLP/Officially recognised testing facilities
Acceptability/Reliability:	Yes

2. Full summary of KCA 7.5/17

Executive Summary

Trifluoroacetic acid (TFA) is an atmospheric breakdown product of the chlorofluorocarbon replacements HCFC-123, HCDC-124, and HFC-134a. Due to its low Henry's law constant, TFA will partition into the various aqueous phases that occur throughout the environment. TFA was detected and measured in fog, rain, snow, and surface water obtained in 1994 - 1996 from several locations in California and Nevada. Fog and rain samples contained 31 - 3779 ng/L TFA. Snow samples taken in more remote areas had 51 - 584 ng/L. Surface water varied from 55 ng/L - 41 µg/L depending on type and location. Washout of TFA from the lower atmosphere was observed in both rain and fog samples. There was a trend toward decreasing TFA in precipitation samples taken at later stages during a single

storm event, indicating cleansing of TFA from the lower atmosphere by precipitation. The magnitude of TFA levels suggest that formation in the environment from HCFC and HFC degradation is occurring more rapidly than expected, or that alternate sources of TFA exist.

I. MATERIAL AND METHODS

Material
A series of sites in California and Nevada were selected for collection of fog, rain, snow and surface water samples to provide information on the aqueous phase washing of TFA from the lower atmosphere.

Sampling method
Site selection was based upon air-conditioned vehicle use in the general vicinity and commonly high atmospheric oxidant levels. California's San Joaquin Valley is adjacent and upwind to the Sierra Nevada range. The valley, which encompasses potential sources, and the mountain range, which represents a downwind depositional site, were chosen as the main focus of sample collection. Samples were also taken from Sonoma County, CA near the Pacific Coast, Luke Tahoe, CA and Reno, NV at the eastern slope of the Sierra Nevadas.

Fog water was collected by a vehicle-mounted high-volume fog sampler, which contained a 50 cm diameter fan in the back, which drew air at a rate of 4400 m^3/h and resulted in the collection of up to 1 L/h of fog water in dense fog. All samples were refrigerated until extracted and analysed. The entire apparatus was rinsed thoroughly with acetone before each collection period and the initial 5 min of sample collected was discarded to provide additional rinsing of the collection device. All amber bottles were cleaned to prevent trace TFA contamination in the laboratory.

Rain samples were collected into 1 and 4 L amber bottles by using large glass funnels (20 cm diameter) or a 1 m^2 stainless steel catch basin. Collection devices were rinsed thoroughly with acetone, followed by Nanopure water prior to use. As with the fog sampler, the first 5 min of rain was discarded.

Snow samples were taken approximately 0.3 m below the surface and placed into 75 L galvanized cans, melted at ambient temperature and then transferred to 4 L amber bottles.

Water sampled from the surface of lakes and rivers approximately 3 - 5 m from shore was collected into 4 L amber bottles. Each bottle was rinsed 3 times with water from the surface water site before the actual sample was collected.

Analytical method
TFA was extracted from 250 mL aqueous samples by rotary evaporation followed by saturation with sodium chloride and back extraction with diethyl ether into alkaline water. Samples were filtered through glass wool and concentrated to a volume between 1 and 2.5 mL, then transferred to graduated conical test tubes to a total volume of 3 mL and acidified with 0.1 mL of H_2SO_4/H_2O (1:1) for every 1 mL of sample. Extraction of the protonated TFA used 3 × 3 mL of diethyl ether which was then placed into a 1.0 mL 0.8 mol/L sodium bicarbonate solution, while vortexing and equilibrating the samples at each step. The majority of the diethyl ether was removed by pasteur pipette and the remainder blown down under a stream of nitrogen.

Derivatisation was carried out in cold headspace (HS) vials partially submerged in an ice bath. All reagents, including the samples, were cooled in a refrigerator for at least 0.5 h prior to derivatisation. 1 mL of sulphuric acid , followed by 0.2 mL of purified dimethyl sulphate, and finally 0.2 mL was added to the HS vial of the aqueous blank, standard, or sample and the vials immediately sealed. The TFA was converted to the volatile methyl ester (MTFA) by heating the sample at 80°C for 1.0 h.

TFA analysis was performed on an Autosystem GC equipped with an electron-capture detector (ECD). A 25 m × 0.32 mm i.d. PoraPLOT Q fused silica capillary column with a 10 - 5 m film thickness was used to resolve TFA.

To confirm the presence of TFA, a quadrupole mass-spectrometer was used in series with a GC equipped with a 10 m × 0.32 mm i.d. (10 - 5 m stationary film thickness) PoraPLOT Q column. Following a 1 h equilibration period at room temperature, the vapour phase from the derivatised samples was manually injected onto the system. The presence of TFA was established by re-quantifying several samples by GC-MS in the selected ion monitoring mode and comparing these results with those determined by GC-ECD. The three ions, m/z 59, 69, 99 monitored in the SIM - electron impact mode, sufficiently characterise the mass spectrum of MTFA.

Limits of detection (LOD) and quantification (LOQ): The LOD was 4.8 µg/L and the LOQ was 9.6 µg/L.

Calibration curve R^2 (coefficient of determination): Ranged from 0.9954 to 0.9994.

II. RESULTS AND DISCUSSION

Blanks consisting of Nanopure water taken through the complete extraction and derivatization process were analysed with the samples. These blanks contained a small peak, barely detectable from baseline/background noise, eluting within the same retention range as MTFA. These blanks were relatively consistent throughout the course of the study, with relative standard deviation (RSD) values ranging from 19 – 48% for a given set of runs. Standard curves were produced by including these blanks as concentration values of zero.

All of the samples analysed were above the LOQ, with even the lowest concentrated sample level being nearly twice this value. Evaporative concentration (250:1 mL) was necessary to bring most aqueous samples above the LOQ and within the range of the standard curve. Some highly concentrated samples were re-diluted with nanopure water prior to re-analysis to bring them into the linear range.

A representative sample from each location was quantified and confirmed by GC-MS to ensure that the peak eluting within the MTFA window was entirely a product of MTFA and not from other co-eluting compounds. Quantification yielded relatively minor differences from the HS-GC method using ECD, in most cases. These differences may be due in part to the reduced sensitivity of the GC-MS as a quantitative tool and the employment of manual injections that could not be continuously temperature controlled.

Trifluoroacetate concentrations measured in rain, fog, snow, and surface waters are reported in Table 7.5.-34. Most samples below 180 ng/L were collected at remote sites in the Lake Tahoe basin or in Sequoia National Park, or were the result of extended rain or fog sampling, where it is believed that the initial part of the event effectively stripped TFA from the lower atmosphere. The majority of snow samples taken in the Sierra Nevada mountains ranged from 50.6 to 172.0 ng TFA/L. Due to the remote location of these sampling sites from precursor "point sources" in California, lower oxidant levels, and continual atmospheric cleansing resulting from washout during winter and spring, these samples were not expected to have the higher concentrations seen in samples taken within urban areas in the Central Valley.

Table 7.5- 34: TFA concentrations in fog, snow and surface waters

Sample Area[1]	Type	Sample collection	Time/Storm event	Volume collected (L)[2]	Concentration (ng/L)
Lake Tahoe, California					
WC	Snow	20/1/96	18/1/96	4	172
	Snow	2/2/96	27/1 – 1/2/96	4	172
	Snow	1/3/96	NA	4	70
	Snow	8/3/96	5/3/96	4	51
Sequoia National Park, California					
WT	Snow	18/1/96	16 - 17/1/96	4	584
MC	River	28/5/96	NA	4	94
KW	River	9/7/96	NA	4	55
	River	15/8/96	NA	4	77
Central Valley, California					
RS	Lake	4/1/96	NA	2.5	5434
WLt	Lake	4/1/96	NA	4	579
PF	Lake	5/1/96	NA	4	62
KA	Fog	4-5/2/96	23:00 – 02:30	0.5	3779
SR	Fog	4/1/95	02:00 – 07:00	4	596
	Fog	4/1/95	07:00 – 10:00	1.0	287
	Fog	3/2/95	02:30 – 07:00	2	1780
	Fog	4/2/96	00:00 – 09:00	4	1640
	Fog	4/2/96	05:25 – 10:45	1	650
	Fog	14/2/96	05:30 – 07:25	1.0	732
	Rain	30/1/96	00:00 – 03:45	1.0	676
	Rain	31/1/96	05:15 – 09:50	4	93
	Rain	31/1/96	09:55 – 13:15	4	40
	Rain	24/2/96	09:45 – 10:35	0.5	580
	Rain	28/3/96	04:00 – 09:00	1.0	1160
Sonoma County, California					
RP1	Rain	28/12/94	NA	2	48[3]
RP2	Fog	29/12/94	03:30 – 06:00	2	750
	Fog	29/12/94	06:00 – 10:00	2	279[3]
RP1	Rain	29/12/94	Evening	1.5	55
RP2	Fog	25/11/95	NA	2	425
Washoe County, Nevada					
SW	Rain	28/9/94	NA	0.2	36
UNR	Rain	28/9/94	NA	0.5	31
	Rain	17/7/95	NA	0.15	90[3]
	Rain	19/1/96	NA	0.5	547
	Rain	4-5/3/96	NA	0.5	796
	Lake	27/5/94	NA	2	3300
	Lake	5/6/94	NA	2	3100
PL	Lake	14/7/94	NA	1	40500[3]

[1]: Sampling sites: WC, Ward Creek; WT, Wolverton; MC, Moro Creek; KW, Kahweah River; RS, Reeding Park Storyland Lake; WL, Woodward Lake; PF, Pine Flat Lake; KA, Kearney Agricultural Station; SR, Selma residential; RP1, Rohnert Park residential; RP2, Rohnert Park foothills; UNR, University of Nevada, Reno campus; SW, South-west Reno residential; PL, Pyramid Lake.
[2]: 250 mL of each sample was concentrated, extracted and analysed, except for SW 28/9/94, SW 17/7/95, and PL 14/7/95, which were 200, 110, and 90 mL.
[3]: Analysed in a previous study.

The "washout" effect was apparent in samples taken in both the Central Valley Selma location and Sonoma County. Fog and rain events occurring in Selma, CA, on 4th Jan 1995 and 31st Jan 1996 and a

fog event in Sonoma County, CA on 29th Dec 1994, resulted in reductions in TFA concentration of over half with continued collection. These extended sampling periods for rain and fog water demonstrated the efficiency of these media for stripping TFA from the atmosphere. By comparing the washout trend observed with fog events on 29th Dec 1994 and 4th Jan 1995 with the rain sample taken 31st Jan 1996, it was apparent that both rain and fog water had removed TFA from the ambient atmosphere with similar effectiveness. The second fog samples taken in series had 45 and 40% of the initial concentration of TFA, while the secondary rain sample had a comparable value of 43%. Both rain and fog samples taken from Selma, CA, were collected over the same approximate time duration. Although fog droplets have a greater surface area to volume ratio than rain drops and are suspended for longer periods of time, the partitioning of TFA into these phases appeared to be governed more by the Henry's law constant and solubility of the dissociated anion.

Two lake samples taken from the city of Fresno contained 0.6 and 5.4 µg/L TFA. These two sites are near two heavily used highway routes (State routes 99 and 41) within a densely populated area. These characteristics may contribute to elevated levels of atmospheric oxidants and precursor compounds, which will increase the quantities of TFA produced. These static lakes have direct input of TFA from precipitation and local runoff with no significant sources of output. The high concentrations of TFA found in these two small lakes may thus be a result of their location within the "point source" and their physical ability to retain deposited TFA.

A rough estimate of expected TFA concentrations were made from averaged rainfall inputs for Woodward Lake and compared to the measured value. A high TFA rainwater value of 1160 ng/L and the average concentration per unit volume of all rainwater samples taken in the Central Valley, 253 ng/L, were used to estimate the annual input of TFA into Woodward Lake from rainfall and the resultant lake water concentration. The volume of Woodward Lake is approximately 28370 m^3 with the surface area estimated at 10400 m^2. The annual averaged rainfall in Fresno County is 267.21 mm. Calculations made with the high TFA rain concentration resulted in an annual TFA input of around 3224 mg/yr and lake water concentration of 114 ng/L. Use of the averaged sample rainfall concentration yielded TFA input of about 703 mg/yr and a resultant lake water concentration of 25 ng/L. The measured value (579 ng/L) was 5 to 20 times the level estimated from a single annual rainwater input. This probably reflects the additive nature of several years input, and evaporative concentration within the lake but there may also be added sources of TFA such as from fog water or dry deposition.

Lower TFA concentrations were seen at Pine Flat Reservoir, CA, located in the foothills of the Sierra Nevada mountains to the east of Fresno. This site contained 62 ng/L of TFA, which was near the levels found in river water samples taken from similar remote Sierra Nevada sites such as Kahweah River and Moro Creek in Sequoia National Park. Pine Flat reservoir has significant output and would not be expected to accumulate TFA by evaporative concentration. With a turnover rate of less than a year, this lake system should remain at a relatively steady concentration, which may slowly increase with increasing use of HFCs and HCFCs.

Pyramid Lake, located north of Reno, contained 40.5 µg/L TFA. This desert lake receives input from the Truckee River and the vast central Sierra Nevada watershed. The Truckee River flows from Lake Tahoe, through the city of Reno, and terminates in Pyramid Lake. Washout and runoff of TFA from winter rains can provide a major source of TFA addition into this system and may be responsible for the high measured concentration. The sample taken on 14th July 1995 also represented a high point in seasonal evaporative concentration of Pyramid Lake. Like many other Great Basin lakes, Pyramid Lake is characterised by a lack of significant out-flow, input of water from in-flowing rivers or streams, and a dry climate that results in a rate of water evaporation that is usually greater than the input. These traits may make Pyramid Lake and other similar lakes accumulators of TFA.

III. CONCLUSIONS

TFA was detected and measured in fog, rain, snow, and surface water from several locations in California and Nevada. Fog and rain samples contained 31 - 3779 ng/L TFA. Snow samples taken in more remote areas had 51 - 584 ng/L. Surface water varied from 55 ng/L - 41 µg/L depending on type and location. Washout of TFA from the lower atmosphere was observed in both rain and fog samples. There was a trend toward decreasing TFA in precipitation samples taken at later stages during a single storm event.

The magnitude of TFA levels suggest that formation in the environment from HCFC and HFC degradation is occurring more rapidly than expected, and/or other sources exist for environmental TFA.

3. Assessment and conclusion

Assessment and conclusion by applicant:

Assessment:

This article contains monitoring (including detailed sampling and analytical methodology) for fog, rain, snow and surface waters from California and Nevada (1994 – 1996). The study was not conducted to GLP or other similar guidelines and there are currently no guidelines for the conduct of monitoring studies.

Conclusion:

The "washout" of TFA effect was apparent in samples taken in both the Central Valley Selma location and Sonoma County. Fog and rain samples contained 31 - 3779 ng/L TFA, snow samples taken in more remote areas had 51 - 584 ng/L and surface water varied from 55 ng/L - 41 µg/L

The information from this article can be regarded as reliable.

Assessment and conclusion by RMS:

Outcome and conclusion of the study: RMS should indicate if they agree to the results and conclusions of the APPL.

1. Information on the published literature article

Data Point:	KCA 7.5/18
Report Author:	Jordan, A.; Frank, H.
Report Year:	1999
Report Title:	Trifluoroacetate in the environment. Evidence for sources other than HFC/HCFCs
Report No:	M-585141-01-1
Document No:	M-585141-01-1
Guideline(s) followed in study:	not applicable
Deviations from current test guideline:	Current Guideline: not applicable
Previous evaluation:	No, not previously submitted
GLP/Officially recognised testing facilities:	No, not conducted under GLP/Officially recognised testing facilities
Acceptability/Reliability:	Yes

2. Full summary of KCA 7.5/18

Executive Summary

The partly halogenated C2-hydro(chloro)fluorocarbons (HFC, HCFC) 1,1,1-trifluoro-2,2-dichloroethane (HCFC-123), 1,1,1,2-tetrafluoro-2-chloroethane (HCFC-124), and 1,1,1,2-tetrafluoroethane (HFC-134a) are CFC substitutes found at increasing levels in the atmosphere. Trifluoroacetate (TFA) is an atmospheric degradation product of these compounds and due to its persistence, potential accumulation in some aquatic ecosystems is of environmental concern. This study presented base level TFA environmental concentrations and determined if model calculations were in line with actual data. Average levels of about 120 ng/L as predicted for the year 2010 were found already in rain in Germany, slightly higher than in rain collected in Switzerland or Nevada. In the major rivers in Germany, TFA was present at average concentrations of 140 ng/L. In air, levels of 45 - 60 pg/m^3 were found in Central Europe. Between March 1995 and September 1996, a period of substantial increase in atmospheric HFC-134a mixing ratio, the TFA concentrations in air and precipitation did not significantly increase. TFA was absent in old groundwater samples, and in river water from remote locations, concentrations were low. These data suggested that the total TFA in both compartments exceeded the formation potential of sources known at the time, that TFA in atmosphere and rain is regionally associated with industrial or population density, and that other unresolved sources must contribute to the concentrations at the time of the publication.

I. MATERIAL AND METHODS

Material

The aim of this work was to extend the database of environmental TFA concentrations in order to enable global budget estimations. Air, precipitation and river water samples were taken regularly and analysed for TFA from March 1995 to September 1996 in Bayreuth (Northern Bavaria, Germany). Surface and ocean waters from several other locations and continents have also been analysed as well as groundwater samples of preindustrial origin.

Sampling method

All glassware used was thoroughly cleaned prior to use. Rain samples were collected in the botanical garden of the University of Bayreuth from May 1995 to June 1996 using Pyrex glass funnels (diameter 40 cm) and 500 mL brown glass bottles. From May 1996 to September 1996, samples of canopy runoff were collected from a conifer forest and from a clearing nearby. Surface water samples were collected

in 250 mL brown glass bottles with screw-caps lined with Teflon-laminated butyl rubber disks. After rinsing five times with the water of the location, the bottle was filled by immersion leaving about 1 mL of air space under the lid. Air samples were collected using glass denuder tubes (2.5 m × 1 cm id) consisting of five segments of 0.5 m length connected with ground-joints and Teflon sleeves on both ends. The denuders were coated with aqueous saturated solution of sodium carbonate in glycerol at the sampling site to avoid contamination from laboratory air. Three denuders were run in parallel, each one connected to a membrane pump followed downstream by a gas-volume counter. In most cases, air volumes of 50 - 60 m^3 per denuder were sampled in the course of 5 days at flow rates of 7 - 8 L/min through each tube. The glycerol film containing the entrapped acids was then eluted with five portions of 2 mL deionized water into a 20 mL test tube with its ground-joint directly connected to the front end of the denuder.

Analytical method

Triplicate aliquots (10 mL) of aqueous samples or denuder eluate were taken in the clean air glove compartment and transferred to a 20 mL test tube with ground-joint stopper. The actual sample volume was determined by weight. Analyses were always performed within 1 day of sample collection, except for those samples collected at remote sites. Sets of 15 - 20 actual samples, three blank samples (10 mL deionized water), and seven calibration samples were always processed in parallel. Pentafluoropropionic acid (PFP) in deionized water was added to each sample as internal standard. Sodium chloride and concentrated sulfuric acid were added, and trifluoroacetic acid was extracted with 1 mL of *tert*-butyl methyl ether by agitation (60 s). After standing for 10 min, 0.9 mL of the supernatant ethereal extract was placed in a silanized 1 mL crimp-cap vial containing 10 µL of a solution of 200 µmol/mL 1-(pentafluorophenyl)diazoethane in *tert*-butyl methyl ether. Derivatization was complete within 1 h at room temperature. The extraction efficiency was determined as 92 ± 3% by spiking river and North Seawater in the concentration range of 20 - 3500 ng/L.

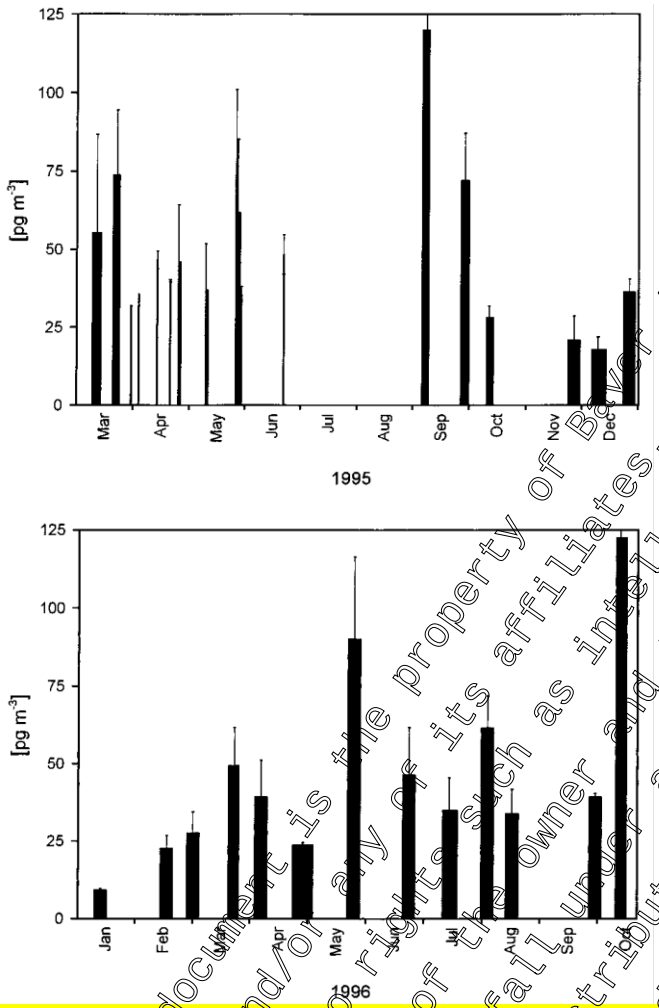
GC-MS analyses were performed on a gas chromatograph interfaced to a quadrupole mass spectrometer equipped with chemical-ionization source. Aliquots (3 µL) of the derivatized sample were injected onto a deactivated fused-silica retention gap (50 cm × 0.53 mm). Gas chromatographic separation was carried out on a fused-silica column coated with methyl-phenyl-(5%)-silicone (CPSil 8 CB-MS, 25 m × 0.25 mm, film thickness 0.25 µm). Helium was used as carrier gas at an inlet pressure of 80 kPa. TFA and the internal standard were detected in the selected-ion monitoring mode as carboxylate anions (TFA: m/z = 113; PFP: m/z = 163).

Each calibration series included seven TFA standard samples ranging from 20 to 4000 ng/L. Relative response factors are known to be variable in the negative chemical-ionization mode; therefore, after each series of 20 samples, a calibration run was included, and response factors were determined by interpolation.

II. RESULTS AND DISCUSSION

Air

TFA air levels ranged from 10 to 125 pg/m^3, with an average value of 44 pg/m^3 (Figure 7.5- 11). Previous authors have determined similar levels; Vista-University campus in Mamelodi (40 pg/m^3) near Pretoria, South Africa (August 1996); Zurich, Switzerland (65 pg/m^3) in September 1995; and at Waldstein, Northern Bavaria, Germany (20 - 40 pg/m^3), in June 1995.



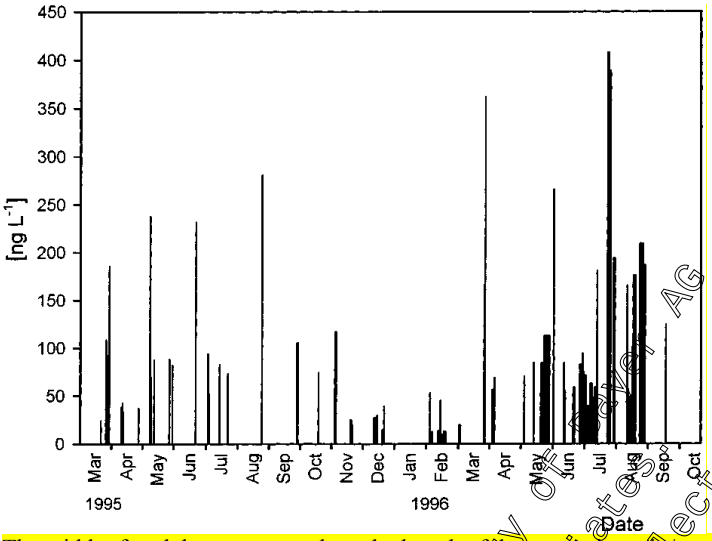
The height of each sample bar represents the average of three replicate analyses; where no standard deviations are indicated, only one analysis was performed. The width of each bar corresponds to the length of the sampling period.

Figure 7.5- 11: TFA in ambient air near Bayreuth, Germany in 1995 (a) and 1996 (b)

Precipitation

TFA concentrations in precipitation collected at the Botanical Garden of the University of Bayreuth and on a forest clearing about 0.5 km to the south ranged from 10 to 410 ng/L (average of 110 ng/L). One sample had a concentration below determination limit (10 ng/L) (Figure 7.5- 12). Comparison of TFA levels in rain samples collected in summer 1995 and in summer 1996 seemed to suggest an upward trend, although statistically not significant. Other authors report TFA levels in rain samples from Switzerland (50 - 80 ng/L) and Nevada (30 - 90 ng/L) in a similar range. TFA was below the determination limit in four rainwater samples collected at Mace Head, Ireland, in October 1995 and in surface runoff water collected after heavy rainfall near Oudtshoorn, South Africa, in October 1996.

Canopy throughfall of a conifer forest was generally higher in TFA by a factor of 2.6 than rain samples collected in parallel on a nearby clearing. This is indicative of evaporative concentration of rain on leaves and needles before collection as canopy throughfall; dry deposition on plant surfaces and subsequent rinse-off or leaching of TFA from needles may also contribute.



The width of each bar corresponds to the length of the respective rain/snowing period. The values represent the means of three replicate analyses (relative standard deviations about 15%).

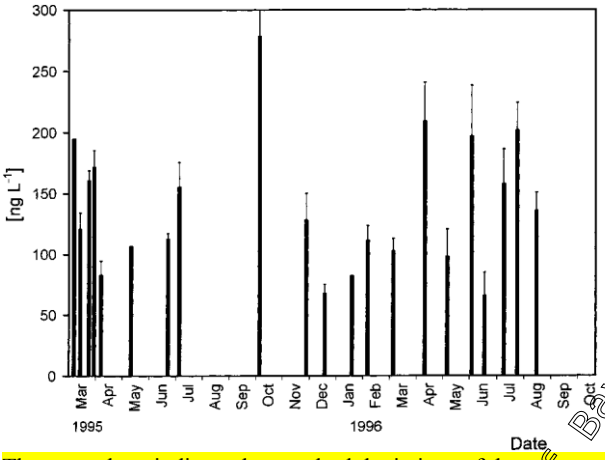
Figure 7.5- 12: TFA in precipitation near Bayreuth, Germany in 1995 and 1996

River water

Water collected in Bayreuth from the Roter Main River contained TFA ranging from 60 to 280 ng/L (average 140 ng/L) (Figure 7.5- 13). Other authors reported similar concentrations previously for eight other German rivers (Table 7.5- 35). The average concentration in river water was 1.3-fold higher than that in precipitation; since evaporation of hydrometeors should entail a concentration increase slightly higher than 2-fold for Germany, this suggested a sink for TFA either in the form of an unaccountable depot or an unknown removal process.

TFA concentrations in the Kemijoki River (Rovaniemi, Finland) near the polar circle were 210 ng/L, suggesting significant contribution of Central European air masses to subarctic TFA deposition due to prevailing southwesterly winds. In contrast, the Jennessej River (Krasnojarsk, Siberia) contained only 40 ng/L in July 1996.

Surface waters were collected on the southern hemisphere in Brazil and South Africa in August 1996. TFA was not detected in water samples from the Rio Tocantins (Cotijuba, Brazil) or from a small river near Tweede Tol (Hottentot-Mountains, South Africa) but was present in the Apies River (15 km north of Pretoria, South Africa) at 500 ng/L and in the Vaal River (Christiana near Kimberley) at 100 ng/L. An intermediate level of 40 ng/L was found in a freshwater pond in the Golden Gate National park about 300 km south of Johannesburg South Africa (Table 7.5- 35).



The errors bars indicate the standard deviations of the average of three independent samples.

Figure 7.5- 13: TFA in the River Roter Main at Bayreuth

Table 7.5- 35:

identity	location	date	concn ± std dev	n
	Rivers			
Elbe	Wittenberg; Germany	24.02.1995	200 ± 20	3
Danube	Regensburg; Germany	25.03.1995	200 ± 1	3[a]
Main	Mainleus; Germany	02.03.1995	10 ± 6	3[a]
Neckar	Tübingen; Germany	23.04.1995	260 ± 13	3[a]
Elbe	Hamburg-Altona; Germany	07.07.1995	100 ± 14	5[a]
Weser	Bremerhaven; Germany	06.07.1995	100 ± 7	3[a]
Rhine	Duisburg-Ruhrort; Germany	06.07.1995	630 ± 100	4[a]
Rhine	Bregenz; Austria	14.09.1995	55 ± 2	3[a]
Warnow	Rostock; Germany	09.07.1995	60 ± 15	4[a]
Naab	Schwandorf; Germany	29.10.1996	130 ± 18	3
Jordan	below Lake Kinneret; Israel	11.11.1995	250 ± 20	3[a]
Jennessej	Krasnojarsk; Russia	28.07.1996	30 ± 9	3
Rio Tocantins	Cotijuba; Brasil	31.08.1996	<15	3
Kemijokj	Rovaniemi; Finland	13.07.1996	210 ± 40	4
Apies River	North of Pretoria; RSA	31.08.1996	500 ± 35	3
Vaal River	Christiana; RSA	30.08.1996	100 ± 10	6
Tweede Tol	Hottentot Mts.; RSA	22.10.1996	<15	3
	Lakes			
Lake Fichtel	Fichtelberg; Germany	17.05.1995	70 ± 18	3[a]
Lake Weissenstadt	Weissenstadt; Germany	17.05.1995	110; 100	2[a]
Lake Constance	Constance; Germany	11.09.1995	60 ± 5	3[a]
Lough Ahalia	Connemara; Ireland	01.11.1995	<10	3
Lough Skannive	Connemara; Ireland	01.11.1995	20 ± 4	3[a]
Lake Kinneret	Capernaum; Israel	11.11.1995	200 ± 8	3[a]
Dead Sea	En Bokek; Israel	10.10.1995	6400 ± 600	3[a]
Borehole	Waterval District; RSA	26.08.1996	45 ± 2	3
Pond	Fourriesburg; RSA	30.10.1996	40 ± 6	3
	Marine Waters			
North Sea	Husum; Germany	07.07.1995	90 ± 15	4[a]
Baltic Sea	Warnemünde; Germany	08.07.1995	40 ± 10	3[a]
Atlantic	Ile d'Yeu; France	07.09.1995	250 ± 25	3[a]
Atlantic	Mace Head; Ireland	31.10.1995	70 ± 18	4[a]
Atlantic	Cape Point; RSA	17.10.1996	160 ± 5	3
Pacific	Noosa Heads; Australia	22.04.1996	200 ± 50	3

a: Analysed earlier.

Table 7.5- 36: TFA concentrations (ng/L) in springs and mineral water wells (some of known

identity	location	date	concn ± std dev	n	age [yr]
Spring Waters					
Saale Spring	Fichtelgebirge (Bavaria; Germany)	17 May 1995	130 ± 20	3	ca. 4
Eger Spring	Fichtelgebirge (Bavaria; Germany)	17 May 1995	110 ± 25	3	ca. 4
Naab Spring	Fichtelgebirge (Bavaria; Germany)	17 May 1995	80 ± 6	3	ca. 4
White Main Spring	Fichtelgebirge (Bavaria; Germany)	17 May 1995	70 ± 8	3	ca. 4
Friesen Spring	Fichtelgebirge (Bavaria; Germany)	17 May 1995	320 ± 20	3	ca. 4
Well Waters					
Antonien Source	Kondrau (Bavaria; Germany)	28 Oct 1996	<10	3	>700
Dippold Source	Kondrau (Bavaria; Germany)	28 Oct 1996	<10	3	unknown
Bayern Source	Kondrau (Bavaria; Germany)	28 Oct 1996	23 ± 3	5	ca. 200
Gerwig Source	Kondrau (Bavaria; Germany)	28 Oct 1996	10 ± 3[a]	3	unknown
Thüringer Wald Source	Schmalkalden (Thuringia; Germany)	04 Nov 1996	<9	3	400 ± 60
Rennsteig Source	Schmalkalden (Thuringia; Germany)	04 Nov 1996	13 ± 3	3	185

[a] Detection limit = 10 ng/L.

Ocean

TFA levels of 70, 250, and 160 ng were determined in Atlantic Ocean water collected directly from the shore at Mace Head (Ireland, 1995), the Ile d'Yeu (France, 1995), and South Atlantic Ocean water taken at Cape Point (Cape of Good Hope, South Africa). TFA concentration of 200 ng/L was determined in the Pacific Ocean water at Noosa Heads (50 km north of Brisbane, Australia), respectively.

Spring and well water

TFA levels in spring waters of young age were found in the same range as surface waters. In groundwater of known old age (determined by radioisotope analysis) TFA was very low (Table 7.5- 36). Two samples with negligible freshwater contents (<1%) ("Antonien Quelle" and "Thüringer Wald Quelle") had TFA at blank levels. The "Bayern Quelle" and the "Rennsteig Quelle" with young water contents of 10% and 15%, respectively, had levels of 13 and 25 ng/L.

TFA as Degradation Product of HFC-134a, HCFC-123 and HCFC-124

High environmental TFA levels call for sources other than the CFC-alternatives. The regional pattern of high TFA levels in river waters in industrialised zones versus low levels in rivers at sparsely industrialized regions (Rio Tocantins, Tweede Tol, Jennessee) suggest other significant industrial contributions. Further evidence is provided by the fact that air and rain levels in Germany do not exhibit significant upward trends (Figure 7.5- 11 and Figure 7.5- 12) during a period of a rapid growth of the atmospheric abundance of HFC-134a. The presence of TFA in spring waters at similar concentrations as in rain and surface waters indicate that TFA is persistent and the absence of TFA in old groundwaters suggest that most of the environmental TFA burden is of modern origin. The fact that TFA is also found in all ocean surface water samples even on the southern hemisphere suggest that there is potentially a large global source.

Other potential TFA sources

The fluorinated inhalation anaesthetics halothane ($CF_3CHClBr$), desflurane ($CF_3CHFOCHF_2$), and isoflurane ($CF_3CHClOCHF_2$) are oxidized in the atmosphere to TFA. To estimate an upper limit for TFA from narcotic gases, the author assumed that 70-80% (i.e. 6000 t) of halogenated inhalation anaesthetics are mainly TFA producing isoflurane. With an atmospheric lifetime of about two years this would yield an average rain concentration of less than 5 ng/L.

Several pesticides (e.g. trifluralin; production volume in 1986, 50000 t) have a trifluoromethyl-substituted aromatic ring system, a fraction of the applied pesticides will volatilize, undergo photooxidation or be wet deposited. Ring-cleavage (for trifluralin) has not been observed to date and is not expected as the electronegative CF_3-group decreases the OH-reactivity of the aromatic ring. Although metabolism of trifluoromethylated aromatics in soils has been suggested to produce TFA, radiolabelled studies showed slow degradation. Even if TFA was formed in soil, it is not conceivable that it is a relevant source of atmospheric TFA.

Electrolytic aluminium production is known to entail emissions of CF_4 and C_2F_6. Formation of TFA was also considered possible, but analysis of a stackgas sample of an aluminium production site did not reveal any TFA. An upper limit of 0.25 g of TFA emitted per ton aluminium as derived from the limit of determination would result in a maximum annual global release of 5 t/a from this source, assuming a global annual aluminium production of 20 million tons.

Most perfluorinated polymers are used in long-term applications with product lifetimes of 20 years and more, it may be expected that TFA from this source will slowly increase in the coming years. The fraction of waste currently being incinerated in Europe is 50%; for nonfluorinated plastics a share of 17% has been stated. Several authors have shown that hexafluoropropene and trifluoroacetylfluoride (TFAF) are pyrolysis products of perfluoroalkyl ethers, polytetrafluoroethene (PTFE) and polyperfluoroethenepropene. Atmospheric reaction of hexafluoropropene with hydroxyl radicals leads to TFAF within ca. 6 days followed by hydrolysis to TFA within days. Due to its hydrophilicity, TFA should predominantly be deposited close to the source regions. On the assumption that 2500 t fluoropolymer waste are presently incinerated in Europe and 10% hexafluoropropene are formed, ca. 200 t TFA may be released annually. This is on a similar scale as the amount of annual wet deposition upon Europe of about 500 t (average concentration = 100 ng/L; annual precipitation rate = 500L/m²). Thus, thermolysis of fluoropolymers may be an important source of the environmental TFA burden.

III. CONCLUSIONS

TFA seems to be predominantly if not exclusively of anthropogenic/industrial origin. As a fully persistent and strongly hydrophilic compound it accumulates in the hydrosphere, particularly in the oceans. Since there are no insoluble salts or stable derivatives known, TFA must be expected to eventually remain and accumulate in the oceans.

3. Assessment and conclusion

Assessment and conclusion by applicant:

Assessment:
This article from public literature reports monitoring results for TFA in air, precipitation, river water, surface waters, and ocean waters, including details of the sample methodology and analytical work. However, the work wasn't carried out according to GLP, and there are currently no guidelines for the conduct of monitoring studies. The reported results are a snap-shot of TFA concentrations in the mid-1990's.

Conclusion:
TFA (at the time of the publication 1999) seemed to be predominantly, if not exclusively, of anthropogenic/industrial origin. As a persistent and strongly hydrophilic compound it accumulates in the hydrosphere, particularly in the oceans. In Germany, TFA concentrations in precipitation ranged from 10 to 410 ng/L, in rivers from 60 to 280 ng/L and in oceans from 70 to 200 ng/L. In spring waters of young age, TFA was found in the same range as surface waters, whereas in groundwater of known old age, TFA was very low.

The information from this article can be regarded as reliable.

Assessment and conclusion by RMS:
Outcome and conclusion of the study: RMS should indicate if they agree to the results and conclusions of the APPL

1. Information on the published literature article

Data Point:	KCA 7.5/19
Report Author:	Cahill, T. M.; Seiber, J. N.; Wujcik, C. E.
Report Year:	1999
Report Title:	Determination of trifluoroacetic acid in 1996-1997 precipitation and surface waters in California and Nevada
Report No:	M-585142-01-1
Document No:	M-585142-01-1
Guideline(s) followed in study:	not applicable
Deviations from current test guideline:	Current Guideline: not applicable
Previous evaluation:	No, not previously submitted
GLP/Officially recognised testing facilities:	No, not conducted under GLP/Officially recognised testing facilities
Acceptability/Reliability:	Yes

2. Full summary of KCA 7.5/19

Executive Summary

The atmospheric degradation of three chlorofluorocarbon (CFC) replacement compounds; HFC-134a, HCFC-123, and HCFC-124, results in the formation of trifluoroacetic acid (TFA). Concentrations of TFA were determined in precipitation and surface water samples collected in California and Nevada during 1996-1997. Terminal lake systems were found to have concentrations 4 - 13 times higher than their calculated yearly inputs, providing evidence for accumulation. The results support dry deposition as the primary contributor of TFA to surface waters in arid and semi-arid environments. Precipitation samples obtained from three different locations contained 20.7 - 1530 ng/L with significantly higher concentrations in fogwater (median = 689 ng/L) over rainwater (median = 63.7 ng/L). Elevated levels of TFA were observed for rainwater collected in Nevada (median = 136 ng/L) over those collected in California (median = 49.5 ng/L), indicating continual uptake and concentration as clouds move from a semi-arid to arid climate. Thus, several mechanisms exist, including evaporative concentration, vapour-liquid phase partitioning, lowered washout volumes of atmospheric deposition water, and dry deposition, which may lead to elevated concentrations of TFA in atmospheric and surface waters above levels expected from usual rainfall washout.

I. MATERIAL AND METHODS

Material

The objective of this study was to determine conditions under which TFA might reach concentrations in the environment above levels typically found in atmospheric precipitation.

Sampling method

Rainwater samples were collected at Robert Park and Selma, CA and Reno, NV from December 1996 to September 1997. Fog events occurring during this period were sampled at both California sites, but not in Reno due to the lack of fog.

Surface waters from the Sierra Nevada Range in both California and Nevada were collected during 1996 - 1997. The Truckee River and Carson River systems were sampled from their headwaters in the Sierra Nevada to their terminal endpoints in the Great Basin. The Truckee River system sampling began with a tributary stream to Lake Tahoe near Eagle Falls, CA in the Sierra Nevadas, through Lake Tahoe to the lower Truckee River and Pyramid Lake, its terminal endpoint. The Carson River system sampling began

in the high Sierra Nevada mountains to Carson City, NV, through Lahontan Reservoir, and ending at the Stillwater National Wildlife Refuge (Stillwater NWR). In addition to the Truckee/Pyramid and Carson/SNWR terminal systems, Mono Lake, CA, was examined along with one of its tributaries, Rush Creek, which flows from the Sierra Nevada mountains in the vicinity of Yosemite National Park.

Fogwater was collected in duplicate by two portable high-volume fog sampling units placed side-by-side. Each unit contained a fan that pulled the foggy air past a four-layer screen of 0.28 mm diameter Teflon filaments. The water coalesced on this screen and ran into the collection device. The entire apparatus, including the separate Teflon screens, had been rinsed thoroughly before each collection period to remove any TFA from surfaces. Several rinse blanks showed that no detectable TFA was leached from the Teflon screens. Depending upon the sampling period, 100 - 500 mL of fogwater was collected in 500 mL amber vials, sealed with aluminium foil lined lids and frozen until the time of extraction and analysis.

Rain samples were collected in 500 mL amber bottles using 25 cm diameter polyethylene funnels. Each rain event was sampled in duplicate with 100 - 800 mL volumes typically collected per event. Funnels were rinsed with acetone (reagent grade), reagent water, and finally HPLC grade acetone between sampling efforts. All bottle caps were lined with aluminium foil before sealing. Rainwater samples were either frozen or refrigerated at 5°C until analysis.

