Bayer CropScience

Document Title

Summary of the fate and behaviour in the environment for Flufenacet

Data Requirements

EU Regulation 1107/2009 & EU Regulation 283/2013

Document MCA

Section 7: Fate and behaviour in the environment

According to the guidance document, SANCO 10181/2013, for preparing dossiers for the approval of a chemical active substance

Date

2014-03-19

Author(s)

[redacted]

Bayer CropScience

M-482174-01-2

OWNERSHIP STATEMENT

The summaries and evaluations contained in this document are based on unpublished proprietary data submitted for the purpose of the assessment undertaken by the regulatory authority.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authorities should not grant, amend, or renew a registration on the basis of the summaries and evaluation of unpublished proprietary data contained in this document unless they have received the data on which the summaries and evaluation are based, either: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 CropScience; or**
- **From other applicants once the period of data protection has expired.**

Version history

Date	Data points containing amendments or additions[1] and brief description	Document identifier and version number

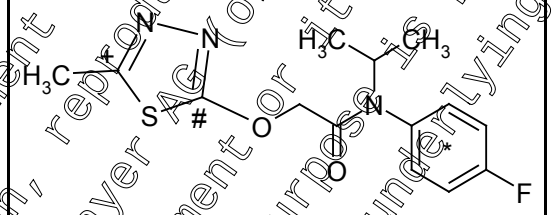
[1] It is suggested that applicants adopt a similar approach to showing revisions and version history as outlined in SANCO/10180/2013 Chapter 4 How to revise an Assessment Report

Table of Contents

CA 7 FATE AND BEHAVIOR IN THE ENVIRONMENT

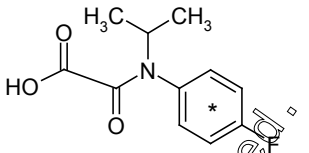
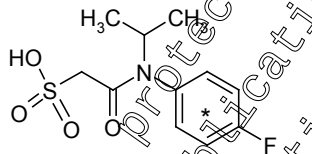
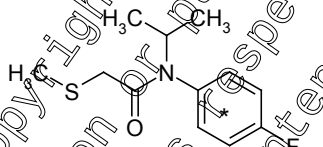
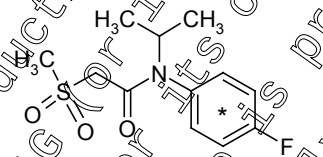
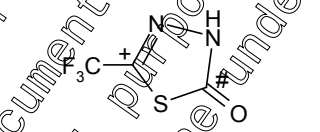
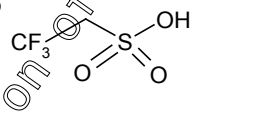
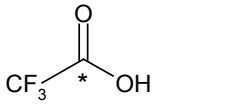
Data on the fate and behavior of flufenacet (FOE 5043) in soil, water, sediment and air were submitted within the EU Dossier (Baseline Dossier), which resulted in the Annex I inclusion under Directive 91/414/EEC in 2003. In the Supplemental Dossier for renewal of approval of flufenacet presented here only those environmental fate studies are described in sections 7.1 to 7.5 which were not submitted within the Baseline Dossier. However, for a better understanding of the behavior of flufenacet in soil, water and sediment and air, short summaries including the results of all environmental fate studies are given additionally in this summary in sections CA 7.1, CA 7.2, CA 7.3. In order to facilitate discrimination between new studies and studies submitted within the Baseline Dossier, the studies submitted with the last Annex I inclusion process of flufenacet are written in grey letters.

The studies concerning the fate and behavior of flufenacet in the environment were conducted using either [phenyl-UL-^{14}C]-, [thiadiazole-2-^{14}C]- or [thiadiazole-5-^{14}C]-labeled flufenacet, as well as unlabeled flufenacet as test item. These radiolabel positions are considered sufficient to define the route of degradation of flufenacet. The structure of flufenacet and the positions of the different radiolabels are depicted below:

Report Name **(Codes and Synonyms)**	**Chemical Structure**	**Radiolabel Positions**
flufenacet (FOE 5043, FFA; formerly: thiafluminde)		* [phenyl-UL-^{14}C] # [thiadiazole-2-^{14}C] + [thiadiazole-5-^{14}C]

The results of the studies are summarized in the sections 7.1 to 7.5. The proposed degradation pathways in soil, water and sediment are given in Figure 7.1.1- 1 and Figure 7.2- 1, respectively.

In addition, studies have been performed with the radiolabelled and unlabeled major degradation products FOE oxalate, FOE sulfonic acid, FOE methylsulfide, FOE methylsulfone, FOE-thiadone, FOE 5043-trifluoroethanesulfonic acid and trifluoroacetic acid. An overview is given in the table below.

Report Name[1] (Codes and Synonyms)	Chemical Structure	Radiolabel Positions
FOE oxalate (M1)		* [phenyl-UL-^{14}C]
FOE sulfonic acid (M2)		* [phenyl-UL-^{14}C]
FOE methylsulfide (M5)		* [phenyl-UL-^{14}C]
FOE methylsulfone (M7, BCS-CO62475)		* [phenyl-UL-^{14}C]
FOE-thiadone (M9, Thiadone)		# [thiadiazole-2-^{14}C]
FOE 5043-trifluoro-ethanesulfonic acid (M44, TFESA)		no radiolabel available
trifluoroacetic acid (M45, TFA, BCS-AZ56567)		* [1-^{14}C]

[1] The structures and report names of degradation products identified in environmentalfate studies reflect in general their uncharged species. The degradation products FOE sulfonic acid, FOE 5043-trifluoro-ethanesulfonic acid and trifluoroacetic acid have pKa-values < 2 and hence, are deprotonated (ionic) under environmental conditions. Therefore, their environmental relevant deprotonated species were used for all studies which were conducted to elucidate the toxicological and ecotoxicological properties of these degradation products as well as their fate in the environment, plants and animals.