Surface water was sampled in duplicate from lakes and rivers by submerging two 1000 mL amber bottles at various shore locations. Bottles were rinsed 3 times with water from the site before sample collection. All samples within a river system were collected within 2 days. After collection, foil-sealed samples were refrigerated at 5°C until analysis

Analytical method

Fogwater, rain, and surface waters were vacuum filtered at 5°C through a 90-mm diameter GF/F filter. Conductivity and pH measurements were made immediately before resealing the sample to limit exposure to room air. Aqueous samples with conductivities less than 500 µS/cm were directly extracted with a conditioned anion exchange SR Empore disk. The sample was pulled under vacuum through the disk at the rate of 35 - 45 mL/min, followed by three 15 mL methanol rinses of the extraction reservoir. The disk was then dried under vacuum, cut into small pieces and placed in a headspace vial with 4.0 mL of 10% sulphuric acid (18M) in methanol. The vial was then capped and vortexed prior to derivatization and analysed by headspace gas chromatography. Environmental samples with conductivities above 500 µS/cm were processed by a liquid-liquid extraction procedure which involved acidifying ≤ 200 mL of aqueous sample in a separatory funnel with 1 mL of sulphuric acid (18 M) for every 10 mL of sample. Cold diethyl ether (100 mL) was added followed by saturation of the aqueous phase with sodium sulphate. In a second separatory funnel, 100 mL of reagent water and 20 mL of 1 M NaOH were added along with the ether layer from the first separatory funnel. This diethyl ether extraction was conducted a total of three times with the initial aqueous sample, with each of the subsequent ether layers added to the second separatory funnel. After vigorously agitating the second funnel containing the alkaline water and ether, the aqueous layer and 2-3 mL of the ether layer were dispensed into a clean bottle. This solution, containing the TFA from the original sample was then passed through the Empore disk as described previously.

A headspace sampler and autosystem GC with an electron capture detector (ECD) were used for derivatization and sample analysis. All headspace samples were thermostated at 50°C for 1 h before injection to promote the quantitative derivatization of TFA to its volatile methyl ester, methyl trifluoroacetate (MTFA), and partitioning of MTFA to the vapour phase. The analytical column was a 25 m x 0.32 mm i.d. Poraplot Q with a 10 µm stationary phase. The carrier and makeup gases were ultrahigh purity nitrogen with flows of 3.2 mL/min at 110°C and 32 mL/min, respectively.

Environmental samples, including Pyramid Lake, NV, Mono, Lake, CA, Stillwater National Wildlife Refuge, NV, and rain from Reno, NV (6/19/97), were confirmed by GC-MS in the selected ion monitoring mode. Ion 69 *m/z*, which corresponds to the CF_3^+ fragment, was scanned to obtain optimal sensitivity and selectivity.

LOQ: The limit of quantification was 36 ng/L for a 400 mL sample and was determined by the average analytical blank plus six times the standard deviation of the analytical blanks.

TFA concentrations below 36 ng/L were detected but quantification was less reliable. Recoveries for spiked (579 and 1160 ng/L) environmental samples passed directly through the anion exchange Empore disk were 94 - 105%. Environmental samples requiring liquid-liquid extraction (i.e., those with conductivities > 500 µS/cm) gave 89 - 104% recovery.

RSDs: Relative standard deviations for all spike-recovery samples fell in the range of 0.7 - 7.9%, demonstrating the consistency of the method.

Statistical calculations were conducted by Minitab software version 10.2. The data sets were tested for normal distribution using an Anderson-Darling normality plot ($P < 0.05$). Since the majority of the data sets were non-normal in distribution, a median and range were reported. Comparisons between two groups of non-normally distributed data were conducted using a Mann-Whitney test with $\alpha = 0.05$.

II. RESULTS AND DISCUSSION

Fogwater and precipitation

There were no significant differences between fogwater from Rohnert Park and Selma (Mann-Whitney test $P > 0.1$). Precipitation samples also showed consistent concentrations between the two sites (Mann-Whitney test $P > 0.1$). In both cases, the median TFA concentrations in the precipitation samples between the two sites were similar (Table 7.5-37). The similar medians combined with a high degree of variability in the data sets caused the lack of statistical differences between the two sites. The similarity in concentrations of TFA found at Selma and Rohnert Park, California may result from similar local TFA production due to population sizes and precursor use, transport of both the precursor HFCs and HCFCs and TFA from California's San Francisco Bay area, and/or a similar region-wide ambient level of TFA not connected with specific local sources. However, rainwater collected at Reno, NV, showed significantly higher concentrations of TFA than the other two sites (Mann-Whitney test $P < 0.001$), with the median TFA concentration being over twice as high. As an arid environment in the rain shadow of the Sierra Nevada mountain range, Reno is expected to have lower rain frequencies and lower rain volumes due to water losses from rainfall and cloudwater evaporation during transport. The effective washout of TFA from the ambient air by a lower volume of rainwater may result in an overall higher rainwater concentration. Build-up of TFA in cloudwater could also occur from continual vapour phase partitioning along its transport route and cloudwater evaporation. TFA transferred to the vapour phase during the evaporation process is expected to be rapidly repartitioned to the bulk cloud mass as a result of its low Henry's Law constant. The complete evaporation of cloudwater containing TFA could elevate ambient atmospheric concentrations as is proven for both formic and acetic acids measured in air in the southwestern United States. Build-up of ambient TFA between rain events resulting from local production and complete cloud and rainwater evaporation, in addition to the potential accumulation of TFA in cloudwater during transport, could explain elevated TFA concentrations in Reno rain. While both California sites are technically classified as semiarid environments, the drier climate of the Reno area provides the means for enhancing evaporation of cloudwater and, consequently, elevating TFA concentration in precipitation and air.

Table 7.5- 37: Concentrations of TFA in rainwater and fogwater samples collected from November 1996 to September 1997

Sample	Number of samples	Median TFA concentration (ng/L)	Range of sample concentrations
Rohnert Park, Sonoma County, CA			
Rainwater	31	46.6[1]	25.1 - 158
Fogwater	6	723	86.6 - 809
Selma, Fresno County, CA			
Rainwater	23	93.9[2]	20.7 - 463
Fogwater	21	689	101 - 1390
Reno, Washoe County, NV			
Rainwater	6	136	108-763

[1]: Ten samples were below LOQ.
[2]: Five samples were below LOQ.

River and lake system

A series of river samples collected upstream of Reno on the Truckee River and Carson City on the Carson River were compared to a series of downstream samples from those same sites, to test for additional inputs from the cities. Since Lake Tahoe has a large volume and complex mixing behaviours, the "upstream" segment of the Truckee River was defined as the distance from the Truckee River outflow from Lake Tahoe to Reno; it does not include any Lake Tahoe samples or tributaries to Lake Tahoe. In both cases, samples taken downstream from the cities trended toward higher TFA concentrations than upstream samples (Mann-Whitney tests, $P < 0.001$ Truckee River, $P < 0.001$ Carson River). This is a tenuous calculation for the Truckee River system because some of the measured values are near or below the method's limit of quantification (36 ng/L). Measured values that fell below the limit of quantification were still used for the statistical calculations as they represented the best estimate of the sample concentration. The Carson River system consistently had concentrations above the LOQ, lending more confidence to the statistical calculations. The median and ranges of TFA concentrations are presented in Table 7.5- 38.

Table 7.5- 38: Concentrations of TFA in the Truckee River, Carson River and Mono Lake

Sample	Number of samples	Median TFA concentration (ng/L)	Range of sample concentrations
Truckee River System			
Upstream of Reno, NV	19	28.9[1]	12.8 – 47.7
Downstream of Reno, NV	8	50.8[2]	31.0 – 66.5
Pyramid Lake, NV	6	79.0	77.1 – 95.1
Carson River System			
Upstream of Carson City, NV	6	45.3	36.6 – 60.5
Downstream of Carson City, NV	8	84.2	76.9 - 154
Stillwater, NWR, NV	6	432.5	314 - 472
Mono Lake System			
Rush Creek, CA	2	51.0	50.1 – 52.0
Mono Lake, CA	10	192	186 - 227

[1]: Seventeen samples were below LOQ.
[2]: One data point was below LOQ.

Concentrations of TFA in the three terminal surface water systems, including Pyramid Lake, Stillwater NWR and Mono Lake, the terminals for rivers flowing east from the Sierra Nevada mountains, were compared to the concentrations of their river sources. In all three cases, the terminals were found to have significantly higher concentrations of TFA than their source rivers (Mann-Whitney Tests, $P < 0.001$ for Pyramid Lake and Stillwater NWR and $P = 0.04$ for Mono Lake), thus demonstrating that TFA is accumulating in terminal water bodies.

Since TFA concentrations have been measured in rain and in-flowing rivers, dry deposition into these lakes can be estimated and it was possible to calculate the approximate time, at current input rates, it would take for these lakes to accumulate to the observed TFA concentrations. The assumptions for these calculations were the following; (1) TFA is only deposited into the lake through streams, wet deposition, and dry deposition. (2) No TFA is removed from the lake by degradation, volatilization, or binding to soil. (3) The volumes of Pyramid and Mono Lakes are maintained at their same level from year to year due to water evaporation. (4) The lake is evenly mixed so the samples are representative of the entire lake. (5) TFA inputs do not vary during a year, hence the input samples are representative of the entire year. (6) TFA vapour and particulate deposition inputs can be estimated from rough flux measurements or by applying the 92% dry deposition estimate for formic and acetic acid to TFA. (7) TFA inputs are constant between years, which is not the case due to the increase in usage rates of HFCs. Therefore, this model will overestimate the overall quantity of TFA input to these lake systems during the introduction of the HCFCs and HFCs. (8) The TFA concentration in rainfall at the lakes is the same as in Reno, NV where the rainfall samples were taken. The volume, surface area, surface water inputs, and rainfall rates for Pyramid Lake and Mono Lake are known. Since the volume and surface area of Stillwater NWR could not be determined, its accumulation rate was not calculated.

The results show that the observed concentration of TFA in Mono Lake could be reached in 4.2 and 7.2 years of current input and Pyramid Lake would have reached its observed concentrations in 6.2 and 13.0 years of current input depending upon the dry deposition flux estimation used. The HFCs and HCFCs were introduced in 1990, which is seven years prior to the sampling. Therefore, the estimated accumulation time for TFA in both Pyramid and Mono Lake correspond generally to the introduction of the CFC replacement compounds. Although wet deposition may be the primary removal and transfer mechanism for TFA in the atmosphere in more temperate climates, dry deposition (vapour and particulate) appears to be the dominant pathway in arid and semi-arid environments. The Henry's Law constant of $8.95 \pm 2 \times 10^3$ mol/kg.atm (at 298.15 K) reinforces the fact that vapour phase TFA will partition immediately into water when present. Since arid climates receive little annual rainfall, and practically none from May to October, vapour partitioning could contribute appreciable quantities of TFA to surface water systems. Particulate deposition, which can contain small quantities of water, may also serve as a significant transport medium during the drier months. Up to 92% of the overall flux of formic and acetic acids to the Sierra Nevada mountain range occurs via dry deposition. In both cases, vapour phase formic and acetic acid dominated the gas-particle distribution of the overall measured dry deposition totals at 94 and 88%, respectively. Since TFA has similar physical-chemical properties to these acids, it should behave like and be transported by similar mechanisms. Assuming that TFA in the environment is derived from the HFCs and HCFCs and no alternate sources, dry deposition should be the major contributor of TFA into arid and semi-arid environments.

III. CONCLUSIONS

Terminal lake systems were found to have concentrations 4 - 13 times higher than their calculated yearly inputs, providing evidence for accumulation. The results support dry deposition as the primary contributor of TFA to surface waters in arid and semi-arid environments. Precipitation samples obtained from three different locations contained 20.7 - 1530 ng/L with significantly higher concentrations in fogwater (median equals 689 ng/L) over rainwater (median equals 63.7 ng/L). Elevated levels of TFA were observed for rainwater collected in Nevada (median equals 136 ng/L) over those collected in California (median equals 49.5 ng/L), indicating continual uptake and concentration as clouds move from a semi-arid to arid climate. Thus several mechanisms exist, including evaporative concentration, vapour-liquid phase partitioning, lowered washout volumes of atmospheric deposition water, and dry deposition, which may lead to elevated concentrations of TFA in atmospheric and surface waters above levels expected from usual rainfall washout.

3. Assessment and conclusion

<u>Assessment and conclusion by applicant</u>:
Assessment:
This article reports TFA concentrations in fogwater, precipitation, rivers and lake systems in California and Nevada during 1996-1997. Details on sampling and analytical work (including LOQ and RSDs) are well reported. However, the work wasn't carried out according to GLP, and there are currently no guidelines for the conduct of monitoring studies.

Conclusion:
The results support dry deposition as the primary contributor of TFA to surface waters in arid and semi-arid environments. Precipitation samples obtained from three different locations contained 20.7 - 1530 ng/L with significantly higher concentrations in fogwater (median = 689 ng/L) over rainwater (median = 63.7 ng/L). Elevated levels of TFA were observed for rainwater collected in Nevada (median = 136 ng/L) over those collected in California (median = 49.5 ng/L), indicating continual uptake and concentration as clouds move from a semi-arid to arid climate.

The information from this article can be regarded as reliable.

<u>Assessment and conclusion by RMS</u>:
Outcome and conclusion of the study: RMS should indicate if they agree to the results and conclusions of the APPL.

1. Information on the published literature article

Data Point:	KCA 7.5/20
Report Author:	Cahill, T. M.; Seiber, J. N.
Report Year:	2000
Report Title:	Regional distribution of trifluoroacetate in surface waters downwind of urban areas in Northern California, USA
Report No:	M-604967-01-1
Document No:	M-604967-01-1
Guideline(s) followed in study:	not applicable
Deviations from current test guideline:	Current Guideline: not applicable
Previous evaluation:	No, not previously submitted
GLP/Officially recognised testing facilities:	No, not conducted under GLP/Officially recognised testing facilities
Acceptability/Reliability:	Yes

2. Full summary of KCA 7.5/20

Executive Summary
To determine the scale of urban enrichment of trifluoroacetate (TFA) in Northern California, a series of streams were sampled in 1998 along a transect upwind and downwind of the San Francisco and Sacramento metropolitan areas. In addition, 17 remote sites were sampled in British Columbia and the Yukon Territory, Canada and in Alaska, U.S.A. to determine the baseline TFA concentrations in Northern Hemisphere surface waters. The results showed elevated TFA concentrations in surface waters around and immediately downwind of urban areas. The enrichment was approximately 5 - 6 times higher

than the concentrations in upwind sites. The northern remote sites showed a median TFA concentration of 21 ng/L, which was statistically indistinguishable from the upwind coastal sites of the Californian transect. The mechanism for the urban enrichment was unknown, but it may have been the result of additional sources of TFA other than the HFC/HCFCs or faster formation of TFA due to higher HFC/HCFC and hydroxyl radical concentrations.

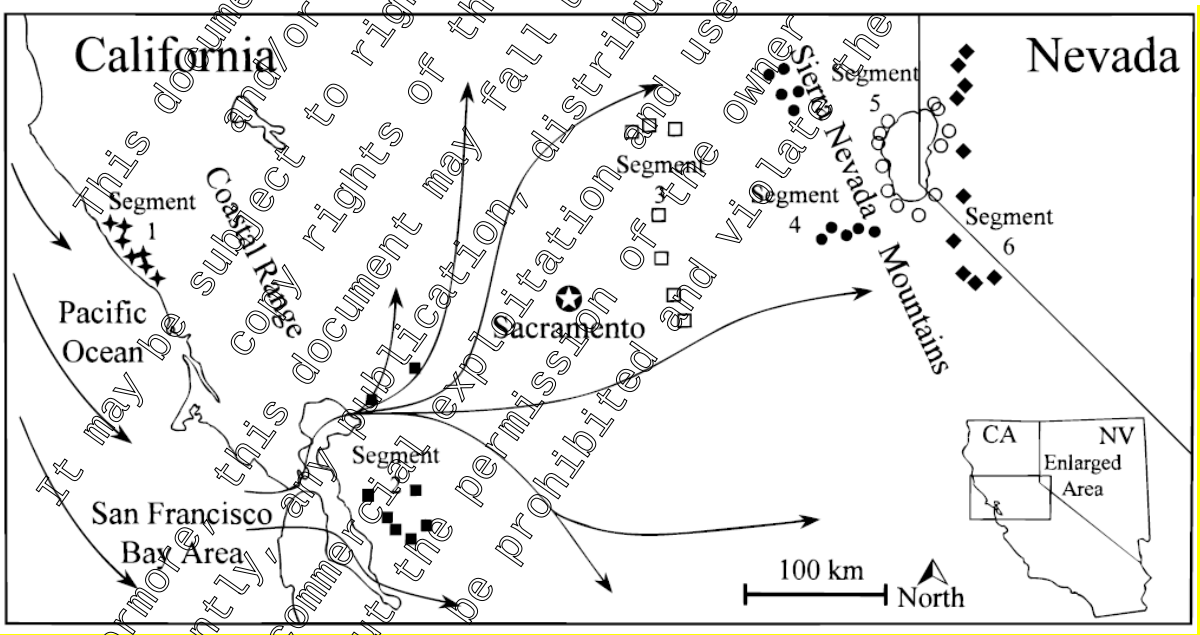
I. MATERIAL AND METHODS

Materials

Environmental samples were collected in two sets during 1998 to determine the distribution of TFA in the environment.

Sampling method

The first set of samples was collected along a transect upwind and downwind of the San Francisco and Sacramento metropolitan areas to test for local and regional urban enrichment of TFA. The transect was divided into six segments representing different regions. The first segment consisted of seven streams along the coast of Northern California. The prevailing northwesterly winds bring clean air mass from the Pacific Ocean, hence these sites should not be impacted by the urban plume of the San Francisco Bay Area. The second segment was a set of streams immediately downwind of the San Francisco Bay area. The third segment was composed of streams in the Sierra Nevada foothills below 500 m in elevation. The last three segments represented the west slope of the Sierra Nevada above 1600 m elevation, the Tahoe Basin, and the east slope of the Sierra Nevada. To reduce temporal variation in the data set, all the samples along the transect were collected during an 8 day period between 23rd August 1998 and 30th August 1998. No significant rain events occurred within a week of sample collection that might have caused mixing or dilution effects. Sampling locations in this region are shown in Figure 7.5-14.



Each sampling segment is marked by a different symbol, and predominant spring and summertime surface wind flow patterns marked by arrows. In winter, when the majority of wet deposition occurs, winds are mostly northerly (25%), southerly (22%) or stagnant (18%) which do not favour transport into the Sierra Nevada Mountains.

Figure 7.5-14: Location of sampling sites in California and Nevada

The second set of samples was collected to determine the baseline concentration of TFA in the remote areas of the Northern Hemisphere. These samples consisted of 17 sites in British Colombia and Yukon

Territory in Canada, and Alaska, U.S.A. The sampling sites ranged from near Lytton, BC to Fairbanks, AK. The sites were remote from urban areas with two exceptions, which were the Chena River in Fairbanks, AK and the Yukon River in Whitehorse, YT. All these samples were collected between 23rd July 1998 and 30th July 1998.

Sampling sites along the Californian transect were chosen to be representative of local TFA deposition using the following criteria: all sites were small flowing streams that originated within the transect segment; sampling sites could not be downstream of a large lake or reservoir that might cause dilution or mixing effects; the streams within a segment needed to be in different watersheds to ensure sites were independent of each other. A similar distribution of stream sizes was sampled in each transect segment to control for stream volume. Small watersheds lacking industrial sites or heavy urban populations were selected to ensure that the predominate, if not only, source of TFA would be through atmospheric deposition. Urban water discharge was avoided. Sample site criteria for the northern samples were relaxed in that larger rivers and two small lakes were sampled in addition to streams.

At each sampling site, two separate samples were collected into 1 L glass bottles by submerging the bottle under the surface of the water. The sample bottles were precleaned in the laboratory and washed 3 times with site water prior to collection of the sample. The bottle caps were lined with aluminum foil to prevent potential contamination from the bottle caps. Two sample bottles were tested for TFA contamination by filling them with 18 MΩ resistance Nanopure water and the water then subsequently analysed. The samples from the northern sites consisted of only one 60 mL bottle of water from each site.

Analytical method

The samples were analysed for TFA using a headspace gas chromatography (HS-GC) method. Both field replicates collected from each stream along the Californian transect were analysed separately, while the northern samples had only a single bottle of water that was analysed. An aliquot (15 mL) to which 1 mL of 0.5 M $(NH_4)_2CO_3$ was added was evaporated to dryness in a two-step process to produce an effective sample volume of 30 mL. After the sample had been evaporated, 4 mL of a 25% methanol/75% 9 M sulfuric acid solution was added and the vial subsequently capped and heated to extract and derivatize the TFA to methyl-TFA which was then analysed using HS-GC equipped with an electron capture detector. Method blanks, consisting of Nanopure water, run along with the samples showed no detectable TFA. Statistical analyses of the data sets were conducted by Minitab statistical software version 12 for Windows. Since some of the data sets were not normally distributed as determined by an Anderson-Darling normality test ($P < 0.05$), a nonparametric Mann-Whitney test with $\alpha = 0.05$ was used to test for differences between data sets.

LOQ: The limit of quantification for TFA was 8 ng/L.

II. RESULTS AND DISCUSSION

The transect results showed enrichment of TFA in local water systems near urban areas. The coastal sites showed consistent and low concentrations of TFA with a median concentration of 24.2 ng/L. In contrast, sites immediately downwind of the San Francisco Bay Area had significantly higher TFA concentrations with a median concentration of 144 ng/L (Mann-Whitney, $P < 0.001$). There was a high degree of variability between streams, although the TFA concentrations in the streams appeared to be independent of the stream size. The concentrations were lower (Mann-Whitney, $P = 0.04$) in the foothills of the Sierra Nevada with a median concentration of 95.4 ng/L. As the transect proceeded into the high elevations of the Sierra Nevada, the TFA concentrations dropped in the last three segments with median values of 24.1, 27.8, and 21.5 ng/L, respectively. These segments were not statistically different from each other ($P > 0.05$), and the combined Sierra sample set was indistinguishable ($P > 0.05$) from the coastal segment. The differences between field replicates from the same stream averaged 11.6%,

although this was elevated by samples near the LOQ of 8 ng/L. Streams with concentrations greater than 30 ng/L had better precision with an average difference between replicates of 6.6%.

The samples collected in Alaska and Canada showed low and fairly consistent concentrations of TFA with a range of < 8 to 40 ng/L and a median value of 21.1 ng/L (Table 7.5- 39). Although, there was one site with a TFA concentration of 63 ng/L. The TFA concentrations were fairly constant between small creeks and large rivers in the same region, which indicates that the size of the water body did not affect the TFA concentrations.

Table 7.5- 39: TFA concentrations in surface waters from British Columbia and the YukonTerritory in Canada and Alaska, U.S.A[a]

Site	Approximate location	TFA concentration (ng/L)
Creek	~18 km S of Lytton, BC	21.7
Lake	~15 km N of Quesnel, BC	39.4
Crooked River	~118 km N of Prince George, BC	23.8
Bijoux Falls	~197 km N of Prince George, BC	10.3
Cache Creek	~48 km E of Hudsons Hope, BC	63.0
Sikanni Falls	~15 km E of Sikanni Chief, BC	30.4
Kledo Creek	~60 km W of Ft. Nelson, BC	24.9
Lake	~4 km W of Summit Lake, BC	29.0
Contact Creek	~67 km E of Watson Lake, YT	18.8
Albert Creek	~13 km W of Watson Lake, YT	16.3
Rancheria Falls	~135 km W of Watson Lake, YT	17.2
Yukon River	At Whitehorse, YT	26.9
Mendenhall River	~85 km W of Whitehorse, YT	21.1
Kluane River	~50km NW of Destruction Bay, YT	< 8.0[b]
Tanana River	~20 km S of Tok, AK	9.5
Shaw Creek	~128 km S of Fairbanks, AK	19.8
Chena River	At Fairbanks, AK	13.7
Median TFA concentration in northern samples		21.1

[a]: With two exceptions, the sites are typically remote and should represent background TFA concentrations. The sites are listed by increasing latitude. Only one sample was collected and analysed from each site.
[b]: While this sample had detectable TFA, the concentration was below the limit of quantification of 8 ng/L.

There was a slight trend toward lower TFA concentrations in the nine northernmost sites in the Yukon Territory and Alaska (median = 17.2 ng/L) compared to the eight southern sites in British Columbia (median = 27.0 ng/L, Mann-Whitney test, $P = 0.02$). The cause of this trend is uncertain, but the author felt that different climatic conditions as well as increasing distance from industrialized areas may have contributed to the trend. The TFA concentrations in the 17 northern sites were statistically indistinguishable ($P > 0.05$) from the TFA concentrations in the coastal transect segment in California, thus demonstrating that the coastal sites selected for sampling were not appreciably impacted by the San Francisco Bay Area.

III. CONCLUSIONS

The effect of urban enrichment appears to be regional, rather than local, and follows predominate surface wind patterns. Since the sampling sites were selected to reduce surface inputs from urban areas, the TFA in the streams was assumed to originate predominantly from atmospheric deposition, both wet and dry.

The results from the northern samples in Alaska and Canada demonstrate that TFA was present in globally remote sites. The northern samples, particularly the ones from the Yukon Territory and Alaska, should represent Northern Hemisphere background concentrations of TFA.

The observed TFA distribution in surface waters appears to follow the wintertime pattern with the bulk of the TFA remaining in the lowlands near the urban areas and minimal TFA transportation/deposition into the Sierra Nevada. This also indicates that the TFA in the urban aerosol transported during the summertime is not being effectively deposited into the Sierra.

3. Assessment and conclusion

Assessment and conclusion by applicant:

Assessment:

The article contains well documented details of monitoring (including sampling and analytical methodology) a series of streams along a transect upwind and downwind of the San Francisco and Sacramento metropolitan areas and 17 remote sites in British Columbia and the Yukon Territory, Canada and in Alaska, U.S.A. to determine the baseline TFA concentrations in Northern Hemisphere surface waters, in 1998. The study was not performed to GLP and there are currently no guidelines for the conduct of monitoring studies, and the quality performance of the analytical method was not given.

Conclusion:

The study identified TFA in all sampled surface waters in California, Nevada, Alaska and Canada, at similar concentrations for coastal and northern sites. TFA was found to be higher in urban areas than in coastal areas and northern territories.

The information from this article can be regarded as reliable.

Assessment and conclusion by RMS:

Outcome and conclusion of the study: RMS should indicate if they agree to the results and conclusions of the APPL.

1. Information on the published literature article

Data Point:	KCA 7.5/21
Report Author:	Scott, B.; Mactavish, D.; Spencer, C.; Strachan, W.; Muir, D.
Report Year:	2000
Report Title:	Haloacetic acids in Canadian lake waters and precipitation
Report No:	M-585144-01-1
Document No:	M-585144-01-1
Guideline(s) followed in study:	not applicable
Deviations from current test guideline:	Current Guideline: not applicable
Previous evaluation:	No, not previously submitted
GLP/Officially recognised testing facilities:	No, not conducted under GLP/Officially recognised testing facilities
Acceptability/Reliability:	Yes

2. Full summary of KCA 7.5/21

Executive Summary

Haloacetic acids (HAAs) were measured in lake water and precipitation in surface water samples from the Great Lakes and four lakes in widely separated geographical areas of Canada to determine prevailing

levels and source regions. These lakes had levels dependent on the degree of isolation from human activity, with the more isolated lakes having lower trifluoroacetic acid (TFA) concentrations. Lake Winnipeg surface waters (downstream of possible urban sources of TFA from southern Manitoba and North Dakota) contained the highest concentrations of TFA (maximum 360 ng/L). Two sites from each of the other Great Lakes were sampled, one close to the inflow of the lake and the other close to the outflow, show that TFA values from Lake Superior are less than those measured in the other Great Lakes.

Concentration levels of TFA in precipitation samples vary from below detection limits to 180 ng/L. Five-day back-trajectories indicated that the sources of the air masses govern the amount of trifluoroacetic acid (TFA) in the precipitation. Urban centres appear to be sources of TFA. The average daily event precipitation fluxes of TFA were reasonably constant across Canada, except for the most remote site (Snare Rapids) where the values were considerably lower.

I. MATERIAL AND METHODS

Material

The objective in this study was to determine the extent of TFA in the Canadian aqueous environment and to infer possible source regions.

Sampling method

The Canadian Air and Precipitation Monitoring Network (CAPMoN) precipitation collection sites used for this study, as well as the locations of the four lakes, are shown in Figure 7.5- 15. All samples were collected and analysed in 1997.

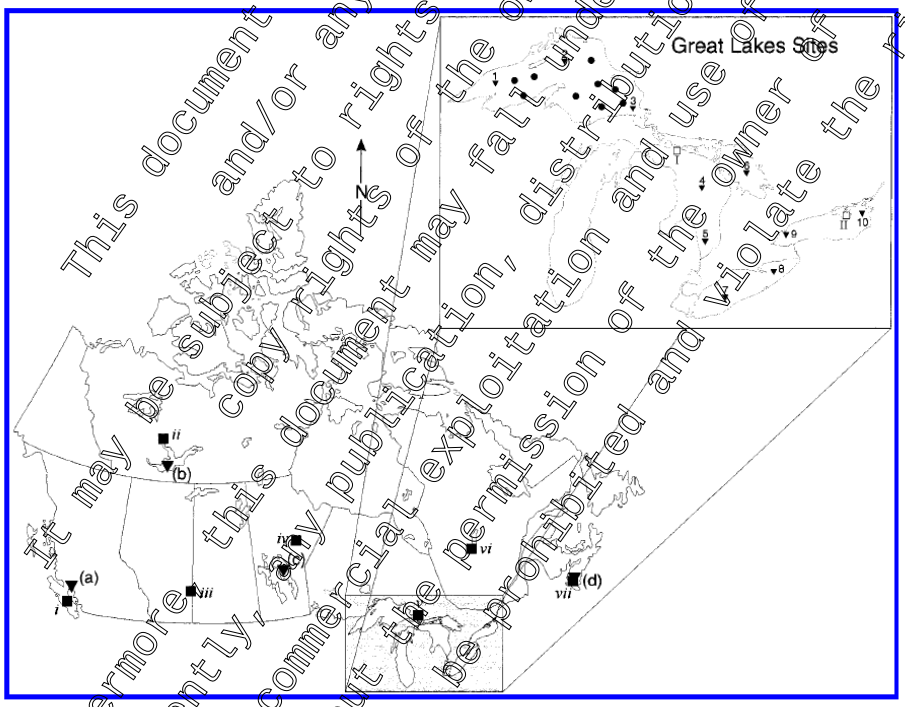


FIGURE 1. Sample collections sites for (■) precipitation: i, Saturna Island; ii, Snare Rapids; iii, Ester; iv, Island Lake; v, Algoma; vi, Chapais; vii, Kejimkujik; (▼) small lake surface water: (a) Loon Lake; (b) Great Slave Lake; (c) Lake Winnipeg and (d) Lake Kejimkujik. Sampling sites of the Great Lakes are denoted in the insert with algebraic number 1–10 and the sites as shown as solid upsidedown traingles (▼). Integrated precipitation samplers are shown as (□) I, Burnt Island; II, Point Petre. Sites in Lake Superior listed in Table 3 as lakehead, mid-lake and outflow are given as 1, 2, and 3, respectively.

Figure 7.5- 15: Sample collection sites for precipitation

Surface water
At single sites on the Great Lakes, except for 2 cruises on Lake Superior, water samples were collected in triplicate from 1 m below the water surface of each lake using a 3 L GO-flo bottle. These samples were placed in precleaned 1 L amber glass bottles with Teflon-lined lids, stored at 4°C, and returned to the laboratory in refrigerated coolers. The Lake Superior samples were individual grab samples collected 1 m below the surface at 11 sites using a Go-flo bottle. During the spring cruise, duplicate samples were taken, with one sample stored in a glass bottle and the other in a polyethylene bag which was heat-sealed at each station. In the four smaller lakes, samples were also collected at a 1 m depth after prerinsing with lake water.

Precipitation samples
24 hour integrated samples were collected at seven sites across Canada operated by the CAPMoN precipitation network. These sites were selected such that they were not influenced by nearby activities. The wet samplers had a collection area of 0.0802 m^2. Each precipitation sample was collected in a polyethylene bag and maintained at 4°C until it was received at a central laboratory where the sample was placed in a 500 mL cleaned amber glass bottle and stored at 4°C in the dark until it was analysed. Samples with volumes of 250 mL or more were analysed individually, but samples that contained less than this amount were combined with the sample collected either before or after the event that had the lower volume. Two other wet only samplers (0.085 m^2 collection area) located on Burnt Island and Point Petre, (sites on the Great Lakes), provided samples collected every fourth week. The precipitation samples were shipped to the laboratories for analysis. None of the precipitation samplers contained Teflon components.

Blanks and Sample Containers.
HAA free water was prepared, 500 mL of this water was placed in an empty bag or bottle for 1 week. The water was then removed and subjected to analysis. In addition, strips of a bag were placed in SPE prepared water for 14 days as were the bottle caps, and the water then analysed. In all cases, there were no enhanced amounts of TFA in the test waters from the sample container material relative to the laboratory blanks analysed concurrently.

Drinking water samples
Triplicate samples from the city of Hamilton (ON) were collected in 1 L amber glass bottles and processed within a day of collection. The Burlington city tap water was taken from the cold water tap in the laboratory and analysed immediately.

Analytical method
Each sample was derivatized and analysed by GC-MS equipped with a splitless injector and a mass selective detector using a DB-17 capillary column, (30 m × 0.25 mm internal diameter) with a liquid-phase thickness of 0.25 µm with He as the carrier gas. During the analysis of each sample set, two standard solutions were also analysed. The intensity of the peak *m/e* 225 amu for TFA was used to determine the concentration.

The minimal detectable limit was 0.5 ng/L for TFA based on a sample of 1 L.

Periodically, recoveries of TFA at environmental concentrations was checked. Quantitative recoveries were obtained from 10-10000 ng/L for TFA.

The flux for each daily event or 4 week integrated sample was calculated from the concentration of TFA present, the precipitation amounts and the collection surface area. Volume weighted fluxes were determined by taking the sum of the flux for all events and dividing by the sum of the amount of precipitation. The average fluxes were the mean of the event flux for each site and the attendant standard was calculated.

Storage stability was investigated using water samples taken from several depths at a single site in Lake Erie. Each sample was divided and placed in two separate storage bottles. In the laboratory one sample was analysed immediately and the other after 4 weeks storage at 4°C in the dark. No decomposition of TFA was found under these conditions.

Ponds treated with TFA at levels of 100 and 1000 ng/L were analysed using both GC-MS and NMR with excellent agreement between the results.

II. RESULTS AND DISCUSSION

Precipitation

All precipitation samples were analysed for TFA. Results for the CAPMoN precipitation samples (positions are depicted in Figure 7.5- 15) are summarized in Table 7.5- 40. Each collection site was distant from an urban centre where the rain may be unduly influenced by nearby human activities. Saturna Island is closest to Loon Lake and often both were subjected to the same precipitation events. Snare Rapids (located 100 km north of Great Slave Lake) had the lowest number of precipitation events and the samples from this site contained the lowest levels of TFA. Island Lake is located northeast of Lake Winnipeg, near the provincial border between Manitoba and Ontario and contained intermediate amounts of TFA. The most easterly site at Kejimkujik is located in southwestern Nova Scotia close to Kejimkujik Lake. The TFA values determined from the precipitation samples from this site were generally higher than those determined at the other sites and the values determined in the adjacent lake. The average precipitation fluxes with 95% confidence limits are plotted in Figure 7.5- 16. This figure shows that the values for TFA are relatively similar from west to east except for the most remote site (Snare Rapids) where the values were considerably lower.

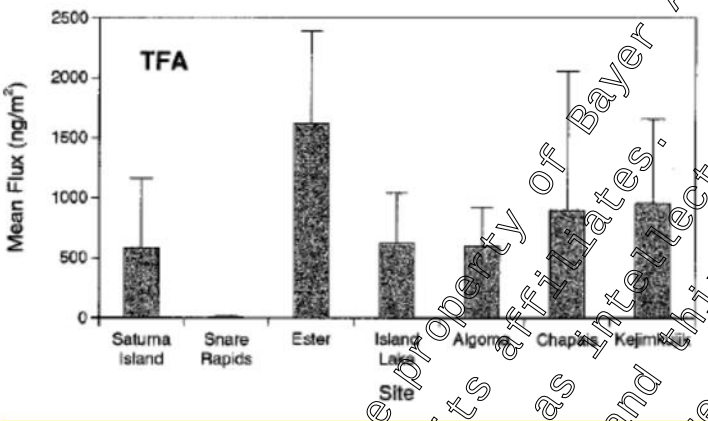
Two sampling sites provided integrated precipitation samples (Burnt Island, northwest coast of Lake Huron and Point Petre, northeast shore of Lake Ontario). As the total amount of rainfall per 28 day period was analysed for these samples, the concentration values were represented as fluxes. The TFA fluxes in the Point Petre samples (Table 7.5- 41) were higher than those detected in Burnt Island samples. Also the fluxes of TFA were considerably lower at Burnt Island during the December to January interval compared to the two collected earlier in the year. The two sites are situated less than 150 km apart and do not receive the same precipitation events.

Table 7.5- 40: Precipitation results for TFA collected at 7 Canadian locations

Site	Saturna Island	Snare Rapids	Ester	Island Lake	Algoma	Chapais	Kejimkujik
Location	48°47'00"N 123°8'00"W	63°31'00"N 116°00'00"W	51°40'00"N 110°12'00"W	53°51'55"N 94°40'00"W	47°2'6"N 84°22'52"W	49°49'20"N 74°49'20"W	44°26'1"N 65°12'21"W
No.of events	9	4	6	9	11	11	11
Avg concn (ng/L)	29	<0.1	85	40	48	24	43
Min, max (ng/L)	<0.1, 170	<0.1, <0.1	38, 160	<0.1, 59	4, 120	<0.1, 69	<0.1, 130
Volume weighted precipitation flux							
TFA (ng/L)	37	0.4	84	36	36	44	45

Table 7.5- 41: Flux of TFA determined at Great Lakes sample stations

Site	Burnt Island 45°49'42"N, 82°56'53"W			Point Petre 43°50'34"N, 77°09'13"W		
	Oct 20 – Nov 17	Nov 17 – Dec 15	Dec 15 – Jan 12 1998	Oct 21 – Nov 18	Nov 18 – Dec 16	Dec 16 – Jan 13 1998
Amt of precipitation (mm)	32	32	32	80	26	88
TFA (ng/m^3)	2330	1260	<3.8	3260	1550	1950



The sites are listed as most western, most northern, then in a west to east order

Figure 7.5- 16: Arithmetic means of precipitation flux of TFA with 95% CI, at seven Canadian precipitation sites

The variation in amounts of TFA at a site may be explained from a consideration of the origins of the air mass from which the precipitation was collected. Using the AES/LRTAP trajectory model (Constant Acceleration Algorithm) a three-dimensional 5-day air parcel back-trajectory computer model, back-trajectories were plotted at pressures of 850, 925, and 1000 hPa. These being related to different altitudes from which the precipitation could descend. Two stations, Saturna Island and Algoma, were considered for three events at each station, 2 events corresponded to samples with low TFA concentrations and the third event corresponded with an elevated TFA concentration.

The 5-day back-trajectories for the sample collected on September 13th are significant given that there were no detectable amounts of TFA. In this case the air associated with the trajectories for all three pressures originated over the Pacific Ocean and the lack of measurable TFA is likely an indication that any TFA that may have been present had the opportunity to be washed out or diluted to the point of non-detection without replenishment from any consequential sources. Conversely, when one of the air masses at the pressures considered passed over an area of population or industry, TFA in the atmosphere was transported and then flushed from the air mass at a later time by dissolving in the precipitation. The back trajectories of the sample collected Sep 17-18 that had high concentrations of TFA (170 ng/L), revealed that air masses passed over areas of California associated with significant industrial activity and large populations. Similar correlations between TFA concentration levels and back-trajectories were obtained for the other events.

Surface Water

Concentrations of TFA in regional lakes are listed in Table 7.5- 42. Loon Lake (the most westerly) contained trace amounts of TFA (< 1 ng/L). Great Slave Lake, the next most westerly lake, contained small amounts of TFA (< 1 to 10 ng/L) and Lake Winnipeg surface water contained high concentrations of TFA (100 to 360 ng/L), this lake is situated downstream of possible urban sources of TFA from southern Manitoba and North Dakota. Lake Kejimkujik, the most easterly lake sampled, is a pristine

lake situated within Kejimkujik National Park, in Nova Scotia. Its surface waters contained comparable amounts of TFA to the Great Slave Lake.

Table 7.5- 42: TFA concentrations of regional lake waters in Canada

Site	Grid reference	TFA (ng/L)
Loon Lake	49°18' N, 122°35' W	< 0.5, < 0.5, < 0.5, < 0.5
Great Slave Lake	60°50'30"N, 113°50'99"W	10, < 0.5
Lake Winnipeg	50°37'03"N, 91°53'13"W	220, 100, 360, 320
Lake Kejimkujik	44°08'28"N, 65°19'05"W	14, 28, 15, 12

The waters of the Laurentian Great Lakes ranged from near pristine areas (Lake Superior) to areas impacted by extensive agricultural and industrial activities as well as high population densities (Lakes Erie and Ontario). Concentrations of TFA from three stations for the Lake Superior spring sampling are listed in Table 7.5- 43. Overall, the concentrations of TFA detected are low (16 - 18 ng/L), slightly higher than those measured in Loon Lake. Also the concentrations are similar between sites on Lake Superior. The concentrations of the samples taken during the summer cruise were lower than those measured for the samples taken in the spring cruise.

Table 7.5- 43: Seasonal variation of TFA in Lake Superior

Sampling	Site 1 (western basin) 47°07'54"N, 91°06'42"W	Site 2 (mid lake) 47°35'00"N, 86°57'06"W	Site 3 (eastern basin) 47°12'48"N, 85°38'00"W
Spring cruise	16	18	17
Summer cruise	2	3	< 0.5

For TFA, the values from Lake Superior are less than those measured in the other Great Lakes. Drinking water values are also included in Table 7.5- 44 to compare with the open lake values.

Table 7.5- 44: Concentration of TFA in the Great Lakes and Drinking Water

Site	Grid reference	TFA (ng/L)
Lake Superior Site 1 (western basin)	47°07'54"N, 91°06'42"W	2
Lake Superior Site 3 (eastern basin)	47°12'48"N, 85°38'00"W	< 0.5
Lake Huron Site 4	43°32'57"N, 82°09'05"W	100
Lake Huron Site 5	44°22'51"N, 82°02'53"W	110
Georgian Bay Site 6	45°21'29"N, 80°59'47"W	74
Lake Erie Site 7	42°30'25"N, 79°53'59"W	130
Lake Erie Site 8	41°36'09"N, 81°29'16"W	140
Lake Ontario Site 9	43°53'13"N, 76°43'58"W	130
Lake Ontario Site 10	43°37'23"N, 79°27'12"W	150
Drinking water (Hamilton)	-	183
Drinking water (Burlington)	-	120

Discussion

Concentration levels of TFA in the precipitation samples vary from below detection limits to 180 ng/L. The precipitation fluxes, either volume weighted or not, indicate that at temperate latitudes, the flux of TFA is reasonably constant from west to east.

TFA was found in the treated water samples, but at concentrations similar to those of Lake Ontario water (190 ng/L) from which the two cities, Burlington and Hamilton, draw their raw water. The treated water eventually returns to its source, sometimes after further chlorination. TFA would not be expected to be broken down as it is considered a refractory compound. The agreement of the TFA concentration values between lake water and treated water suggests that TFA is not formed during the treatment process.

III. CONCLUSION

The results from this analysis show that TFA is present in the Canadian environment, including remote or isolated areas. Frequent detection of TFA in rain samples from stations across Canada indicated that atmospheric transport and deposition may play an important role in delivering this compound to the Canadian aquatic ecosystems. The back trajectory models imply that urban centres are sources for TFA.

3. Assessment and conclusion

Assessment and conclusion by applicant:
This article from public literature reports monitoring results for TFA in precipitation and surface waters, including details of the sample methodology and analytical work. However, the work wasn't carried out according to GLP, and there are currently no guidelines for the conduct of monitoring studies.

Conclusion:
TFA is present in the Canadian environment, including remote or isolated areas. Frequent detection of TFA in rain samples from across Canada indicated that atmospheric transport and deposition may play an important role in delivering this compounds to the Canadian aquatic ecosystems. The back trajectory models imply that urban centres are sources for TFA.

The information from this article can be regarded as reliable.

Assessment and conclusion by RMS:
Outcome and conclusion of the study - RMS should indicate if they agree to the results and conclusions of the APPL.

1. Information on the published literature article

Data Point:	KCA 7.5/22
Report Author:	Roempp, A.; Klemm, O.; Frank, H.
Report Year:	2001
Report Title:	Haloacetates and nitrophenols in fog and rain
Report No:	M-604971-01-1
Document No:	M-604971-01-1
Guideline(s) followed in study:	not applicable
Deviations from current test guideline:	Current Guideline: not applicable
Previous evaluation:	No, not previously submitted
GLP/Officially recognised testing facilities:	No, not conducted under GLP/Officially recognised testing facilities
Acceptability/Reliability:	Yes

2. Full summary of KCA 7.5/22

Executive Summary

Concentrations of haloacetates and nitrophenols were analysed in 96 fogwater and more than 100 rainwater samples collected in Bavaria (Germany), during 1998 and 1999. Application of an assessment factor of 100 gave concentrations of trifluoroacetate (TFA), monofluoroacetate (MCA) and trichloroacetate (TCA) that all exceeded the projected no-effect concentration. Therefore, these 3 haloacetates in fog must be regarded as ecotoxicologically relevant, and their way of deposition into forest ecosystems must not be ignored. All analysed substances showed higher average concentrations in fog than in rain.

MATERIAL AND METHODS

Materials

Sampling of fog and rainwater was undertaken between July 1998 and March 1999 and samples analysed for a number of haloacetates including trifluoroacetate (TFA).

Sampling procedures

Between July 1998 and March 1999, 96 fogwater and more than 100 rainwater samples were collected at an ecological research site (800 m above sea level) in Northeastern Bavaria, Germany. From November through March, fogwater samples were collected using a Caltech Heatable Rods Cloudwater Collector. During the summer season a Caltech Active Strand Cloudwater Collector with higher collection efficiency was used.

Analytical procedures

Haloacetates including trifluoroacetate (TFA), were extracted with *tert*.-butyl methyl ether and derivatized with 1-(pentafluorophenyl)-diazoethane. The analytes were separated by gas chromatography and detected by negative chemical-ionization mass-spectrometry.

II. RESULTS AND DISCUSSION

Concentrations of TFA in fog are shown in Table 7.5- 45.

Table 7.5- 45: TFA concentrations in fog

	Median (µg/L)	Min/max (µg/L)
TFA	0.23	0.02 / 1.9

90th -percentile TFA concentrations for fog events with westerly and easterly winds are 0.65 µg/L and 0.43 µg/L, respectively. The origin of the air masses associated with fog events in October 1998 were analysed in more detail using backward trajectories. Trajectories were calculated for three pressure levels (ground, 900, and 850 hPa). The two lower trajectories were used to characterize the air masses at the sampling site. TFA concentrations were found to be higher in air masses that were not of marine origin. All analysed substances showed higher average concentrations in fog than in rain. The fog/rain concentration ratio of TFA was 6.6.

III. CONCLUSION

Using the average rain and fogwater concentrations, the deposition of TFA by fog was estimated to be 70% to 90%. The author concluded that the contribution of fog to the input of TFA into the forest ecosystem may be higher than that of rain.

Backward trajectory of air masses associated with fog events showed that concentrations of TFA were higher in air masses that were not of marine origin and predominantly of anthropogenic origin.

3. Assessment and conclusion

Assessment and conclusion by applicant:

Assessment:

This article from public literature reports monitoring results for TFA in fog and rainwater samples between July 1998 and March 1999 in Bavaria, Germany. The article has major restrictions (e.g. no details on sampling sites, sampling methodology, analytical controls, storage and results cannot be related to definite times). In addition, the work wasn't carried out according to GLP, and there are currently no guidelines for the conduct of monitoring studies.

Conclusion:

TFA was recorded in fog samples at concentrations between 0.02 and 1.9 µg/L and had a TFA fog/rain ratio of 6.6. Backward trajectory of air masses suggest TFA sources were of anthropogenic origin.

The information from this article can be regarded as supportive information.

Assessment and conclusion by RMS:

Outcome and conclusion of the study: RMS should indicate if they agree to the results and conclusions of the APPL.

1. Information on the published literature article

Data Point:	KCA 7.5/23
Report Author:	Wallington, T. J.; Hurley, M. D.; Fedotov, V.; Morrell, C.; Hancock, G.
Report Year:	2002
Report Title:	Atmospheric chemistry of CF3CH2OCHF2 and CF3CHClOCHF2: Kinetics and mechanisms of reaction with Cl atoms and OH radicals and atmospheric fate of CF3C(O.bul.)HOCHF2 and CF3C(O.bul.)ClOCHF2 radicals
Report No:	M-605021-01-1
Document No:	M-605021-01-1
Guideline(s) followed in study:	not applicable
Deviations from current test guideline:	Current Guideline: not applicable
Previous evaluation:	No, not previously submitted
GLP/Officially recognised testing facilities:	No, not conducted under GLP/Officially recognised testing facilities
Acceptability/Reliability:	Yes

2. Full summary of KCA 7.5/23

Executive Summary

An investigation of the chemical kinetics relating to the atmospheric fate of isoflurane, $CF_3CHClOCHF_2$ (an anaesthetic), is reported. Trifluoroacetic acid is a major product of the atmospheric degradation of isoflurane. Relative rate techniques were used to measure $k(Cl + CF_3CH_2OCHF_2) = (1.2 \pm 0.1) \times 10^{-14}$, $k(Cl + CF_3\text{-}CHClOCHF_2) = (5.4 \pm 0.5) \times 10^{-15}$, $k(Cl + HC(O)OCHF_2) = (2.0 \pm 0.2) \times 10^{-14}$, and $k(Cl + CF_3C(O)\text{-}OCHF_2) \leq 4 \times 10^{-17}$ cm^3 molecule/s at 295 K. Cl atoms react with $CF_3CHClOCHF_2$ (isoflurane, HCFE-235da2) via H-atom abstraction to give $CF_3C(\bullet)ClOCHF_2$ and $CF_3CHClOC(\bullet)F_2$ radicals in yields of 92% and 8%. OH radicals react with $CF_3CHClOCHF_2$ via H-atom abstraction to give $CF_3C(\bullet)ClOCHF_2$ and $CF_3\text{-}CHClOC(\bullet)F_2$ radicals in yields of 95% and 5%. $CF_3C(\bullet)ClOCHF_2$ and $CF_3CHClOC(\bullet)F_2$ add O_2 to give peroxy radicals which react with NO to give the alkoxy radicals $CF_3C(O\bullet)ClOCHF_2$ and $CF_3CHClOC(O\bullet)\text{-}F_2$. The atmospheric fate of $CF_3C(O\bullet)ClOCHF_2$ radicals is decomposition via elimination of a Cl atom to give $CF_3C(O)OCHF_2$ and is unaffected by the method used to generate the $CF_3C(O\bullet)ClOCHF_2$ radicals. Reaction of Cl atoms with $CF_3CH_2OCHF_2$ (HFE-245fa2) proceeds via H-atom abstraction to give $CF_3C(\bullet)HOCHF_2$ radicals in a yield which is indistinguishable from 100%. The fate of the alkoxy radical $CF_3C(O\bullet)HOCHF_2$ is affected by the method in which it is generated. There are two competing fates for $CF_3C(O\bullet)HOCHF_2$ radicals formed by the reaction of $CF_3C(OO\bullet)HOCHF_2$ with other peroxy radicals; bimolecular reaction with O_2 to give $CF_3C(O)OCHF_2$ and unimolecular decomposition via C-C bond scission to give a CF_3 radical and $HC(O)OCHF_2$. In contrast, decomposition is the only observable fate of $CF_3C(O\bullet)HOCHF_2$ produced via the $CF_3C(OO\bullet)HOCHF_2 + NO$ reaction. This observation is ascribed to the formation of vibrationally excited $CF_3C(O\bullet)HOCHF_2$ radicals in the $CF_3C(OO\bullet)HOCHF_2 + NO$ reaction. The atmospheric oxidation of isoflurane gives trifluoroacetic acid in a molar yield of 95 ± 3%. Isoflurane was emitted to the atmosphere (at the end of the 1990s) at a rate of 750 tonnes per year, and its contribution to the global trifluoroacetic acid budget was 440 tonnes per year.

I. MATERIAL AND METHODS

Material

The aim of the study was to provide a better understanding of the atmospheric chemistry of isoflurane (an anaesthetic), its oxidation, and contribution to trifluoroacetic acid in rainwater.

Analytical procedure

All experiments were performed using a 140 L Pyrex reactor interfaced to a fourier transform infrared (FTIR) spectrometer. The reactor was surrounded by 22 fluorescent black lamps which were used to photochemically initiate the experiments. The oxidation of $CF_3CHClOCHF_2$ and CF3CH$_2$OCHF$_2$ was initiated by reaction with Cl atoms or OH radicals in 700 Torr of N_2/O_2 diluent at 295 ± 2 K. The loss of $CF_3CHClOCHF_2$ and $CF_3CH_2OCHF_2$ and the formation of products were monitored by the FTIR spectrometer using an infrared path length of 27 m and a spectral resolution of 0.25 cm^{-1}. Infrared spectra were derived from 32 co-added interferograms.

Three sets of experiments were performed. First, relative rate techniques were used to study the kinetics of the reactions of Cl atoms with $CF_3CHClOCHF_2$ and $CF_3CH_2OCHF_2$. Second, the products of the Cl atom initiated oxidation of $CF_3CHClOCHF_2$ and $CF_3CH_2OCHF_2$ were investigated by irradiating $CF_3CHClOCHF_2/Cl_2/O_2/N_2$ and $CF_3CH_2OCHF_2/Cl_2/O_2/N_2$ mixtures. Third, the products of the OH radical initiated oxidation of $CF_3CHClOCHF_2$ were determined by irradiating mixtures containing $CF_3CHClOCHF_2$, CH_3ONO, and NO in air. All experiments were performed at 295 K.

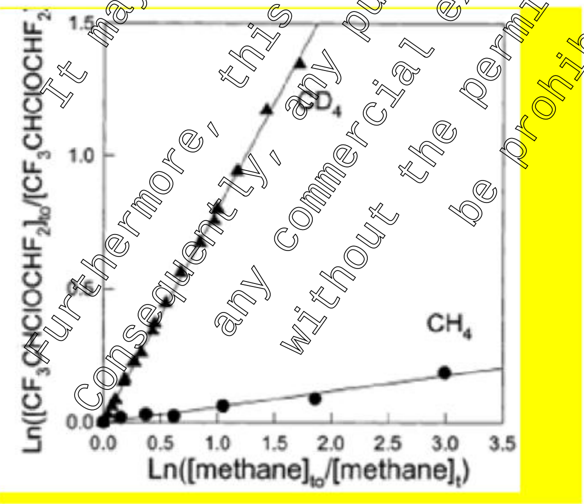
II. RESULTS AND DISCUSSION

The uncertainties reported are two standard deviations unless otherwise stated. Standard error propagation methods were used to combine uncertainties where appropriate.

Relative Rate Studies of the Reactions of Cl with $CF_3CHClOCHF_2$ and $CF_3CH_2OCHF_2$
Prior to investigating the atmospheric fate of alkoxy radicals, relative rate experiments were performed.

The observed losses of $CF_3CHClOCHF_2$ and $CF_3CH_2OCHF_2$ versus those of reference compounds in the presence of Cl atoms are shown in Figure 7.5- 17. Linear least-squares analysis of the data in Figure 7.5- 17 gives $k8/k10$ = 0.06 ± 0.01, $k8/k11$ = 0.80 ± 0.07, $k9/k10$ = 0.12 ± 0.01, and $k9/k11$ = 1.90 ± 0.10. Multiplication of these ratios by literature values for $k10$ and $k11$ provides two independent determinations of $k8$ and $k9$. Using $k10 = 1.0 \times 10^{-13}$ and $k11 = 6.1 \times 10^{-15}$ gave $k8 = (6.0 \pm 1.0) \times 10^{-15}$, $k8 = (4.9 \pm 0.5) \times 10^{-15}$, $k9 = (1.20 \pm 0.10) \times 10^{-14}$, and $k9 = (1.16 \times 0.06) \times 10^{-14}$ cm^3/molecule/s.

Estimated potential systematic errors associated with uncertainties in the reference rate constants contributed an additional 10% uncertainty range for $k8$ and $k9$. Propagating this additional uncertainty gives $k8 = (6.0 \pm 1.2) \times 10^{-15}$, $k8 = (4.9 \pm 0.7) \times 10^{-15}$, $k9 = (1.20 \pm 0.16) \times 10^{-14}$, and $k9 = (1.16 \pm 0.13) \times 10^{-14}$ cm^3/molecule/s. The authors cited final values of $k8$ and $k9$ which were averages of those determined using the two different reference compounds together with error limits which encompass the extremes of the individual determinations. Hence, $k8 = (5.5 \pm 1.7) \times 10^{-15}$ and $k9 = (1.2 \pm 0.2) \times 10^{-14}$ cm^3.



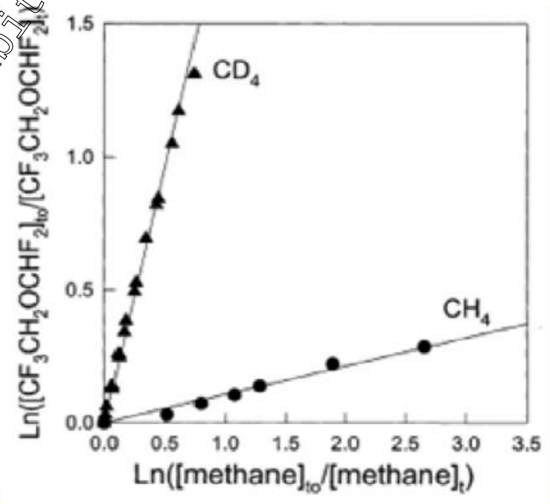


Figure 7.5- 17: Decay of $CF_3CHClOCHF_2$ (left panel) and $CF_3CH_2OCHF_2$ (right panel) versus CD_4 (triangles) and CH_4 (circles) in the presence of Cl atoms in 700 Torr of air at 295 K

Mechanism of the Reaction of Cl Atoms with $CF_3CH_2OCHF_2$ and $CF_3CHClOCHF_2$

Experiments were conducted using $CF_3CH_2OCHF_2/Cl_2/N_2$ mixtures to provide information on the mechanism of the reaction of Cl atoms with $CF_3CH_2OCHF_2$. $CF_3CHClOCHF_2$ was the only product observed in these experiments. Linear least-squares analysis of the corrected data gave a molar yield of $CF_3CHClOCHF_2$ of 95 ± 8%. The UV irradiation of $CF_3CH_2OCHF_2/Cl_2/N_2$ mixtures produced $CF_3CHClOCHF_2$ in a yield which is indistinguishable, within the experimental uncertainties, from 100%. The authors concluded that the reaction of Cl atoms with $CF_3CH_2OCHF_2$ proceeded essentially exclusively via attack at the -CH_2- site to give $CF_3C(•)HOCHF_2$ radicals which then reacted with molecular chlorine to give $CF_3CHClOCHF_2$.

Using $k8/k10 = 0.06 \pm 0.01$, $k8/k11 = 0.80 \pm 0.07$, $k9/k10 = 0.12 \pm 0.01$, and $k9/k11 = 1.90 \pm 0.10$, two independent determinations were derived of $k8/k9 = 0.50 \pm 0.09$ and $k8/k9 = 0.42 \pm 0.05$. Substitution of one of the two hydrogens at the -CH_2- site by a chlorine atom (i.e., $CF_3CH_2OCHF_2 \rightarrow CF_3CHClOCHF_2$) led to a reduction in reactivity of the molecule of approximately a factor of 2. The authors speculated that the majority of the reaction of Cl atoms with $CF_3CHClOCHF_2$ occurred at the secondary carbon atom. It appeared that the CHF_2 group made a minor contribution to the overall reactivity of $CF_3CH_2OCHF_2$ and $CF_3CHClOCHF_2$.

Atmospheric Fate of the Alkoxy Radical $CF3C(O•)ClOCHF_2$

The reaction of Cl atoms with $CF_3CHClOCHF_2$ generated $CF_3C(•)ClOCHF_2$ radicals, which were expected to react rapidly with O_2 to give peroxy radicals. The peroxy radicals undergo self-reaction to give the alkoxy radical, $CF_3C(O•)ClOCHF_2$. The Cl atom initiated oxidation of $CF_3CHClOCHF_2$ in air and provided a convenient method to study the atmospheric fate of $CF3C(O•)ClOCHF_2$ radicals.

There are three possible fates for the $CF_3CC(O•)OCHF_2$ radical: elimination of either a Cl atom, CHF_2O radical, or CF_3 radical.

$CF_3C(O•)ClOCHF_2 \rightarrow Cl• + CF_3C(O)OCHF_2$ (1)

$CF_3C(O•)ClOCHF_2 \rightarrow CF_3C(O)Cl + •OCHF_2$ (2)

$CF_3C(O•)ClOCHF_2 \rightarrow CF_3• + ClC(O)OCHF_2$ (3)

The absence of any observable $CF_3C(O)Cl$ or $CF_3O_2CF_3$ showed that pathways 2 and 3 were of minor importance and by a process of elimination, the authors concluded that pathway 1 showed the major fate of $CF_3C(O•)ClOCHF_2$ radicals.

Subtraction of IR features attributed to COF_2 from panel C in Figure 7.5- 18 gave the residual spectrum shown in panel E, which suggested that they are attributable to one product. The author assigned the spectrum in panel E to $CF_3C(O)OCHF_2$ formed in reaction 1.

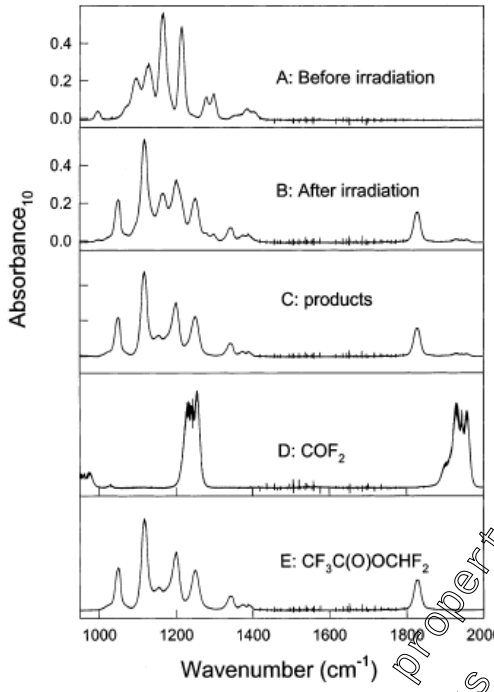


Figure 7.5- 18: IR spectra of a mixture of 6 mTorr of $CF_3CHClOCHF_2$, 207 mTorr of Cl_2, and 10 Torr of O_2 in 700 Torr of N2 before (A) and after (B) 3 min UV irradiation. Panel C is the product spectrum obtained by subtracting features attributable to $CF_3CHClOCHF_2$ from panel B (C = B - 0.28A). Panel D shows a COF_2 reference spectrum. Subtraction of COF_2 features from panel C gives the features shown in panel E assigned to $CF_3C(O)OCHF_2$

Experiments were conducted using $CF_3CHClOCHF_2/Cl_2/O_2/N_2$ mixtures with the oxygen partial pressure varied over the range 3-700 Torr. There was no discernible O_2 effect on the observed COF_2 and $CF_3C(O)OCHF_2$ yield. Linear least-squares analysis of the COF_2 data gave a molar yield of 8.2 ± 0.6%.

There are two possible mechanisms by which COF_2 can be formed following the UV irradiation of $CF_3CHClOCHF_2/Cl_2/O_2/N_2$ mixtures. The simplest explanation is that reaction 4 proceeds via two channels with $k_{8b}/(k_{8a} + k_{8b}) = 0.082 \pm 0.006$ and that reaction 5 was the source of COF_2.

$Cl + CF_3CHClOCHF_2 \rightarrow CF_3CCl(\bullet)OCHF_2 + HCl$ (4a)

$Cl + CF_3CHClOCHF_2 \rightarrow CF_3CHClOC(\bullet)F_2 + HCl$ (4b)

$CF_3CHClOCF_2O(\bullet) \rightarrow CF_3CHClO(\bullet) + CF_2O$ (5)

The concentration of $CF_3C(O)OCHF_2$ increased linearly with the loss of $CF_3CHClOCHF_2$. This linearity suggested that the reactivity of Cl atoms toward $CF_3C(O)OCHF_2$ was substantially lower than that toward $CF_3CHClOCHF_2$. The reactivity of Cl atoms toward $CF_3C(O)OCHF_2$ was quantified by irradiating $CF_3CHClOCHF_2/Cl_2$/air mixtures until all (> 98%) of the $CF_3CHClOCHF_2$ was consumed, adding CD_4, resuming UV irradiation, and monitoring the subsequent loss of $CF_3C(O)OCHF_2$ and CD_4. In such experiments there was no observable loss (< 2%) of $CF_3C(O)OCHF_2$ while there was up to 96% consumption of CD_4. Using $k(Cl + CD_4 = 6.1 \times 10^{-15}$,1 an upper limit of $k(Cl + CF_3C(O)OCHF_2) < 4 \times 10^{-17}$ cm^3 molecule^{-1} s^{-1} was derived

Alkoxy radicals formed in the reaction of peroxy radicals with NO possessed vibrational excitation which may influence the importance of decomposition pathways. To check for such effects, experiments

were performed using the irradiation of $CF_3CHClOCHF_2/Cl_2/NO$ mixtures in 700 Torr of N_2/O_2. The $CF_3C(O)OCHF_2$ yield in the presence of NO was indistinguishable, within experimental uncertainties, from that in the absence of NO. The author concluded that the atmospheric fate of $CF_3C(O•)ClOCHF_2$ radicals was decomposition via elimination of a Cl atom to give CF_3 $C(O)OCHF_2$ and was unaffected by the method used to generate the $CF_3C(O•)ClOCHF_2$ radicals (reaction of $CF_3C(OO•)ClOCHF_2$ with either NO or with other peroxy radicals). A possible explanation for this observation is that $CF_3CHClO(•)$ radicals are converted into $CF_3CO(•)$ (either by intramolecular HCl elimination or via Cl atom elimination followed by secondary reaction of CF_3CHO with Cl atoms) and that these radicals add O_2 and then NO_2 to give the relatively stable peroxy nitrate $CF_3C(O)OONO_2$, thereby preventing further COF_2 formation. At the concentrations expected in this experiment (< 0.5m Torr), $CF_3C(O)OONO_2$ would escape detection by FTIR analysis.

Atmospheric Fate of the Alkoxy Radical CF3C(O•)HOCHF2

To investigate the atmospheric fate of $CF_3C(O•)HOCHF_2$ radicals, $CF_3CH_2OCHF_2/Cl_2/N_2/O_2$ mixtures were introduced into the chamber and subjected to UV irradiation. The Cl atom-initiated oxidation of $CF_3CH_2OCHF_2$ generated four carbon-containing products: COF_2, $CF_3O_3CF_3$, $CF_3C(O)OCHF_2$, and an unknown compound.

Experiments were performed using O_2 partial pressures varied over the range 50 - 700 Torr. Increasing O_2 partial pressure led to an increase in the $CF_3C(O)OCHF_2$ yield and a corresponding decrease in the yield of the unknown product. The simplest explanation of the experimental observations is that reactions 6 and 7 compete for the available $CF_3C(O•)HOCHF_2$ radicals and that the unknown is $HC(O)OCHF_2$.

$CF_3C(O•)HOCHF_2 \rightarrow CF_3 + HC(O)OCHF_2$ (6)

$CF_3C(O•)HOCHF_2 + O2 \rightarrow HO2 + CF_3C(O)OCHF_2$ (7)

Figure 7.5- 19A shows the observed formation of $HC(O)OCHF_2$, $CF_3C(O)OCHF_2$, and COF_2 following successive UV irradiations of the mixture of 6 mTorr of $CF_3CH_2OCHF_2$, 740 mTorr of Cl_2, and 400 Torr of O_2 in 700 Torr total pressure of N_2 diluent. The formation of $CF_3C(O)OCHF_2$ increased linearly with the $CF_3CH_2OCHF_2$ loss. In contrast to the behaviour of $CF_3C(O)OCHF_2$, the data plots for $HC(O)OCHF_2$ and COF_2 in Figure 7.5- 19A are distinctly curved, which suggested that $HC(O)OCHF_2$ is consumed and COF_2 is formed via secondary reactions involving Cl atoms.

As in the case of the decomposition pathway of $CF_3C(O•)ClOCHF_2$, the effect of vibrational excitation on the decomposition pathway of the $CF_3C(O•)HOCHF_2$ alkoxy radical needs to be considered. To check for such effects, experiments were performed using the irradiation of the same mixture used for the experiments reported in Figure 7.5- 19A but with the addition of 16 mTorr of NO. Following UV irradiation two products were observed: $HC(O)OCHF_2$ and COF_2. There was no observable formation of $CF_3C(O)OCHF_2$ (< 5% yield). Figure 7.5- 19B shows a plot of the formation of $HC(O)OCHF_2$ versus loss of $CF_3CH_2OC HF_2$ in the presence of NO. The filled symbols are the observed data; the open symbols have been corrected for loss of $HC(O)OCHF_2$ via reaction with Cl atoms. The straight line in Figure 7.5- 19B is a linear least-squares fit to the corrected data which gives a molar $HC(O)OCHF_2$ yield of 99 ± 6%. Clearly, within the experimental uncertainties, the yield of $HC(O)OCHF_2$ accounts for 100% of the loss of $CF_3CH_2OCHF_2$. The presence of NO has a major impact on the product distribution.

The authors concluded that chemical activation is an important factor in the fate of $CF_3C(O•)HOCHF_2$ radicals. Alkoxy radicals formed via the self-reaction of peroxy radicals have little, if any, internal excitation while alkoxy radicals formed via reaction of peroxy radicals with NO can possess significant internal excitation. The experimental results suggest that reaction of $CF_3C(OO•)HOCHF_2$ radicals with

NO produces vibrationally excited $CF_3C(O•)HOCHF_2$ radicals that possess internal energy exceeding that necessary to overcome the barrier for C-C bond scission.

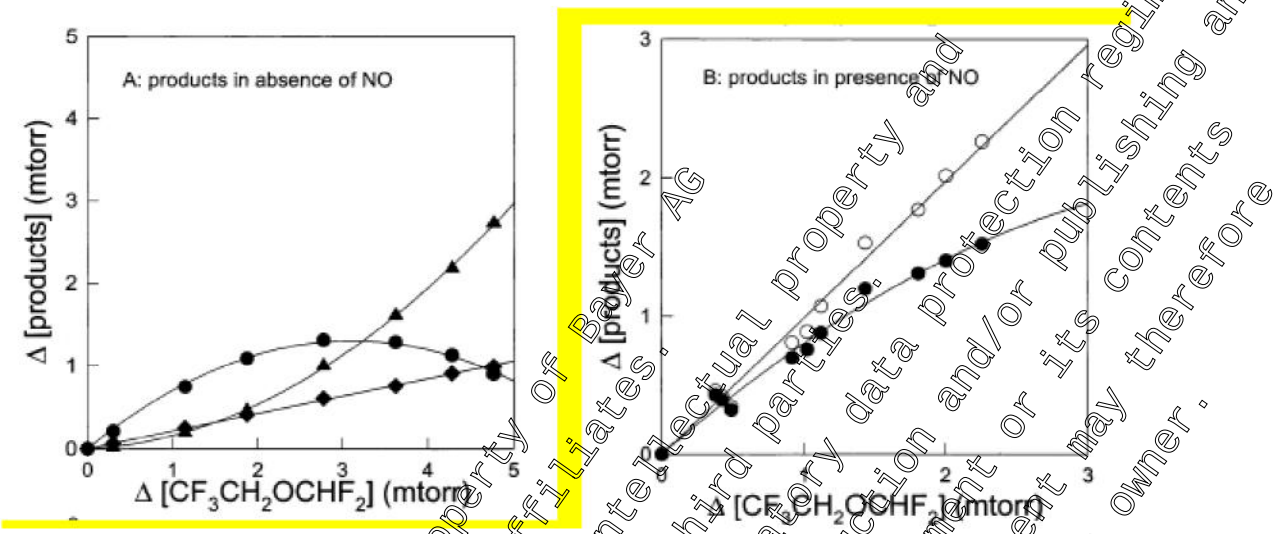


Figure 7.5- 19: Formation of COF_2 (triangles), $HC(O)OCHF_2$ (circles), and $CF_3C(O)OCHF_2$ (diamonds) versus loss of $CF_3CH_2OCHF_2$ following irradiation of mixtures of 6 mTorr of $CF_3CH_2OCHF_2$, 740 mTorr of Cl_2, 400 Torr of O_2, and either 0 (Panel A) or 16 mTorr (Panel B) of NO in 700 Torr total pressure of N_2 diluent. The open symbols in the lower panel show the result of correction for secondary reactions involving Cl atoms

Products of the OH radical initiated oxidation of $CF_3CHClOCHF_2$

To provide insight into the mechanism of the reaction of OH radicals with $CF_3CHClOCHF_2$, the products of the OH radical initiated oxidation of $CF_3CHClOCHF_2$ in air in the presence of NO were determined. In this work the loss of the reactant ($CF_3CHClOCHF_2$) was monitored indirectly by observing the loss of a more reactive tracer compound (C_2H_4). In 700 Torr of air diluent OH radicals react with C_2H_4 with a rate constant $k_{23} = 8.5 \times 10^{-12}$ cm^3 molecule/s.

Experiments were performed using mixtures of 4 – 5 mTorr of C_2H_4, 438 – 672 mTorr of $F_3CHClOCHF_2$, 157 - 316 mTorr of CH_3ONO, and 5 - 6 mTorr of NO in 700 Torr of air diluent. UV irradiation for periods of 0.5 – 30 min led to consumption of 30 - 95% of the C_2H_4 with corresponding (calculated) CF_3-$CHClOCHF_2$ consumptions of 0.079 - 0.66%. Two carbon containing products were observed: $CF_3C(O)OCHF_2$ and COF_2. $CF_3C(O)OCHF_2$ and COF_2 increased linearly with $CF_3CHClOCHF_2$ loss. Linear least squares analysis of the data gave molar yields of 85 ± 10% for $CF_3C(O)OCHF_2$ and 5 ± 1% for COF_2. The formation of $CF_3C(O)OCHF_2$ in reaction 1 was accompanied by the production of Cl atoms which can react with $CF_3CHClOCHF_2$ and raises the question, "to what extent does Cl atom initiated oxidation of $CF_3CHClOCHF_2$ contribute to the observed $CF_3C(O)OCHF_2$ and COF_2 product yields."

Using $k(Cl + CF_3CHClOCHF_2) = 5.4 \times 10^{-15}$, $k(Cl + C_2H_4) = 9.3 \times 10^{-11}$, $k(Cl + CH_3ONO = 2.1 \times 10^{-12}$ cm^3/molecule/s, and the average initial experimental conditions given above, it can be calculated that only 0.2% of the Cl atoms generated in the system will react with $CF_3CHClOCHF_2$. Cl atom initiated oxidation of $CF_3CHClOCHF_2$ is of negligible importance.

The yields of $CF_3C(O)OCHF_2$ and COF_2 provide information concerning the relative importance of reaction pathways 8a and 8b.

$CF_3CHClOCHF_2 + OH \rightarrow CF_3C(•)ClOCHF_2 + H_2O$ (8a)

$CF_3CHClOCHF_2 + OH \rightarrow CF_3CHClOC(•)F_2 + H_2O$ (8b)

$CF_3C(•)ClOCHF_2$ radicals formed in reaction 8a are converted into $CF_3C(O)OCHF_2$ while $CF_3CHClOC(•)F_2$ radicals are converted into COF_2. From the yields of $CF_3C(O)OCHF_2$ and COF_2 observed from the OH radical initiated oxidation of $CF_3CHClOCHF_2$ and assuming that in the presence of NO each $CF_3CHClOC(•)F_2$ radical is converted into either one or two molecules of COF_2, the author derived the reactions $k_{1a}/(k_{1a} + k_{1b}) = 0.95 \pm 0.03$ and $k_{1b}/(k_{1a} + k_{1b}) = 0.05 \pm 0.03$.

III. CONCLUSIONS

In the atmosphere $CF_3C(•)ClOCHF_2$ radicals will add O_2 rapidly to give $CF_3C(OO(•)ClOCHF_2$ which will be converted by reaction with NO into $CF_3C(O(•)ClOCHF_2$ radicals. The sole fate of $CF_3C(O(•)ClOCHF_2$ radicals is decomposition via Cl atom elimination to give the ester $CF_3C(O)OCHF_2$ which is relatively unreactive toward further gas-phase chemistry. By analogy to similar fluoroesters, $CF_3C(O)OCHF_2$ is expected to be removed from the atmosphere by incorporation into cloud rain-fog water followed by hydrolysis to give $CF_3C(O)OH$, CO_2, and HF. The atmospheric oxidation of isoflurane gives trifluoroacetic acid in a molar yield of 95 ± 3%. Isoflurane is emitted into the atmosphere at a rate of approximately 750 metric tons/yr and its contribution to the global trifluoroacetic acid budget is 750 × 0.95 × (114/184.5) = 440 metric tons/yr.

With an atmospheric lifetime of approximately 3 years, isoflurane will be well mixed in the atmosphere. To provide an estimate for the contribution of isoflurane oxidation to trifluoroacetic acid levels in rainwater, the authors combined the 440 metric tons/yr flux with the annual global rainfall of 4.9×10^{17} L to arrive at approximately 1 ng/L. This value can be compared to the levels of trifluoroacetic acid that are observed in rainwater which were (in late 1990s) typically of the order of 10 - 100 ng/L. Isoflurane oxidation makes a small, but non-negligible, contribution to trifluoroacetic acid observed in precipitation.

3. Assessment and conclusion

Assessment and conclusion by applicant:
This article from public literature reports the atmospheric chemistry of $CF_3CH_2OCHF_2$, and $CF_3CHClOCHF_2$ (isoflurane). The article has details on analytical procedures, but the work was not carried out according to GLP and there are currently no guidelines for the conduct of these study types.

Conclusion:
The atmospheric oxidation of isoflurane gives trifluoroacetic acid in a molar yield of 95 ± 3%. An estimate for the contribution of isoflurane oxidation to trifluoroacetic acid levels in rainwater arrived at approximately 1 ng/L which is a small, but non-negligible, contribution to trifluoroacetic acid observed in precipitation.
The information from this article can be regarded as supportive information.

Assessment and conclusion by RMS:
Outcome and conclusion of the study: RMS should indicate if they agree to the results and conclusions of the APPL.

1. Information on the published literature article

Data Point:	KCA 7.5/24
Report Author:	Wilson, S.; Tang, X.; Solomon, K.
Report Year:	2007
Report Title:	Changes in tropospheric composition and air quality due to stratospheric ozone depletion and climate change
Report No:	M-457426-01-1
Document No:	M-457426-01-1
Guideline(s) followed in study:	not applicable
Deviations from current test guideline:	Current Guideline: not applicable
Previous evaluation:	No, not previously submitted
GLP/Officially recognised testing facilities:	No, not conducted under GLP/Officially recognised testing facilities
Acceptability/Reliability:	Yes

2. Full summary of KCA 7.5/24

Executive Summary

In agreement with known usage and atmospheric loss processes, tropospheric concentrations of HFC-134a, the main human-made source of trifluoroacetic acid (TFA), is increasing rapidly. As HFC-134a is a potent greenhouse gas, this increasing concentration has implications for climate change. However, the risks to humans and the environment from substances, such as TFA, produced by atmospheric degradation of hydrochlorofluorocarbons (HCFCs) and hydrofluorocarbons (HFCs) are considered minimal.

I. MATERIAL AND METHODS

Materials

Several of the HCFCs and HFCs, including halothane, isoflurane, HCFC 123, HCFC-124, HFC-134a, and HFC-143a can break down into TFA.

Method

Literature and studies have been summarised to understand the impacts of ozone depletion, ozone depleting chemicals and their replacements on atmospheric composition and how these may interact with climate change. This paper was an update of information presented in a previous report.

II. RESULTS AND DISCUSSION

Observations in both hemispheres (Mace Head, Ireland and Cape Grim, Tasmania) between 1998 and 2002 showed that the concentration of HFC-134a had increased rapidly (3 picomol/mol/year) equivalent to 12% a year based on measured concentrations of approximately 25 picomol/mol/year measured in the troposphere at Mace Head, Ireland in 2002. This increase was in agreement with the known usage and atmospheric loss processes.

The final environmental sink for TFA is in the oceans and landlocked lakes. Concentrations of TFA in rainwater ranged from < 0.5 to 350 ng/L, depending on location and distance from anthropogenic activity. The predominant source of TFA in non-oceanic surface waters is likely to be anthropogenic as concentrations in surface water samples > 2000 years old obtained from groundwater and ice cores in

Greenland were not detectable (< 2 ng/L). Reports of TFA concentrations in oceans are generally less than or equal to 200 ng/L, and much of this appears to have pre-industrial natural origins. In seawater, relatively large TFA concentrations have occasionally been detected in close proximity to undersea volcanic vents, suggesting natural sources. TFA concentrations up to 350 ng/L in flowing surface waters have been reported from several locations and in landlocked lakes, concentrations may be as large as 40 000 ng/L.

Based on historical production of HFCs and HCFCs that are potential sources of TFA as well as projections of future uses, an estimate of total production was made (Table 7.5- 46). A worst-case estimate of TFA release from complete conversion of HFCs and HCFCs to TFA produced a total of 22 × 10^6 tonnes of TFA. After dilution and complete mixing in the volume of the oceans (1.34 × 1021 L), the increase in concentration above a nominal base level of 200 ng/L would be small (0.016 ng/L). Even if mixing were slow, concentrations in receiving zones would be less than those in flowing fresh waters or less than double the nominal base concentration. Considering other sources of TFA, the added inputs from anthropogenic activity will be insignificant.

Table 7.5- 46: Historical and projected production of HFCs and HCFCs in tonnes

	HCFC-124	HFC-134a	HFC-143a
Total production as of 2003	32253	1172891	39615
Estimated annual production in 2015	1000	446000	72000
Estimated total production by 2020/2040[1]	93681	19402446	3351615

[1]: Phaseout projected for 2020 in developed countries and 2040 in developing countries, half of the total use attributed to developed countries and half to developing countries.

III. CONCLUSIONS

Concentrations of TFA in various environmental compartments were: < 0.5 to 350 ng/L in rainwater; up to 40000 ng/L in landlocked lakes; up to 350 ng/L in flowing surface waters; ≤ 200 ng/L in oceans. In seawater, relatively large concentrations have occasionally been detected in close proximity to undersea volcanic vents, suggesting natural sources of TFA.

A worst-case estimate of cumulative TFA release up to the year 2040 from complete conversion of HFCs and HCFCs to TFA produced a total of 22 × 10^6 tonnes of TFA.

3. Assessment and conclusion

Assessment and conclusion by applicant:

Assessment:

This article summarises information on ozone depletion and climate change due to the the impact of hydrochlorofluorocarbons (HCFCs) and hydrofluorocarbons (HFCs) on the troposphere and air quality. Monitoring results for TFA in surface water and oceans from several monitoring literature articles have been included, without reference to sampling or analytical technique. A calculation has been made to estimate potential TFA concentrations from projected production of HFCs and HCFS in the mid-21st century. There are currently no guidelines for the conduct of monitoring studies.

Conclusion:

Measurements of TFA in various environmental compartments were: < 0.5 to 350 ng/L in rainwater; up to 40,000 ng/L in landlocked lakes; up to 350 ng/L in flowing surface waters; ≤ 200 ng/L in oceans. In seawater, relatively large concentrations have occasionally been detected in close proximity to undersea volcanic vents, suggesting natural sources of TFA.

A worst-case estimate of cumulative TFA release up to the year 2040 from complete conversion of HFCs and HCFCs to TFA produced a total of 22 × 10^6 tonnes of TFA.

The information from this article can be regarded as supportive information.

<u>Assessment and conclusion by RMS</u>:
Outcome and conclusion of the study: RMS should indicate if they agree to the results and conclusions of the APPL.