In original reports study authors may have used different names or codes for degradation products of flufenacet. In this summary, a single name or a single code is used for each degradation product. A full list containing structural formula, various names, short forms, codes and occurrences of degradation products is provided in Document N3 submitted with this dossier.

CA 7.1 Fate and behavior in soil

CA 7.1.1 Route of degradation in soil

The route of degradation of flufenacet under aerobic conditions was studied in a number of soils at different temperatures and soil moistures, using either [phenyl-UL-^{14}C]-, [thiadiazole-2-^{14}C]- or [thiadiazole-5-^{14}C]-labeled flufenacet as test item. Flufenacet was stable to photolysis, while degradation was observed in microbial active soil.

Under aerobic conditions in the dark in the laboratory flufenacet formed six major degradation products: FOE oxalate (max. occurrence 26.5% of applied radioactivity (AR)), FOE sulfonic acid (max. occurrence 26.3% AR), FOE methylsulfone (max. occurrence 6.6% AR), FOE-thiadone (max. occurrence 5.9% AR), FOE 5043-trifluoroethanesulfonic acid (max. occurrence 6.0% AR) and trifluoroacetic acid (max. occurrence 81.5% AR). Additionally, a number of minor degradation products were formed. Significant mineralization to carbon dioxide was observed for all three labeling positions (5 to 51% AR) accompanied by the formation of non-extractable residues (7 to 58% AR).

On request of the US environmental protection agency (EPA) the route of degradation of FOE-thiadone under aerobic conditions was additionally studied in a number of soils at 20 °C, using either [phenyl-UL-^{14}C]- or [thiadiazole-2-^{14}C]-labeled FOE-thiadone as test item. FOE-thiadone was stable to photolysis, while degradation was observed in microbial active soil, forming carbon dioxide as final major degradation product.

The route and rate of degradation of flufenacet under anaerobic conditions was studied in three soils at 20 °C, using either [phenyl-UL-^{14}C]- or [thiadiazole-2-^{14}C]-labeled flufenacet as test item. During the first phase of the study the soils were maintained under aerobic conditions for approx. one half-life of flufenacet in the respective soil (30 or 15 days). Afterwards, the samples were flooded with water and maintained under anaerobic conditions. Under these conditions flufenacet formed five major degradation products. FOE oxalate (max. occurrence 11.2% AR aerobic and 14.5% AR anaerobic), FOE sulfonic acid (6.6% AR aerobic and anaerobic), FOE-thiadone (max. occurrence 5.9% AR aerobic and 13.6% AR anaerobic), FOE 5043-trifluoroethanesulfonic acid (max. occurrence 6.0% AR aerobic and 5.0% AR anaerobic) and trifluoroacetic acid (max. occurrence 37.5% AR aerobic and 53.2% AR anaerobic). FOE oxalate, FOE sulfonic acid, FOE-thiadone and FOE 5043-trifluoro-ethanesulfonic acid were formed under aerobic conditions. Under anaerobic conditions their amounts increased initially before they decreased again or their amounts decreased directly after soil flooding, depending on the test system. Trifluoroacetic acid was formed under aerobic and anaerobic conditions. Volatile organic compounds were not formed in significant amounts (≤ 0.5% AR) during the aerobic or the anaerobic incubation phase. Mineralization to carbon dioxide was observed for both labeling positions during the aerobic incubation phase (1.4 to 1.9% AR) accompanied by the formation of non-extractable residues during the aerobic incubation phase (8.4 to 16.9% AR) and the anaerobic incubation phase (24.5 to 32.6% AR).

The degradation pathway of flufenacet in the environment is shown in Figure 7.1.1- 1. A summary of maximum occurrences in soil of major degradation products derived from laboratory studies is shown in Table 7.1.1- 1.