1. Information on the published literature article

Data Point:	KCA 7.5/25
Report Author:	Luecken, D. J.; Waterland, R. L.; Papasavva, S.; Taddonio, K. N.; Hutzell, W. T.; Rugh, J. P.; Andersen, S. O.
Report Year:	2010
Report Title:	Ozone and TFA impacts in North America from degradation of 2,3,3,3-tetrafluoropropene (HFO-1234yf) - A potential greenhouse gas replacement
Report No:	M-599310-01-1
Document No:	M-599310-01-1
Guideline(s) followed in study:	not applicable
Deviations from current test guideline:	Current Guideline: not applicable
Previous evaluation:	No, not previously submitted
GLP/Officially recognised testing facilities:	No, not conducted under GLP/Officially recognised testing facilities
Acceptability/Reliability:	Yes

2. Full summary of KCA 7.5/25

Executive Summary
A regional-scale, three-dimensional atmospheric model was used to evaluate U.S. air quality effects that would result from replacing HFC-134a in automobile air conditioners in the U.S. with HFO-1234yf. Although HFO-1234yf produces tropospheric ozone, the incremental amount is small, averaging less than 0.01% of total ozone formed during the simulation. This production of ozone could be compensated for by a modest improvement in air conditioner efficiency. Atmospheric decomposition of HFO-1234yf produces trifluoroacetic acid (TFA), which is subject to wet and dry deposition. Deposition and concentrations of TFA are spatially variable due to HFO-1234yf's short atmospheric lifetime, with more localised peaks and less global transport when compared to HFC-134a. Over the 2.5 month simulation, deposition of TFA in the U.S. from mobile air conditioners averaged 0.24 kg/km^2, substantially higher than previons estimates from all sources of current hydrofluorocarbons. Automobile air conditioning HFO-1234yf emissions are predicted to produce concentrations of TFA in Eastern U.S. rainfall at least double the values currently observed from all sources, natural and man-made. This model predicts peak concentrations in rainfall of 1264 ng/L, a level that is 80× lower than the lowest level considered safe for the most sensitive aquatic organisms.

I. MATERIAL AND METHODS

Material

Atmospheric degradation of HFCs can produce trifluoroacetic acid (CF_3COOH, TFA) via hydrolysis of trifluoroacetyl fluoride (CF_3COF, TFF).

The aim of this work was to address the question: While substitution of HFC-134a with HFO-1234yf would benefit the environment by decreasing global climate forcing, might it also degrade air quality by increasing tropospheric ozone or cause other multipollutant problems?

Analytical method
The Community Multiscale Air Quality Model, CMAQ v.4.7 performed simulations on a continental-scale domain with 36-km horizontal grid resolution and 24 vertical layers. Chemical boundary conditions for VOCs and inorganic species were derived from the GEOS-CHEM global model. Cloud and aerosol processes were included, and meteorological fields were obtained from the Pennsylvania State University/NCAR MM5 model, v. 3.6.1. Simulations were performed for June, July, and August 2005, using the first two weeks in June to allow concentrations of radicals and TFF to stabilise. Therefore, the model results are presented for the last two weeks in June, and all of July and August.

As HFO-1234yf is not currently in widespread use, there were no measurements or global modelling studies with which to initialize concentrations or characterize cross boundary transport, so boundary conditions and initial conditions were set to zero. Initial analyses showed that this did not adversely impact concentrations at the eastern or western boundaries, due to the short lifetime of HFO-1234yf, which varies from 2 days to 11 days depending on conditions, and the rapid solubility of TFA. Neglecting transport from the southern and northern boundaries may slightly have impacted on areas close to the boundaries of the U.S.

The CMAQ cloud module included parameterisations for sub-grid convective precipitating and nonprecipitating clouds, and gridscale resolved clouds, diagnosed at each hour and grid cell. When clouds were present, gas and aerosol-phase pollutant concentrations in the CMAQ model were affected by convective mixing, wet scavenging, aqueous chemistry and removal by wet deposition. Subgrid-scale cloud effects were simulated by diagnosing the fraction of grid covered by cloud, performing aqueous chemistry, transport and deposition on this fraction and mixing into the entire grid, on a weighted basis, at each time step.

The chemical degradation of HFO-1234yf and production of ozone and TFA by extending the base CB05 chemical mechanism with chlorine to include reactions of HFO-1234yf and its products is represented by:

$$HFO\text{-}1234yf + OH \rightarrow CF_3COF + HCHO + HO_2 + XO2 \quad (1)$$

$$HFO\text{-}1234yf + Cl \rightarrow 0.92^{*}CF_3COF + 0.56^{*}TFMCl + 2.0^{*}XO2 + CO \quad (2)$$

$$HFO\text{-}1234yf + O_3 \rightarrow 0.5^{*}CF_3COF + 0.74^{*}HCHO + 0.44^{*}HO_2 + 0.220^{*}XO2 + 0.1^{*}OH + 0.330^{*}CO + PAR \quad (3)$$

$$HFO\text{-}1234yf + NO_3 \rightarrow 0.91^{*}CF_3COF + 0.91^{*}HCHO + 0.91^{*}XO2 + 0.09^{*}XO2N + NO_2 \quad (4)$$

The dominant degradation pathway of HFO-1234yf is reaction with hydroxyl radical (OH) with a rate constant of $1.26 \times 10^{-12} \exp(-35/T)$ cm^3/molecule/s, where addition at either end of the double bond produces TFF, formaldehyde, hydroperoxy radical (HO_2), and oxidation of NO to NO_2. In reactions 1 - 4, XO2 and XO2N are CB05 model operators representing NO to NO_2 conversion and NO to organic nitrate conversion over multiple steps, and PAR represents single-bonded carbon.

In the gas phase, the only major reaction of TFA is with OH:

$TFA + OH \rightarrow XO2 + COF_2$ (5)

with a rate constant of 9.35×10^{-14} cm^3/molecule/s. It was assumed there was no nitrate formation and 100% formation of peroxy radical operator XO2. Formation of organic nitrate from reactions of NO and peroxy radicals was not needed to fit recent smog chamber studies.

As TFF is unreactive in the gas phase, but hydrolyses to TFA in water, this was the only route considered by the author in the modelling. A Henry's Law constant of 3 M atm^{-1} and hydrolysis rate of 150 s^{-1} converted most TFF into TFA when cloudwater was present. Partitioning of TFF and TFA into cloudwater and formation of TFA from TFF in grid cells and times when cloudwater was present was accounted for by integrating over the time used to resolve clouds in CMAQ (300 s) with a 0.25 s time step for aqueous cloud chemistry. There were no data for effect of pH on hydrolysis of TFF or dehydration of TFA; therefore, the author assumed that hydrolysis occurred irreversibly.

TFA partitions into the gas phase when cloudwater evaporates and is highly soluble in cloudwater, so the author removed aqueous TFA by both wet scavenging and deposition and via dry deposition by similarity to nitric acid.

Non-refrigerant emissions for the June-August Base Case period were extracted from the 2005 National Emission Inventory for point and area sources, the BEIS model for biogenic emissions, and the Mobile Source Model for on-road and off-road emissions. These were then allocated spatially and temporally to grid cells using the SMOKE emissions processor.

The refrigerant emission inventory for HFO-1234yf takes into consideration direct and indirect emissions associated with the manufacturing, operation, shipping, and end-of-life of MACs. Refrigerant emissions from normal operation, vehicle accidents, servicing, and end-of-life vehicle scrapping were considered. It was assumed that all vehicles in the US were equipped with HFO-1234yf systems in 2017. This overestimated the HFO-1234yf emissions since it did not account for the fraction of the 2017 fleet manufactured before 2011 and equipped with HFC-134a systems, but it gave a better estimate of future-year emissions. Due to uncertainty in accurately estimating refrigerant leaks, a Low and High leak Scenario was considered for the number and mix of vehicles in calendar year 2017, when the switch took place. Emissions in the Low Scenario were roughly 67% of the High Scenario for the three summer months simulated (June - August). State-level emissions were allocated to county-level based on population weighting and further allocated to 36-km grids covering the continental U.S using the SMOKE model, and based on vehicle miles travelled (VMT), roadway distribution, and profiles of on-road activity data. No emissions inventories were available from Mexico and Canadian mobile sources, so this analysis considered only the effect of U.S. emissions on concentrations in the U.S.

Every refrigerant transition requires redesign and re-optimization of components/controls and application of regulatory standards. Studies have shown that current MAC system efficiency can be improved by more than 30%. While HFO-1234yf is approximately 5% less efficient than HFC-134a based on chemical and physical properties, engineering innovations are expected to result in at least a 10% improvement in coefficient of performance (COP).

To study effects of MAC improvements that might occur with transition to HFO-1234yf, an additional simulation incorporating the effect of a 10% increase in COP over existing systems was performed. An equivalent incremental engine efficiency for both systems for relating work to fuel usage, and a linear relationship between fuel use and exhaust emissions was assumed. Tailpipe emissions from operation of an optimized MAC based on HFO-1234yf were derived based on tailpipe emissions in a current system with HFC-134a.

Four emissions scenarios were simulated:

1. Base Case Scenario: Using 2005 emissions, this scenario provided a baseline of ozone concentrations and radicals from current sources of organic and inorganic emissions. TFA was not calculated because HFC-134a, the current refrigerant, has a very low reactivity;
2. Low Scenario: Using the lower estimate of HFO-1234yf emissions added to Base Case emissions;
3. High Scenario: Using the upper estimate of HFO-1234yf emissions added to Base Case emissions; and
(4) High Scenario with COP Improvement: Using emissions from the High Scenario combined with reduced mobile source emissions assuming a 10% increase in COP.

II. RESULTS AND DISCUSSION

Figure 7.5- 20 shows the average predicted summer concentrations of HFO-1234yf in the High Scenario. The Low Scenario predicted concentrations that ranged from 65% (in the north) to 70% (in the south). The concentration distributions reflected the spatial distribution of emissions of HFO-1234yf which have been previously reported, with high concentrations in areas of high automobile density. Although there are grids with average concentrations on the order of 100-300 ppt, mean HFO-1234yf concentrations over the U.S. are 5.0 ppt (Low Scenario) and 7.4 ppt (High).

CMAQ with a 36-km resolution cannot predict every observed value, however comparison of Base Case predictions against point observations at 1189 ozone monitoring sites was good with mean bias values of 7.6 (July) and 5.8 ppb (August), and mean absolute gross errors of 11 ppb (July) and 10 ppb (August).

Figure 7.5- 21 shows predicted dry, wet, and total deposition of TFA from the High Scenario during the 2.5 month period. Dry deposition comprised of 10 - 75% of the total, depending on location and with a different spatial pattern than wet. Production of TFA depended on the presence of cloudwater, so the highest deposition occurred in areas with high cloudwater. Average TFA deposition was 0.16 kg/km^2 in the Low Scenario and 0.24 kg/km^2 in the High Scenario. Average precipitation concentrations of TFA in the High Scenario ranged from 100 to 1000 ng/L. The largest concentrations occurred in areas with small precipitation but large emissions, such as southern California. Deposition of TFA from the Low Scenario was 67 - 68% of the High Scenario, roughly linear with emissions difference between scenarios.

The 3 months modelled, provided a baseline for estimating production and deposition of TFA under longer-term simulations. Although an entire year has not been simulated, the 2.5 months presented include ca. 52% of the annual emissions with the majority of MAC leaks occurring during the summer when MACs are more likely to be pressurised and serviced. If deposition of TFA varies approximately linearly with emission rate, then a full year estimated emissions from MACs would result in about twice as much deposition as reported. Production and deposition of TFA depends on the presence of liquid water in the atmosphere and radical concentrations, both of which vary seasonally, so the pattern and magnitude of deposition may change seasonally.

The potential production of TFA in liquid water on atmospheric aerosols was ignored by the author due to the lack of laboratory data on partitioning and reactions in aerosols and the high uncertainty in characterising nonideal solutions on aerosols. For typical summer temperatures and the acidic aerosols seen in the U.S., liquid partitioning would be small. In contrast, there is nearly complete removal of TFF and TFA when clouds are present (the processes presented).

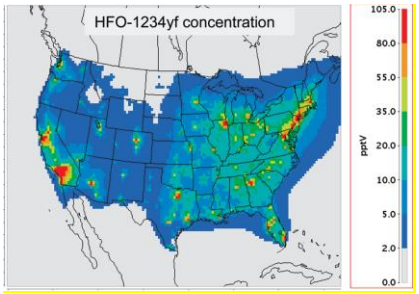


Figure 7.5- 20: Average concentration of HFO-1234yf, pptv - Model results for the high scenario

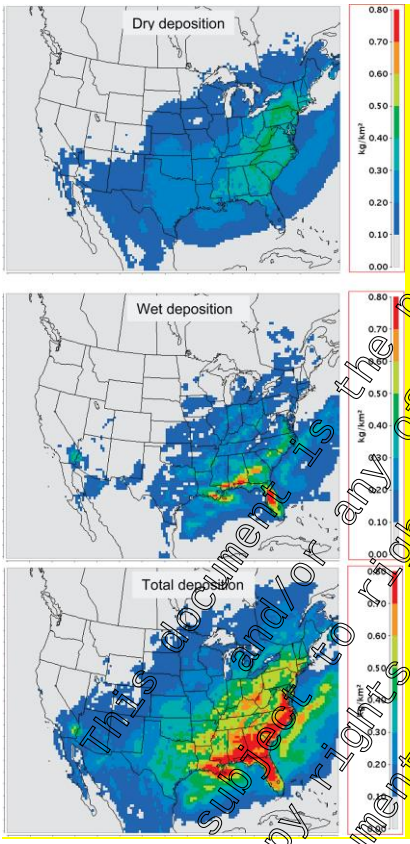


Figure 7.5- 21: Predicted total deposition of TFA in the high scenario

III. CONCLUSIONS

Deposition and concentrations of TFA are spatially variable due to HFO-1234yf's short atmospheric lifetime, with more localised peaks closer to major urban areas with less global transport when compared to HFC-134a. Over the 2.5 month simulation, deposition of TFA in the U.S. from mobile air conditioners averaged 0.24 kg/km², substantially higher than previous estimates from all sources of current hydrofluorocarbons. Automobile air conditioning HFO-1234yf emissions are predicted to produce TFA rainfall concentrations of 1264 ng/L (at least double the values observed from all sources, natural and man-made up to the publication date (2010)).

3. Assessment and conclusion

Assessment and conclusion by applicant:

Assessment:

This article contains three-dimensional atmospheric modelling to evaluate U.S. air quality effects that would result from replacing HFC-134a in automobile air conditioners in the U.S. with HFO-1234yf. The study was not performed to GLP and there are currently no guidelines for the conduct of modelling studies.

Conclusion:

Deposition and concentrations of TFA are spatially variable due to the short atmospheric lifetime of HFO-1234yf, with more localised peaks closer to major urban areas with less global transport when compared to HFC-134a. Automobile air conditioning HFO-1234yf emissions are predicted to produce TFA rainfall concentrations of 1264 ng/L.

The information from this article can be regarded as supportive information.

Assessment and conclusion by RMS:

Outcome and conclusion of the study. RMS should indicate if they agree to the results and conclusions of the APPL.

1. Information on the published literature article

Data Point:	KCA 7.5.26
Report Author:	Henne, S.; Shallcross, D. E.; Reimann, S.; Xiao, P.; Brunner, D.; Buchmann, B.; Hill, M.
Report Year:	2012
Report Title:	Environmental impacts of HFO-1234yf and other HFOs
Report No:	M-464526-01-1
Document No:	M-464526-01-1
Guideline(s) followed in study:	not applicable
Deviations from current test guideline:	Current Guideline: not applicable
Previous evaluation:	No, not previously submitted
GLP/Officially recognised testing facilities:	No, not conducted under GLP/Officially recognised testing facilities
Acceptability/Reliability:	Yes

2. Full summary of KCA 7.5.26

Executive Summary

HFO-1234yf (2,3,3,3-tetrafluoropropene may replace HFC-134a (1,1,1,2-tetrafluoroethane) in mobile air conditioners, and thus be an important compound in terms of expected future emissions and trifluoroacetic acid (TFA) yield. Previous findings on TFA in the environment were reviewed and more recent TFA measurements in Switzerland were compared to those from the 1990s when HFCs with considerable TFA yields were introduced. Changes in rainwater concentrations were not significant for two sites in northern Switzerland but were positive for one site in southern Switzerland, where photochemistry was accelerated. The latter may indicate enhanced production of TFA from increased

HFC background concentrations during the last decades but could not be generalised due to the large variability and sparsity of the observations.

Atmospheric chemistry and transport modelling investigations were made of the TFA concentrations in rainwater and TFA deposition rates that would result from a complete switch of the European vehicle fleet to HFO-1234yf. It was estimated that total European HFO-1234yf emissions would be 1.1.0 to 19.2 Gg/yr for 2020. Since the lifetime of HFO-1234yf is relatively short, maximal TFA concentrations and deposition rates were simulated close to emission centres. Predicted maximal summer-time TFA concentrations in European rainwater reached up to 7700 ng/L, with maximal annual TFA concentrations predicted to stay below 2500 ng/L.

I. MATERIAL AND METHODS

Material

TFA concentrations in rainwater from Switzerland (April – October 2011) were compared with measurements made at the same site or close to and within similar environments from 1996 - 1997. Future TFA concentrations in rainwater and TFA deposition rates in Europe were evaluated based on emission predictions and atmospheric chemistry and transport simulations.

Sampling method

Samples were collected for 33 weeks between April - October 2011 at three sites in Switzerland which formed part of the Swiss air pollution monitoring network (NABEL). The sites were: Dübendorf (DUE), a sub-urban site in Northern Switzerland, 430 m above sea level (asl); Magadino (MAG), a rural site in Southern Switzerland, 203 m asl; Rigi-Seebodenalp (RIG), an elevated rural site in the foothills of the Northern Alps, 1031 m asl.

Samples were collected using a Digitel DRA-92 HK wet-only rain collector. During sampling and transport the samples were kept at 4 - 8°C and stored at -20°C until analysis.

Analytical method

TFA was quantified in the rain samples by liquid chromatography / mass spectrometry (LC/MS) without any sample pre-treatment. Samples were thawed and transferred into LC-vials, which were rinsed twice with the sample. Chromatography was performed on a mixed mode anion exchange column (Shodex RSpak JJ-50 2D) under isocratic conditions (10 mM NH_4OAc in acetonitrile/water (3:1, v/v). The MS was operated in the negative ion electrospray mode. For TFA, the transition m/z 113 to m/z 69.1 was acquired. Quantification was done by external calibration. Standard additions demonstrated equal response in rain samples and standard solutions. The laboratory blank (18 - 25 ng/L) and the field blank (14 ng/L) were subtracted for the final concentration in the rain samples.

Limit of quantification: The LOD was 48 - 75 ng/L (laboratory blank sample + 10 times the standard deviation of the laboratory-blank sample).

II. RESULTS AND DISCUSSION

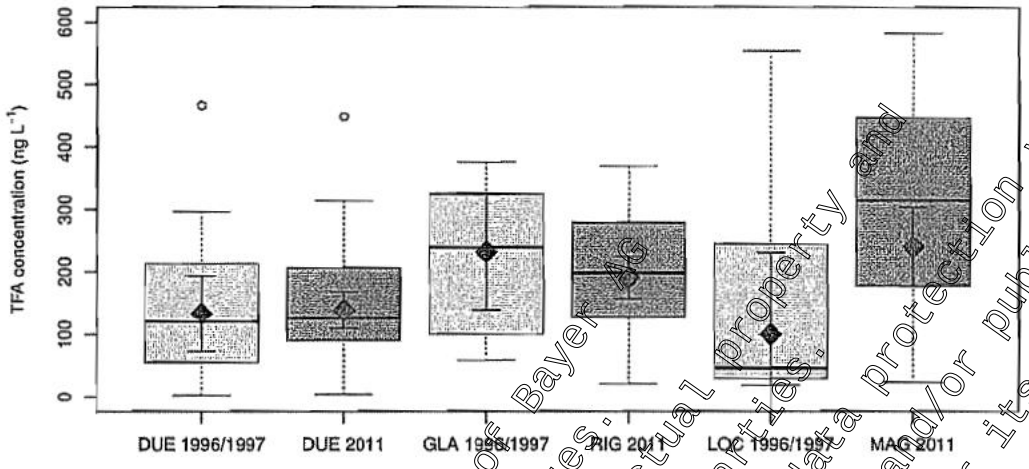
Median TFA concentrations were 126 ng/L for DUE, 315 ng/L for MAG and 198 ng/L for RIG. A direct comparison of these concentrations with previously reported TFA concentrations in rainwater across Central Europe (Table 7.5- 47) did not reveal any significant changes in observed TFA concentrations since the 1990s, although this was complicated by the large variability in observed concentrations and the fact that TFA concentrations in rainwater depend on the available precipitation amount. Since precipitation amounts varied from year to year, it could not be concluded that TFA concentrations and especially TFA deposition remained unchanged since the 1990s.

Table 7.5- 47: Published TFA concentration ranges in precipitation in chronological order (mean concentration in brackets)

Location	Concentration (ng/L)	Samples	Period
Europe			
Germany, urban	25 - 280 (100)	29	1995
Switzerland, urban/rural	40 - 80	n.a.	1995
Germany, urban/rural	10 - 410 (110)	> 10	1995/96
Germany, rural	ca. 20 - 580 (ca. 100)		1998/99
Switzerland, various	< 3 - l, 553 (151)	73	1996/97
Ireland, remote	2 - 92 (39)	8	1996
Poland, urban	26 - 1100 (318)	4	1996
Outside Europe			
USA, Nevada	21 - 763		1996/97
Canada, remote	40 (84)		1997
South Africa, suburban	40		1996
U.S.A., suburban	10 - 2400	62	1998/99
U.S A., rural	3 - 360	80	1998/99
China, urban	25 - 235		2000/01
Canada, remote	4 - 220	42	2002
Canada, suburban	43 - 170	8	2003/04
Canada, urban	87 - 270	7	2003/04
Japan, urban	39 - 76		2007

n.a: Not available.

Site DUE was one of the same sites as reported by a previous author (reported as “Switzerland, various” in Table 7.5- 47). As part of that study, TFA measurements were carried out at DUE in the years 1996 and 1997. The other two sites of the current study (RIG and MAG) were situated relatively close to and within similar environments as two other sites (Glarus (GLA) and Locarno (LOC)) used in the same 1996/1997 study. Measurements in that previously reported study consisted of 47 individual rain events taken in the months March to October compared to 33 weekly samples taken between April to October 2011 in the present study. Observed TFA concentrations did not differ significantly between the two periods for DUE and GLA/RIG (Figure 7.5- 22) with precipitation weighted average concentrations of 133 ng/L and 138 ng/L for 1996/1997 and 2011 in DUE, respectively, and 233 ng/L and 191 ng/L in GLA/RIG. For LOC/MAG a significant increase from 100 ng/L to 240 ng/L was observed. Taking the precipitation weighted average TFA concentrations and the annual precipitation amount at the individual sites and the individual years of measurement, total annual TFA deposition rates of 127, 228, and 321 g/km^2/yr for 2011 were calculated for DUE, RIG and MAG, respectively. In the earlier period, deposition rates were not consistently different. 159, 348, and 193 g/km^2/yr, for DUE, GLA, and LOC, respectively. The increase in rainwater concentrations and deposition rates at the site LOC/MAG in the southern part of Switzerland, where photochemistry is accelerated due to higher temperatures and increased solar radiation, potentially indicated that TFA concentrations and deposition in Switzerland had increased since the 1990s, which was expected from the increase of the main atmospheric precursor HFC-134a, from ca. 2 ppt in 1995 to ca. 58 ppt in 2010 in the northern hemisphere.



♦: Averaged TFA in rainwater concentration weighted by precipitation amount
○: Outliers.
Error bars indicate 95% confidence levels at different sites in Switzerland. The central line of the box indicates the median estimate, while the outer borders of the box give the 25th and 75th percentile range. The error bars depict the range of "connected" (smallest/largest data point within +/- 1.5 times the interquartile range) data.

Figure 7.5- 22: Boxplots of observed TFA in rainwater concentration and averaged TFA in rainwater concentration weighted by precipitation amount and their 95% confidence levels at different sites in Switzerland

Envisaged future HFO-1234yf emissions in Europe

To estimate the potential future impact of TFA deposition from HFO-1234yf degradation a detailed European emission inventory for HFO-1234yf for the year 2020 was developed. Only emissions from mobile air conditioners (MAC) were considered since these were expected to be the major application of HFO-1234yf. A complete transition from HFC-134a to HFO-1234yf was assumed. Emissions from the whole life cycle of MACs were considered, comprising regular diffusive emissions, irregular emissions due to system failures, initial filling and refilling emissions, and end of life emissions during decommission. Emission factors were based on those estimated for present day HFC-134a emissions from MACs. Two different emission scenarios were developed that assumed different regular emission rates and different fractions of trained and untrained personnel handling refill and end of life treatment. Predicted vehicle counts for all European Union countries plus Croatia, Norway, Switzerland and Turkey (EU27+) were taken from the TREMOVE 2.7b database and multiplied with the emission factors to derive country total emissions for the year 2020. Country total emissions were then disaggregated on a 0.1° by 0.1° regular grid based on population densities and carbon monoxide emissions from traffic. No temporal variability was assumed in the emissions.

European (EU27+) total envisaged HFO-1234yf emissions for the year 2020 were estimated to be between 11.0 Gg/yr (low scenario) and 19.2 Gg/yr (high scenario). These numbers were comparable to those predicted by a previous author for the U.S. car fleet for 2017 of 11.4 Gg/yr to 24.7 Gg/y. As the predicted size of the European and the U.S. car fleet were very similar (290 million and 280 million for EU27+ and U.S., respectively) these estimates were very consistent.

Future TFA concentrations and deposition

Two different atmospheric chemistry and transport models were set up to simulate atmospheric degradation of European HFO-1234yf emissions, based on the predicted emission scenarios. The first model was an extended version of the Lagrangian Particle Dispersion Model FLEXPART (Version 8.1). The model was modified to represent the main reactions of the HFO-1234yf degradation chain to TFA, but used an external (and therefore fixed) OH field. No feedback of HFO-1234yf on the OH field was simulated. The second model, CRI-STOCHEM, incorporated a comprehensive atmospheric chemistry scheme and included feedbacks of HFO-1234yf on OH levels. These feedbacks remained negligible at the encountered HFO-1234yf levels. Transport was described in more detail in FLEXPART, whilst chemistry was more complete in CRI-STOCHEM. Both models were run for the period of one whole year in order to analyse the seasonal behaviour of HFO-1234yf dispersion and degradation. Two emission scenarios were run for both models, based on the low and high emission estimates. Due to the linearity of results, only results from the high emission scenario are presented. An additional simulation was analysed that used a higher resolution meteorological input nest for the Alpine domain (0.2° by 0.2° horizontal resolution), while the current study used meteorological input on a 1° by 1° regular grid.

Table 7.5- 48 summarises some of the model results in terms of simulated atmospheric mole fractions of HFO-1234yf and TFA, TFA concentrations in rainwater and total TFA deposition rates. For comparison, results from a previous study for the U.S. are also included. Average simulated HFO-1234yf concentrations were comparable between the studies, considering that in the U.S. study 61% of the annual HFO-1234yf emissions occurred during the summer months, while in the current study a constant emission rate was used and only 25% of the annual total was released in the summer months. The mole fraction maxima indicated that the main differences between the current study and that for the U.S. stems from different reference grid resolutions. Maxima steadily increased with model grid resolution. For TFA mole fractions in air the model results were more similar because this compound was much more dispersed in the atmosphere than the freshly released HFO-1234yf.

European mean TFA concentrations in rainwater were predicted by FLEXPART to be 580 ng/L whilst mean concentrations for the Alpine domain were slightly greater (960 ng/L). The highest rainwater concentrations (up to 1700 ng/L) were predicted for hot spots in the Czech Republic and southern Germany when looking at the European scale simulation, while the nested simulation for the Alpine region showed highest precipitation concentrations in the western Po valley (up to 2200 ng/L). These differences were most likely caused by the better representation of topographic flow in the nested simulations that more realistically simulates situations of weak atmospheric dispersion encountered in Northern Italy.

Table 7.5- 48: Summary of modelled mole fractions, rainwater concentrations and deposition rates from this study compared to a previous study in the USA

	Europe (annual) FLEXPART		Europe (annual) STOCHEM		Europe (summer) FLEXPART		Alpine region (summer) FLEXPART		USA[1] (summer)	
	Mean	Max	Mean	Max	Mean	Max	Mean	Max	Mean	Max
HFO-1234yf (ppt)	2.6	18	1.5	3.7	1.5	15	3.9	28	7.4	300
TFA (ppt)	0.1	0.6	0.12	0.35	0.15	0.94	0.26	0.78	n.a.	> 0.8
TFA in rainwater (ng/L)	580	1700	800	2160	1200	12000[2]	1600	7700	500	1264
Combined TFA deposition (kg/km^2/yr)	0.65	2.5	0.76	1.9	0.0[3]	4.4[3]	2.48	6.4	0.48[1]	2.34

n.a: Not available.
[1]: Only summer time average available (mid-June to end of August), deposition rates up-scaled assuming 50% of annual emission in this period.
[2]: Maximal values observed over Eastern Mediterranean during low precipitation rain events. Maxima over continental Europe were 5000 ng/L.
[3]: Seasonal results up-scaled to annual flux.

The results for the nested simulation show that TFA concentrations in the inner Alpine domain may have been significantly lower than in the surroundings. Rain events in the Alps are often triggered by topographic lifting and extend from the foothills towards the inner Alpine domain. Since TFA is quickly washed out from the atmosphere most TFA does not reach the inner Alpine domain, but is deposited in the foothills and adjacent plains. This model result matched the observations by a previous author, who measured the smallest concentrations of TFA in rainwater within Switzerland in the eastern Alpine part of Switzerland (Davos and Weissfluejoch). Although TFA formed in the atmosphere at the time of those measurements did not result from HFO-1234yf degradation, the washout mechanism would still be the same.

When compared with the annual average, simulated mean and maximum summer time rainwater concentrations were higher, with values up to 12000 ng/L reached over the Eastern Mediterranean, where infrequent rainfall in the summer months encountered outflow of European HFO-1234yf emissions that underwent degradation over the Mediterranean. These concentrations may have included relatively large uncertainties due to large uncertainties in precipitation amounts and location for isolated rain events. Previous and current measurements of TFA in rainwater in Europe were in the range of 10 to ca. 1500 ng/L with a current average for a site in northern Switzerland of ca. 125 ng/L.

Annual average total deposition rates of TFA for Europe were 0.65 kg/km^2/yr in the FLEXPART simulations and only slightly higher, 0.79, in the CRI-STOCHEM simulations. Simulated maxima were located in the Po Valley of northern Italy and southern Germany, relatively close to the HFO-1234yf emission maxima. This was in contrast to TFA formed from present HFC and HCFC degradation that, due to the longer lifetimes of these compounds, was expected to show maxima in the Tropics, the region with largest OH concentrations. The higher resolution results suggested that deposition rates would be largest in the plains and foothills directly adjacent to the Alps. North of the Alps a maximum of about 2.2 kg/km^2/yr was predicted for Switzerland, while the maximum value south of the Alps increased to 3.4 kg/km^2/yr. The mean summer-time European deposition rate of 0.25 kg/km^2 (value in Table 7.5- 48 multiplied by 4 to scale to annual total) was very similar to that predicted in the U.S. (0.24 kg/km^2). Considering that summer-time emissions were larger in the U.S study as compared to the current one, European deposition rates may be a factor of 2 larger than those for the U.S. Reported deposition rates for Germany and Switzerland ranged from 0.05 to 0.2 kg/km^2/yr. Future annual deposition rates may

thus be an order of magnitude larger than these previously reported values when HFO-1234yf replaces HFC-134a.

III. CONCLUSIONS

Median TFA concentrations in rainwater samples taken between April - October 2011 at three sites in Switzerland ranged from 126 ng/L to 315 ng/L. A direct comparison of these concentrations with previously reported TFA concentrations in rainwater across Central Europe did not reveal any significant changes in observed TFA concentrations since the 1990s, although variabilities in observed concentrations and quantity of available precipitation amount meant that it could not be concluded that TFA concentrations and TFA deposition had remained unchanged since the 1990s.

Model simulations average predicted TFA concentration in rainwater of 1200 ng/L would result from HFO-1234yf emissions in Europe.

Previous estimates suggested annual TFA deposition of 50 - 100 Gg/yr for the next 100 years would lead to an average increase of 3.7 - 7.4 ng/L in the oceans, a value much smaller than present day concentrations. This calculation assumed oceanic mixing on the same time scale as TFA input (100 yr), although larger increases in surface waters (by at least one order of magnitude) were likely. Furthermore, the assumption of TFA production of 50 - 100 Gg/yr seemed to be too low considering that a complete replacement of HFC-134a by HFO-1234yf would lead to emission of about 150 Gg/yr of HFO-1234yf and, hence, the same amount of TFA production in the atmosphere. As a conservative estimate, the authors assumed that annual TFA production (from HFO-1234yf and other HFOs) would be in the order of 300 Gg/yr.

The total accumulation in the oceans after 100 year of TFA deposition would be 22 ng/L if complete oceanic mixing was assumed and 200 ng/L as a conservative estimate for oceanic surface waters if mixing was not complete.

3. Assessment and conclusion

Assessment and conclusion by applicant:

Assessment:

This article from public literature describes a small rainwater monitoring study for TFA, comparison of results with other studies in public literature, and modelling simulations to extrapolate future TFA concentrations and deposition from HFO-1234yf. Sampling and analytical methods were reported, both laboratory and field blanks were included, and a LOQ of 48-75 ng/L determined. The study was not conducted according to GLP. There are currently no guidelines for monitoring studies.

Conclusion:

Median TFA concentrations in rainwater samples taken between April - October 2011 at three sites in Switzerland ranged from 126 ng/L to 315 ng/L. Model simulations predicted TFA concentration in rainwater of 1200 ng/L would result from HFO-1234yf emissions in Europe.

The information from this article can be regarded as reliable.

Assessment and conclusion by RMS:

Outcome and conclusion of the study: RMS should indicate if they agree to the results and conclusions of the APPL

1. Information on the published literature article

Data Point:	KCA 7.5/27
Report Author:	Wang, Q.; Wang, X. (.; Ding, X.
Report Year:	2014
Report Title:	Rainwater trifluoroacetic acid (tfa) in guangzhou, south china: levels, wet deposition fluxes and source implication
Report No:	M-754605-01-1
Document No:	M-754605-01-1
Guideline(s) followed in study:	not applicable
Deviations from current test guideline:	Current Guideline: not applicable
Previous evaluation:	No, not previously submitted
GLP/Officially recognised testing facilities:	No, not conducted under GLP/Officially recognised testing facilities
Acceptability/Reliability:	Yes

2. Full summary of KCA 7.5/27

Executive Summary

Hydrochlorofluorocarbons and hydrofluorocarbons (HCFCs/HFCs) as replacements of chlorofluorocarbons (CFCs) are precursors of trifluoroacetic acid (TFA) in the atmosphere, their contribution to rainwater TFA is a concern as their ambient mixing ratios are continually growing. Rainwater TFA monitored from April 2007 to March 2008 in urban Guangzhou, a central city in south China's highly industrialized and densely populated Pearl River Delta region (PRD) showed TFA levels ranged from 45.8 - 974 ng/L (median of 166 ng/L). TFA levels negatively correlated with rainfall amount. The yearly rainfall-weighted average for TFA was 152 ng/L. The annual TFA wet deposition flux was estimated to be 229 g/km²/yr, and the total wet deposition of TFA reached ca.1.7 t/yr in Guangzhou. The Two-Box model was applied to estimate attributions of HCFCs/HFCs and fluoropolymers to rainwater TFA assuming TFA generated was proportional to gross domestic product (GDP), gross industrial product (GIP) or number of private cars. The results revealed that the degradation of HCFCs/HFCs and fluoropolymers could explain 131.5 - 152.4 ng/L rainwater TFA, quite near the observed rainfall-weighted annual mean of 152 ng/L, suggesting rainwater TFA in Guangzhou was predominantly originated from these anthropogenic precursors. HCFCs/HFCs accounted for 83.3 – 96.5% of rainwater TFA observed, while fluoropolymers' contributions were minor (ca. 5%). HFC-134a alone could explain 55.9 – 90.0% of rainwater TFA, and its contribution would be greatly enhanced with its wide use in mobile air conditioning systems and rapid increase in ambient mixing ratios.

I. MATERIAL AND METHODS

Material

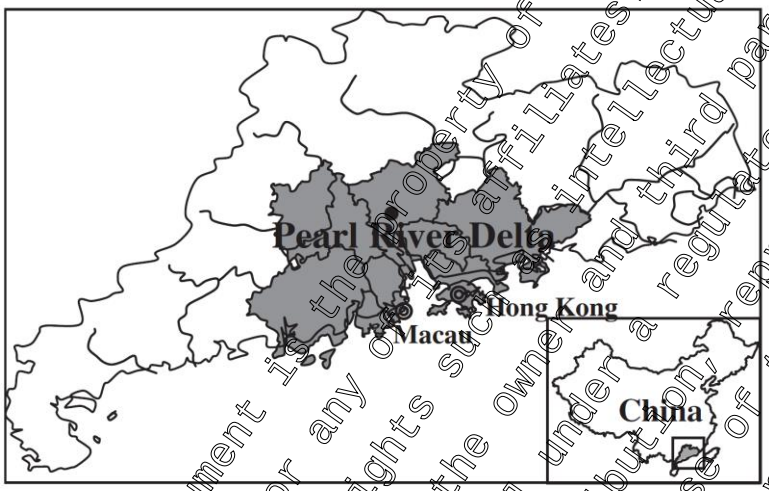
In this present study, rainwater TFA was monitored in urban Guangzhou. The aim of this work was to obtain rainwater TFA data from extensive field monitoring, to estimate its wet deposition in this region and to assess source contributions to rainwater TFA, particularly the role played by CFC-replacement HCFCs/ HFCs.

Sampling method

The rain sampling location is shown in Figure 7.5- 23. Rainwater samples were simultaneously collected using two 50 cm cube glass containers on the rooftop of a 4-story building with an elevation of 37.5 m above sea level. The containers were opened once a rain event started and closed when the rain stopped

to avoid dry deposition. Except for keeping separate as parallel samples, two rainwater samples for each rain event were combined and transferred to a 1 L polypropylene bottle immediately as one sample and stored at 4°C in dark until analysis. After sampling, the glass containers were carefully cleaned by methanol and then by ethyl acetate to avoid cross contamination in the next collection. If rainwater samples collected were less than 100 mL, they were combined to the nearest rainwater samples. A total of 40 rainwater samples were collected from April 2007 to March 2008. The data of rainfall amount, air temperature and relative humidity (RH) for each rainy day were obtained from the Guangzhou Meteorological Satellite Ground Station (GMSS), which is less than 2 km away from the sampling site.

All glassware and rainwater collection containers were solvent rinsed before use. Reagent water was double distilled purified water, and excluded for possible TFA contamination that might occur in the laboratory environment.



The bottom right corner is the location of Guangdong province in south China.

Figure 7.5- 23: Location of the Pearl River Delta region (grey) and the sampling site (solid circle)

Analytical method

Rainwater samples were warmed to room temperature. TFA was derivatized using 2,4-difluoroaniline (DFA). The sample was purified by separating the aqueous and the organic phases. The ethyl acetate solution was gently reduced to dryness with a rotary evaporator. 10 mL of toluene was added to extract the precipitate. After filtration, the sample was finally reduced to 1 mL in volume and kept at −20°C until analysis.

Derivatized samples were analysed by gas chromatography with a mass selective detector (GC/MSD) equipped with a 50 m FFAP capillary column in the electron impacting ionization and selected ion monitoring mode. Helium was used as carrier gas with a flow rate of 1.5 mL/min. 2 µL of each sample was injected in the splitless mode. The oven temperature was initially maintained at 100°C for 2 min, then raised at a rate of 7°C/min to 215°C, and kept isothermally for 10 min. The target ion selected for the 2,4-difluoroanalide derivatives of TFA was m/z 225. During the instrumental analysis, a calibration run was performed each day to determine the response factor (RF) and recalibrated if the relative deviation of the RF was beyond 10%.

Three laboratory blank samples (reagent water) were treated in the same way as rainwater samples. TFA concentrations were less than MDL in these blank samples, indicating that no TFA was introduced by either inevitable exposure to laboratory air or the multi-step sample treatment processes. Recoveries of spiked blank samples (n = 7) and spiked rainwater samples (n = 4) were 87 ± 6% and 83 ± 6%, respectively.

Method detection limit (MDL): calculated to be 1.7 ng/L based on a 500 mL sample.

Calibration curve linear correlation (R^2) = 0.997

Relative standard deviation (RSD): < 10%

II. RESULTS AND DISCUSSION

Rainwater TFA levels

TFA levels in collected rainwater samples ranged from 45.8 to 974 ng/L with a median concentration of 166 ng/L and an average of 225 ng/L (Figure 7.5-24). Higher TFA concentrations were related to lower rainfalls. TFA level exhibited a significant negative correlation with rainfall ($p < 0.01$) during the sampling period. Larger rainfall probably diluted TFA in rainwater and resulted in the relatively lower concentrations observed.

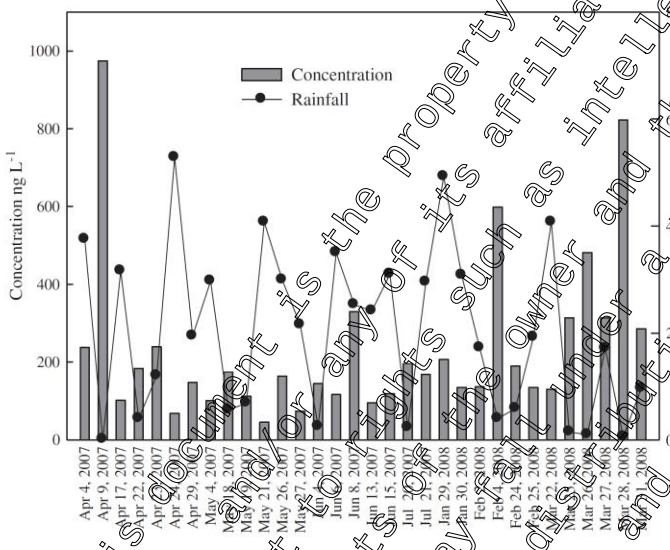


Figure 7.5- 24: Observed rainwater TFA levels and rainfall from April 2007 to March 2008

This relationships between TFA levels and rain amount indicated that, especially for TFA wet precipitation flux estimation, rainfall-weighted average concentration at a site should be used rather than an arithmetic mean of rainwater concentration.

Due to the accumulation of CF$_3$COX or TFA on non-raining days, TFA levels should be the highest at the beginning of a rain event and then decrease with time. To determine the washout effect for TFA, continuous sampling during one rain event was conducted. Two continuous samples (sampling in the morning and in the afternoon, separately) during one event were collected in each of two rainy days. A sharp decrease (42.9% on March 22, 2008 and 41.7% on March 31, 2008) of TFA levels were clearly observed from morning to afternoon. The gradual decrease of TFA levels was observed during a thunderstorm (29.9 mm rainfall within only 20 min) on May 26, 2007. TFA concentrations in the three continuous samples collected during 0–2 min, 2–10 min and 10–20 min were 176, 164 and 154 ng/L, respectively. Washout effect was also found in samples collected in continuous rainy days.

Due to the influence of monsoons, the PRD has a clear division between the arid and rainy seasons. The rainy season, accounted for about 80% of annual total rainfall and is typically from April to September, while October to March is the arid season. Rainfall-weighted rainwater TFA level in arid seasons (191.3 ng/L) was higher than that in rainy seasons (135.1 ng/L). In rainy seasons including summer, higher temperature, elevated RH and more intensive solar radiation result in relatively higher

photochemical oxidants and therefore promote the formation of TFA from precursors. However, more rainfall amount in the rainy season led to comparatively lower rainwater TFA levels due to frequent washout and more dilution. On the contrary, with lower rainfall washout in arid seasons, TFA in the atmosphere would accumulate in non-rainy days and lower rainfalls further lead to elevated rainwater TFA levels during arid season.

Annual TFA wet deposition estimation in the region

In the PRD region, wet deposition is predominantly through rainfall. The TFA deposition for each rain event, calculated by TFA level multiplying rainfall amount, ranged from 97 to 10177 ng/m^2.

Taking the calculated rainfall-weighted average level (152 ng/L) as the annual rainfall-weighted average concentration of TFA in Guangzhou, with the total rainfall of 1500 mm during April 2007 to March 2008, the annual wet deposition flux of TFA in Guangzhou was estimated to be 229 g/km^2/yr. According to this annual wet deposition flux, there would be 1.7 t/yr of TFA deposited through rainfall in Guangzhou within an area of 7434 km^2. The PRD has an area of 42,898 km^2 with the annual average rainfall of about 1900 mm. When extrapolated to PRD using the annual wet deposition flux observed, annual wet deposition of TFA in PRD reached 12.1 t/yr.

Source implication

The "Two-Box model" was used to evaluate the contributions of precursors, such as HCFCs/HFCs and fluoropolymers, to rainwater TFA in Guangzhou. The two boxes were set in the model with the smaller box representing Guangzhou city within the larger one representing China. The fluxes of TFA into and out of the smaller box (Guangzhou) and the larger box (China) were all considered to establish steady-state equations. In this model calculation, a key parameter is the proportion of TFA generated in the small box to that in the large box. Generated TFA was allocated assuming that it was proportional to 1) gross domestic production (GDP), 2) gross industrial production (GIP), and 3) number of private vehicles possessed. The model results revealed rainwater TFA of 131.5 – 152.4 ng/L (Table 7.5- 49) in Guangzhou from three halocarbons and fluoropolymers, assuming the mass of TFA generated was proportional to the GDP, GIP or number of private cars. These levels were quite near the observed annual rainfall-weighted mean TFA of 152 ng/L in Guangzhou. This suggested that the degradation of HCFCs/HFCs and fluoropolymers could explain TFA in rainwater, and rainwater TFA in Guangzhou was therefore predominantly anthropogenic in its origin.

Table 7.5- 49: Contribution of precursors to TFA as estimated by the Two-Box Model

Compound	Atmospheric mixing ration (pptv)	Yearly molar yield for TFA	Generated TFA in rainwater (ng/L)	Contribution to rainwater TFA
Scheme 1: TFA generated is proportional to GDP (Guangzhou/China = 2.85%)				
HCFC-123	0.3	100%	31.8	20.9%
HCFC-124	0.7	100%	16.6	10.9%
HCFC-134a	50.0[1]	20%	98.3	64.7%
Fluoropolymers[2]		0.1%[3]	5.7	3.7%
Total			152.4	100%
Scheme 2: TFA generated is proportional to GIP (Guangzhou/China = 2.44%)				
HCFC-123	0.3	100%	27.4	18.0%
HCFC-124	0.7	100%	14.3	9.4%
HCFC-134a	50.0[1]	20%	84.9	55.9%
Fluoropolymers[2]		0.1%	4.9	3.2%
Total			131.5	86.5%
Scheme 3: TFA generated is proportional to numbers of private cars (Guangzhou/China = 2.63%)				
HCFC-123	0.3	100%	29.5	19.49%
HCFC-124	0.7	100%	15.4	10.1%
HCFC-134[1]	50.0[1]	20%	91.2	60.0%
Fluoropolymers[2]		0.1%[3]	5.3	3.5%
Total			141.4	93.0%

[1]: The average mixing ration of HFC-134a in the north hemisphere.
[2]: The reserve of fluoropolymers in China in the last 5 years was estimated to be 981,000 t.
[3]: Percentage of fluoropolymers that ultimately undergo thermal degradation per year.

The three HCFCs/HFCs altogether accounted for 83.3 – 96.5% of the rainfall TFA in Guangzhou. HFC-134a contributed 84.9 – 98.3 ng/L or 55.9 – 64.7% of rainwater TFA observed in Guangzhou, suggesting that it was already the dominant halocarbon precursor of TFA in this region. If the mixing ratio of atmospheric HFC-134a in China was higher than the average background level in the northern hemisphere as expected, its contribution to rainwater TFA would reach up to 90%.

Other organo-fluorinated chemicals like HFC-227ea (CF_3CHFCF_3), halothane and isoflurane anaesthetics were also reported to produce TFA. However, halothane and isoflurane anaesthetics formed TFA mainly through metabolism other than oxidative degradation in the atmosphere. Mixing ratios of HFC-227ea reported in the northern mid-latitudinal upper troposphere were lower than 1.0 pptv. Therefore, its potential contribution to TFA was negligible. The PRD region is adjacent to the South China Sea, which is a large reservoir of TFA. However, owing to its strong solubility, TFA in seawater is difficult to re-evaporate to atmosphere and transfer to coast area. The re-evaporation from the South China Sea could not contribute to rainwater TFA in Guangzhou.

III. CONCLUSIONS

A year-round monitoring of rainwater TFA from April 2007 to March 2008 in urban Guangzhou revealed that rainwater TFA levels ranged from 45.8 – 974 ng/L (median concentration of 166 ng/L) with a rainfall-weighted annual average of 152 ng/L. The annual TFA wet deposition flux was estimated to be 229 g/km^2/yr and the total wet deposition of TFA reached ca. 1.7 t/yr in Guangzhou. By applying the Two-Box model with the assumption that TFA generated was proportional to GDP, GIP or number of private cars, the author found that the degradation of HCFCs/HFCs and fluoropolymers could explain 131.5 – 152.4 ng/L rainwater TFA, quite near the observed rainfall weighted annual average of 152 ng/L, which suggested rainwater TFA in Guangzhou was predominantly anthropogenic. HCFCs/HFCs were precursors that could explain 83.3 – 96.5% of observed rainwater TFA, while fluoropolymers' contributions were minor. HFC-134a alone could explain 55.9 – 64.7% of rainwater TFA, even up to 90.0%, and a larger contribution would be expected with rapid growth of its ambient

mixing ratios over China for its prevalent use as cooling agent in mobile air conditioning systems. As a strongly persistent and hydrophilic compound, TFA would eventually accumulate in the hydrosphere.

3. Assessment and conclusion

<u>Assessment and conclusion by applicant</u>:

Assessment:

This article from public literature reports monitoring results for TFA concentrations in rainwater in Guangzhou, China from April 2007 to March 2008. Details on sampling and analytical work (including LOQ and RSDs) are well reported. However, the work wasn't carried out according to GLP, and there are currently no guidelines for the conduct of monitoring studies.

Conclusion:

Rainwater TFA levels ranged from 45.8 – 974 ng/L (median concentration of 166 ng/L) with a rainfall-weighted annual average of 152 ng/L. The annual TFA wet deposition flux was estimated to be 229 g/km^2/yr, and the total wet deposition of TFA reached ca. 1.7 t/yr in Guangzhou. TFA level exhibited a significant negative correlation with rainfall.

The information from this article can be regarded as reliable.

<u>Assessment and conclusion by RMS</u>:

Outcome and conclusion of the study: RMS should indicate if they agree to the results and conclusions of the APPL.

1. Information on the published literature article

Data Point:	KCA 7.5/28
Report Author:	Vollmer, M. K.; Reimann, S.; Hill, M.; Brunner, D.
Report Year:	2015
Report Title:	First observations of the fourth generation synthetic halocarbons hfc-1234yf, hfc-1234ze(e), and hcfc-1233zd(e) in the atmosphere
Report No:	M-757135-01-1
Document No:	M-757135-01-1
Guideline(s) followed in study:	not applicable
Deviations from current test guideline:	Current Guideline: not applicable
Previous evaluation:	No, not previously submitted
GLP/Officially recognised testing facilities:	No, not conducted under GLP/Officially recognised testing facilities
Acceptability/Reliability:	Yes

2. Full summary of KCA 7.5/28

Executive Summary

First multiyear atmospheric measurements of the hydrofluorocarbons HFC-1234yf, and HFC-1234ze(E), and the hydrochlorofluorocarbon HCFC-1233zd(E) are reported from the high-altitude observatory at Jungfraujoch and from urban Dubendorf (Switzerland).

In 2011, HFC-1234yf was undetectable at Jungfraujoch (mole fractions < 0.003 ppt, parts-per-trillion, 10^{-12}) but since then the percentage of measurements with detectable mole fractions has steadily increased to 4.5% in 2014. By contrast, in 2014 HFC-1234ze(E) was detectable in half of samples at Jungfraujoch and in all samples at Dubendorf demonstrating the wide use of this compound within the air mass footprints of the stations. Back trajectory analysis for the Jungfraujoch observations suggests high emission strength of HFC-1234ze(E) in the Belgium/Netherlands region. HCFC-1233zd(E) is present at very low mole fractions (typically < 0.03 ppt) at both stations, and features pronounced seasonality and a general absence of pollution events during 2013–2014 measurements. This is indicative of the presence of significant emissions from source locations outside the footprints of the two stations. Based on a simple one-box model calculation HCFC-1233zd(E) emissions are estimated to globally increase from 0.2 Gg/yr in 2013 to 0.5 Gg/yr for 2014.

I. MATERIAL AND METHODS

Material

Measurements of HFC-1234yf, HFC-1234ze(E), and HCFC-1234zd(E) were made at the high-altitude (3580 m above sea level) observatory at Jungfraujoch, Switzerland and from the laboratory roof-top at Dubendorf (suburban Zurich).

Sampling method

At both the Jungfraujoch and Dubendorf sites air was drawn into the laboratory through 12 mm OD Synflex-1300 tubing. Routine ambient measurements at the two sites were characterised by a pair of hourly ambient air sample measurements from cryogenically preconcentrated 2 L samples interspersed by weekly laboratory air measurements and blank measurements.

The air samples were passed through an air sampling unit including a small sampling pump with EPMD membranes and flaumers (which were routinely vacuum baked at 60°C to avoid contamination by the pumps). The author concluded that there was no evidence of pump contamination as a large fraction of the in-situ air samples collected through these pumps showed the absence of HFC-1234yf and HFC-1234ze(E).

At Jungfraujoch, HFC-1234yf measurements began at the end of 2010, HFC-1234ze(E) measurements started in mid-2011 and HCFC-1234zd(E) measurements started in 2013. In Dubendorf, measurements began in 2013.

Analytical method

The samples were analysed using gas chromatography – mass spectrometry (GCMS) with “Medusa-GCMS” type instruments. Routine ambient measurements at the two sites were characterised by a pair of hourly ambient air sample measurements from cryogenically preconcentrated 2 L samples, bracketed by calibration standard measurements. These standards were measured to track and correct for short-term MS detector sensitivity changes. All mole fractions below the detection limits were designated as “zero/undetectable”, despite a positive (but not integrated) above-baseline detector response in some of the measurements. There was no GCMS baseline disruption in the blank measurements, which were performed as internal system blanks without trapping a sample, and by measuring purified synthetic air. No other atmospheric constituent was detectable which could otherwise interfere with the integration of the HFC-1234yf, HFC-1234ze(E), and HCFC-1234zd(E) peaks. These findings, along with a linear system response, as shown by measurements of the detector response to variable-volume injections of a standard and a molar dilution series of a standard with purified synthetic air, suggested the absence of major systematic measurement errors even for very small mole fractions. There were no commercial calibration standards at low mole fractions available for these halocarbons, so reference standards were internally generated. The Empa-2013 calibration scales had estimated scale accuracies of 15% for each of the compounds. The precisions of the measurements were determined from flask measurements at various mole fractions. They were estimated for HFC-1234yf at 6 ppq (parts per quadrillion, 10^{-15}) or

5%, for HFC-1234ze(E) at 6 ppq or 7%, and for HCFC-1233zd(E) at 3 ppq or 5%, whichever was greater, respectively.

LOD: The detection limits (LOD) were defined as the mole fractions corresponding to the lowest integrated peaks. These corresponded roughly to 2-3 times the height of the noise. Detection limits were ~0.003 ppt for HFC-1234yf and HFC-1234ze(E), and ~0.001 ppt for HCFC-1233zd(E).

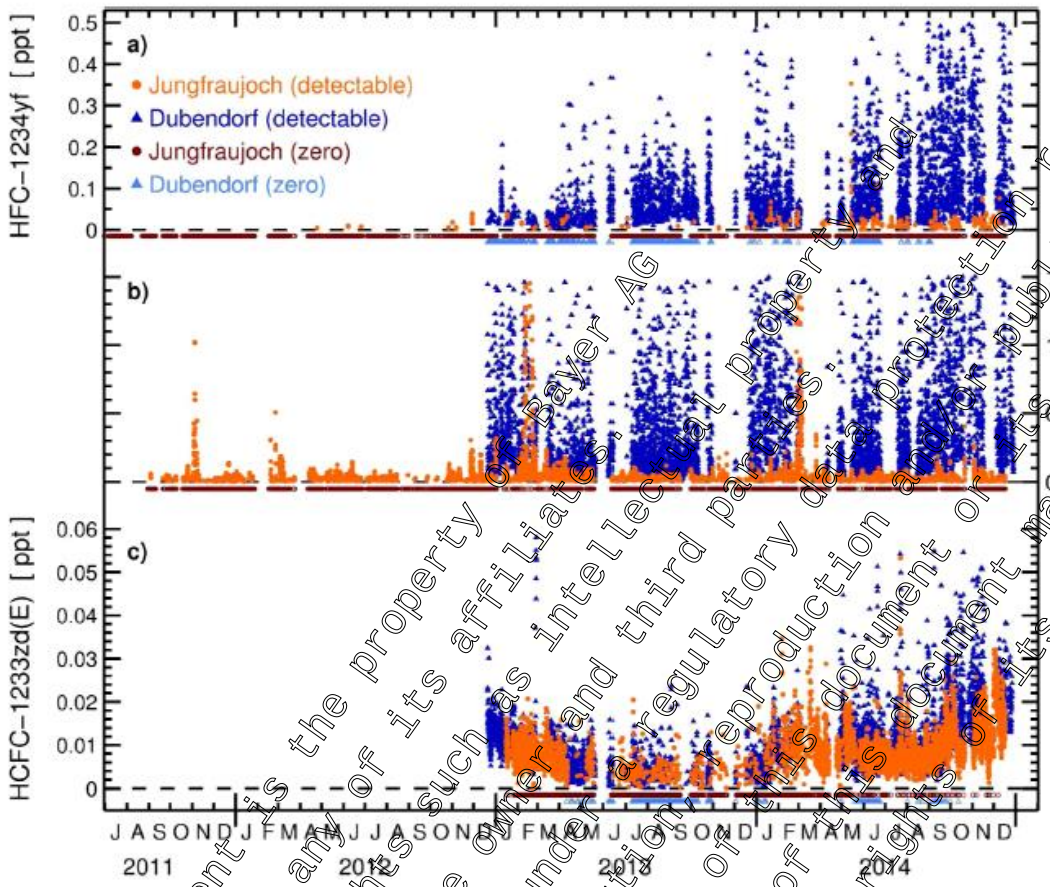
II. RESULTS AND DISCUSSION

HFC-1234yf

At Jungfraujoch first detectable mole fractions were observed at the end of 2012 (Figure 7.5- 25). The percentage of detectable mole fractions in the measurements increased from 0.0% in 2011 (number of observations n = 4160) to 4.4% in 2014 (n = 3849). Correspondingly the mean mole fractions (including zeros) increased from undetectable (< 0.003 ppt) to 0.003 ppt, respectively (Table 7.5- 50). The magnitude of HFC-1234yf generally increased and first typical pollution events have reached the site. Measured mole fractions in such pollution events were 0.02 − 0.05 ppt.

At Dubendorf, the percentage of detectable HFC-1234yf in air amounted to 87% in 2014 (n = 2648) and the site received frequent pollution events since measurements began in 2013, with magnitudes > 0.8 ppt for the 10 biggest events. Mean mole fractions at Dubendorf increased from 0.032 ppt in 2013 to 0.14 ppt in 2014. This compares with model predictions for 2020 for Europe of 0.073 − 15 ppt (mean: 1.5 ppt) for the summer months and 0.76 − 29 ppt (mean: 4.1 ppt) for the winter months under the assumption of a complete conversion to HFC-1234yf in the European car fleet.

The results indicated that HFC-1234yf was being used in Switzerland and the author suspected the emissions arose from the mobile air conditioners of those cars, which were now equipped with HFC-1234yf.



Junfraujoch data are in orange (detectable mole fractions) and brown (zeros, < detection limits). Dubendorf data are in navy blue and light blue. Zeros are slightly shifted to negative for better visual distinction. HFC-1234ze(E) at Dubendorf was never zero. To expand the y-axes for better illustration of some of the smaller mole fractions, the results are omitted above the largest tick mark labels for each compound.

Figure 7.5- 25: Atmospheric measurements of the hydrofluorocarbons HFC-1234yf and HFC-1234ze(E) and the hydrocarbonfluorocarbon HCFC-1233zd(E) at Jungfraujoch (3580 m above sea level) and urban Dubendorf

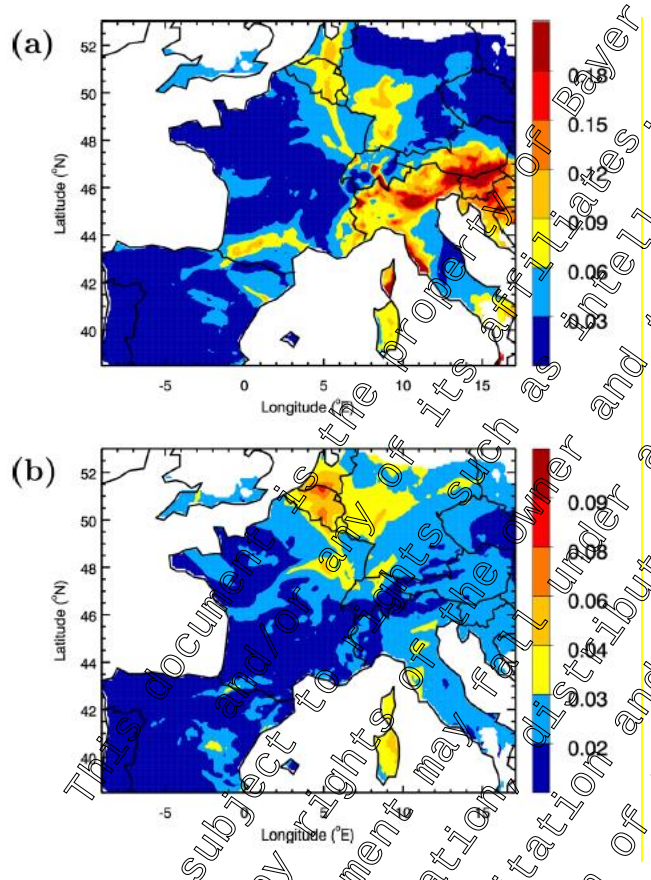
HFC-1234ze(E)

At Jungfraujoch, measurements of HFC-1234ze(E) started in mid 2011. The percentage of detectable mole fractions steadily increased from 27% in 2011 (n = 1501) to 52% in 2014 (n = 3867). Frequent pollution events reached the site with the largest three pollution periods in November 2011, February 2013, and March 2014 with mole fractions ranging up to 1− 4 ppt (Figure 7.5- 25). These findings indicated widespread use of HFC-1234ze(E) in large parts of Europe.

At Dubendorf, HFC-1234ze(E) was always above detection limits and rarely declined to the “baseline” lower mole fractions observed at Jungfraujoch. Such a pattern is typical for compounds with nearby large emissions.

The Jungfraujoch HFC-1234ze(E) record exhibited sufficient structure and detectable mole fractions to allow for a back trajectory analysis to assess the potential source regions within the footprint of the site. Measurements were combined with simulations of the Langrangian particle dispersion model FLEXPART to calculate qualitative emission maps (Figure 7.5- 26). The European emission distribution for the combined >3 yr measurements, was dominated by three pollution events with large (> 1 ppt) mole fractions (Figure 7.5- 25). The November 2011 event was linked to air masses from Northern Italy, a source region typical for many halogenated compounds. Whereas, the February 2013

event (peaking at > 6 ppt) was linked to air masses with predominant origin in Northeastern Italy and Slovenia, and the March 2014 event (peaking at 4.5 ppt) was attributed to the Balkan area, both rather unusual source regions in the regular HFC emission map calculations. The strong enhancements during these events was unusual compared with other similar meteorological conditions during the observational period. While local sources were excluded at Jungfraujoch, it is possible that these events were caused by distant accidental releases of HFC-1234ze(E) rather than regular usage. If these three events are excluded, then HFC-1234ze(E) shows pronounced emission sources in the Belgium/Netherlands border regions (Figure 7.5- 26b). This source distribution is also rather different to those found for the established HFCs.



Dark red colours indicate regions with potentially large emissions, dark blue regions with low emissions. The analysis covered the entire measurement record from August 2011 to December 2014. The three dominant pollution episodes were included in the upper panel (a) but excluded in the lower panel (b). Units are arbitrary. Regions without colour denote insufficient model sensitivity.

Figure 7.5- 26: Qualitative maps of the sources of HFC-1234ze(E) over central Europe based on Jungfraujoch measurements

HCFC-1233zd(E)

The records of HCFC-1233zd(E) at the two sites were similar in magnitude for the 2-year measurement period. The mole fractions were much smaller compared to the two HFCs. Seasonally varying mole fractions were exhibited, and pollution events occurred rarely, which the author suggested was due to the absence of major sources within the footprints of the two sites. The percentage of detectable mole fractions increased from 2013 to 2014, from 31% to 74% at Jungfraujoch and from 63% to 94% at Dubendorf (Table 7.5- 50). For the same years the mean mole fractions increased from 3 ppq to 8 ppq at Jungfraujoch and from 5 ppq to 12 ppq at Dubendorf. The author interpreted these increases as increasing emissions but they could also be caused by sources getting closer to the sites. The seasonality characterised by mole fractions less than half in the summer months compared to the winter was likely due to the seasonality in the hydroxyl radical and less likely a cause of seasonally varying emissions.

Table 7.5- 50: Measured dry-air mole fractions in ppt (parts-per-trillion, 10^{-12}) of the hydrofluorocarbons HFC-1234yf and HFC-1234ze(E), and the hydrochlorofluorocarbon HCFC-1233zd(E) at the Junfraujoch and Dubendorf stations

	2011	**2012**	**2013**	**2014**	**Combined years**
HFC-1234yf					
Jungfraujoch					
Mean (ppt)	< LOD	< LOD	< LOD	0.003	< LOD
Median (ppt)	< LOD	< LOD	< LOD	< LOD	< LOD
Number of observations	4160	3240	3260	3850	14500
% detectable	0.00	0.37	0.92	4.44	1.47
Dubendorf					
Mean (ppt)			0.032	0.136	0.085
Median (ppt)			< LOD	0.067	0.036
Number of observations			2510	2650	5160
% detectable			44.3	87.0	66.2
HFC-1234ze(E)					
Jungfraujoch					
Mean (ppt)	0.013	0.014	0.041	0.035	0.027
Median (ppt)	< LOD	< LOD	0.008	0.007	< LOD
Number of observations	1500	3380	3260	3870	12000
% detectable	26.9	35.5	51.2	51.5	43.9
Dubendorf					
Mean (ppt)			0.704	0.928	0.820
Median (ppt)			0.217	0.405	0.294
Number of observations			2480	2660	5140
% detectable			100	100	100
HFC-1233zd(E)					
Jungfraujoch					
Mean (ppt)			0.003	0.008	0.005
Median (ppt)			0.001	0.007	0.004
Number of observations			3120	3830	6950
% detectable			31.4	74.3	55.0
Dubendorf					
Mean (ppt)			0.005	0.012	0.009
Median (ppt)			0.004	0.010	0.008
Number of observations			2500	2860	5350
% detectable			63.5	94.2	79.9

Mean and median values include measurements with undectable mole fractions. Instead of assigning those a value of zero, a value was assigned equal to half LOD. Detection linits are 0.003 ppt for HFC-1234yf and HFC-1234ze(E) and 0.001 ppt for HCFC-1234zd(E).

Estimation of emissions

In order to estimate the emissions that were compatible with the observations, a rough 1-box calculation was performed in which the northern hemisphere troposphere was treated as a single isolated box (7.06×10^{19} mol) with no exchange to the southern hemisphere or the stratosphere. Jungfraujoch and Dubendorf observations were assumed to be representative for this box and seasonality in emissions and destruction of HCFC-1233zd(E) was ignored. With the additional assumption of a temporal steady-state in sources and sinks, emissions were calculated based on the simple definition of lifetime = burden/emission rate. The burden was calculated from the average of the monthly mean observations of the two records (Figure 7.5- 25) and used a lifetime of 46 days. Using the observations (including zeros) emissions were calculated of 0.18 Gg/yr for 2013 and 0.43 Gg/yr for 2014.

III. CONCLUSIONS

The presence of HFC-1234yf, HFC-1234ze(E) and HCFC-1233zd(E) steadily increased at the sampling sites, Jungfraujoch and Dubendorf, in Switzerland. HFC-1234yf was initially undetectable at Jungfraujoch but detectable mole fractions steadily increased to 4.5% in 2014. By 2014 HFC-1234ze(E) was detectable in half of samples at Jungfraujoch and in all samples at Dubendorf, demonstrating the wide use of this compound within the air mass footprints of the stations. Back trajectory analysis for the Jungfraujoch observations suggested high emission strength of HFC-1234ze(E) in the Belgium/Netherlands region. HCFC-1233zd(E) was present at very low mole fractions (typically < 0.03 ppt) at both stations and featured pronounced seasonality and a general absence of pollution events during 2013 to 2014 measurements; indicative of the presence of significant emissions from source locations outside the footprints of the two stations. Based on a simple one-box model calculation HCFC-1233zd(E) emissions were estimated to globally increase from 0.2 Gg/yr in 2013 to 0.5 Gg/yr for 2014.

3. Assessment and conclusion

Assessment and conclusion by applicant:

Assessment:

HFC and HCFC concentrations were sampled at two sites in Switzerland (August 2011 to December 2014). Locations, sampling and analytical methodologies are described and included some performance criteria (e.g. LOD and blanks), but the work wasn't carried out according to GLP and there are currently no guidelines for the conduct of monitoring studies.

Conclusion:

HFC-1234yf, HFC01234z(E) were shown to be present in increasing quantities in air samples from two sites in Switzerland (detections increased to 4.5% and ca. 50% at Jungfraujoch and Dubendorf, respectively). HCFC-1234zd(E) was present at low concentrations at both stations with pronounced seasonality, indicating source emissions further away. Modelling calculated increased HCFC-1233zd(E) emissions from 0.2 Gg/yr in 2013 to 0.5 Gg/yr for 2014.

The information from this article can be regarded as supportive information.

Assessment and conclusion by RMS:

Outcome and conclusion of the study: RMS should indicate if they agree to the results and conclusions of the APPL.

1. Information on the published literature article

Data Point:	KCA 7.5/29
Report Author:	Scheurer, M.; Noedler, K.; Freeling, F.; Janda, J.; Happel, O.; Riegel, M.; Mueller, U.; Storck, F.; Fleig, M.; Lange, F.; Brunsch, A.; Brauch, H
Report Year:	2017
Report Title:	Small, mobile, persistent: Trifluoroacetate in the water cycle Overlooked sources, pathways, and consequences for drinking water supply
Report No:	M-603993-01-1
Document No:	M-603993-01-1
Guideline(s) followed in study:	not applicable
Deviations from current test guideline:	Current Guideline: not applicable
Previous evaluation:	No, not previously submitted
GLP/Officially recognised testing facilities:	No, not conducted under GLP/Officially recognised testing facilities
Acceptability/Reliability:	Yes

2. Full summary of KCA 7.5/29

Executive Summary

Elevated concentrations of trifluoroacetate (TFA) of more than 100 µg/L in a major German river led to the occurrence of more than 20 µg/L TFA in bank filtration-based tap waters. Several spatially resolved monitoring programs were conducted and discharges from an industrial company were identified as the point source of TFA contamination. Treatment options for TFA removal were investigated at full-scale waterworks and in laboratory batch tests. Commonly applied techniques like ozonation or granulated activated carbon filtration are inappropriate for TFA removal, whereas TFA was partly removed by ion exchange and completely retained by reverse osmosis.

Further investigations identified wastewater treatment plants (WWTPs) as additional TFA dischargers into the aquatic environment. TFA was neither removed by biological wastewater treatment, nor by a retention soil filter used for the treatment of combined sewer overflows. WWTP influents can even bear a TFA formation potential, when appropriate CF_3-containing precursors are present. Biological degradation and ozonation batch experiments with chemicals of different classes (flurtamone, fluopyram, tembotrione, flufenacet, fluoxetine, sitagliptine and 4:2 fluorotelomer sulfonate) proved that there are yet overlooked sources and pathways of TFA.

I. MATERIAL AND METHODS

Material

An extended monitoring program was initiated to identify potential trifluoroacetate (TFA) dischargers and emission routes responsible for high concentrations in rivers and streams.

Sampling Method

Several monitoring programs with different spatial scopes were conducted. Samples were taken as grab samples in 250 mL brown glass bottles and stored at 4°C for < 1 week until analysis. A river water sample was analysed weekly over a period of eight weeks (stored in a glass container at 4°C) and no losses of TFA due to biodegradation and/or sorption were observed.

In the Neckar region, a highly resolved spatial monitoring program was conducted in order to identify the point source(s) responsible for the elevated concentrations of TFA measured in the tap and surface water samples from the city of Heidelberg. In total, grab samples were taken at 34 surface water

sampling locations up to three times in August and September 2016. Sampling locations were adjusted during the monitoring program to identify the potential industrial emission source. The surface water samples were taken in approx. 1 - 1.5 m distance from the riverbank. Additional samples were taken on a regular basis between October 2016 and May 2017 at the mouth of the Neckar (city of Mannheim, a few kilometres upstream of the confluence of the rivers Rhine and Neckar) in order to elucidate the time profile of TFA concentrations and to clarify if TFA is continuously discharged. Samples were also taken from the Rhine River (km 507) for the same time period, in order to assess the impact of the Neckar River on the water quality of the Rhine River. Samples were taken during a five month monitoring program between November 2016 and May 2017. Sampling locations regularly sampled were at Basel, Karlsruhe, Mainz, Schierstein (close to Mainz), Cologne and Düsseldorf for the Rhine River, Mannheim for the Neckar River and Frankfurt for the Main River. To assess the impact of the Neckar River on the TFA concentrations of the Rhine River in comparison to other substantial tributaries, the longitudinal profile of the Main River was sampled to evaluate its individual role.

In order to determine if elevated TFA concentrations also occurred in another region where fluorochemical industry was suspected, the catchment of the Alz River in Bavaria (mean annual discharge approx. 70 m^3/s) was additionally investigated. Sampling locations are shown in Figure 7.5-27.

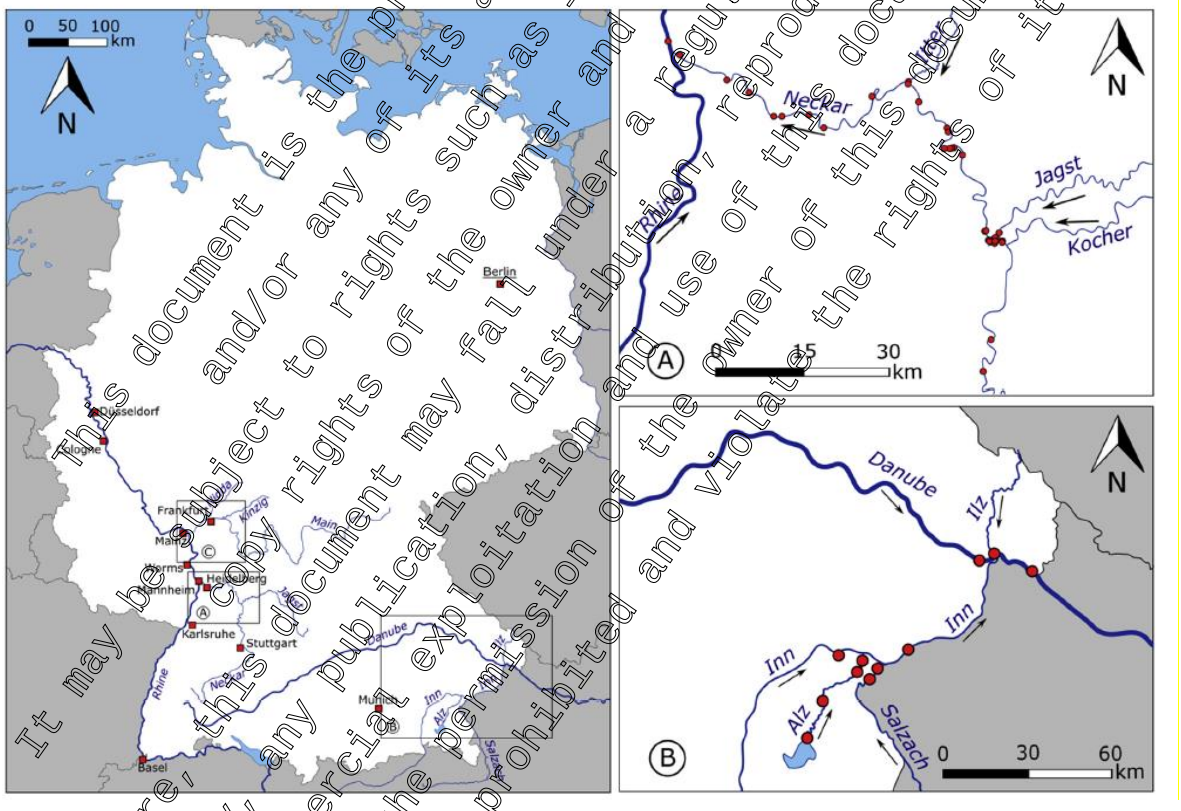


Figure 7.5-27: Map of sampling locations of monitoring programs along the Rhine River (left), the Neckar River (A) and the Alz (B)

Three full-scale waterworks, which applied a wide range of different treatment techniques, were sampled in February and March 2017. In waterworks A, water from the Rhine River was mechanically treated before pre-ozonation and flocculation with $FeCl_3$. Main ozonation was followed by a second flocculation step, before the water passed through a multi-layer filter where residual ozone was removed. Biologically active granular activated carbon (GAC) filters completed the treatment. The treated water is used for irrigation and groundwater recharge.

Waterworks B used surface water from the Main River, which is used for groundwater recharge and irrigation. First, the raw water was mechanically treated with coarse and fine screens, before flocculation and filtration over gravel and GAC were applied. The water was then infiltrated in a sandy aquifer where it mixed with local groundwater.

Waterworks C serves 40,000 people and uses spring water from the Gallusquelle in a Karstic region (Swabian Jura) as raw water. The average discharge of the spring is 500 L/s, draining a rural catchment (4000 inhabitants) of approximately 45 km^2 and approx. 40% of the catchment is used for agriculture. Treatment in the waterworks consisted of a multi-layer filtration step (hydroanthracite and quartz gravel), ozonation (~0.4 mg/L ozone) followed by activated carbon filtration (loading 70 m^3/kg), and disinfection by addition of ClO_2 (0.1 mg/L).

Analytical method

Ion exchange liquid chromatography electrospray tandem mass spectrometry (LC-ESI-MS/MS) analysis with an electrospray interface operated in negative ionization mode was applied for the detection of TFA. Water samples (10 mL) were centrifuged for 15 min at 4000 g (3500 rpm) to separate suspended matter. An aliquot (1 mL) of the supernatant was transferred to a HPLC vial and spiked with a defined volume of 10 µL (0.1 mg/L) of an internal standard (IS). Chromatographic retention and separation was achieved using a Dionex IonPac AS17-C column (2 mm × 250 mm) equipped with a Dionex IonPac AG17-C precolumn with ultra-pure water containing 50 mM ammonium bicarbonate (A) and methanol (B) as eluents. To minimize matrix suppression by co-eluting components, the gradient was optimized regarding the separation of TFA from major anions (chloride, nitrate, sulphate) by using conductivity detection. A gradient program with a flow rate of 0.3 mL/min was used. The gradient started with 20% of eluent A, increased to 50% A within 10 min and finally decreased to the initial conditions within 1 min. Before each injection, the column was re-equilibrated for 5 min. Separation took place at 40°C and an injection volume of 100 µL was used. The developed IC-method does not require suppression of the eluent as the buffer does not contain any non-volatile components.

LOQ: The limit of quantification (LOQ) was 0.05 µg/L, determined according to DIN 32645 (DIN, 2008) by equidistant calibration levels. Further quality measures were taken by the implementation of the isotopically labelled IS $^{13}C_2$-TFA for the correction of matrix effects.

II. RESULTS AND DISCUSSION

Based on spatially resolved monitoring of the longitudinal profile of the Neckar River, a point source of TFA close to the city of Bad Wimpfen was identified. Downstream of Bad Wimpfen, concentrations of TFA between 5.4 µg/L and 140 µg/L were measured. Upstream of the point of discharge the concentrations were much lower but TFA was still present with concentrations around 1 µg/L.

The discharger was identified as a producer of inorganic and organic fluorinated chemicals. Besides the production of TFA as a final product, the compound is also used for the production of CF_3- containing building blocks. After identification of the point source, local authorities, water utilities along the Neckar River as well as associations of water supply companies in the Rhine basin area were informed. Following dialogue with the discharger, it was agreed to stop the TFA production and to optimize production processes to minimize the TFA discharge. However, due to the continuous usage of TFA as an intermediate in chemical synthesis, elevated concentrations in the rivers Neckar and Rhine can still be measured. The concentration profile at the sampling point at the Rhine River corresponded to the profile of the Neckar, indicating that no other substantial TFA sources existed in between.

TFA concentrations were also tracked along the Rhine River, which is used in its lower course for the production of drinking water after bank filtration. The elevated concentrations of the Neckar River have a direct impact on the TFA concentrations measured in the Rhine River as it can be seen from the sharp

increase between the sampling points in Karlsruhe and Mainz. At the two sampling points at the upper Rhine (Basel and Karlsruhe), the mean concentration was below 0.5 µg/L and increased to 1.1 µg/L in Mainz. The river discharge considerably increased between Mainz and Cologne due to several tributaries. Thus, dilution of elevated TFA concentrations was expected, but a further increase of concentrations along the river course to approx. 1.4 µg/L in Düsseldorf was observed. This led to the assumption that additional point sources like WWTPs might be continuously discharging TFA.

In the two other surface waters, in which elevated concentrations due to industrial activities were suspected (rivers Main and Alz), different concentration patterns were found. In the Main River no concentration increase from the most upstream sampling point to the river mouth was observed. TFA was detected in a narrow concentration range between 1.0 µg/L and 1.4 µg/L and was randomly distributed along the Main River. In the two Main tributaries Kinzig and Nidda 0.60 µg/L and 0.72 µg/L TFA were measured, respectively.

At the Alz, a small stream in Bavaria, elevated TFA concentrations were expected, due to a chemical park in the Alz catchment. In the upper Alz, TFA concentrations were below 0.5 µg/L, whereas downstream of the chemical park much higher TFA concentrations up to 22 µg/L were measured at two sampling locations. Due to high dilution, there was only a minor effect on the receiving streams Inn and Danube. TFA concentrations at all other sampling points apart from those at the lower Alz were below 1 µg/L.

In three full-scale waterworks, the presence of TFA was confirmed by sampling. At waterworks A and B, TFA was present in the surface waters (rivers Rhine and Main) used for direct abstraction with average concentrations of more than 1 µg/L. Removal of TFA was neither achieved by flocculation and ozonation nor by filtration over biologically active or adsorptive filter media. In fact, in the water utilities using surface water even a slight increase of TFA concentrations along the treatment train was observed. Biologically active treatment steps seemed to contribute to the largest extent to the TFA formation, but differences in concentrations were low. No change in TFA concentrations was observed at waterworks C, which uses spring water for drinking water production, although a relatively high ozone concentration was used. The author concluded that the water matrix of waterworks A and B contained compounds, which were oxidatively transformed to TFA.

II. CONCLUSIONS

TFA occurs ubiquitously in surface water. The routes of discharge for TFA are diverse. The release of TFA into the aquatic environment is not limited to photochemical degradation of precursors in the atmosphere and subsequent entry of TFA by precipitation. Further sources are industrial emissions, municipal WWTPs, and possibly the biological degradation of micropollutants like plant protecting agents or pharmaceuticals. Industrial point sources of TFA can have a substantial impact on downstream areas even with large distances from the point of discharge.