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

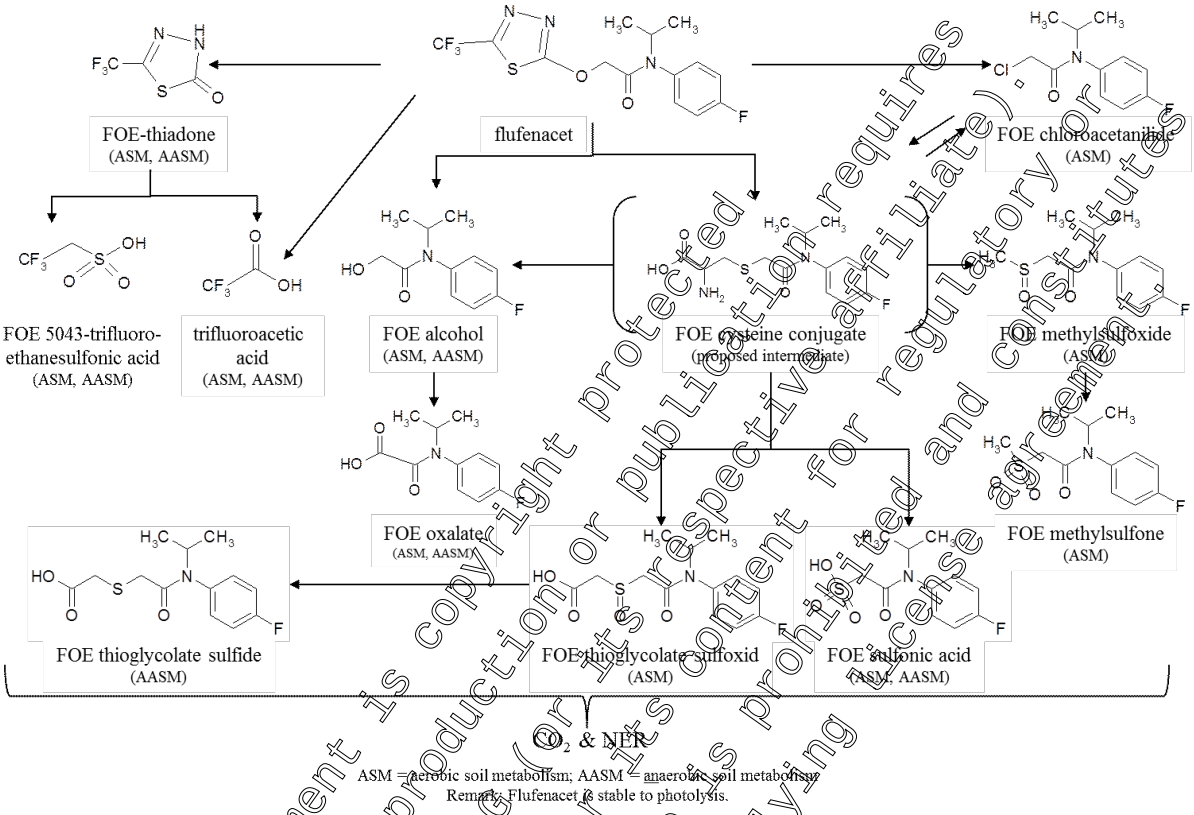


Table 7.1.1- 1: Summary of maximum occurrences in soil of major flufenacet degradation products derived from laboratory studies (in percentage of applied radioactivity [% AR])

Degradation Product	Aerobic Soil [% AR]	Anaerobic Soil [% AR]
FOE oxalate	26.5	14.5
FOE sulfonic acid	26.3	6.6
FOE methylsulfone	6.6	-
FOE-thiadone	5.9	13.6
FOE 5043-trifluoroethanesulfonic acid	6.0	5.0
trifluoroacetic acid	81.5	53.2

CA 7.1.1.1 Aerobic degradation

The route of degradation of flufenacet in soil under aerobic conditions in the dark in the laboratory was evaluated during the Annex I Inclusion and was accepted by the European Commission (7469/VI/98-Final – 3rd July 2003). The following studies are included in the Baseline Dossier:

Annex Point / Reference No	Author(s)	Year	Document No
KCA 7.1.1.1/01	[redacted], N. C.; [redacted], D. M.	1994	M-002166-01-1
KCA 7.1.1.1/02	[redacted], N. C.; [redacted], D. M.	1994	M-002165-01-1
KCA 7.1.1.1/03	[redacted], I. V.; [redacted], M.	1995	M-002146-01-1

Two additional studies have been performed for flufenacet to further elucidate the fate of the thiadiazole heterocylce and are submitted within this Supplemental Dossier for the flufenacet renewal of approval.

A summary of the route of degradation of flufenacet in soil is given in section CA 7.1.1 and Figure 7.1.1- 1.

Report:	**KCA 7.1.1.1 /04; [redacted], E. M., 2013**
Title:	Amendment No 1 - [thiadiazole-5-^{14}C]flufenacet: Aerobic Degradation / Metabolism in One European Soil
Report No:	MEF-11/937
Document No:	M-439105-02-1
Guidelines:	• OECD Test Guideline No. 307 • OCSPP Test Guideline No. 835.4100/4200
GLP:	Yes

Executive Summary

The degradation of [thiadiazole-5-^{14}C]flufenacet was investigated in one soil under aerobic conditions in the dark in the laboratory for 120 days at 19.7 °C and soil moisture of 55 ± 5% of the maximum water holding capacity:

Soil	Source	Texture (USDA)	pH [1]	OC [%]
Hoefchen am Hohenseh	Burscheid, Germany	silt loam	6.7	2.5

[1] pH in 0.01 M $CaCl_2$

The study application rate was 162.3 µg/100 g soil (dry weight), equal to 1.6 mg flufenacet/kg soil (dry weight).

Duplicate test systems were processed and analyzed 0, 2, 4, 7, 10, 14, 35, 60, 87 and 120 days after treatment.

In the following those parts of the study are summarized which were performed to elucidate the route of degradation in soil. Parts concerning evaluation of rate of degradation are reported in section CA 7.1.2.1.1 (study KCA 7.1.2.1.1 /05) of this document.

Overall mean material balance was 99.5% of applied radioactivity (% AR).

The maximum amount of carbon dioxide was 5.6% AR at DAT-120 (study end). Formation of volatile organic compounds was not significant, values being ≤ 0.1% AR for all sampling intervals.

Extractable residues decreased from 99.7% AR at DAT-0 to 78.8% AR at DAT-120.

Non-extractable residues increased from 0.5% AR at DAT-0 to 13.5% AR at DAT-60 and slightly decreased to 12.5% AR at DAT-120.

The amount of flufenacet decreased from 99.7% AR at DAT-0 to 0.9% AR at DAT-120.

Besides the formation of carbon dioxide (5.6% AR at DAT-120), three major degradation products were identified: FOE-thiadone (max. 5.8% AR at DAT-10), FOE 5043-trifluoroethanesulfonic acid (max. 6.0% AR at DAT-14) and trifluoroacetic acid (max. 77.7% AR at DAT-87).

I. MATERIALS AND METHODS

A. MATERIALS

1. Test Item

[thiadiazole-5-^{14}C]flufenacet	
CAS No	142459-58-3
Specific activity	1.54 MBq/mg
Radiochemical purity	> 99% HPLC with radioactivity-detector and TLC, scan

2. Test Soils

The soil (Table 7.1.1.1-1) was sampled freshly from the field (upper horizon of 0 to 20 cm) and sieved to a particle size of ≤ 2 mm. The soil was taken from agricultural use area representing one of the common agricultural soils of this region.

Table 7.1.1.1- 1: Physico-chemical properties of test soils

Parameter		Results / Units
Soil Designation		Hoefchen am Hohenseh
Geographic Location		
City		Burscheid
State		North-Rhine Westphalia
Country		Germany
GPS Coordinates		N 51° 04.0' E 007° 06.3'
Soil Taxonomic Classification (USDA)		loamy, mixed, mesic, Typic Argudalf
Soil Series		no information available
Textural Class (USDA)		silt loam
Sand [%]	[50 µm – 2 mm]	29
Silt [%]	[2 µm – 50 µm]	56
Clay [%]	[< 2 µm]	15
pH		
- in $CaCl_2$ (soil/$CaCl_2$ 1/2)		6.7
- in water (soil/water 1/1)		7.0
- in water (saturated paste)		7.0
- in KCl		6.3
Organic Carbon [%]		2.5
Organic Matter [%] [1]		4.3
Cation Exchange Capacity [meq/100 g]		12.9
Water Holding Capacity		
maximum [g H_2O *ad* 100 g soil DW]		61.1
at 0.1 bar (pF 2.0) [%]		29.8
Bulk Density (disturbed) [g/cm³]		1.04
Microbial Biomass [mg microbial carbon / kg soil DW] [2]		
DAT-0 (BIO-)		841
DAT-58 (BIO- / BIO+)		693 / 638
DAT-121 (BIO- / BIO+)		563 / 506

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

[2] BIO- samples were left untreated, BIO+ samples were applied with solvent of application solution

DAT: days after treatment
DW: dry weight
GPS: global positioning system
USDA: United States Department of Agriculture

B. STUDY DESIGN

1. Experimental Conditions

Static test systems were used, consisting of Erlenmeyer flasks filled with soil and equipped with solid trap attachments for collection of carbon dioxide and volatile organic compounds.

100 g of the sieved soil (dry weight equivalents) were weighed into each flask and the soil moisture was adjusted to 55 ± 5% maximum water holding capacity by addition of de-ionized water, taken into

account the water content of the application solution. The untreated test systems were closed with the trap attachments and equilibrated to study conditions for 4 days prior to application.

The study application rate (SAR) was based on a single field application rate of flufenacet of 600 g/ha, resulting in a nominal study application rate 160 µg/100 g soil (dry weight), equal to 1.6 mg /kg soil (dry weight). The actual SAR was 162.3 µg/100 g soil (dry weight), equal to 1.6 mg flufenacet/kg soil (dry weight).

The application solution was prepared in methanol/water (1:1, *v/v*). 358 µL of the application solution were applied drop wise onto the soil surface of the respective test systems using a pipette. After application, the test vessels were closed with the trap attachments (except DAT-0 samples).

The test systems were incubated under aerobic conditions in the dark for 120 days at 19.7 °C and soil moisture of 55 ± 5% of the maximum water holding capacity in a walk-in climatic chamber.

2. Sampling

Ten sampling intervals were distributed over the entire incubation period of 120 days. Duplicate test systems were processed and analyzed 0, 2, 4, 7, 10, 14, 35, 60, 87 and 120 days after treatment (DAT). Microbial soil biomass was determined at DAT-0, DAT-60 and DAT-120.

3. Analytical Procedures

At each sampling interval, the trap attachments were removed from the test systems and the entire soil of each test system was extracted four times at ambient temperature using acetonitrile/water (1:1, *v/v*), followed by two microwave-accelerated extractions: first with acetonitrile/water (1:1, *v/v*) at 70 °C and second with methanol at 70 °C (DAT-0 and DAT-2) or 50 °C (DAT-4 to DAT-120). After each extraction step supernatant and soil were separated by centrifugation and decantation.

Soil extracts were characterized by liquid scintillation counting and HPLC/radiodetection and TLC/radiodetection. The limit of detection (LOD) for the HPLC/radiodetection method was 0.5% AR. The amount of volatiles and non-extractable residues was determined by liquid scintillation counting and combustion/ liquid scintillation counting, respectively.

The identity of the test item and its degradation products was elucidated by HPLC-MS and/or HPLC-MS/MS including accurate mass determination and/or by co-chromatography with reference items.

II. RESULTS AND DISCUSSION

A. EXTRACTION AND QUANTITATION OF RADIOACTIVITY IN SOIL SAMPLES

Table 7.1.1.1- 2 summarizes the degradation of [thiadiazole-5-^{14}C]flufenacet and the formation and degradation of its degradation products as a function of time.