3. Assessment and conclusion

Assessment and conclusion by applicant:

Assessment:

This article contains well documented details of monitoring for TFA in three rivers and WWTPs, including analytical methodology. However, no detail of the precautions taken to avoid contamination of environmental samples was reported. The study was not performed to GLP and there are currently no guidelines for the conduct of monitoring studies.

Conclusion:

TFA was detectable in all sampled surface water sources at levels from < 0.5 µg/L to 140 µg/L, the higher concentrations deriving from industrial point sources.

The information from this article can be regarded as reliable.

Assessment and conclusion by RMS:
Outcome and conclusion of the study: RMS should indicate if they agree to the results and conclusions of the APPL.

1. Information on the published literature article

Data Point:	KCA 7.5/30
Report Author:	Tian, Y.; Yao, Y.; Chang, S.; Zhao, Z.; Zhao, Y.; Yuan, X.; Wu, F.; Sun, H.
Report Year:	2018
Report Title:	Occurrence and phase distribution of neutral and ionizable per- and polyfluoroalkyl substances (pfass) in the atmosphere and plant leaves around landfills: a case study in tianjin, china
Report No:	M-758268-01-1
Document No:	M-758268-01-1
Guideline(s) followed in study:	not applicable
Deviations from current test guideline:	Current Guideline: not applicable
Previous evaluation:	No, not previously submitted
GLP/Officially recognised testing facilities:	No, not conducted under GLP/Officially recognised testing facilities
Acceptability/Reliability:	Yes

2. Full summary of KCA 7.5/30

Executive Summary

A total of 23 per- and polyfluoroalkyl substances (PFASs) including trifluoroacetic acid (TFA) were investigated in the air, dry deposition, and plant leaves at two different landfills and one suburban reference site in Tianjin, China. The potential of landfills as sources of PFASs to the atmosphere and the phase distribution therein were evaluated. Spatially, the distribution trend of TFA in all three kinds of media consistently showed the central landfill > the downwind > the upwind > the reference sites, indicating that landfills are important sources of TFA in the environment. Plant leaves were found to be effective in uptake of TFA, thus capable of acting as a passive air sampling approach for air monitoring.

The maximum measured concentrations of TFA at the two landfills were up to 3.0 ng/m^3 in the air, 3.7 μg/g in dry deposition, and 42 μg/g lipid in leaves.

I. MATERIAL AND METHODS

Materials

The levels of 7 neutral and 16 ionizable PFASs (including TFA) in air samples, dry deposition, and plant leaves collected from surroundings of two landfills and one reference site in Tianjin, China, were investigated.

Sampling method

Sampling campaigns were carried out at and around two landfills, and at one reference site from May 8th to June 9th, 2016. Figure 7.5- 28 shows the geographic information on all 12 sampling sites. The

Shuangkou (SK) landfill opened in 2001, with a daily capacity of 1500 t, covers an area of 800 hectares and accepts the waste from the urban areas of Tianjin. The Baodi (BD) landfill opened in 2010, with a daily capacity of 160 t, covers an area of 340 hectares and accepts the waste from Baodi (a suburb area of Tianjin, China). JN, a suburban reference site far away from any known point sources of PFASs, is about 40 km and 71 km away from SK and BD landfills, respectively.

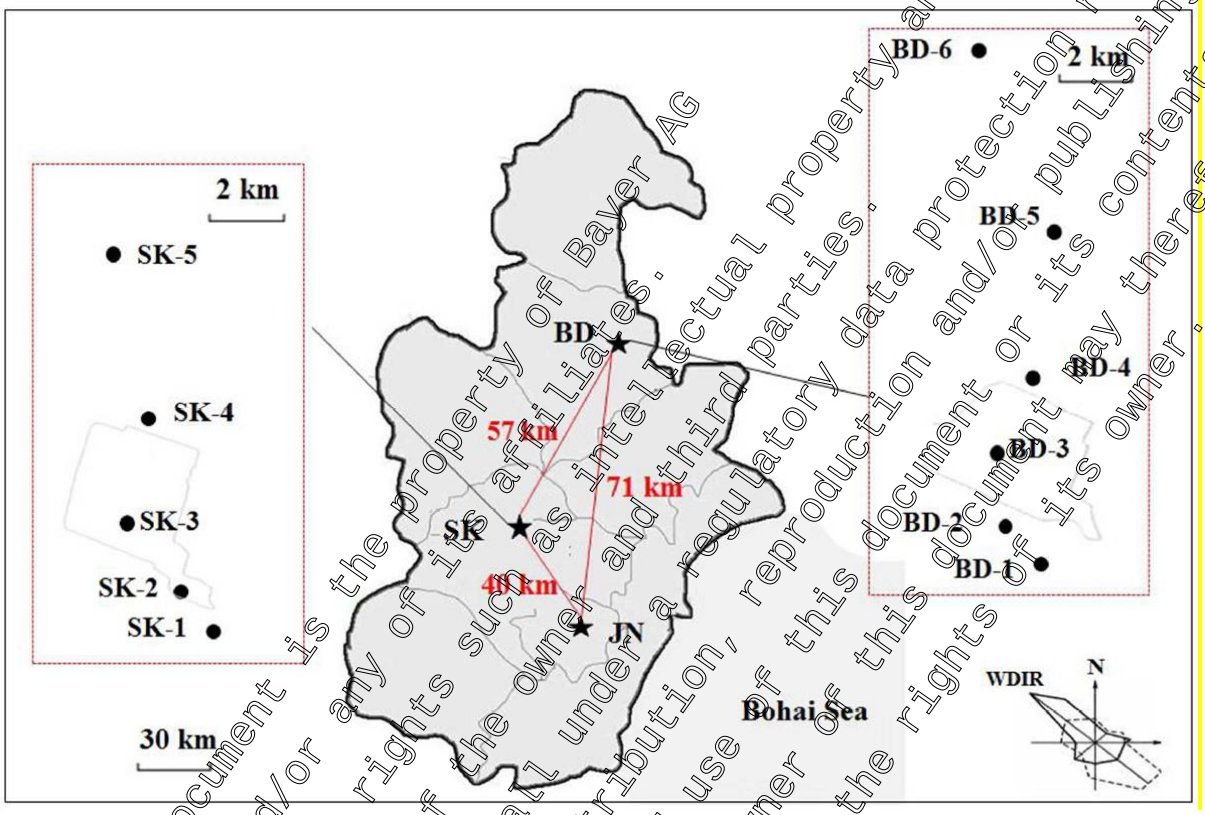


Figure 7.5- 28: The sampling sites for PFASs investigation around 2 landfills (SK and BD) and a suburb reference site (JN) in Tianjin, China

Plant leaves (n = 72) and air samples (n = 12) were collected at the 12 sites, and dry deposition samples were collected in duplicate (n = 10) at SK-Central, SK-Down-5 km, BD-Central, BD-Down-5 km, and JN. During the sampling campaign, the predominant wind direction was south or southeast with a speed of 11 km/h ~ 28 km/h and the temperature varied between 16°C and 29°C.

Air samples were collected with a passive sampling technique using pre-cleaned sorbent-impregnated polyurethane foam (SIP) disks. A rate of 4 m^3/d was used for calculation of the effective air volume during the 30-day sampling period. All passive samplers were assembled and loaded with SIP disks immediately on site to avoid contamination in transit. Three SIP disks were exposed to the atmosphere at SK, BD, and JN for about 8 h, and taken back to the laboratory for measurement of field blanks.

Dry deposition samples were collected with pre-cleaned stainless steel cylinder buckets (40 cm in diameter × 70 cm in height). Plant leaves of local species were collected by precleaned scissors, including Chinese pine (*Pinus tabulaeformis Carr*), Oriental plane (*Platanus orientalis Linn*), and Abele (*Populusalba*). At the end of the sampling campaign, all the samples were carefully wrapped in foil, put in pre-cleaned polypropylene bags, and kept at -20°C before extraction.

Analytical method

The 16 ionizable PFASs (including TFA) were analysed using HPLC–MS/MS. Lipid contents of leaves were measured by weight difference before and after the extraction.

For air samples, the SIP disks were Soxhlet-extracted with ethyl acetate and methanol each for 24 h, successively. Before extraction, 5 ng of each mass-labelled standard was added. Both extracts were concentrated to less than 5 mL via rotary evaporation, transferred to PP tubes, further dried with anhydrous sodium sulphate and concentrated to 500 mL under a gentle stream of pure nitrogen. 25 mg dispersive Envi-Carb was added to the final concentrate. After being gently shaken for 5 min, the Envi-Carb was removed by centrifugation at 15000 g for 10 min. 100 µL of the ethyl acetate supernatant was transferred into an auto-sampler vial to be analysed for neutral PFASs, whilst another 100 µL of the ethyl acetate supernatant was evaporated to dryness under a gentle stream of pure nitrogen in an auto-sampler vial and re-dissolved with 100 µL of the methanol extract to be analysed for ionic PFASs (including TFA).

For dry deposition, 5 ng of each mass-labelled internal standard was spiked in ca. 500 mg of sieved dry deposition (< 250 µm). The sample was extracted in 5 mL methanol under sonication for 30 min and centrifuged at 4200 g for 10 min. The supernatant was collected and a second 5 mL methanol was added to repeat the procedure. The supernatants were combined and further reduced to 500 µL by evaporation under a gentle stream of nitrogen. The concentrate was cleaned by 25 mg dispersive Envi-Carb and then centrifuged at 15000 g for 10 min. A 500 µL supernatant was transferred to an auto-sampler vial to be analysed.

Plant leaf samples were purified by deionized water to remove the particulate matter on the surface, and then processed by vacuum freeze drying. 1 g of freeze-dried homogenised leaves and 5 ng of each mass-labelled standard were added in a PP tube. For ionic PFASs (including TFA), 5 mL of methanol was added and the mixture was sonicated for 30 min at 40 °C. The tube was centrifuged at 4200 g for 10 min. This procedure was repeated and the supernatants combined. The combined extracts were cleaned up with GCB-Carbon cartridge and dried under a gentle stream of pure nitrogen to 500 µL before being transferred to an auto-sampler vial.

The lipid content of leaves were measured by Soxhlet-extracting 2 g of freeze-dried homogenised leaves for 2 h with petroleum ether, and the weight difference before and after the extraction was measured as the lipid content of each kind of leaves. In this way, the lipid content of Chinese pine, Abele, and Oriental plane leaves were measured as 13.0%, 6.80%, and 8.85%, respectively.

For ionic PFASs (including TFA), a liquid chromatograph interfaced with a triple quadrupole mass spectrometer and operated in the electrospray negative ionization multiple-reaction monitoring (MRM) mode was used. Nitrogen with a purity of 99.9% was used as desolvation gas at a flow rate of 10 L/min and a manipulating temperature of 350°C. A 2D ion-exchange column (2 mm i.d. × 150 mm, 5µm) was used for separating C2-C4 PFCAs. A 20 µL aliquot of the extract was injected. The mobile phase compositions were 20% of 50 mM ammonium acetate (at pH 9) and 80% of methanol (v/v) under isocratic conditions, at a flow rate of 250 L/min. For TFA the parent and daughter ions measured were 113.0 and 69.0, respectively.

Plant and dry deposition samples were numbered randomly and analysed in duplicate. TFA was normalised against the recovery of the internal standard, ^{13}C4-PFBA spiked prior to extraction. Limit of detection (LOD) and the limit of quantification (LOQ) were defined as a signal-to-noise of 3:1 and 10:1, respectively. The final concentration of the TFA was adjusted by field blank values, which were very low compared to levels in air samples. The method detection limit (MDL) was derived from three times the standard deviation of the field blank values and for analytes not detected in field blank, MDLs were derived directly from three times their corresponding LODs. All the values below MDLs were considered as not detected (n.d.). For each batch of 10 samples, one procedural blank was processed to avoid background contamination. The SPSS 22 software was used for statistical analysis. Spearman rank and Pearson correlation analyses were used to examine possible correlations among various PFASs in different samples.

Recoveries for TFA were: leaf (n = 70) 85 ± 9%; air (n = 12) 90 ± 4%; dry deposition (n = 10) 80 ± 2%. All frequencies of recovery were 100%.

Limit of quantification: The LOQ for TFA was 0.16 µg/L.

Method detection limits: The MDLs for TFA were: leaf = 0.25 ng/g dw, 1.92 ng/g lipid; Air = 0.02 pg/m^3; particulate matter (PM) = 0.66 ng/g.

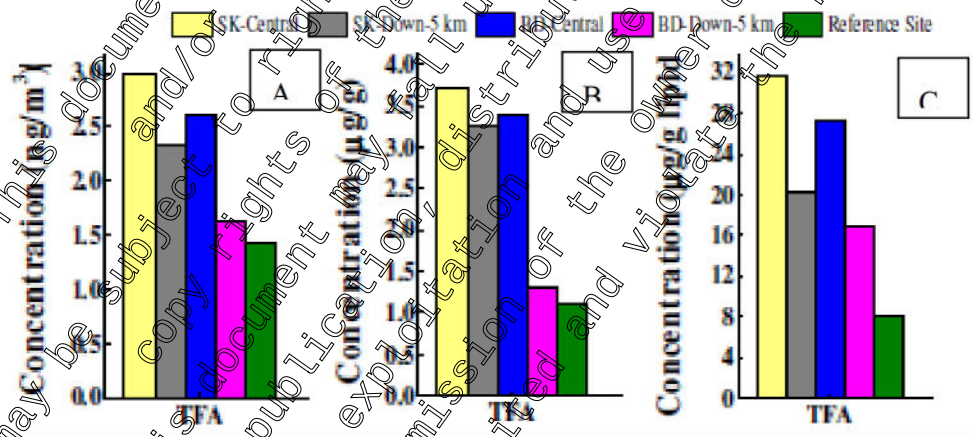
II. RESULTS AND DISCUSSION

TFA in the Environment

Figure 7.5- 29 shows, the concentrations of TFA in air, dry deposition and leaves around the 2 landfills (SK and BD) and the suburb reference site (JN). TFA was detected in all air samples with a predominant concentration range of 1.4 ng/m^3 to 3.0 ng/m^3, which contributed to 80% of the ΣPFCAs profiles.

In dry deposition, TFA also contributed to the majority of ΣPFCAs profiles with a concentration range of 1.1 ug/g to 3.7 ug/g.

In plant leaves, TFA was also dominant with a concentration range of 6.3 ng/g lipid to 42 µg/g lipid (0.56 µg/g dw to 3.0 µg/g dw) contributing to over 86% of ΣPFCAs profiles at each site. The concentrations of TFA in the present study were higher than that in pine needles (0.47 µg/g dw) from North America. The overall spatial distribution of these ultrashort-chain PFCAs followed a similar trend to that of medium- and long-chain PFASs. The elevated levels suggested additional sources of these ultra-short-chain PFCAs, which were different from medium- and long-chain PFCAs.



SK-Central and BD-Central represent the central area of the two landfills. SK-Down-5km and BD-Down-5km represents downwind sites 5 km from the central area. (A) in the air; (B) in dry deposition; (C) in leaves.

Figure 7.5- 29: The concentrations and spatial distributions of TFA around two landfills (SK and BD) and a suburb reference site (JN) in Tianjin, China

III. CONCLUSIONS

Spatially, the distribution trend of TFA in all three kinds of media consistently showed the central landfill > the downwind > the upwind > the reference sites, indicating that landfills are important sources of TFA in the environment. Plant leaves were found to be effective in uptake of TFA, thus capable of acting as a passive air sampling approach for air monitoring.

The maximum measured concentrations of TFA at the two landfills were up to 3.0 ng/m^3 in the air, 3.7 µg/g in dry deposition, and 42 µg/g lipid in leaves.

3. Assessment and conclusion

Assessment and conclusion by applicant:
This article from public literature reports results from a total of 23 per- and polyfluoroalkyl substances (PFASs) including trifluoroacetic acid (TFA) investigated in the air, dry deposition, and plant leaves at two different landfills and one suburban reference site in Tianjin, China (May – June 2016). Sampling methodology was well reported (including LOD and LOQ). However, the work wasn't carried out according to GLP, and there are currently no guidelines for the conduct of monitoring studies.

Conclusion:
Spatially, the distribution trend of TFA in all three kinds of media consistently showed the central landfill > the downwind > the upwind > the reference sites, indicating that landfills are sources of TFA in the environment. The maximum measured concentrations of TFA at the two landfills were up to 3.0 ng/m^3 in the air, 3.7 µg/g in dry deposition and 42 µg/g lipid in leaves.

The information from this article can be regarded as reliable.

Assessment and conclusion by RMS:
Outcome and conclusion of the study: RMS should indicate if they agree to the results and conclusions of the APPL.

1. Information on the published literature article

Data Point:	KCA 7.5/31
Report Author:	Wang, Z.; Wang, Y.; Li, J.; Henne, S.; Zhang, B.; Hu, J.; Zhang, J.
Report Year:	2018
Report Title:	Impacts of the degradation of 2,3,3,3-tetrafluoropropene into trifluoroacetic acid from its application in automobile air conditioners in china, the united states, and europe
Report No:	M-757883-01-1
Document No:	M-757883-01-1
Guideline(s) followed in study:	not applicable
Deviations from current test guideline:	Current Guideline: not applicable
Previous evaluation:	No, not previously submitted
GLP/Officially recognised testing facilities:	No, not conducted under GLP/Officially recognised testing facilities
Acceptability/Reliability:	Yes

2. Full summary of KCA 7.5/31

Executive Summary
HFO-1234yf (2,3,3,3-tetrafluoropropene) was proposed as an automobile air conditioner (MAC) refrigerant worldwide. Its atmospheric degradation product is trifluoroacetic acid (TFA), which persists in aquatic environments. A global three-dimensional chemical transport model was used to assess the potential environmental effects resulting from complete future conversion of the refrigerant in all MAC to HFO-1234yf in China, the United States, and Europe. The annual mean atmospheric concentrations

of HFO-1234yf were 2.62, 2.20, and 2.73 parts per trillion by volume (pptv), and the mean deposition rates of TFA were 0.96, 0.45, and 0.52 kg/km^2/yr, in the three regions. The regional TFA deposition sources mainly came from emissions within the same region. The annual TFA deposition in the North Pole region was lower than the global average and mainly originated from European emissions. A potential doubling in the future HFO-1234yf emissions in China mainly affected the local TFA depositions. The TFA concentrations in rainwater were strongly affected by the regional precipitation rates. North Africa and the Middle East, regions with scant rainfall, had extremely high TFA concentrations.

I. MATERIAL AND METHODS

Material

A global-scale atmospheric chemistry transport model was used to examine the potential environmental impact of a complete transition to HFO-1234yf as the cooling agent in MACs in China, the US, and EU. A one-year simulation was used to predict the amount of atmospheric HFO-1234yf and its conversion to TFA, local deposition, regional transport, and interactions.

Analytical method

The refrigerant emission inventory of HFO-1234yf in China was developed based on a former inventory using a bottom-up method that considered direct and indirect emissions from the manufacturing, operation, servicing, and end-of-life disposal of MACs. Two emissions scenarios were considered: (1) a current scenario using the current number of vehicles in the year 2016 and (2) a future scenario that used projected vehicle numbers for the year 2030. Both scenarios assumed that all vehicles were equipped with HFO-1234yf as a refrigerant and used adapted high-leak factors. State-level emissions were allocated to county-level data based on the GDP and population weighting and further re-griding to 1° × 1° grids based on roadway distributions and on-road activity data.

Seasonal allocations of annual emissions were made assuming that all the operation leakage, irregular leakage, and servicing leakage occur during the summer and were equally distributed into June, July, and August. End-of-life leakages were allocated across all 12 months equally. Emissions from different regions were tagged as HFO-1234yf-CH, HFO-1234yf-US, and HFO-1234yf-EU in models to track their transport and impacts. Regional and inter-regional impacts were researched by setting different emission inputs: (1) input all three emission regions; (2) input CH emissions and zero out the US and EU emissions; and (3) repeat step 2 for the US and EU emissions.

In this study, only emissions from the world's three largest automobile ownership regions (China, US and EU) were included, and both the regional and inter-regional environmental effects from these regions were considered.

The global three-dimensional chemical transport model (CTM) GEOSChem version v11-02 was used. The GEOS-Chem simulation was conducted for the whole year of 2016 following 2 months of spin-up with 2° × 2.5° horizontal grid resolution and 72 vertical layers.

For chemical degradation of HFO-1234yf and production of TFA, the NO_x-O_x- hydrocarbon-aerosol simulation was extended to include HFO-1234yf reactions with: (1) OH radicals as the dominant degradation pathway and an ~100% yield of TFF (trifluoracetyl fluoride, a product of the reaction of HFO-1234yf with OH and Cl radicals, which hydrolyses rapidly to TFA), (2) Cl radicals with a 92% yield of TFF, (3) O_3 with a 50% yield of TFF and (4) NO_3 radicals with a 91% yield of TFF. GEOS-Chem simulated OH, O_3, Cl, and NO_3 were used in this study.

A hydrolysis process was added to the heterogeneous chemistry of GEOS-Chem and a Henry's Law solubility constant of 3 M atm^{-1} at a standard temperature of 298.15 K and a hydrolysis rate of 150 s^{-1} of the dissolved TFF was applied. It was assumed that the partitioning of TFF between the gaseous and

aqueous phases is at a pseudosteady state, and dissolved quantities of TFF were calculated in grid boxes using its Henry's Law constant and the total volume of cloudwater presented in the grids.

II. RESULTS AND DISCUSSION

Atmospheric mixing ratios

The model results are presented at different levels of temporal and spatial aggregations. The results of HFO-1234yf emissions from three sources under scenario I are shown in Table 7.5- 51. Scenario II was calculated for China's future scenario with emissions of 88.4 Gg/yr. The US and EU emissions in scenario II were the same as those used in scenario I.

Table 7.5- 51: Summary of model results for HFO-1234yf and TFA

State	China annual[1]	US annual[1]	US summer[1]	EU annual[1]	North Pole annual	Globe annual[2]	Other global regions annual
HFO emissions (Gg)	42.65	24.53	15.21	19.16			
Mean HFO (pptv)	2.62	2.20	4.49	2.73	0.40	0.34	0.10
Max HFO (pptv)	30.96	19.44	40.95	19.08	1.09	30.96	
Mean TFA (pptv)	0.48	0.33	0.83	0.43	0.04	0.07	0.03
Max TFA (pptv)	3.77	1.15	3.26	1.78	0.14	3.77	
Mean TFA deposition (kg/km^2/yr)	0.96	0.45	0.59	0.52	0.08	0.12	0.05
Max TFA deposition (kg/km^2/yr)	7.94	2.12	2.90	2.95	0.56	7.94	
Mean rainwater concentration of TFA (ng/L)	638	480	1277	620	144		
Max rainwater concentration of TFA (ng/L)	23574	4485	15417	2099	549		

[1]Results under scenario I are given and the mean and maximum are various spatial aggregates (China, the US, EU, the North Pole, and the globe) from the annual and seasonal (summer) means.
[2]The global rainwater concentration of TFA was not presented because extreme values affected the comparability of the data.

Figure 7.5- 30 shows the spatial distributions of the annual mean mixing ratios of HFO-1234yf and TFA for scenario I. The annual TFA mixing ratio globally was 0.07 pptv and regionally was 0.48 pptv for China, 0.33 pptv for the US, 0.43 pptv for EU, 0.04 pptv for the North Pole, and 0.03 pptv for other areas globally.

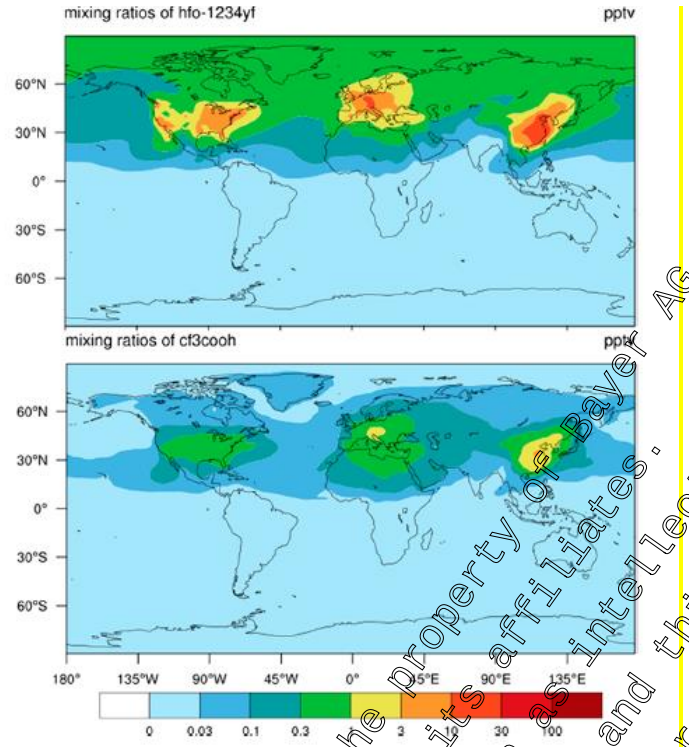


Figure 7.5- 30: Global annual mean surface mixing ratios (pptv) of HFO-1234yf (upper) and TFA (bottom) under scenario 1

Despite China's emissions being twice as large as those of the US and EU, all three regional HFO-1234yf and TFA atmospheric concentrations were very similar. These differences can partly be explained by (1) the area of China (2.26 × 107 km^2) being larger than those of the US (1.45 × 107 km^2) and EU (9.76 × 106 km^2) and (2) more TFA deposition in China (23392 tons) than in the US (7505 tons) and EU (5869 tons).

The largest annual mean atmospheric concentrations of TFA were 3.77 pptv for China, 1.15 pptv for the US, and 1.78 pptv for EU. All these peak concentrations occurred in regions with high HFO-1234yf emissions. There were considerable variations in the seasonal mean HFO-1234yf and TFA concentrations throughout the year. In the three emission regions, values peaked in the summer and reached a minimum in the spring.

Differences in the chemical mechanism that was used could also affect the OH levels and consequently the lifetime of HFO-1234yf in the atmosphere if the concentrations of oxidants or photolytic fluxes were different. The results also showed that, in spring, autumn, and winter, the seasonal atmospheric concentrations agreed closely for TFA (0.09 − 0.18 pptv in CH, 0.11− 0.23 pptv in the US, and 0.11− 0.27 pptv in EU). However, different meteorological conditions in the three seasons would impact the atmospheric chemistry and deposition, causing differences in the seasonal concentrations.

The global annual mean mixing ratio of TFA was 0.10 pptv under scenario II. Applying a factor of 2.08 to emissions in China, the atmospheric concentrations increased from 0.48 to 0.95 pptv for TFA. The mixing ratios in the US, EU, and the North Pole increased only slightly. Changes in the emissions of an area can affect the local atmospheric concentrations directly and considerably, but have little effects on the atmospheric components of other regions.

TFA Deposition

Figure 7.5- 31 shows the predicted dry, wet, and total deposition of TFA under scenario I in 2016. The annual global total TFA deposition from HFO-1234yf emissions from three main sources was 59.71 Gg/yr (69% of the total emissions). The remainder of the TFA was mainly remaining emissions either accumulated in the atmosphere in the gaseous and aqueous phases during the simulation period or lost through TFA degradation by OH. Dry deposition comprised of 5 − 30% of the total deposition loss, dependant on spatial and temporal variations. The maximum deposition occurred during the summer (of both dry and wet depositions), which accounted for 71% of the global yearly depositions, followed by autumn (12%). TFA deposition depends on the HFO-1234yf emissions as the primary factor, as well as meteorological conditions such as convective mass flux and the amount of precipitation.

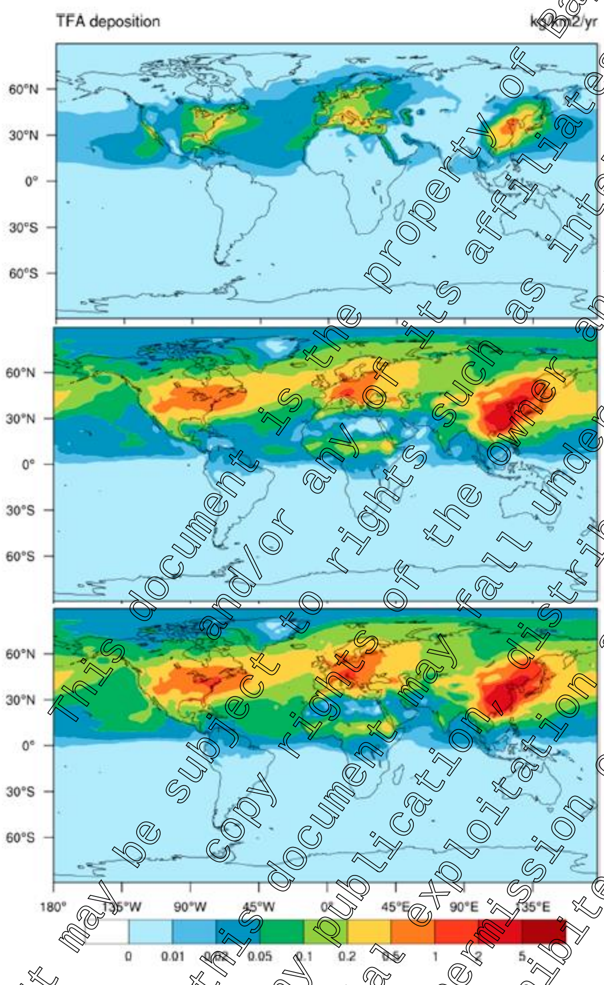


Figure 7.5- 31: Predicted annual total deposition rates of TFA (kg/km^2/yr) under scenario I from dry deposition (top), wet deposition (middle) and both processes (bottom)

The annual total depositions of TFA over the three emission regions were 23.39 Gg/yr in China, 7.50 Gg/yr in the US, and 5.87 Gg/yr in EU, accounting for 55%, 31%, and 31% of their local emissions, respectively. The remainder of the deposition occurred outside the emission areas and was more widely dispersed. The ratio of domestic deposition to emissions reached a minimum during the winter (40% for China, 17% for the US, and 13% for EU) because the meteorological conditions in winter accelerated atmospheric transport and had less precipitation. This ratio peaked during autumn (149% for China, 35% for the US, and 31% for EU) because the HFO-1234yf and TFA that had accumulated in the

atmosphere during the high, summertime emissions continued to deposit in September. In summer, the deposition to emission ratio in the US increased to 35%.

The global annual total deposition rate of TFA was estimated to be 0.12 kg/km^2/yr, while the regional rates had averages of 0.96, 0.45, and 0.52 kg/km^2/yr and maxima of 7.94, 2.12, and 2.95 kg/km^2/yr for China, the US, and EU, respectively. As wet deposition dominated the total TFA deposition distribution pattern was similar to that of wet depositions only. The mean summertime total deposition rates of TFA were 0.83 kg/km^2 for China, 0.29 kg/km^2 for the US, and 0.35 kg/km^2 for EU.

Under scenario II, with the doubled emissions of HFO-1234yf from China, the annual total depositions of TFA from HFO-1234yf in China increased linearly to 45.34 Gg/yr (with a factor of 1.94) and increased slightly in the US and EU to 8.27 and 6.14 Gg/yr (with factor of 1.10 and 1.05), respectively. Deposition rates increased with a similar pattern, to 1.85, 0.50, 0.54, and 0.18 kg/km^2/yr for China, the US, EU, and the whole globe, respectively. During the summer, the TFA deposition rate in China reached a mean of 1.52 kg/km^2 and a maximum of 12.89 kg/km^2.

Inter-regional Transport and Effects

The atmospheric amounts of HFO-1234yf and TFA and the amount of TFA depositions of the three emissions regions mostly came from emissions within the region, which accounted for ~75 − 95% of the total values. The local emission contributions were smallest during the winter and largest in the summer, due to the shorter chemical lifetime of HFO-1234yf, more efficient wet deposition by rain in summer than winter; and transport of the emission region is faster in winter than summer because of higher wind speed. The meteorological conditions in winter accelerate the transport of substances, and those in summer restrain it, which causes more inter-regional transmission and exchange in winter and local emissions increased dramatically during the summer compared with the other three seasons, making local emissions the primary factor affecting the regional atmospheric processes.

The largest source of TFA emissions in the North Pole was EU, contributing to 51% of the TFA mixing ratios, and 51% of the TFA depositions (in terms of the annual means). EU contributions were relatively stable across the four seasons, ranging from 45 − 61% for the TFA mixing ratios, and 50 − 59% for the TFA depositions. This is not only because northern EU is geographically closest to the North Pole but also because meteorological conditions facilitate the dispersion of EU emissions northward to the North Pole. In contrast, China and the US had much smaller effects on the North Pole, with China contributing 15%, and 21% of the North Pole's annual TFA mixing ratios, and TFA depositions, respectively, and the US contributing 34%, and 28%, respectively. For the other regions, the greatest impacts came from China's emissions, which were the largest of the three sources. China's emissions mostly affected neighbouring areas, especially for East Asia, including Japan, Korea, and the Pacific coast, and had lower impacts on more remote areas, especially for intercontinental transport. Emissions from the US were mainly transported eastwards to the Atlantic Ocean, even reaching EU, and westwards to the Pacific Ocean, with little dispersion to the north (Canada) or the south (Mexico). EU emissions were also mostly transported to the east and west, reaching as far east as the Caspian Sea, Russia and Kazakhstan, and as far west as the Atlantic Ocean and even eastern America.

Under scenario II, with more-than-doubled HFO-1234yf emissions from China, China's contributions to the annual mean TFA mixing ratios and depositions of the US increased from 4.5% to 10.8% and from 7.2% to 15.8%, while the effect on those of EU increased from 1.4% to 3.6% and from 3.0% to 7.2%, respectively. Regional amounts of HFO-1234yf and TFA in the US and EU still came primarily from local emissions. Despite the increased amounts of HFO-1234yf and TFA at the North Pole coming from China as its emissions increased, the North Pole's primary source of emissions was still EU. Scenario II is the maximum hypothesized emissions from China with no changes to those from the US and EU. These small, insignificant changes in the substance compositions of other regions suggest that future China emissions would cause environmental effects focused on a local scale, rather than globally. Future substitution of HFO-1234yf for HFCs could ease the global problem of climate change but

potentially cause regional environmental risks, particularly by increasing local TFA depositions. EU emissions exert the largest effects on regions near the North Pole.

III. CONCLUSIONS

This study presented the projected potential future TFA levels in rainwater over a global scale from three emission regions, and the concentrations were calculated using the rain events in the GEOS-Chem meteorological data after a period of TFA formation in the atmosphere. The annual mean rainwater concentrations of TFA were projected to be 638 ng/L in China, 480 ng/L in the US, 620 ng/L in EU, and 144 ng/L in the North Pole. The largest TFA depositions were predicted in the summertime, when the mean rainwater concentration of these four regions increased to 1451, 1277, 1762, and 313 ng/L, respectively. The highest monthly concentrations of TFA in three emission regions were 1.81×10^5 ng/L in the southern plateau of Tibet in China during November, 22223 ng/L around California and Oregon in the US during August and 9467 ng/L in the southern Mediterranean in the EU during July. These regions all have scant rainfall during certain seasons, so the TFA is highly concentrated.

Although the total amounts of TFA were higher in the source regions, the TFA rainwater concentrations were extremely high over the regions of North Africa and the Middle East, with monthly mean concentrations in August of 2.22×10^8 ng/L, approximately 5 orders of magnitude larger than that of China, the US, and EU. This area was simulated with the world's lowest amount of rainwater, averaging 1.78×10^{-6} kg/m^2/s, with a minimum value of 2.42×10^{-10} kg/m^2/s. This is in contrast to China, the US, and EU, which have minimum amounts of rainwater of 6.97×10^{-7}, 8.05×10^{-8}, and 5.39×10^{-8} kg/m^2/s, respectively.

3. Assessment and conclusion

Assessment and conclusion by applicant:

Assessment:

This article from public literature reports estimated potential atmospheric concentrations of HFO-1234yf and the degradation product trifluoroacetic acid (TFA) based on automobile air conditioner use China, the US and the EU in 2016 and predictions of increased use in China in 2030. The modelling methodology is well described and referenced to previous similar studies, but there are many sources of uncertainty attached to the modelling assumptions. There are currently no guidelines for the conduct of global modelling studies available.

Conclusion:

The mean deposition rates of TFA were 0.96, 0.45, and 0.52 kg km2 yr, in China, the US and EU, respectively. The regional TFA deposition sources mainly came from emissions within the same region. The annual TFA deposition in the North Pole region was lower than the global average, and mainly originated from European emissions. A potential doubling in the future HFO-1234yf emissions in China mainly affected the local TFA depositions. The TFA concentrations in rainwater were strongly affected by the regional precipitation rates. North Africa and the Middle East, regions with scant rainfall, had extremely high TFA concentrations

The information from this article can be regarded as supportive information.

Assessment and conclusion by RMS:

Outcome and conclusion of the study: RMS should indicate if they agree to the results and conclusions of the APPL

1. Information on the published literature article

Data Point:	KCA 7.5/32
Report Author:	Bjoernsdotter, M. K.; Yeung, L. W. Y.; Kaerrman, A.; Jogsten, I. E.
Report Year:	2019
Report Title:	Ultra-short-chain perfluoroalkyl acids including trifluoromethane sulfonic acid in water connected to known and suspected point sources in sweden
Report No:	M-758273-01-1
Document No:	M-758273-01-1
Guideline(s) followed in study:	not applicable
Deviations from current test guideline:	Current Guideline: not applicable
Previous evaluation:	No, not previously submitted
GLP/Officially recognised testing facilities:	No, not conducted under GLP/Officially recognised testing facilities
Acceptability/Reliability:	Yes

2. Full summary of KCA 7.5/32

Executive Summary

Ultra-short-chain PFAAs, including trifluoroacetic acid (TFA), were analysed in water connected to potential point sources in Sweden using supercritical fluid chromatography coupled with tandem mass spectrometry. 34 Samples were collected (in 2017 or 2018) in connection with firefighting training sites, landfills, and a hazardous waste management facility.

Ultra-short-chain PFAAs were detected in all samples at concentrations up to 84000 ng/L (ΣC1− C3), representing up to 69% of the concentration of 29 per- and polyfluoroalkyl substances (PFASs). Trifluoroacetic acid (TFA) was detected at concentrations up to 14000 ng/L. Principal component analysis suggests that TFA is associated with landfills. These findings reveal the presence of high concentrations of ultra-short-chain PFAAs released into the environment from various sources and emphasize the large fraction of ultra-short-chain PFAAs to the total concentration of PFASs in water.

I. MATERIAL AND METHODS

Material

Concentrations of 29 PFASs, including TFA, were measured in environmental waters in Sweden from suspected point sources.

Sampling method

A total of 20 samples were taken from five firefighting training sites (FFTSs) where either aqueous film-forming foams (AFFFs) had been used for firefighting training purposes or where there were rock shelters equipped with sprinkler systems for fire protection and subsequent system tests. At FFTS A, two samples were collected in December 2017 (T1) and February 2018 (T2). The samples were taken from outflowing water from a rock shelter consisting of a combination of groundwater, storm water, and surface water from the nearby areas. Three different types of samples were collected at FFTS B in January (T1) and April (T2) 2018: outflowing water from rock shelter (B1) and groundwater before (B2) and after (B3) treatment with granular activated carbon (GAC) filters. The outflowing water from a rock shelter consisted of a combination of groundwater, storm water, and surface water from the nearby areas. During the first sampling occasion in January 2018 (T1), the GAC filters had been in place for 11 months, filtering about 6.5 million litres of water. During the second sampling occasion in April 2018 (T2), the filters had just been replaced. At sampling site C, one surface water sample was collected from

a creek downstream from a FFTS in February 2017. Sampling was performed at different locations at sampling site D in May 2018. One sample (FFTS D2) was from a pond at a FFTS and another sample (FFTS D1) was from the upstream of the pond. The third sample (FFTS D3) was from a stream close to the training site, not connected to the pond, but was suspected to be contaminated with PFASs from the nearby AFFF usage. At FFTS E, eight groundwater samples were collected at (E1) and downstream (E2 − E8) from the firefighting training ground during December 2017. Sampling was performed along an esker in two directions downstream from the FFTS.

Samples were collected in connection with three municipal and industrial landfills (LFs) (n = 9). LF leachate and storm water samples were collected at LF A in July and August 2017. At LF B, samples were collected from a non-active LF (LF B1), an active non-hazardous waste LF (LF B2), and an active hazardous waste LF (LF B3) in August 2017. At LF C, samples were collected from an active non-hazardous waste LF (LF C1) and an active hazardous waste LF (LF C2) in August 2017.

Samples were collected downstream from one hazardous waste management facility (HWMF) (n = 5) in May 2018. One sample (A1) was from the outlet of the HWMF. Sample A2 was collected downstream from the outlet while samples A3 and A4 were from two lakes receiving water from the stream in which effluent from the HWMF is discharged. Sample A5 was from a stream further downstream from the lake from which sample A4 was collected.

Drinking water (n = 2) was collected from water treatment facilities for comparison.

All samples were collected in polyethylene containers and stored in a refrigerator until processing. All sample containers were pre-cleaned with Milli-Q water followed by methanol and rinsed three times with the sample matrix before collecting the sample. Table 7.5.-52 includes details of all the sampling locations.

Analytical procedures
Water samples were ultrasonicated for 10 min to prevent adsorption of target analytes to the inner surface of the polypropylene containers and then passed through glass microfibre filters (1.2 µm) to remove particulate matter.

Separation and quantification of C1-C3 PFAAs in water samples were performed using supercritical fluid chromatography (SFC) coupled to tandem mass spectrometry operated in negative electrospray ionization mode. An SFC Torus DIOL column maintained at 35°C was used to achieve chromatographic separation. The mobile phase consisted of CO_2 (A) and 0.1% NH_4OH in MeOH (B). Only one multiple reaction monitoring (MRM) transitions was measured for TFA (112.90 → 68.96).

Quantification of TFA was by direct injection (after 1:1 dilution in methanol) and isotope dilution using mass labelled PFBA as an internal standard; results are therefore tentative. TFA was not measured in drinking water. Data is reported after blank subtraction. The LOD and LOQ of TFA were defined as three and ten times the standard deviation of repeated blank direct injections (n = 4) consisting of water and methanol (1:1). Ion signal effects were assessed by spiking native standard (2 ng) to selected test samples (n = 3). Non-spike test samples were spiked with an equal volume of methanol. Ion signal effects were then evaluated by comparing the spiked test samples with a standard after subtraction of the non-spiked samples. TFA suffered slightly from ion suppression (19 ± 0.4%) during electrospray ionization. Ion suppression on PFBA was 4 ± 11%. The difference in ion signal effects between TFA and PFBA has not been compensated for. Instrumental matrix effects on samples directly injected into the SFC-MS/MS system for TFA were 81%, 82% and 81% for surface water, groundwater and landfill leachate, respectively.