Table 7.1.1.1- 2: Degradation of flufenacet in Soil Hoefchen am Hohenseh under Aerobic Conditions (expressed as percent of applied radioactivity; mean value of duplicates)

Compound	DAT									
	0	2	4	7	10	14	35	60	87	120
flufenacet	99.7	92.2	87.8	75.6	64.1	54.8	13.8	3.7	1.6	0.9
FOE-thiadone	n.d.	3.4	4.5	5.5	5.8	3.4	1.6	0.6	< LOD	< LOD
FOE 5043-trifluoroethanesulfonic acid	n.d.	0.9	2.3	4.2	5.4	6.0	4.9	2.6	< LOD	< LOD
trifluoroacetic acid	n.d.	1.2	3.7	9.6	16.7	25.1	61.1	73.0	77.7	77.6
Unid./Diff. Radioactivity [1]	n.d.	< LOD	0.9	0.9	1.5	1.8	1.8	0.8	< LOD	< LOD
Total Extractable Residues	99.7	98.2	99.3	95.8	93.4	91.1	83.2	80.7	79.6	78.5
Carbon Dioxide	n.a.	< 0.1	0.1	0.3	0.7	1.1	3.2	4.5	5.2	5.6
Volatile Organic Compounds	n.a.	< 0.1	< 0.1	0.1	< 0.1	< 0.1	< 0.1	0.1	0.1	0.1
Non-extractable Residues	0.5	1.4	2.1	3.7	5.3	7.0	12.5	13.6	13.1	12.5
Material Balance	**100.2**	**99.9**	**101.6**	**100.2**	**99.8**	**99.5**	**99.1**	**98.9**	**98.6**	**97.0**

[1] Minor degradation products were summed up to unidentified radioactivity, the maximum amount of a single degradation product was 1.8% AR.

B. MATERIAL BALANCE

The amount of dosed test item was determined at DAT-0 before, during and after the application and was set to 100% AR for all samples. The total radioactivity recovery (mean of duplicates) of all sampling intervals ranged from 99.0 to 101.6% AR (overall mean 99.5% AR, RSD 1.2%), see also Table 7.1.1.1- 2.

The complete material balance found at all sampling intervals demonstrated that no significant portion of radioactivity dissipated from the vessels or was lost during processing of theses samples.

C. EXTRACTABLE AND NON-EXTRACTABLE RESIDUES

Extractable residues decreased steadily from 99.7% AR at DAT-0 (study start) to 78.8% AR at DAT-120.

The formation of non-extractable residues increased from 0.5% AR at DAT-0 to 13.5% AR at DAT-60 and slightly decreased at study end (DAT-120) to 12.5%. See also Table 7.1.1.1- 2 for details.

D. VOLATILIZATION

The maximum amount of carbon dioxide formed in the test systems was 5.6% AR at DAT-120 (study end). Formation of volatile organic compounds was insignificant as demonstrated by values of ≤ 0.1% AR at all sampling intervals. See also Table 7.1.1.1- 2 for details.

E. DEGRADATION OF TEST ITEM

The amount of [thiadiazole-5-^{14}C]flufenacet in the combined soil extracts decreased from 99.7% AR at DAT-0 to 0.9% AR at DAT-120.

Besides carbon dioxide, three major degradation products were identified: FOE-thiadone (max. 5.8% AR at DAT-10), FOE 5043-trifluoroethanesulfonic acid (max. 6.0% AR at DAT-14) and

trifluoroacetic acid (max. 77.7% AR at DAT-87). The total unidentified radioactivity amounted to a maximum of 1.8% AR at DAT-14 and DAT-35.

III. CONCLUSIONS

[thiadiazole-5-^{14}C]flufenacet was rapidly degraded in soil under aerobic conditions in the dark in the laboratory.

Formation of carbon dioxide was observed up to 5.6% AR in the tested soil. Besides carbon dioxide, three major degradation products were identified: FOE-thiadione (max. 5.8% AR), FOE 5043-trifluoro-ethanesulfonic acid (max. 6.0% AR) and trifluoroacetic acid (max. 77.7% AR). Formation of non-extractable residues (max. 13.5% AR) was observed in parallel, decreasing towards study end (12.5% AR).

The formation of carbon dioxide indicates the potential for mineralization of the test item and its degradation products. Therefore, flufenacet is not expected to have a potential for accumulation in the environment.

*****

Report:	**KCA 7.1.1.1 /05; [redacted] E. M.; 2013**
Title:	Amendment No 1 to: [thiadiazole-5-^{14}C]flufenacet: Aerobic Degradation / Metabolism in Three European Soils
Report No:	MEF-11/938
Document No:	M-440348-02-1
Guidelines:	• OECD Test Guideline No. 307 • OCSPP Test Guideline No. 835.4100/4200
GLP:	Yes

Executive Summary

The degradation of [thiadiazole-5-^{14}C]flufenacet was investigated in three soils under aerobic conditions in the dark in the laboratory for 121 days at 19.8 °C and soil moisture of 55 ± 5% of the maximum water holding capacity:

Soil	Source	Texture (USDA)	pH [1]	OC [%]
Laacherhof AXXa	Monheim, Germany	loamy sand	6.1	2.4
Dollendorf II	Blankenheim, Germany	clay loam	7.2	5.3
Laacherhof Wurmwiese	Monheim, Germany	loam	5.4	2.2

[1] pH in 0.01 M $CaCl_2$

The study application rate was 152.0 µg/100 g soil (dry weight), equal to 1.5 mg flufenacet//kg soil (dry weight).

Duplicate test systems were processed and analyzed 0, 1, 2, 4, 7, 10, 14, 35, 63, 91 and 121 days after treatment.

In the following those parts of the study are summarized which were performed to elucidate the route of degradation in soil. Parts concerning evaluation of rate of degradation are reported in section CA 7.1.2.1.1 (study KCA 7.1.2.1.1 /06) of this document.

Overall mean material balance was 99.1% of applied radioactivity (% AR) for soil Laacherhof AXXa, 99.7% AR for soil Dollendorf II and 98.7% AR for soil Laacherhof Wurmwiese.

The following maximum amounts of carbon dioxide were detected at DAT-121 (study end): 5.6% AR in soil Laacherhof AXXa, 6.5% AR in soil Dollendorf II and 4.5% AR in soil Laacherhof Wurmwiese. Formation of volatile organic compounds was not significant, values being ≤ 0.2% AR at all sampling intervals in all soils.

Extractable residues decreased from 98.7% AR at DAT-0 to 76.0% AR at DAT-121 in soil Laacherhof AXXa, from 99.9% AR at DAT-0 to 82.1% AR at DAT-121 in soil Dollendorf II and from 98.7% AR at DAT-0 to 75.0% AR at DAT-121 in soil Laacherhof Wurmwiese.

Non-extractable residues (NER) increased from 0.4% AR at DAT-0 to 18.6% AR at DAT-63 and slightly decreased to 17.2% AR at DAT-121 in soil Laacherhof AXXa. In soil Dollendorf II NER increased from 1.1% AR at DAT-0 to 11.5% AR at DAT-63 and slightly decreased to 10.6% AR at DAT-121. In soil Laacherhof Wurmwiese NER increased from 0.7% AR at DAT-0 to 18.6% AR at DAT-35 and DAT-63 and slightly decreased to 17.2% AR at DAT-121.

The amount of flufenacet decreased from 98.7% AR at DAT-0 to 1.4% AR at DAT-121 in soil Laacherhof AXXa, from 99.9% AR at DAT-0 to 0.9% AR at DAT-121 in soil Dollendorf II and from 98.7% AR at DAT-0 to 1.0% AR at DAT-121 in soil Laacherhof Wurmwiese, respectively.

Besides the formation of carbon dioxide one major degradation product was identified. Trifluoroacetic acid was detected with maximum amounts of 74.1% AR at DAT-121 in soil Laacherhof AXXa, 81.5% AR at DAT-91 in soil Dollendorf II and 74.8% AR at DAT-91 in soil Laacherhof Wurmwiese.

I. MATERIALS AND METHODS

A. MATERIALS

1. Test Item

[thiadiazole-5-^{14}C]flufenacet
CAS No 142459-58-3
Specific activity 1.54 MBq/mg
Radiochemical purity > 99% HPLC with radioactivity-detector and TLC, scan

2. Test Soils

The soils (Table 7.1.1.1- 3) 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 areas representing different geographical origins and different soil properties as required by the guidelines.

Table 7.1.1.1- 3: Physico-chemical properties of test soils

Parameter	Results / Units		
Soil Designation	Laacherhof AXXa	Dollendorf II	Laacherhof Wurmwiese
Geographic Location			
City	Monheim	Blankenheim	Monheim
State	North-Rhine Westphalia	North-Rhine Westphalia	North-Rhine Westphalia
Country	Germany	Germany	Germany
GPS Coordinates	N 51° 04.647 E 006° 53.517'	N 50° 22.899' E 006° 43.001'	N 51° 04.857' E 006° 55.251'
Soil Taxonomic Classification (USDA)	sandy, mixed, mesic typic Cambudolls	fine-loamy, mixed, active, frigid Typic Eutrudept	loamy, mixed, mesic Typic Argudalfs
Soil Series	no information available		
Textural Class (USDA)	loamy sand	clay loam	loam
Sand [%] [50 µm – 2 mm]	75	29	49
Silt [%] [2 µm – 50 µm]	20	38	34
Clay [%] [< 2 µm]	5	33	17
pH			
- in $CaCl_2$ (soil/$CaCl_2$ 1/2)	6.1	7.2	5.4
- in water (soil/water 1/1)	6.4	7.4	5.7
- in water (saturated paste)	6.5	7.2	5.8
- in KCl	5.9	7.0	5.2
Organic Carbon [%]	2.4	5.3	2.2
Organic Matter [%] [1]	4.1	9.1	3.8
Cation Exchange Capacity [meq/100 g]	9.9	20.9	10.8
Water Holding Capacity			
maximum [g H_2O *ad* 100 g soil DW]	49.1	79.8	59.9
at 0.1 bar (pF 2.0) [%]	18.7	46.0	23.3
Bulk Density (disturbed) [g cm^3]	1.19	0.95	1.12
Microbial Biomass [mg microbial carbon / kg soil DW] [2]			
DAT-0 (BIO-)	1077	3447	862
DAT-121 (BIO- / BIO+)	451 / 422	2164 / 2032	341 / 338

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

[2] BIO- samples were left untreated, BIO+ samples were applied with solvent of application solution

DAT: days after treatment GPS: global positioning system

DW: dry weight USDA: United States Department of Agriculture

B. STUDY DESIGN

1. Experimental Conditions

Static test systems were used, consisting of Erlenmeyer flasks filled with soil and equipped with solid trap attachments for collection of carbon dioxide and volatile organic compounds.

100 g of the sieved soil (dry weight equivalents) were weighed into each flask and the soil moisture was adjusted to 55 ± 5% maximum water holding capacity by addition of de-ionized water, taken into account the water content of the application solution The untreated test systems were closed with the trap attachments and equilibrated to study conditions for 3 days prior to application.

The study application rate (SAR) was based on a single field application rate of flufenacet of 600 g/ha, resulting in a nominal study application rate 160 µg/100 g soil (dry weight), equal to 1.6 mg /kg soil (dry weight). The actual SAR was 152.0 µg/100 g soil (dry weight), equal to 1.5 mg flufenacet /kg soil (dry weight).