LOD: The limit of detection for TFA was 34 ng/L.

% RSD: The relative standard deviation was 28%.

II. RESULTS AND DISCUSSION

Ultra-short-chain PFAAs were detected over a wide concentration range in all water samples analysed (Table 7.5- 52). TFA was detected in 20 out of 33 samples at concentrations ranging from < 34 to 14000 ng/L (median concentration 110 ng/L). The highest concentration of TFA (14000 ng/L) was found in water from a rock shelter (FFTS B1 T2) with previous usage of AFFFs in sprinkler systems. TFA was more frequently detected at higher concentrations in LF leachate (<34 − 6900 ng/L), indicating that leaching from LFs may be a relevant source for TFA into the environment.

Table 7.5- 52: Concentration and detection frequency of TFA and description of sampling locations, sample matrix

Location	Site [1]	Sample matrix and sample description	TFA Concentration (ng/L)
		Detection frequency (%)	61
		Median (ng/L)	110
Firefighting Training Sites (FFTSs)	A T1	outflowing water from a rock shelter representing a combination of groundwater, storm water, and surface water from the nearby areas	100[2]
	A T2	outflowing water from a rock shelter representing a combination of groundwater, storm water, and surface water from the nearby areas	< 34
	B1 T1	outflowing water from a rock shelter representing a combination of groundwater, storm water, and surface water from the nearby areas	610
	B1 T2	outflowing water from a rock shelter representing a combination of groundwater, storm water, and surface water from the nearby areas	14000
	B2 T1	water connected to B1 T1 collected before treatment with GAC filter	520
	B2 T2	Water connected to B1 T2 collected before treatment with GAC filter	370
	B3 T1	water connected to B2 T1 collected after treatment with GAC filter. Sampling was done 1 week past the date for exchange of the filter	880
	B3 T2	water connected to B2 T2 collected after treatment with GAC filter. Sampling was done just after installation of a new filter	390
	C	surface water collected downstream from a FFTS	< 34
	D1	surface water collected from a stream just before the inlet to a pond (D2) at a FFTS	< 34
	D2	surface water collected from a pond at a FFTS (downstream D1)	< 34
	D3	surface water collected from a stream at FFTS D	< 34
	E1	groundwater collected close to the firefighting training ground at a FFTS	< 34
	E2	groundwater collected downstream from FFTS E (downstream E1)	< 34
	E3	groundwater collected downstream from FFTS E (downstream E1)	69[2]
	E4	groundwater collected downstream from FFTS E (downstream E1)	< 34
	E5	groundwater collected downstream from FFTS E (downstream E1)	120
	E6	groundwater collected downstream from FFTS E (downstream E5)	< 34
	E7	groundwater collected downstream from FFTS E (downstream E6)	< 34
	E8	groundwater collected downstream from FFTS E (downstream E2)	< 34
Landfills (LFs)	A1 T1	LF leachate	4400
	A1 T2	LF leachate	2800
	A2 T1	LF storm water	1200
	A2 T2	LF storm water	1000
	B1	leachate from a nonactive (covered) LF	6900
	B2	leachate from active non-hazardous waste LF	1200
	B3	leachate from active hazardous waste LF	500
	C1	leachate from active non-hazardous waste LF	1200

Location	Site [1]	Sample matrix and sample description	TFA Concentration (ng/L)
	C2	leachate from active hazardous waste LF	< 34
Hazardous waste management facility (HWMF)	A1	surface water collected at the outlet from an HWMF	n.q.[3]
	A2	surface water collected downstream from the HWMF (downstream A1)	2700
	A3	surface water collected from a lake downstream from the HWMF (downstream A2)	< 34
	A4	surface water collected from a lake downstream from the HWMF (downstream A2)	74[2]
	A5	surface water collected from a stream downstream from the HWMF	150

Quantified by direct injection onto the SFC-MS/MS system
[1]: Different sampling sites (letters), locations at the same site (numbers), and sampling occasions (T followed by a number) are indicated.
[2]: Below LOQ (111 ng/L)
[3]: n.q. not quantified

Ultra-short-chain PFAAs represented between 0.4 and 98% of the total concentration of 29 PFASs measured in connection with FFTSs, between 4.3 and 69% in LF leachate and between 6.4 and 69% downstream from the HWMF. Ultra-short-chain PFAAs represented a large fraction of the total concentration of measured PFASs in two samples collected at a FFTS (FFTS B3) on two occasions after treatment with GAC filter. Shorter-chain compounds are not as efficiently removed by GAC filter treatment as longer-chain PFASs. The smallest molecules, including TFA, were not removed at all. An increase was observed for TFA (107%) in water collected after water treatment.

The fraction of individual ultra-short-chain PFAAs to the total concentration of measured PFASs varied between different sampling sites. TFA was the most abundant ultra-short-chain PFAA representing more than 30% of the total PFAS concentration measured in 12 out of 34 samples. TFA was detected in eight out of nine LF leachate samples and represented between 0.1 and 66% to the total PFAS concentration (> 80% in six LF leachate samples). TFA was observed at the highest concentrations in LF leachate samples (< 34 − 6800 ng/L) (after the water sample collected from the rock shelter FFTS B1 T2).

Generally, ultra-short-chain PFAAs were found at higher concentrations and represented a larger fraction of the total concentration of PFASs at FFTS B1 T2 compared to other FFTSs. However, in one sample (FFTS B1 T2), the concentration of TFA was 1 order of magnitude higher than in sample FFTS B1 T1. This considerable increase of TFA along with the increase of other abundant PFASs indicated that the source of TFA at this site may be of the same origin as the other PFASs, that is, the use of AFFFs. Furthermore, TFA could be a degradation product of precursor compounds such as heptafluoropropane (HFC-227ea) and perfluoro-2-methyl-3-pentanone that are used in fire suppression systems.

At FFTS E, samples were collected at the firefighting training ground (E1) which is located near a small lake and at other locations downstream from the firefighting training ground along an esker in two directions (E2 − E8). TFA was not detected above the LOD in the sample collected closest to the source but was found at concentrations 1 order of magnitude higher than the LOD in samples collected downstream of the firefighting training ground. The relatively low concentrations observed at FFTS E suggest that this site is not a point source for ultra-short-chain PFAAs. Relatively low concentrations of ultra-short-chain PFAAs were also observed at FFTSs C and D. The presence of ultra-short chain PFAAs at these sites is likely a result of input from diffuse sources, such as atmospheric degradation of precursor compounds, which has previously been shown for TFA.

III. CONCLUSIONS

TFA was frequently detected (61%) and often at high concentrations in the water samples analysed. Concentrations of TFA ranged between < 34 ng/L (< LOD) to 14000 ng/L at FFTS, < 34 – 6900 ng/L at LF and < 34 – 2700 ng/L at HWMF. The detection of TFA in samples collected in connection with different types of potential point sources reveals the diversity of sources of this compound. The presence of TFA at locations with no point source identified may be a result of diffuse sources.

3. Assessment and conclusion

Assessment and conclusion by applicant:

Assessment:

This article from public literature reports results from a total of 29 per- and polyfluoroalkyl substances (PFASs) including trifluoroacetic acid (TFA) investigated in surface water from three types of possible point source contamination in Sweden. Sampling and analytical methodology were well reported (including LOD). However, the analytical method for TFA generated 'tentative' results only, the work wasn't carried out according to GLP, and there are currently no guidelines for the conduct of monitoring studies.

Conclusion:

TFA was frequently detected (61%) and often at high concentrations in the water samples analysed. Concentrations of TFA ranged between < 34 ng/L (< LOD) to 14000 ng/L at FFTS, <34 – 6900 ng/L at LF and <34 – 2700 ng/L at HWMF. The detection TFA in samples collected in connection with different types of potential point sources reveals the diversity of sources of this compound. The presence of TFA at locations with no point source identified may be a result of diffuse sources.

The information from this article can be regarded as supportive information.

Assessment and conclusion by RMS:

Outcome and conclusion of the study: RMS should indicate if they agree to the results and conclusions of the APPL.

1. Information on the published literature article

Data Point:	KCA 7.5/33
Report Author:	Chen, H.; Zhang, L.; Li, M.; Yao, Y.; Zhao, Z.; Munoz, G.; Sun, H.
Report Year:	2019
Report Title:	Per-and polyfluoroalkyl substances (pfass) in precipitation from mainland china: contributions of unknown precursors and short-chain (c2-c3) perfluoroalkyl carboxylic acids
Report No:	M-758267-01-1
Document No:	M-758267-01-1
Guideline(s) followed in study:	not applicable
Deviations from current test guideline:	Current Guideline: not applicable
Previous evaluation:	No, not previously submitted
GLP/Officially recognised testing facilities:	No, not conducted under GLP/Officially recognised testing facilities
Acceptability/Reliability:	Yes

2. Full summary of KCA 7.5/33

Executive Summary

A nationwide survey was conducted on per- and polyfluoroalkyl substances (PFASs) in precipitation across mainland China. Twenty-two PFASs, including precursors to perfluoroalkyl acids (pre-PFAAs), were investigated in 39 precipitation samples collected from 28 cities. Trifluoroacetate (TFA), perfluorooctanoic acid, and perfluorooctane sulfonic acid (PFOS) were ubiquitous in precipitation. TFA was detected at generally higher concentrations than other PFASs and displayed a unique trend with elevated levels occurring in coastal cities such as Shantou (ST, 1.6×10^4 ng/m^2/d), Tianjin (TJ, 6.9×10^3 ng/m^2/d), and Xiamen City (XM-11.08.2016, 9×10^3 ng/m^2/d), rather than sites impacted by fluorochemical manufacture activities. These results highlighted that TFA in the atmosphere may originate from multiple sources.

I. MATERIAL AND METHODS

Material

The objectives of this study were: (i) to investigate the occurrence, spatial distribution, and fluxes of PFAAs (mainly perfluoroalkyl carboxylic acids (PFCAs) and, PFASs) and infrequently monitored PFASs (including TFA) in precipitation at a nationwide scale in urban areas from mainland China; and (ii) to estimate the contribution of total pre-PFAAs (including potential unknown/untargeted precursors) to PPFASs.

Sampling method

Thirty-nine precipitation samples were collected from 28 cities across mainland China (Figure 7.5- 32). Sampling was conducted from May to September 2016 using stainless steel buckets (30 cm in diameter × 20 cm in height). The sampling equipment and sample containers (polypropylene (PP) bottles) were all pre-cleaned using Milli-Q water and methanol in a sequence. On collection, precipitation samples were transferred to a PP bottle and stored at 20°C.

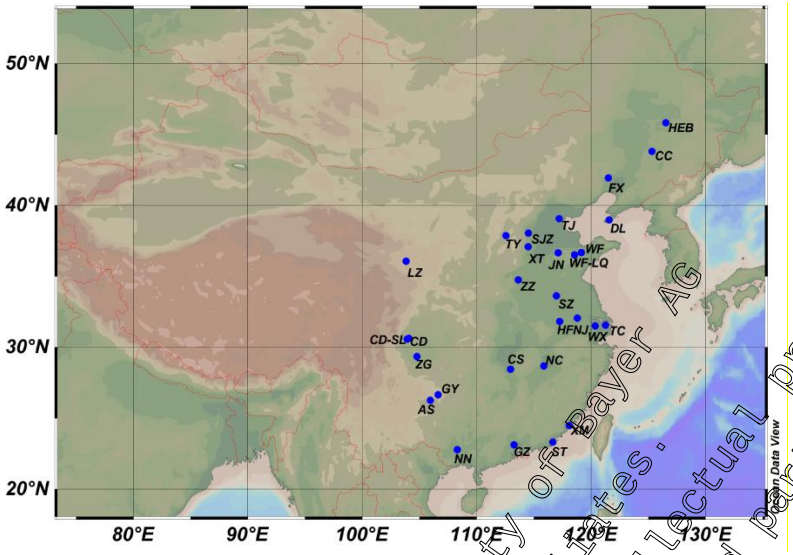


Figure 7.5- 32: Locations of sampling sites in China

Analytical method

Prior to extraction, 50 mL of the oxidized and 200 mL of the unoxidized precipitation samples were spiked with 5 ng of each internal standard (IS). The WAX SPE cartridges were sequentially conditioned and the water samples were then loaded onto the SPE cartridges. The cartridges were washed and centrifuged for 10 min at 3000 rpm for water removal. PFASs were eluted with 5 mL of methanol and 5 mL of methanol containing 0.1% ammonium hydroxide. The combined eluates were concentrated to 0.5 mL under pure nitrogen at 40°C and then transferred to autosampler vials for analysis.

PFASs were analysed using high-performance liquid chromatography coupled to tandem mass spectrometry (HPLC-MS/MS) in negative electrospray ionization (ESI) mode. The extracts were analysed using different LC-MS/MS methods for specific classes of analytes.

Field blanks and procedural blanks were prepared using Milli-Q water to monitor contamination during sample collection, oxidation, and solid-phase extraction. For unoxidized precipitation samples, triplicate matrix spike recovery experiments were performed. Due to the high ionic strength of oxidised samples, the recoveries of short-chain PFCAs were poor in oxidized precipitation samples, which precluded reporting TFA. The instrumental limits of detection (iLODs) and limit of quantification (iLOQs) were defined as the peak of analyte that yielded a signal-to-noise (S/N) ratio of 3 and 10, respectively. For unoxidized precipitation samples, the PFAS method quantification limits (MQLs) were derived from the iLOQs by multiplying with the corresponding enrichment factor by 400×.

iLOD: 96 ng/L for TFA

iLOQ: 320 ng/L for TFA

MQL: 1.46 ng/L, 200 mL for TFA (but note; blanks yielded 1.1 ± 0.12 ng/L)

The internal standard calibration curve consisted of samples with incremental levels of native standards (0.5, 1, 2, 5, 10, 20, 50, 100, 200 µg/L), prepared in MeOH (prior instrumental analysis) and spiked with 5 ng internal standard. The calibration curves showed suitable determined coefficients for all target analytes ($r^2 > 0.99$). Although internal standards were added prior to extraction, exact matching internal standards could not be used for some compounds. A potential pitfall was noted regarding the IS correction of trifluoroacetate (TFA). Since $^{13}C_2$-labelled TFA was not available at the time of quantification, $^{13}C_1$- labelled TFA was used, however, the signal of 1-fold labelled TFA could be

impacted from natural isotopic overlap in native TFA. The artifact could significantly affect TFA quantification for those highly contaminated samples (underestimation of TFA concentration due to unwanted signal increase of $^{13}C_1$-TFA). Therefore, in this study, the use of $^{13}C_1$-TFA in cencentration correction was avoided and correction with the $^{13}C_4$-labelled PFBA internal standard was applied.

II. RESULTS AND DISCUSSION

TFA displayed generally higher concentrations than other targeted PFCA homologues. TFA concentrations (ranged 8.8 – 1.8 × 10^3 ng/L; average 1.5 × 10^2 ng/L and fluxes (ranged: 1.2 × 10^2 – 7.4 × 10^4 ng/m^2/d; average 2.2 × 10^3 ng/L ng/m^2/d) were 1 – 2 orders of magnitude higher than those of other individual PFAAs. The author observed that dominance of TFA over other targeted PFASs in precipitation was consistent with previous studies in North America and other regions worldwide.

Table 7.5- 53: Locations of sampling sites in China

Sampling site	City	Daily precipitation amounts (mm/day)	Concentration of TFA in precipitation (ng/L)	Flux of TFA in precipitation samples (ng/m^2/d)
AS	Anshun	24	9.1	1.3 × 10^2
GY	Guiyang	13	12	1.6 × 10^2
CD	Chengdu	14	1.6 × 10^2	2.3 × 10^2
ZG	Zigong	23	86	2.0 × 10^3
CD-SL	Chengdu-Shuangliu District	16.2	3.2 × 10^2	5.2 × 10^3
GZ	Guangzhou	16	9.1	1.5 × 10^2
ST	Shantou	9	1.8 × 10^3	1.6 × 10^4
NN	Nanning	40	11	4.5 × 10^2
XM-05.08.2016	Xiamen	10	3.2 × 10^2	3.2 ×10^3
XM-11.08.2016	Xiamen	55	1.6 × 10^2	9.0 × 10^3
XM-12.08.2016	Xiamen	12	93	1.1 × 10^3
HF	Hefei	30	16	4.7 × 10^2
SZ	Suzhou	30	1.0 × 10^2	3.1 × 10^3
CS	Changsha	14	8.8	1.2 × 10^2
NC-02.06.2016	Nanchang	64	27	1.7 × 10^3
NC-15.06.2016	Nanchang	50	13	6.6 ×10^2
NC-20.06.2016	Nanchang	20	21	4.3 ×10^2
NJ-XW	Nanjing-Xuanwu District	13	30	4.0 ×10^2
NJ-QH	Nanjing-Qinhuai District	13	13	1.7 × 10^2
TC-LH	Taicang-Litine Town	16	1.8 × 10^2	2.8 × 10^3
TC	Taicang	3	98	2.9 × 10^2
WX	Wuxi	15	15	2.3 × 10^2
JN	Jinan	12	1.3 × 10^2	1.6 × 10^3
WF-LQ	Weifang-Linqu Count	18	1.5 × 10^2	2.6 × 10^3
WF	Weifang	12	1.0 × 10^2	1.2 × 10^3
ZZ-1	Zhengzhou	15	27	4.0 × 10^2
ZZ-2	Zhengzhou	20	15	3.1 × 10^2
ZZ-3	Zhengzhou	22	2.5 × 10^2	5.5 × 10^3
SJZ	Shijiazhuang	15	16	2.4 × 10^2
XT	Xingtai	18	93	1.7 × 10^3
TJ	Tianjin	9	7.7 × 10^2	6.9 × 10^3

Sampling site	City	Daily precipitation amounts (mm/day)	Concentration of TFA in precipitation (ng/L)	Flux of TFA in precipitation samples (ng/m²/d)
TY	Taiyuan	24	59	1.4×10^3
LZ	Lanzhou	14	1.4×10^2	1.9×10^3
FX-1	Fuxin	6	1.4×10^2	8.5×10^2
FX-2	Fuxin	12	1.3×10^2	1.5×10^3
FX-3	Fuxin	12	1.0×10^2	1.2×10^3
DL	Dalian	20	1.8×10^2	3.5×10^3
CC	Changchun	18	25	4.5×10^2
HEB	Haerbin	15	2.0×10^2	3.0×10^3

The highest levels of TFA were generally found in coastal cities (Figure 7.5-33) such as Shantou (ST, 1.6×10^4 ng/m²/d), Tianjin (TJ, 6.9×10^3 ng/m²/d), and Xiamen City (XM-I1.08.2016, 9×10^3 ng/m²/d), rather than sites impacted by fluorochemical manufacture activities. The author considered this trend was consistent with the spatial distribution of TFA in the United States. Urbanization levels and number of private vehicles are higher in these coastal cities in China. Thus, the emissions of refrigerants (HCFCs, HFCs and other related chemicals) are assumed to be greater in this region. More OH radicals and marine derived chlorine atom precursors are expected close to coastal regions under stronger solar radiation. Therefore, these refrigerants could be converted to TFA with greater efficiency under the large amounts of OH radicals and chlorine atoms present in such environments. Enhanced TFA formation may also proceed from non-PFAS products (pharmaceuticals, pesticides, or volatile precursors with carbon-bound -CF_3) with industrial and/or domestic origins.

Although not as high as in the surveyed coastal cities, substantial TFA fluxes were observed in Fuxin City (FX-2,1.5 × 10³ ng/m²/d) and Linqu County (WF-LQ, 2.6 × 10³ ng/m²/d), which are heavily influenced by fluoropolymers production. This was also consistent with the authors' earlier assessment of the surface environment at these sites, where even higher levels of TFA were reported. While TFA is manufactured and/or used in manufacturing processes at these sites, it may also proceed from environmental degradation of acknowledged PFAS precursors.

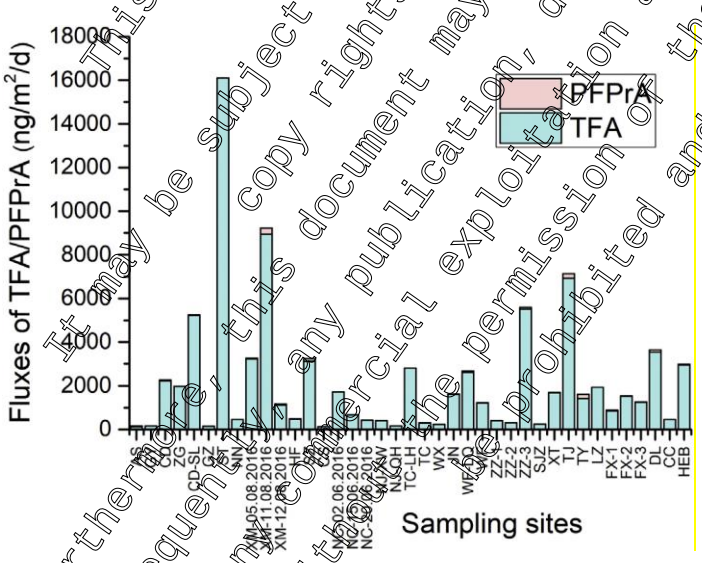


Figure 7.5-33: TFA and PFPrA (perfluoropropionic acid) fluxes (ng/m²/d) (stacked bars) in individual precipitation samples from 28 cities in mainland China

Multivariate statistical analysis was used to discriminate trends among PFASs. The component/cluster explains 18% of the variability in PFASs and grouped two ultra-short chain PFCAs (TFA and PFPrA) suggesting additional sources of TFA/PFPrA other than the degradation of fluoropolymers (and/or fluorotelomers) in urban areas. Although high fluxes of TFA were observed both for fluorochemical production sites (FX-3 and WFLQ) and coastal city sites (ST and XM-11.08.2016), the sampling sites were grouped separately in the cluster analysis, suggesting differences in source contribution. TFA may essentially originate from its use in manufacture or the degradation of fluoropolymers at industrial sites while its primary source at other sampling sites may involve the degradation of novel fluorine-containing refrigerants.. The third (including PFBA and PFOA) and fourth (including PFOS) components explained 16% and 11% of the variability, respectively. The underlying factor may be geographic differences in usage and production category in China. PFBA, PFOA, and fluorotelomer-based PFASs were mainly produced in Eastern and Northern China, while PFOS and PFOS-related electrochemical fluorination products (ECF) were mainly produced in Eastern and Southern China.

III. CONCLUSIONS

TFA was detected at generally higher concentrations than other PFASs and displayed a unique trend with elevated levels occurring in coastal cities such as Shantou (ST, 1.6×10^4 ng/m^2/d), Tianjin (TJ, 6.9×10^3 ng/m^2/d), and Xiamen City (XM-11.08.2016, 9×10^3 ng/m^2/d). These results highlighted that TFA in the atmosphere may originate from multiple sources. Although not as high as in the surveyed coastal cities, substantial TFA fluxes were observed in Fuxin City (FX-2, 1.9×10^3 ng/m^2/d) and Linqu County (WF-LQ, 2.6×10^3 ng/m^2/d), which are heavily influenced by fluoropolymers production.

3. Assessment and conclusion

Assessment and conclusion by applicant:

Assessment:

This article from public literature reports monitoring results from 39 precipitation samples from 28 cities across mainland China (May to September 2016). Sampling methodology was well reported (including LOD, LOQ and the precautions taken to avoid TFA contamination). However, the work wasn't carried out according to GLP, and there are currently no guidelines for the conduct of monitoring studies.

Conclusion:

TFA was detected at generally higher concentrations than other PFASs and displayed a unique trend with elevated levels occurring in coastal cities such as Shantou (ST, 1.6×10^4 ng/m^2/d), Tianjin (TJ, 6.9×10^3 ng/m^2/d), and Xiamen City (XM-11.08.2016, 9×10^3 ng/m^2/d). These results highlighted that TFA in the atmosphere may originate from multiple sources.

The information from this article can be regarded as reliable.

Assessment and conclusion by RMS:

Outcome and conclusion of the study. RMS should indicate if they agree to the results and conclusions of the APPL.

1. Information on the published literature article

Data Point:	KCA 7.5/34
Report Author:	Dorgerloh, U.; Becker, R.; Kaiser, M.
Report Year:	2019
Report Title:	Evidence for the formation of difluoroacetic acid in chlorofluorocarbon-contaminated ground water
Report No:	M-758271-01-1
Document No:	M-758271-01-1
Guideline(s) followed in study:	not applicable
Deviations from current test guideline:	Current Guideline: not applicable
Previous evaluation:	No, not previously submitted
GLP/Officially recognised testing facilities:	No, not conducted under GLP/Officially recognised testing facilities
Acceptability/Reliability:	Yes

2. Full summary of KCA 7.5/34

Executive Summary

The concentrations of difluoroacetic acid (DFA) and trifluoroacetic acid (TFA) in rainwater and surface water from Berlin, Germany resembled those reported for similar urban areas. The TFA concentration levels at the investigated groundwater sites (historically contaminated with 1,1,2-trichloro-1,2,2-trifluoroethane (R113)) are similar to those of surface water. The local geology displays a low permeability of barrier layers and hydrodynamic flow direction from the canal towards the ground water site. This, and the absence of CFCs containing the CF_3 group in the ground water as a potential source for TFA, suggested a surface water origin for the TFA in the ground water.

I. MATERIAL AND METHODS

Material

TFA is very stable in the environment with an estimated half-life of several hundreds of years and is found worldwide in oceans and water bodies.

Sampling method

The rainwater samples were collected in open glass beakers for 1 h (rainwater 1) and for 12 h (rainwater 2), respectively. The aggregated amounts (sample 1: 4 L, sample 2: 2 L) were immediately processed. The surface water samples were taken about 50 cm below the surface in 1 L glass bottles and cooled to 4 – 6°C. In the laboratory, the processing started immediately (between 1 and 12 h after sampling). The first surface water sample was from the Teltow canal near a sewer drain close by the rainwater sampling point and the contaminated ground water site (historically contaminated with 1,1,2-trichloro-1,2,2-trifluoroethane (R113)). The second sample was from a Havel lake in the periphery of Berlin. The ground water samples were taken by pump sampling (35 m under ground level) from two monitoring wells positioned over the contamination hot spot and the plume (Berlin Oberspree) originating from industrial contamination with R113. The samples were filled in 1 L brown glass bottles, closed, and cooled (4°C) until processed in the laboratory. A separate sample was used for each determination.

Analytical method

Each water sample (1 L) was buffered with ammonium carbonate at pH 9 to ensure that TFA was retained completely as acetate during evaporation of the water until the samples were dry. Each vial containing a dried sample was crimped and cooled down to -28°C. Then, 800 µL of a mixture of H_2SO_4

and methanol (3:1, v:v) were added by syringe through the closed septum. The formed fluoroacetic acid methyl esters were volatile and could be determined by gas chromatography (GC) from the headspace.

For method calibration in a range from 1 to 4000 ng absolute per sample, different amounts of TFA stock solutions in methanol were added to closed headspace vials through the septa and derivatised. The recovery rate for the drying procedure at 20 and 2000 ng/L was between 70% and 100%, the relative standard deviation (n = 3) was between 10% and 17%.

GC coupled with a mass selective detector (MSD) autosampler were used for quantification of TFA by analysing its methyl ester. Gas chromatographic separation was achieved using a VF624 standard capillary column. After conditioning of the headspace vial containing the methyl esters (70°C, 15 min), 1 mL of the headspace volume was injected into the gas chromatograph (split 1:5). The oven program started at 40°C (held for 10 min) and was ramped to 140°C (10°C/min) and further to 240°C (40°C/min). The MSD (electron impact, 70 eV) was run in the single ion mode (SIM), and the methyl ester of TFA was quantified using the target ion *m/z* 69. The overall detection limit for TFA was 2 ng per sample. The linear working range was up to 4000 ng per sample.

LOD: The limit of detection (LOD) was 10 ng/L for the full method, based on an initial water volume of 1 L and the matrix effect of real-world water samples.

II. RESULTS AND DISCUSSION

Table 7.5- 54 shows relatively similar levels of TFA in rainwater, lake water and ground water. The high TFA concentration in the first rainfall after a long dry period (rainwater 1) and the sewer drain sampling point at the Teltow canal are consistent with a long accumulation period of air contaminants prior to washout. For the TFA concentration in rainwater 2 collected after a first depuration (rainwater 1), surface water (Havel lake) and the ground water samples displayed a largely similar level of around 500 ng/L (from 370 to 676 ng/L).

Table 7.5- 54: TFA concentrations in rainfall, surface water and groundwater

Water sample	Mean TFA (ng/L)	Relative standard deviation % (n = 2)
Rainwater 1 (1h of rain after a long dry period)	1556[1]	-
Rainwater 2 (after 12h of heavy rainfall)	370	3.7
Surface water: Teltow canal	1908	0.9
Surface water: Havel lake	676	7.1
Contaminated groundwater hot spot[2]	639	19.0
Contaminated groundwater plume[2]	425	3.3

[1]: No replicate determination due to the collected volume of just 1 L after 1 h.
[2]: Historically contaminated with 1,1,2-trichloro-1,2,2-trifluoroethane (R113).

The TFA concentration levels at the investigated contaminated ground water sites are similar to those of surface water. The local geology displays a low permeability of barrier layers and hydrodynamic flow direction from the canal towards the ground water site. This, and the absence of CFCs containing the CF3-group in the ground water as a potential source for TFA, suggest a surface water origin of the TFA in the ground water.

III. CONCLUSIONS

The high TFA concentration in the first rainfall after a long dry period is consistent with a long accumulation period of air contaminants. The TFA concentration levels at the ground water sites and surface water are similar. The local geology and the absence of CFCs containing the CF_3-group in the

ground water as a potential source for TFA, suggest a surface water origin of the TFA in the ground water.

3. Assessment and conclusion

Assessment and conclusion by applicant:

Assessment:

This article from public literature reports monitoring results for TFA in rainwater, surface water and contaminated groundwater sites from Berlin, Germany. Measures taken to prevent contamination were not reported, and nor were control/field blanks, and the date and exact location of sampling was also not reported. The work wasn't carried out according to GLP, and there are currently no guidelines for the conduct of monitoring studies.

Conclusion:

The high TFA concentration in the first rainfall after a long dry period is consistent with a long accumulation period of air contaminants. The TFA concentration levels at the ground water sites and surface water are similar. The local geology and the absence of CFCs containing the CF_3-group in the ground water as a potential source for TFA, suggest a surface water origin of the TFA in the groundwater.

The information from this article can be regarded as supportive information.

Assessment and conclusion by RMS:

Outcome and conclusion of the study: RMS should indicate if they agree to the results and conclusions of the APPL.

1. Information on the published literature article

Data Point:	KCA 7.5/35
Report Author:	Joachim, J.; Karsten, N.; Heinz-Jurgen, B.; Christian, Z.; T, L. F.
Report Year:	2019
Report Title:	Robust trace analysis of polar (c2-c8) perfluorinated carboxylic acids by liquid chromatography-tandem mass spectrometry: method development and application to surface water, groundwater and drinking water
Report No:	M-765202-01-1
Document No:	M-765202-01-1
Guideline(s) followed in study:	not applicable
Deviations from current test guideline:	Current Guideline: not applicable
Previous evaluation:	No, not previously submitted
GLP/Officially recognised testing facilities:	No, not conducted under GLP/Officially recognised testing facilities
Acceptability/Reliability:	Yes

2. Full summary of KCA 7.5/35

Executive Summary

A simple and robust analytical method for the determination of perfluorinated carboxylic acids (PFCAs) with C_2 to C_8 chains, based on solid-phase extraction (SPE) and liquid chromatography-tandem mass spectrometry (LC-MS/MS), was developed, validated and applied to tap water, groundwater and surface

water. Two stationary phases for LC (Obelisc N and Kinetex C_{18}) and two materials with weak anion-exchange properties for SPE (Strata X-AW and Oasis WAX) were evaluated. Robust separation and retention was achieved with the reversed phase column and an acidic eluent.

SPE quantitative extraction recoveries were generally achieved for PFCAs with C greater than 3, however trifluoroacetate (TFA) extraction efficiencies were 14 to 99% using the Strata X-AW and 40 to 103% using the Oasis WAX. The sample pH was identified as a key parameter in the extraction process. One-step elution-filtration was introduced in the workflow, in order to remove sorbent particles and minimise sample preparation steps. Validation resulted in limits of quantification for all PFCAs between 0.6 and 26 ng/L. Precision was between 0.7 and 15% and mean recoveries ranged from 83 to 107%. In groundwater samples from sites impacted by per- and polyfluoroalkyl substances (PFASs), PFCA concentrations ranged from 0.056 µg/L (perfluoropropanoate (PFPrA)) to 2.2 µg/L (TFA). TFA was found in concentrations between 0.045 and 17 µg/L in drinking water, groundwater and surface water, not impacted by PFASs.

I. MATERIAL AND METHODS

Material

The aim of this study was to establish and validate a robust analysis method for short-chain PFCAs (C_2-C_8) in different types of aqueous samples. The analytical method was then applied to surface water, groundwater and drinking water samples with a focus on the occurrence of TFA compared to other PFCAs (C_3-C_8).

Sampling method

Water samples for validation purposes were taken from the in-house water supply (tap water), from a well in Karlsruhe (groundwater), from the Rhine river close to Karlsruhe (surface water) and bought at a supermarket (natural spring water), respectively. Surface water and groundwater samples were taken using amber glass bottles and were collected from the rivers Rhine (Lower Rhine, Middle Rhine, Upper Rhine), Danube, Neckar and Dreisam, from Lake Constance and its tributaries and from groundwater sampling sites in northern, central and southern Baden-Württemberg. Tap water samples were collected either in amber glass bottles or polypropylene bottles and were collected from private and public taps in northern and central Baden-Württemberg. Glass bottles were cleaned successively by rinsing with methanol (MeOH) and demineralised water and by pyrolysis at 550°C. Polypropylene bottles were rinsed with MeOH and demineralised water. Samples were stored at 4°C up to a maximum of 3 weeks before analysis.

The optimised SPE method was used for the analysis of surface water, groundwater and drinking water: Internal standards (12.5 ng of isotopically labelled TFA (TFA-M1) and 2 ng of each other isotopically labelled PFCA) and 0.25 mL MeOH were added to a 50 mL water sample and the pH adjusted to 3.9 ± 0.4. SPE cartridges (Oasis WAX, 6 mL) were placed on a vacuum and preconditioned. The sorbents were loaded with samples (ca. 1.0 - 1.5 mL/min flow rate) and dried in a gentle stream of nitrogen. Before elution of the analytes, the SPE cartridges were connected to regenerated cellulose syringe filters and placed on a vacuum manifold, which did not contain any fluoropolymer parts. The eluates were collected in 20-mL glass vials and blown down to dryness. The residues were dissolved in 0.4 mL of H$_2$O/MeOH solution (7:3, v/v) and transferred into 1.1 mL conical crimp glass vials for further analysis.

Analytical method

Liquid chromatography-mass spectrometry

All analyses were performed using an LC-MS/MS system coupled to a triple-quadrupole mass spectrometer via a two-position diverter valve. The MS was equipped with a Turbo V electrospray ionisation (ESI) source. Chromatographic separation was carried out using a Kinetex C_{18} column and a binary gradient. Additional LC separation experiments were performed with an Obelisc N column,

which is zwitterionic and combined the retention mechanisms of ion (IC), hydrophilic interaction (HILIC) and normal-phase chromatography.

Validation and quality control

As groundwater and surface water were expected to contain considerable amounts of TFA, natural spring water was used as the calibration matrix (background contamination approximately equals the decision limit (LOD)). The natural spring water samples were spiked; for each analyte two overlapping calibration functions with at least five points were used in a low (TFA: 10 to 250 ng/L) and a high concentration range (TFA: 200 to 1500 ng/L).

The working ranges for the analytes were estimated by direct injections of calibration standards. Due to observed matrix effects, the 'total method' working ranges, linearity and analytical limits were determined using calibration standards prepared in spring water, spring water aliquots were spiked at different analyte levels and the whole sample preparation procedure was applied. Linearity was evaluated applying least squares regression on ten equidistant concentration levels spanning the whole working range. The determination of LODs and LOQs were according to DIN 32645 using ten calibration standards (also equidistant levels) in the lower working range (10 to 200 ng/L for TFA). After linear regression, LOD and LOQ were deviated considering the residual standard deviation, method standard deviation and confidence levels of 95%. The analyte signals were used without blank correction in these calculations.

In the analysis of environmental samples, each series of 12 samples contained one procedural blank (demineralised water) for detection of blank contamination and at least one spiked spring water, tap water, groundwater or surface water sample for recovery measurements (control sample). Procedural blanks and recovery control samples were treated as per environmental samples. Instrumental performance was monitored by repeated injections (after every series of 12 samples) of another control sample and was considered acceptable as long as the deviation was less than 10% relative standard deviation (RSD).

Matrix effects were determined by the preparation of a series of six 'blank' samples for each matrix, five of which were spiked after the elution step with equidistant (Δ = 100 ng/L) concentration levels. The resulting calibration curves were used for the calculation of relative matrix effects based on slope ratios relative to a calibration curve with the same spiked concentration levels prepared in demineralised water.

PFASs dissolved in aqueous liquids have varying degrees of tendency to adsorb onto vessel walls e.g. glass or polypropylene. Impairment by such effects was not observed for the investigated analytes under the conditions of the study.

Method validation

LODs, LOQs and working ranges were determined for the individual PFCAs, as well as matrix effects, precision and mean recoveries in four different water matrices. The reporting limit (RL) was set based on the LOQ and precision data.

Precision and bias in tap water, groundwater and surface water were studied in repeatability and intermediate reproducibility experiments. Repeatability was determined using five aliquots of a sample (per matrix), which were spiked at the same concentration levels and prepared the same day. For determination of intermediate reproducibility (within-laboratory reproducibility), several variations were considered: Different days of sample preparation, different spiking levels and different real samples which were used for spiking. TFA repeatability experiments resulted in mean recoveries of 97 ± 0.7%, 99 ± 4.4% and 101 ± 1.4% for tap water, groundwater and surface water, respectively. The mean recoveries from the intermediate reproducibility experiments resulted 97 ± 0.7%, 99 ± 4.4% and 101 ± 1.4% for tap water, groundwater and surface water, respectively.

Procedural blanks were prepared from spring water with each series of environmental samples in order to monitor for blank contamination. For TFA, , there was a systematically occurring signal (below LOQ) in each blank due to the spring water matrix and the internal standard. This signal was integrated and monitored but no actions due to blank contamination were required during the period in which the analyses were carried out. The overall method performance was found suitable for the analysis of environmental samples.

TFA limits of detection (LOD) and quantification (LOQ): The demineralised water LOD and LOQ were 3.3 and 15 ng/L and the natural spring water LOD and LOQ were 5.5 and 26 ng/L, respectively.

TFA R^2 (linearity): 0.998.

TFA reporting limit (RL): 30 ng/L

II. RESULTS AND DISCUSSION

In groundwater samples taken from five polluted sampling sites in the state of Baden-Württemberg, Germany, all seven PFCAs were detected and ranged from 0.056 µg/L (PFPrA in GW 2) to 2.2 µg/L (TFA in GW 1), with TFA and PFOA being the predominant analytes (Figure 7.5- 34).

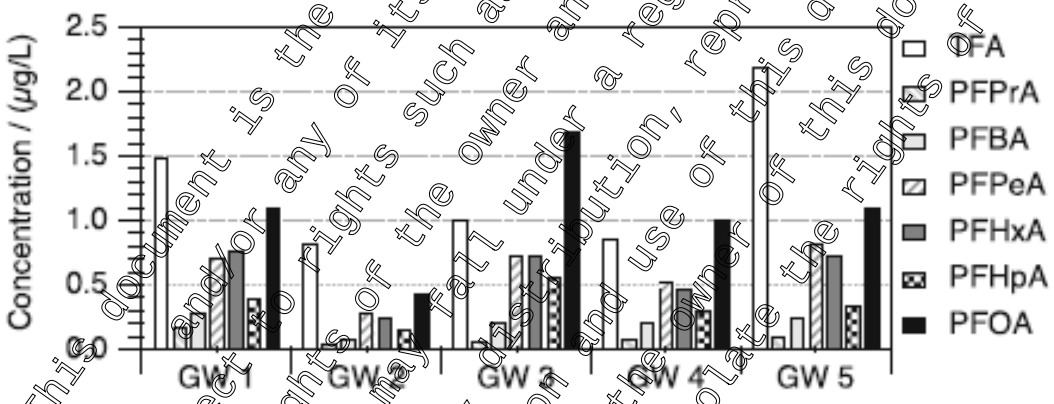


Figure 7.5- 34: Concentrations of PFCAs in five contaminated groundwater samples

The contamination sources at the sampled sites were not entirely elucidated, but further investigations revealed that paper chemicals played a major role. The concentration levels were generally higher than reported for background contamination due to diffuse sources and therefore point sources have to be taken into consideration.