The application solution was prepared in methanol/water (1:1, *v/v*). 346 µL of the application solution were applied drop wise onto the soil surface of the respective test systems using a pipette. After application the test vessels were closed with the trap attachments (except DAT-0 samples).

The test systems were incubated under aerobic conditions in the dark for 121 days at 19.8 °C and soil moisture of 55 ± 5% of the maximum water holding capacity in a walk-in climatic chamber.

2. Sampling

Eleven sampling intervals were distributed over the entire incubation period of 121 days. Duplicate test systems were processed and analyzed 0, 1, 2, 4, 7, 10, 14, 35, 63, 91 and 121 days after treatment (DAT).

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

3. Analytical Procedures

At each sampling interval, the trap attachments were removed from the test systems and the soils were extracted three times at ambient temperature using acetonitrile/water (1 x 4:1, *v/v* and 2 x 1:1, *v/v* at DAT-0) or acetonitrile/water (3 x 1:1, *v/v*, from DAT-1 to DAT-121), followed by two microwave-accelerated extractions; first with acetonitrile/water (1:1, *v/v*) at 70 °C and second with methanol at 50 °C. After each extraction step, supernatant and soil were separated by centrifugation and decantation.

Soil extracts were characterized by liquid scintillation counting and the primary chromatographic methods (HPLC/radiodetection and TLC/radiodetection). The limit of detection (LOD) for the HPLC/radiodetection method was 0.4% AR. The amount of volatiles and non-extractable residues was determined by liquid scintillation counting and combustion/ liquid scintillation counting, respectively.

The identity of the test item and its degradation products was elucidated by HPLC-MS(/MS) and/or assigned by comparison of the retention times with those of reference items.

II. RESULTS AND DISCUSSION

A. EXTRACTION AND QUANTITATION OF RADIOACTIVITY IN SOIL SAMPLES

Table 7.1.1.1- 4 to Table 7.1.1.1- 6 summarizes the degradation of [thiadiazole-5-^{14}C]flufenacet and the formation and degradation of its degradation products as a function of time.

Table 7.1.1.1- 4: Degradation of flufenacet in Soil Laacherhof AXXa under Aerobic Conditions
(expressed as percent of applied radioactivity; mean value of duplicates)

Compound	DAT 0	1	2	4	7	10	14	35	63	91	121
flufenacet	98.7	97.0	91.8	89.9	81.4	70.6	59.9	25.7	7.6	3.2	1.4
FOE-thiadone	n.d.	1.8	1.9	2.5	2.8	2.5	2.7	1.6	1.0	< LOD	< LOD
FOE 5043-trifluoro-ethanesulfonic acid	n.d.	n.d.	< LOD	1.7	3.2	4.4	3.2	2.7	1.2	< LOD	0.5
trifluoroacetic acid	n.d.	n.d.	1.6	2.7	7.2	13.9	22.1	48.2	65.9	71.5	74.1
Unid./Diff. Radioactivity [1]	n.d.	n.d.	n.d.	n.d.	n.d.	< LOD	n.d.	1.8	1.0	n.d.	n.d.
Total Extractable Residues	98.7	98.8	95.2	96.6	94.7	91.7	87.9	80.0	76.5	75.0	76.0
Carbon dioxide	n.a.	< 0.1	< 0.1	0.1	0.4	0.5	1.1	2.9	4.0	5.0	5.6
Volatile Organic Compounds	n.a.	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	0.1	0.1	0.1	0.1
Non-extractable Residues	0.4	1.0	1.9	4.1	4.0	7.1	9.3	16.0	18.6	18.4	17.2
Material Balance	**99.1**	**99.9**	**97.1**	**100.9**	**99.1**	**99.3**	**98.4**	**99.0**	**99.3**	**98.8**	**98.8**

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

[1] Minor degradation products were summed up to unidentified radioactivity, the maximum amount of a single degradation product was 1.0% AR.

Table 7.1.1.1- 5: Degradation of flufenacet in Soil Dollendorf H under Aerobic Conditions
(expressed as percent of applied radioactivity; mean value of duplicates)

Compound	DAT 0	1	2	4	7	10	14	35	63	91	121
flufenacet	99.9	96.8	88.2	87.7	77.0	65.1	55.9	15.3	2.5	1.2	0.9
FOE-thiadone	n.d.	2.1	2.5	3.9	4.0	5.6	4.8	3.2	0.7	n.d.	n.d.
FOE 5043-trifluoro-ethanesulfonic acid	n.d.	n.d.	n.d.	< LOD	2.2	3.4	1.7	1.6	0.6	n.d.	< LOD
trifluoroacetic acid	n.d.	n.d.	2.0	5.7	9.7	19.0	28.1	66.8	78.6	81.5	81.0
Unid./Diff. Radioactivity [1]	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	< LOD	1.0	n.d.	n.d.	n.d.
Total Extractable Residues	99.9	98.9	92.8	97.7	92.8	93.1	91.0	88.0	82.4	82.7	81.9
Carbon dioxide	n.a.	0.1	0.1	0.2	0.5	1.0	1.4	3.7	5.2	5.9	6.5
Volatile Organic Compounds	n.a.	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	0.2	0.1	< 0.1
Non-extractable Residues	1.1	1.8	2.9	3.0	4.9	5.7	6.5	11.2	11.5	11.2	10.6
Material Balance	**101.0**	**100.7**	**95.7**	**101.1**	**98.3**	**99.8**	**98.9**	**103.0**	**99.2**	**99.9**	**99.2**

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

[1] Minor degradation products were summed up to unidentified radioactivity, the maximum amount of a single degradation product was < LOD.