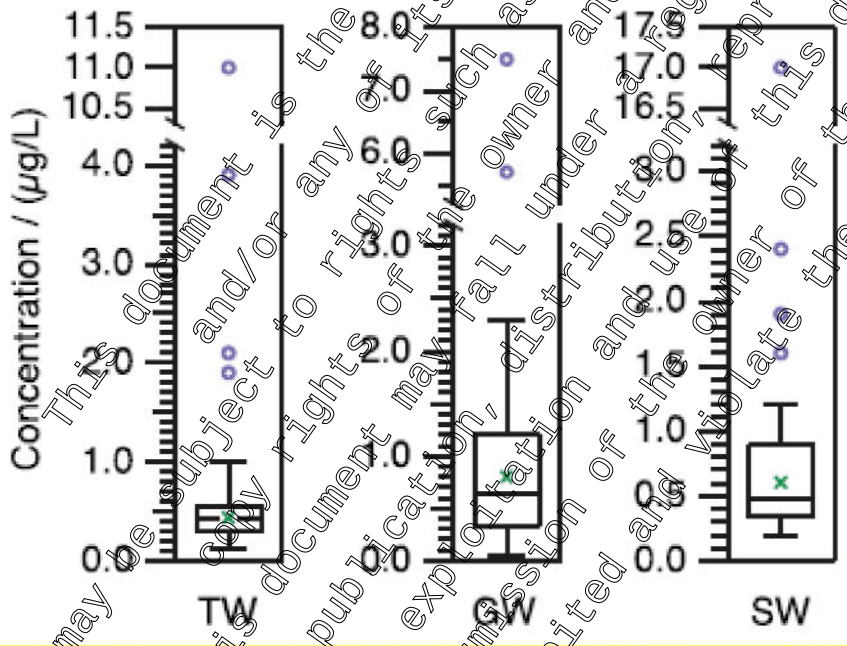
The decomposition of FT compounds ultimately lead to formation of PFCAs in a way, that an x:2 FT precursor with x being the number of perfluorinated C-atoms can yield PFCAs with C_{x+1}, C_x, C_{x-1} and C_{x-2}. Assuming that the contamination of the investigated groundwater samples was also related to the degradation of FT compounds, the distribution patterns shown in Figure 7.5- 34 have possibly been caused by a mixture of precursors with 8:2 FT, 6:2 FT and due to the presence of PFPrA 4:2 FT substructures. TFA can be derived from 4:2 FT precursors, though, considering the present PFPrA levels, TFA concentrations resulting from the degradation of PFASs would be expected to be lower than the measured concentrations.

The considerably higher spread of TFA concentrations (53% RSD) compared to PFBA and its higher homologues (≤ 24%) may indicate another TFA source e.g. from atmospheric deposition. Thus, a

contribution to the measured TFA levels resulting from the degradation of PFASs could neither be concluded nor excluded.

In the individual groundwater samples, the sum of the organofluorine fractions of TFA and PFPrA account for 17 to 35% compared to the sums of the organofluorine of all seven PFCAs. Thus, analysis of TFA and PFPrA (in addition to other PFASs) may partially fill the gap uncovered by analyses of 'extractable organic fluorine' (EOF) in water samples.

Due to the high levels of TFA in the PFAS-impacted groundwater, further water samples (tap water, groundwater, surface water) with no known PFAS contamination were analysed. In these samples, PFCAs other than TFA were typically below LOQ with a few exceptions. The measured TFA levels are displayed in Figure 7.5- 35, the results (arranged in groups according to water types) were not normally distributed and outliers were identified applying the Hampel test. Fifty percent of the investigated surface waters, mostly rivers, contained TFA between 0.48 and 1.2 µg/L, which is in the same order of magnitude, as other authors recently reported for Chinese surface water samples. In contrast, the upper 50% of concentrations in tap water (0.43 - 0.89 µg/L) and groundwater (0.64 - 2.3 µg/L) were considerably higher than concentrations reported earlier. Individual samples exhibited even higher microgram per litre levels e.g. 11 µg/L in tap water, 7.5 µg/L in groundwater and 17 µg/L in surface water and initiated investigations beyond this study, in which industrial discharges of TFA into the Neckar river were identified as the cause for the unusually high concentrations.



Tap water (n = 21), groundwater (n = 42) and surface water (n = 43). Outliers are marked as circles.

Figure 7.5- 35: TFA concentrations in tap water, groundwater and surface water

III. CONCLUSIONS

In groundwater samples from sites impacted by per- and polyfluoroalkyl substances (PFASs), PFCA concentrations ranged from 0.056 µg/L (perfluoropropanoate (PFPrA)) to 2.2 µg/L (TFA). TFA was found in concentrations between 0.045 and 17 µg/L in drinking water, groundwater and surface water, not impacted by PFASs.

3. Assessment and conclusion

Assessment and conclusion by applicant:

Assessment:
This article contains TFA groundwater monitoring (including sampling and analytical methodology) from sites impacted by per- and polyfluoroalkyl substances (PFASs) and TFA monitoring in drinking water, groundwater and surface water, not impacted by PFASs. The study was not conducted to GLP or other similar guidelines and there are currently no guidelines for the conduct of monitoring studies.

Conclusion:
In groundwater samples from sites impacted by per- and polyfluoroalkyl substances (PFASs), PFCA concentrations ranged from 0.056 µg/L (perfluoropropanoate (PFPrA)) to 2.2 µg/L (TFA). TFA was found in concentrations between 0.045 and 17 µg/L in drinking water, groundwater and surface water, not impacted by PFASs.

The information from this article can be regarded as reliable.

Assessment and conclusion by RMS:
Outcome and conclusion of the study: RMS should indicate if they agree to the results and conclusions of the APPL.

1. Information on the published literature article

Data Point:	KCA 7.5/36
Report Author:	Bjoernsdotter, M. K.; Yeung, L. W. Y.; Kaerrman, A.; Ericson Jogsten, I.
Report Year:	2020
Report Title:	Challenges in the analytical determination of ultra-short-chain perfluoroalkyl acids and implications for environmental and human health
Report No:	M-765262-01-1
Document No:	M-765262-01-1
Guideline(s) followed in study:	not applicable
Deviations from current test guideline:	Current Guideline: not applicable
Previous evaluation:	No, not previously submitted
GLP/Officially recognised testing facilities:	No, not conducted under GLP/Officially recognised testing facilities
Acceptability/Reliability:	Yes

2. Full summary of KCA 7.5/36

Executive Summary
The present review gives an overview of analytical methods and summarises the findings of potential analytical challenges regarding ultra-short-chain perfluoroalkyl acids (PFAAs), including trifluoroacetic acid (TFA). In addition, the current state of knowledge regarding TFA and other PFAAs has been reviewed. Both known and potential sources as well as environmental concentrations are summarized and discussed together with their fate and the environmental and human implications.

I. MATERIAL AND METHODS

Materials
The present review assesses and summarizes existing analytical methods and the potential analytical challenges for ultra-short-chain PFAAs, including TFA.

Analytical method

Table 7.5- 55 summarises analytical methodologies, quantification methods, extraction efficiencies and limits of detection and quantification used to determine TFA in various sample matrices by 5 authors.

Different extraction techniques included ion-exchange based methods or liquid-liquid extraction (LLE). The former allowed large-volume samples to be extracted and concentrated at the same time while the latter often required a concentration step by rotary evaporation. Furthermore, extraction of aqueous samples by WAXSPE allowed for simultaneous extraction of a wide range of PFASs including long-, short-, and ultra-short-chain PFAAs as well as neutral PFASs. The extraction time with WAX-SPE depended on volume of the sample and the sample matrix; filtration of water sample prior to extraction was needed when samples contained large amounts of particles and/or biological material. Concentration by rotary evaporation was a limiting factor for sample throughput.

Table 7.5- 55: Summary of analytical methods and method performance for quantification of ultra-short-chain PFAAs in water samples

Sample preparation	Separation detection technique	Quantification	Sample matrix	Sample volume (mL)	Instrument run time (min)	Extraction efficiency (%) based on matrix spike	LOD/ LOQ (ng/L)
Sample volume reduction to 50 mL by rotary evaporation at 55°C. Derivatization and salting-out LLE with ethyl acetate. Removal of water and evaporation to dryness at 30°C. Re-dissolution in benzene/toluene followed by volume reduction to 2 mL.	GC-MSD (SIM)	Internal standard calibration using ^{13}C-labeled trichloroacetic acid	Rain (n = 2) Snow (n = 3) Groundwater (n = 2) Surface water (n = 4) Subsurface water (n = 3) Drinking water (n = 3)	500 – 1000	40	89 ± 7	0.1 – 1[1]/–
Extraction by anion-exchange SR Empore disk, derivatization. Surface water samples with salinity > 500 µS were cleaned up by LLE prior to extraction	GC-ECD	External standard calibration	Rain (n = 2) Tap water (n = 2) Surface water (n = 6)	400	30	Rain 97 ± 4 Tap water 105 ± 0.3 Surface water 102 ± 4	32/36
WAX-SPE	Ion-exchange HPLC-MS/MS	Internal standard calibration using ^{13}C$_4$-PFBA and ^{13}C$_4$-PFOS	Rain (n = 4)	100	30	76 ± 9	–/0.5[2]
WAX-SPE	SFC-MS/MS		Rain (n = 2) Surface water (n = 2)	200	8	79 ± 10	–/ 0.2 - 0.5[2]
WAX-SPE after adjusting the pH to 3.8 - 4.0	RP-LC-ESI-MS/MS	Internal standard calibration using ^{13}C$_2$-TFA	Spring water (n = 1) Tap water (n = 21) Groundwater (n = 42) Surface water (n = 43)	50	20	Tap water 97 ± 0.7 Groundwater 99 ± 4 Surface water 101 ± 1	5.5/26[3]
Direct injection	SFC-MS/MS	Internal standard calibration using ^{13}C-PFBA	Surface water Groundwater Landfill leachate	0.25	11	81 ± 0.4	34[4]/–

LLE: Liquid-liquid extraction.

Analytical techniques developed for TFA have different strengths and limitations. GC separation offered increased performance compared with LC but the analyte needed derivatization, which increased the

time needed for sample preparation and added one chemical reaction that can affect the method recoveries and robustness. Using MS/MS over MS increased the selectivity and often the sensitivity since measuring product ions decreases the chemical noise. Supercritical fluid chromatography (SFC) was the most time-efficient separation technique reported and consumed relatively little organic solvent as the mobile phase mainly consisted of supercritical carbon dioxide with organic solvent added as modifier.

TFA can be expected to be ubiquitous in the atmosphere and blank concentrations can be expected to be high and varied between batches of samples. Investigations showed that TFA was present in ambient air, sulphuric acid and methyl tertbutyl ether that were used in the extraction. Many studies applied precautions during sample preparation, but few studies reported contamination sources. It is possible that a large contribution of TFA blank contamination originated from the ambient air and in that case, the contamination might depend on season and the diurnal cycle. Other potential sources included solvents, chemicals, laboratory equipment and consumables.

Environmental occurrence of TFA had been reported since the mid-1990s. A variety of different analytical methods (sample preparation and instrumental analysis) have been employed and the majority of data obtained without mass-labelled TFA as the internal standard, with surrogate standards such mass-labelled PFBA or trichloroacetic acid, or an external calibration curve used. Different extraction efficiencies and quantification methods made comparison of data difficult. Since TFA is a degradation product of volatile HFCs globally distributed, it can be expected to be found in the laboratory environment, precaution should be taken to ensure that any mass-labelled standard used is not contaminated with native TFA.

In the methods described in Table 7.5-1, extraction efficiencies were reported for TFA ranging from 76 ± 9% to 105 ± 4 in rain, with extractions efficiencies in other matrices falling between these values.

Limit of detection (LOD) and limit of quantification (LOQ): LOD range 0.1 - 34 ng/L; LOQ range 0.1 - 36 ng/L. However, the majority of studies have reported the LOD and/or LOQ based on the linear range of the instrument even if the concentration of TFA observed in the blank was not well below the LOQ of the instrument.

II. RESULTS AND DISCUSSION

Reported concentrations of TFA in precipitation and in surface water, using different analytical methods, are listed in Table 7.5- 56 and Table 7.5- 57.

TFA has been reported in precipitation at concentrations ranging from < 0.1 ng/L - 2.4 µg/L (measured near an urban area in the USA). TFA seemed to be ubiquitous in precipitation even at very remote sites. TFA was the most abundant PFCA in Japan, the USA and in Canada. In the precipitation collected in the USA and Canada, TFA was detected in all samples analysed (n = 196). A 17-fold increase from 23 - 98 ng/L to 345 - 828 ng/L was observed for TFA concentrations in urban landscape waters in China between 2002 and 2012, which indicated that the environmental concentrations of TFA are increasing, likely as a result of the introduction of HFCs after the phase out of ozone depleting chlorofluorocarbons (CFCs).

In surface water, the concentration of TFA ranged from < 0.5 ng/L - 140 µg/L (observed in a river downstream from a chemical industry producing fluorinated chemicals). Higher concentrations of TFA were observed in surface waters in industrialised areas compared to less industrialized areas. Concentrations of TFA were also reported in groundwater (< 5 ng/L - 7.5 µg/L), ocean water (1 – 250 ng/L), fog water (20 ng/L - 2.2 µg/L), in municipal (90 - 600 ng/L) and industrial wastewater effluent (< 100 ng/L - 206 µg/L), in air (10 ng/L - 6.3 µg/L), in drinking water (16 ng/L - 11 µg/L), in soil (< 0.1 - 9.4 ng/L) and conifer needles (< 2 - 420 ng/L). [It should be noted that the highest levels

reported in water (e.g. 11 µg/L in tap water, 7.5 µg/L in groundwater and 17 µg/L in surface water) were found to be due to industrial point source contamination (see M-765202-01-1)].

Atmospheric concentrations of TFA have been shown by other authors to be higher in spring/summer compared with autumn/winter and that airborne TFA measured in the north of China peaked in the afternoon and reached a minimum during early morning, following a diurnal cycle. These findings suggest that degradation of volatile precursors is a major source of airborne TFA.

Table 7.5- 56: Reported concentrations of TFA in precipitation using different analytical techniques

Sampling year	Country	Number of samples (*n*)	Concentration range (ng/L)	Analytical technique
1995 – 1996	Germany	20	10 – 410	Derivatization, LLE, GC-MS
1996	Poland	4	26 – 1100	Rotary evaporation, derivatization, GC-MS
1996	Ireland	8	2 – 92	Rotary evaporation, derivatization, GC-MS
1996 – 1997	The USA	60	20 – 760	Anion-exchange SR Empore disk, derivatization, HS-GC-ECD
1996 – 1997	Switzerland	73	< 3 – 1600	LLE, derivatization, GC-MS
1997	The USA	1	215 – 230	Anion-exchange SR Empore disk, derivatization, HS-GC-ECD
1999	Canada	7	< 0.1 – 170	Rotary evaporation, derivatization, LLE, GC-MS
1999	Malawi	1	4 – 15	Rotary evaporation, derivatization, LLE, GC-MS
1999	Canada	3	< 0.5 – 230	Rotary evaporation, derivatization, LLE, GC-MS
1999	Chile	2	5 – 87	Rotary evaporation, derivatization, LLE, GC-MS
2001 – 2002	China	12	25 – 240	Rotary evaporation, derivatization, HS-GC-ECD
1998 – 2004	The USA and Canada	206	3 – 2400	Rotary evaporation, derivatization, LLE, GC-MS
2007	Japan	4	39 – 76	WAX-SPE, ion-exchange HPLC-MS/MS
2007 – 2008	China	32	46 – 970	Rotary evaporation, derivatization, LLE, GC-MS
2012	China	2	280 ± 68	Rotary evaporation, derivatization, LLE, GC-MS

LLE: Liquid-liquid extraction; HS, headspace.

Table 7.5- 57: Reported concentrations of TFA in surface water using different analytical techniques

Sampling year	Country	Number of samples (*n*)	Concentration range (ng/L)	Analytical technique
1995 – 1996	Germany	47	10 – 630	Derivatization, LLE, GC-MS
1995	Austria	3	55	Derivatization, LLE, GC-MS
1995	Israel	9	200 – 2400	Derivatization, LLE, GC-MS
1996	Russia	3	35	Derivatization, LLE, GC-MS
1996	Brazil	3	< 15	Derivatization, LLE, GC-MS
1996	Finland	4	210	Derivatization, LLE, GC-MS
1996	South Africa	21	15 – 500	Derivatization, LLE, GC-MS
1995	Ireland	10	< 10 – 70	Derivatization, LLE, GC-MS
1995	France	3	250	Derivatization, LLE, GC-MS
1996	Australia	3	200	Derivatization, LLE, GC-MS
1996 – 1997	The USA	66	13 – 470	Anion-exchange SR Empore disk, derivatization, HS-GC-ECD[1]
1997	Canada	14	< 0.5 – 360	Rotary evaporation, derivatization, LLE, GC-MS
1996 – 1997	Switzerland	102	12 – 360	LLE, derivatization, GC-MS
1997	The USA	3	51 – 86	Anion-exchange SR Empore disk, derivatization, HS-GC-ECD[1]
1998 – 2000	Africa	5	1 – 5	Rotary evaporation, derivatization, LLE, GC-MS
1998 – 2000	The USA and Canada	8	51 – 99	Rotary evaporation, derivatization, LLE, GC-MS
2001	China	17	6.8 – 220	Rotary evaporation, derivatization, HS-GC-ECD
2012	China	5	350 – 830	Rotary evaporation, derivatization, LLE, GC-MS
2016	Germany	25	5400 – 140000	Direct injection ion-exchange LC-MS/MS
–	Germany	48	Up to 17000	WAX-SPE, mixed-mode ion-exchange HPLC-MS/MS
2017 – 2018	Sweden	8	< 34 – 2700	Direct injection SFC-MS/MS

[1]: Samples with conductivity > 500 µS were cleaned up by LLE prior to extraction.

Atmospheric degradation of HFCs and HCFCs result in formation of TFA. Measurements of TFA in the environment, mainly in precipitation and surface waters, have revealed that the observed environmental concentrations cannot be explained by the degradation of HFCs and HCFCs alone. Furthermore, HFCs used in other applications besides cooling agents may also play a role in the environmental concentrations of TFA, as TFA is a degradation product of 2Hheptafluoropropane (HFC-227ea) used in fire extinguishers. Formation of TFA can also occur via oxidation of precursor compounds, such as n:2 fluorotelomer alcohols (FTOHs), that are major raw materials used in surfactant and surface protecting products; perfluoroalkane sulphonamide derivatives having four perfluorinated carbon atoms (e.g., perfluorobutane sulfonamide, FBSA) and N-methyl perfluorobutane sulfonamidoethanol (N-MeFBSE), which is used as stain protectants for carpets, fabrics, and paper products. Atmospheric concentrations of TFA has been shown to be higher in spring and summer compared with autumn and winter, and the airborne TFA measured in the north of China peaked in the afternoon and reached a minimum during early morning, following a diurnal cycle. These findings suggest that degradation of volatile precursors is a major source of airborne TFA. TFA may also be formed during thermolysis of fluoropolymers in industrial and consumer products. Other potential sources of TFA include industrial wastewaters, hazardous waste management facilities, landfills, and firefighting training sites.

III. CONCLUSIONS

TFA has been detected in many different aqueous based compartments in the environment. The many sources of environmental TFA include atmospheric degradation of HFCs and HCFCs, products in fire extinguishers, thermolysis of fluoroploymers, industrial wastewaters, hazardous waste management facilities, landfills and firefighting training sites.

3. Assessment and conclusion

Assessment and conclusion by applicant:

Assessment:

This paper from public literature is a review of other published environmental monitoring studies. The strengths and limitations of the analytical and quantification methodologies are discussed. No guidelines exist for monitoring studies.

Conclusion

TFA is ubiquitous in precipitation, even in remote areas, with reported concentrations ranging from < 0.1 ng/L to 2.4 µg/L. A 17-fold increase from 23 - 98 ng/L to 345 - 828 ng/L was observed for TFA concentrations in urban landscape waters in China between 2002 and 2012, which indicated that the environmental concentrations of TFA are increasing, likely as a result of the introduction of HFCs after the phase out of ozone depleting chlorofluorocarbons (CFCs).

In surface waters, the concentration of TFA ranged from < 0.5 ng/L to 140 µg/L. Higher concentrations of TFA have been observed in surface waters in industrialized areas. Concentrations of TFA were also reported in groundwater (< 5 ng/L - 7.5 µg/L), ocean water (1 - 250 ng/L), fog water (20 ng/L - 2.2 µg/L), in municipal (90 - 600 ng/L) and industrial wastewater effluent (< 100 ng/L - 206 µg/L), in air (10 ng/L - 6.3 µg/L), in drinking water (16 ng/L - 11 µg/L), in soil (< 0.1 - 9.4 ng/L) and conifer needles (< 2 - 420 ng/L). [It should be noted that the highest levels reported in water (e.g. 11 µg/L in tap water, 7.5 µg/L in groundwater and 17 µg/L in surface water) were found to be due to industrial point source contamination (see M-765202-01-1).

The many sources of environmental TFA include atmospheric degradation of HFCs and HCFCs, products in fire extinguishers, thermolysis of fluoroploymers, industrial wastewaters, hazardous waste management facilities, landfills and firefighting training sites.

The information from this article can be regarded as reliable.

Assessment and conclusion by RMS:

Outcome and conclusion of the study. RMS should indicate if they agree to the results and conclusions of the APPL.

1. Information on the published literature article

Data Point:	KCA 7.5/37
Report Author:	Holland, R.; Khan, M. A. H.; Driscoll, I.; Chhantyal-Pun, R.; Derwent, R. G.; Taatjes, C. A.; Orr-Ewing, A. J.; Percival, C. J.; Shallcross, D. E.
Report Year:	2021
Report Title:	Investigation of the production of trifluoroacetic acid from two halocarbons, hfc-134a and hfo-1234yf and its fates using a global three-dimensional chemical transport model
Report No:	M-765301-01-1
Document No:	M-765301-01-1
Guideline(s) followed in study:	not applicable
Deviations from current test guideline:	Current Guideline: not applicable
Previous evaluation:	No, not previously submitted
GLP/Officially recognised testing facilities:	No, not conducted under GLP/Officially recognised testing facilities
Acceptability/Reliability:	Yes

2. Full summary of KCA 7.5/37

Executive Summary

Trifluoroacetic acid (TFA), a highly soluble and stable organic acid, is photochemically produced by certain anthropogenically emitted halocarbons such as HFC-134a and HFO-1234yf. Both of these halocarbons are used as refrigerants in the automobile industry, and the high global warming potential of HFC-134a has promoted regulation of its use, with industries transitioning to the use of HFO-1234yf as a more environmentally friendly alternative. The environmental effects of this change suggest a 33-fold increase in the global burden of TFA from an annual value of 65 tonnes formed from the 2015 emissions of HFC-134a to a value of 2220 tonnes formed from an equivalent emission of HFO-1234yf. The percentage increase in surface TFA concentrations resulting from the switch from HFC-134a to HFO-1234yf remains substantial with an increase of up to 250-fold across Europe. The increase in emissions greater than the current emission scenario of HFO-1234yf is likely to result in significant TFA burden as the atmosphere is not able to disperse and deposit relevant oxidation products. The Criegee intermediate initiated loss process of TFA reduces the surface level atmospheric lifetime of TFA by up to 5 days (from 7 days to 2 days) in tropical forested regions.

I. MATERIAL AND METHODS

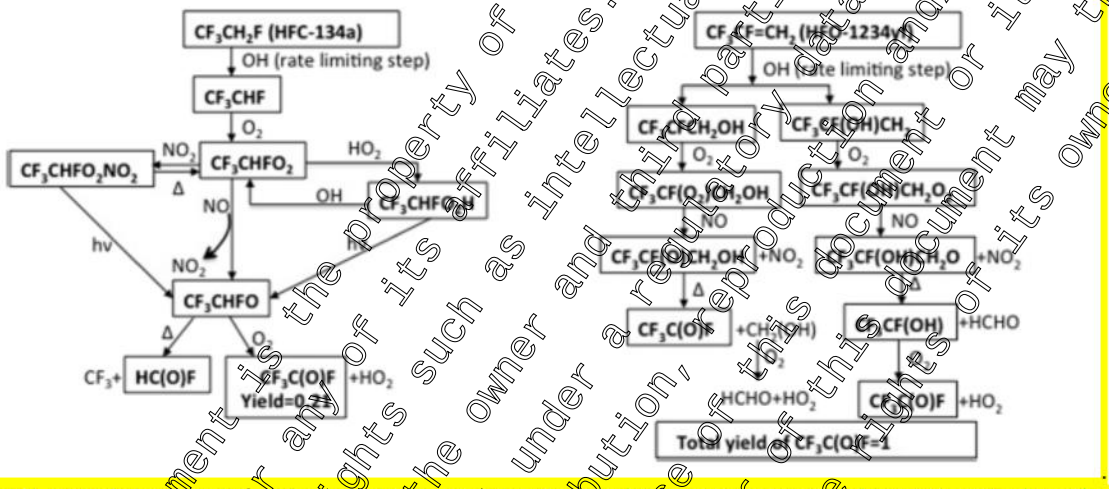
Material

This study examined the effect of the transition from use of HFC-134a to HFO-1234yf on atmospheric TFA formation, distribution, and deposition, and investigated the mechanisms by which TFA was lost from the atmosphere.

Analytical method

STOCHEM-CRI, a 3D tropospheric chemical transport model, operates such that chemistry and transport processes are uncoupled (allowing timesteps to be determined locally) and is driven by archived meteorological data from the UK Meteorological Office (Met. Office). The “offline” model functions at the atmospheric resolution of the Met. Office unified model (1.25° longitude × 0.83° latitude × 12 uneven vertical levels). The data outputs include: pressure, temperature, humidity, interpolated wind data, tropopause height, cloud amount, precipitation, boundary layer height, and surface parameters.

In this study, the reduced chemical CRI mechanism was utilized. Optimisation of this reduced mechanism was achieved using Master Chemical Mechanism 3.1 (MCM v3.1) with ozone generation as the key principle. OH initiated oxidation mechanisms of HCF-134a and HFO-1234yf (Figure 7.5-36) and TFA were added in the CRI mechanism. HCF-134a and HFO-1234yf reacted with OH at distinct rates of 7.3×10^{-13} exp(−1540/T) and 1.26×10^{-12} exp(−35/T) cm^3/s, respectively. TFA formation from the degradation mechanisms for both HFC-134a and HFO-1234yf went via $CF_3C(O)F$ formation with yields of 0.21 and 1, respectively, followed by hydrolysis. As the secondary chemistry/partitioning was fast, 100% TFA formation from $CF_3C(O)F$ was assumed. The main differences between the TFA formation paths from the two degradation mechanisms were the initiation step and the branching ratios of the final products (investigated in this study). Following the inclusion of the oxidation mechanisms of HFC-134a/HFO-1234yf and TFA, the air parcels in the model contained concentrations of 231 individual species that competed in 531 chemical reactions.



For HFO-1234yf, the formation of organic hydroperoxides (reaction between a peroxy radical and HO_2 radicals) and peroxy nitrates (reaction of peroxy radicals with NO_x) from the OH-initiated oxidation products and their fates, occur in the same way as shown for HFC-134a but are not shown in the diagram.

Figure 7.5-36: Degradation mechanisms of HFC-134a and HFO-1234yf oxidation by OH

The addition of Criegee intermediate chemistry to the CRI mechanism involved the inclusion of 17 individual SCIs along with explicit formation and loss processes. The added chemistry included: formation reactions of SCIs from their parent alkenes, unimolecular decomposition of SCIs, and bimolecular reactions of SCIs with water (and water dimer). As all SCIs included were expected to have similar reaction rates with TFA, all individual SCIs were grouped into a singular class labelled "SCI". This class accounted for the total concentration of all the included SCIs and assumed a consistent rate coefficient for all SCIs with TFA (3.4×10^{-10} cm^3/s). Following the inclusion of the Criegee intermediate chemistry, each air parcel now contained concentrations of a total of 248 species that competed in 578 chemical reactions and utilised a timestep of 5 min. Further addition of the hydroperoxyester product (termed HETFA) from the reaction of TFA and SCIs and its reactions (considered the same for all HETFA) was implemented in the model.

Global anthropogenic emission fluxes for HFC-134a of 0.21 Tg/yr were taken from the Department for Business, Energy and Industrial Strategy (BEIS) report for the year 2015 and as a full transition in use was assumed, were taken to be the same for HFO-1234yf. Atmospheric TFA production was modelled only as a result of degradation of these hydrocarbons (i.e., no biogenic TFA emissions or direct anthropogenic emissions were included). Emissions of HFC-134a and HFO-1234yf from anthropogenic sources (industrial process and product use) were distributed using an annual source map of HFC-134a for the year 2010 at a resolution of 5° longitude by 5° latitude extracted from EDGARv4.2 with a resolution of 0.1° longitude by 0.1° latitude. As the distribution over China was poor in the EDGAR

emission inventory, collected HFC-134a emission distribution for China was merged with the EDGAR emission inventory to derive a more accurate global distribution of HFC-134a. The emission totals of the other species employed in STOCHEM were adapted from the Precursor of Ozone and their Effects in the Troposphere (POET) inventory.

Physical deposition processes were accounted for where relevant. Dynamic and convective scavenging coefficients were calculated using the correlation between Henry's Law constant and scavenging coefficient. Excluding a brief sensitivity analysis, TFA was represented using a dry deposition velocity (over land and sea), dynamic scavenging coefficient, and convective scavenging coefficient of 1.9 m/s, 1.9 cm^{-1}, and 3.8 cm^{-1}, respectively. Depositions of HFC-134a and HFO-1234yf were not included as these processes were not expected to be significant given the high volatilities of the species.

In this investigation, six key simulations (STO-HFC, STOHFC-SCI, STO-HFC-HETFA, STO-HFO, STO-HFO-SCI and STO-HFO-HETFA) were performed. A collection of the basic features of each simulation and the differences between them can be found in Table 7.5- 58. "STO-HFC" and "STO-HFO" employed the addition of an emission inventory of HFC/HFO as well as their atmospheric fates in the CRI mechanism. The fates of TFA (reaction with OH, dry deposition, and wet deposition) were also accounted for in these simulations. All subsequent simulations (STO-SCI and STO-HETFA) included the addition of Criegee intermediate chemistry. The STO-HETFA simulations included the explicit atmospheric fates (e.g. OH oxidation, dry deposition, and wet deposition) of the SCI-mediated HETFA. Each simulation was run with meteorological data from 1997/98 for a period of 24 months with the first 12 months discarded.

Table 7.5- 58: Details of each simulation

Simulation (STO-)	Total species	Additional species	Number of gas phase reactions	Criegee field included (Y/N)	Additional reactions/physical processes
HFC	231	HFC, TFA	531	N	OH + HFC → $CF3COF^{1}$ + HO_2 + HF OH + TFA → P1 TFA → dry deposition TFA → wet deposition
HFC-SCI	248	SCIs[2]	578	Y	SCI + TFA → P2
HFC-HETFA	249	HETFA	580	Y	SCI + TFA → HETFA[2] HETFA + OH → CO2 + HF HETFA+ OH → TFA + HCOOH HETFA → dry deposition HETFA→ wet deposition
HFO	231	HFO, TFA	531	N	OH + HFO → CF_3COF^{2} + HO_2 + HCHO OH +TFA → P1 TFA → dry deposition TFA → wet deposition
HFO-SCI	248	SCIs[2]	578	Y	SCI + TFA → P2
HFO-HETFA	249	HETFA	580	Y	SCI + TFA → HETFA[3] HETFA + OH → CO2 + HF HETFA + OH → TFA + HCOOH HETFA → dry deposition HETFA → wet deposition

[1]: Assuming 100% conversion of TFA from CF_3COF.
[2]: SCIs represent the "Criegee Field".
[3]: The reaction product "P2" has been replaced by "HETFA".

II. RESULTS AND DISCUSSION

TFA global budget
The only source of TFA was via "Chemical Production" which refers to oxidation of HFC-134a or HFO-1234yf in the foremost simulations (STO-HFC, STO-HFO, STO-HFC-SCI, and STO-HFO-SCI) with the addition of TFA production via the degradation of HETFA in the final simulations (STO-HFC-HETFA and STO-HFO-HETFA).

The global burdens of TFA across the simulations (Table 7.5- 59) followed a similar trend where the "STO-HFC" simulated outcomes were consistently around 3% of their "STO-HFO" counterparts, not surprising given the increased rate and yield of TFA formation from the oxidation of HFO-1234yf compared with HFC-134a. These results suggested the transition to HFO-1234yf from HFC-134a (assuming consumption is matched) would generate a 33-fold increase in the global atmospheric TFA burden, corresponding to over 2150 tonnes of TFA. Successive simulations for each precursor had significant effects on the overall global burden of TFA (Table 7.5- 59). The addition of Criegee intermediate reactive loss gave a global burden reduction of TFA by ca. 0.6 and 15 tonnes in the STO-HFC-SCI and STO-HFO-SCI scenarios, respectively. Globally, SCI-mediated oxidation was shown to account for only ca. 0.4% of the total loss, meaning that deposition processes accounted for a much more significant overall removal, which was not unexpected given that SCI oxidation reactions are not significant at high altitudes, as SCIs do not form in significant quantities at low pressures. Whereas physical processes may operate across a wider zonal range resulting in an increased tropospheric average deposition loss. As such, it was important to consider SCI-mediated loss processes at the surface level where their contributions were likely to be more significant. Furthermore, OH-initiated HETFA degradation to TFA only represented a minor route to atmospheric TFA production (ca. 0.13% in relevant simulations). Thus, inclusion of the atmospheric fate of the SCI-mediated oxidation product, HETFA, does not have a significant effect on the overall global burden of TFA.

Table 7.5- 59: Global budget of TFA from successive simulations

	STO-HFC	STO-HFC-SCI	STO-HFC-HETFA	STO-HFO	STO-HFO-SCI	STO-HFO-HETFA
Production process						
Chemical production (Gg/yr)	7.77	7.77	7.78	207.30	207.30	207.57
Loss processes						
OH removal (Gg/yr)	0.48	0.48	0.48	12.96	12.94	12.95
SCI removal (Gg/yr)	N/A	0.03	0.03	N/A	0.84	0.84
Dry deposition (Gg/yr)	0.58	0.57	0.57	23.83	23.74	23.78
Wet deposition (Gg/yr)	6.70	6.68	6.69	170.33	169.59	169.76
Global burden (tonnes)	65.72	65.15	65.16	22.35×10^2	22.20×10^2	22.22×10^2

N/A: Not applicable.

Impact of transition from HFC-134a to HFO-1234yf on TFA surface concentration

Surface distribution plots showed high TFA concentrations closer to the equator and northern mid latitudes produced from HFC-134a and HFO-1234yf, which were in good agreement with other modelling studies both in concentration magnitudes and spatial distributions. With the industrial productions of HFC-134a and HFO-1234yf predominantly between 30°N and 60°N and with OH abundances highest in the tropics, the peak levels of TFA reached up to 0.05 and 3 ppt from the oxidation of HFC-134a and HFO-1234yf, respectively. Growth in absolute TFA concentration following the transition to HFO-1234yf usage, showed the most significant increases occurred in the mid latitudes due to an increase in OH oxidation productivity.

Despite accounting for an additional loss process for TFA by the reaction with Criegee intermediates, this investigation showed that a transition from HFC-134a to HFO-1234yf use would result in a significant overall increase in tropospheric TFA as loss processes cannot compensate sufficiently. As such, natural cycles of TFA and the proportions that reside in air, land, and sea reservoirs will be altered as environmental contamination increases. Even with consideration of the effects of SCIs, the percentage increase in tropospheric TFA resulting from the switch to HFO use remains substantial, with a maximum 250-fold increase in the northern hemisphere. As a result of the more rapid degradation of HFO-1234yf compared with HFC-134a, the transition not only increases the global burden of TFA but also concentrates it over landmass, most notably the northern hemisphere, although significant increases (up to 50-fold) were also seen in regions of the southern hemisphere.

Impact of Criegee intermediate loss on the regional lifetime of TFA

Removal of TFA by OH is generally accepted to be a minor loss process, giving a lifetime of around 4 months, whereas wet deposition is expected to be the most significant loss process, with a corresponding lifetime close to 9 days. This investigation predicted a global TFA lifetime of 5 - 10 days, with the spatial variation shown in Figure 7.5- 37. The shorter predicted surface TFA lifetime from this investigation was a consequence of the inclusion of the Criegee intermediate reactive loss. A recent author showed that the inclusion of SCIs may result in an TFA atmospheric lifetime as short as 4 days over forested regions. The model predictions presented, with Criegee intermediate chemistry, showed that this lifetime may be as little as 2 days over forested regions, such as the Amazon and Congo (Figure 7.5- 37b). Although the global tropospheric lifetime of TFA was consistent between simulations, the addition of the updated Criegee intermediate chemistry resulted in significant regional surface lifetime reductions. SCIs exist in the greatest concentrations over forested regions, where biogenic alkene emissions are high, and thus significant impacts on TFA lifetimes are seen over the Amazon, boreal, and Congo forests, as shown in Figure 7.5- 37.

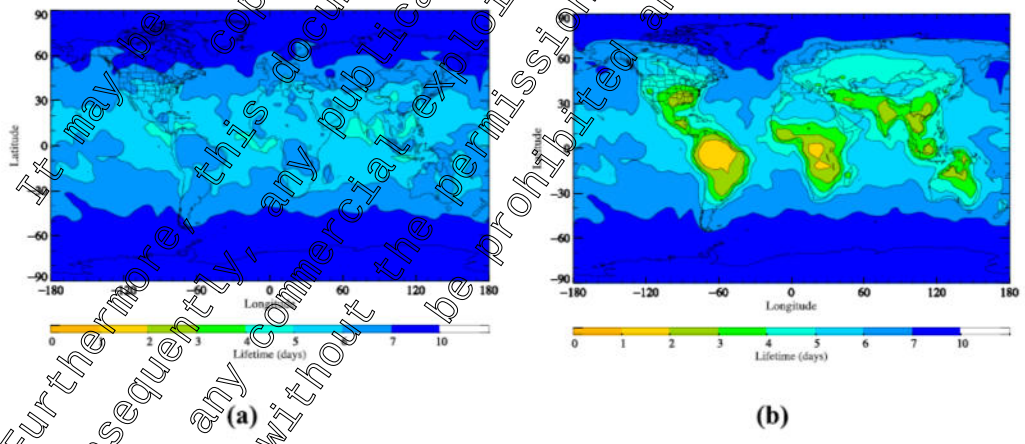


Figure 7.5- 37: Surface level distribution plots depicting the lifetime of TFA with respect to (a) OH removal and deposition processes only and (b) OH removal, deposition processes, and removal by SCIs (extracted from the STO-HFC-SCI simulation)

SCI-mediated loss of TFA was significant over land masses, but was mostly negligible over water and ice-covered regions. Large reductions of up to ca. 5 days were seen over parts of South America and central Africa, which are covered by tropical rainforests (Figure 7.5- 37). Significant reductions of ca. 3 days were also seen over the boreal forests of Canada and Russia, as well as the forest regions of Australia and Southeast Asia (Figure 7.5- 37). The implication of this finding is a more concentrated loss of TFA in some regions than would previously have been suggested.

Formation of HETFA and its impact on TFA concentration

The reaction of TFA with SCIs may only temporarily remove TFA from the atmosphere as some of the reaction products formed can degrade by OH-initiated oxidation to regenerate TFA. This possibility was investigated in the STO-HFC-HETFA and STO-HFO-HETFA simulations, which included consideration of the atmospheric fates of the SCI-mediated oxidation products of TFA. The further oxidation of the SCI-mediated oxidation product, HETFA, did not have an overall significant effect on the atmospheric concentration or distribution of TFA. However, it was important to consider the condensed phase hydrolysis of HETFA, reforming TFA that can then partition into the gas phase. The deposition losses of HETFA (15 tonnes/yr for STO-HFC-HETFA and 468 tonnes/yr for STO-HFO-HETFA) are comparatively higher than the chemical loss processes which could be responsible for the regeneration of TFA by biological degradation in the aqueous phase, but the contribution to TFA abundances from this process could not be accounted for with the current model. As rapid reactions of TFA with SCIs are the dominant sink over biodiverse forested areas.

Impact of increased dry deposition on TFA concentration

Dry deposition fluxes of TFA were modelled as an upper limit to investigate the impact of this loss mechanism on tropospheric TFA levels under the future emission scenario for HFO-1234yf. A dry deposition velocity of 0.43 cm/s was employed in these simulations, hereafter referred to as "STO-HFC-SCI-DD and STO-HFO-SCI-DD". The global burden of TFA was reduced by 6.9 and 7.3% when operated under maximum deposition velocities compared with STO-HFC-SCI and STO-HFO-SCI simulations, respectively. An increase in the contribution of dry deposition to overall TFA loss was also observed (ca.14 − 20% in STO-HFC-SCI-DD and STO-HFO-SCI-DD as opposed to ca. 8 − 12% in STO-HFC-SCI and STO-HFO-SCI simulations), along with a corresponding decrease in the contributions of other loss processes. Deposition fluxes in this integration were significantly higher than those previously reported in the literature due to the implementation of a greater deposition velocity. The increased dry deposition flux of TFA from 0.19 to 0.43 cm/s decreased its global surface level by between 5 and 40%, with the most significant reductions occurring in the tropical region. However, the greater dry deposition of TFA into oceans could have an impact on the environment due to its high solubility, accumulation, and persistence in aqueous phases.

III. CONCLUSIONS

A 33-fold increase (equivalent to ca. 2160 tonnes) in global atmospheric TFA burden was predicted following a complete transition from HFC-134a to HFO-1234yf. Criegee intermediate chemistry was shown to result in minor contributions to overall global TFA loss, although more significant regional effects were seen when considering only the surface layer. Despite inclusion of these previously neglected loss processes, the HFC-134a to HFO-1234yf transition resulted in significant global increases of surface level TFA (i.e. a maximum 250-fold increase over Europe) as loss processes could not compensate with the increase in emissions of TFA precursors. The atmospheric lifetime of surface level TFA was predicted to be between 5 and 9 days, whereas inclusion of the Criegee intermediates sees the TFA lifetime decrease to as little as 2 days over areas with significant SCI-mediated loss (i.e. the terrestrial tropics).

Using a model to assess increased emission scenarios suggested that a significantly greater global TFA burden would accompany the transition to HFO-1234yf.

3. Assessment and conclusion

Assessment and conclusion by applicant:

Assessment:

This article from public literature reports a fate modelling study for atmospheric TFA production considering a transition of use from HFC-134a to HFO-1234y using the STOCHEM-CRI chemical transport model. The model had been parameterised to consider the impact of stabilised Criegee intermediates on the atmospheric fate of organic acids. There are currently no guidelines for the conduct of global modelling studies available..

Conclusion:

A 33-fold increase of TFA is predicted following a complete transition of use from HFC-134a to HFO-1234y, equivalent to ca. 2150 tonnes at the global scale. The atmospheric lifetime of surface level TFA is predicted to be between 5 and 9 days, whereas inclusion of the Criegee intermediates sees the TFA lifetime decrease to as little as 2 days over areas with significant SCI-mediated loss. A first approach using a model to assess increased emission scenarios suggests that a significantly greater global TFA burden will accompany the transition to HFO-1234y.

The information from this article can be regarded as reliable.

Assessment and conclusion by RMS:

Outcome and conclusion of the study: RMS should indicate if they agree to the results and conclusions of the APPL.