Table 7.1.1.1- 6: Degradation of flufenacet in Soil Laacherhof Wurmwiese under Aerobic Conditions
(expressed as percent of applied radioactivity; mean value of duplicates)

Compound	DAT										
	0	1	2	4	7	10	14	35	63	91	121
flufenacet	98.7	96.8	90.5	86.2	74.4	63.4	47.4	13.3	3.6	1.3	1.0
FOE-thiadone	n.d.	1.5	2.0	3.1	4.6	3.3	3.1	1.7	0.7	n.d.	n.d.
FOE 5043-trifluoro-ethanesulfonic acid	n.d.	n.d.	< LOD	0.7	1.6	1.9	0.5	< LOD	< LOD	< LOD	< LOD
trifluoroacetic acid	n.d.	n.d.	1.3	5.2	11.5	19.1	31.6	60.0	70.0	74.8	73.8
Unid./Diff. Radioactivity [1]	n.d.	n.d.	n.d.	n.d.	0.5	1.0	2.4	2.3	< LOD	n.d.	n.d.
Total Extractable Residues	98.7	98.3	93.8	95.2	92.5	88.8	83.0	77.3	75.1	76.4	74.8
Carbon dioxide	n.a.	< 0.1	< 0.1	0.2	0.4	0.8	1.3	2.8	3.7	4.4	4.5
Volatile Organic Compounds	n.a.	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	0.1	0.1	0.1	0.1
Non-extractable Residues	0.7	1.2	2.3	4.1	6.7	10.1	13.3	18.6	18.6	18.2	17.2
Material Balance	**99.3**	**99.5**	**96.2**	**99.5**	**99.7**	**99.8**	**99.7**	**98.9**	**97.7**	**98.8**	**96.7**

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

[1] Minor degradation products were summed up to unidentified radioactivity, the maximum amount of a single degradation product was 1.4% AR.

B. MATERIAL BALANCE

The amount of dosed test item was determined at DAT-0 before, during and after the application and was set to 100% AR for all samples. The total radioactivity recovery (mean of duplicates) of all sampling intervals ranged from 97.1 to 100.9% AR in soil Laacherhof AXXa (overall mean 99.1% AR, RSD 0.9%), from 95.7 to 103.0% AR in soil Dollendorf II (overall mean 99.7% AR, RSD 1.8%) and from 96.2 to 99.8% AR in soil Laacherhof Wurmwiese (overall mean 98.7% AR, RSD 1.2%), see also Table 7.1.1.1- 4 to Table 7.1.1.1- 6.

The complete material balance found at all sampling intervals (mean of duplicates) in all soils demonstrated that no significant portion of radioactivity dissipated from the vessels or was lost during processing of these samples.

C. EXTRACTABLE AND NON-EXTRACTABLE RESIDUES

Extractable residues decreased steadily from 98.7% AR at DAT-0 to 76.0% AR at DAT-121 in soil Laacherhof AXXa, from 99.9% AR at DAT-0 to 82.1% AR at DAT-121 in soil Dollendorf II and from 98.7% AR at DAT-0 to 75.0% AR at DAT-121 in soil Laacherhof Wurmwiese.

The formation of non-extractable residues (NER) increased from 0.4% AR at DAT-0 to 18.6% AR at DAT-63 and slightly decreased to 17.2% AR at DAT-121 in soil Laacherhof AXXa. In soil Dollendorf II NER increased from 1.1% AR at DAT-0 to 11.5% AR at DAT-63 and slightly decreased to 10.6% AR at DAT-121. In soil Laacherhof Wurmwiese NER increased from 0.7% AR at DAT-0 to 18.6% AR at DAT-35 and DAT-63 and slightly decreased to 17.2% AR at DAT-121.See also Table 7.1.1.1- 4 to Table 7.1.1.1- 6 for details.

D. VOLATILIZATION

The maximum amount of carbon dioxide formed in the test systems was 5.6% AR in soil Laacherhof AXXa, 6.5% AR in soil Dollendorf II and 4.5% AR in soil Laacherhof Wurmwiese.

Formation of volatile organic compounds was insignificant as demonstrated by values of ≤ 0.2% AR at all sampling intervals in all soils. See also Table 7.1.1.1- 4 to Table 7.1.1.1- 6 for details.

E. DEGRADATION OF TEST ITEM

The amount of [thiadiazole-5-^{14}C]flufenacet in the combined soil extracts decreased from 98.7% AR at DAT-0 to 1.4% AR at DAT-121 in soil AX, from 99.9% AR at DAT-0 to 0.9% AR at DAT-121 in soil DD and from 98.7% AR at DAT-0 to 1.0% AR at DAT-121 in soil WW.

Besides carbon dioxide, one major degradation product was identified. Trifluoroacetic acid was detected with maximum amounts of 74.1% AR at DAT-121 in soil AX, 81.5% AR at DAT-91 in soil DD and 74.8% AR at DAT-91 in soil WW. The known degradation products FOE-thiadone and FOE 5043-trifluoroethanesulfonic acid were detected with maximum amounts of 2.8% AR at DAT-7 and 4.4% AR at DAT-10, respectively, in soil Laacherhof AXXa, with maximum amounts of 5.6% AR at DAT-10 and 3.4% AR at DAT-10, respectively, in soil Dollendorf II and with maximum amounts of 4.6% AR at DAT-7 and 1.9% AR at DAT-10, respectively, in soil Laacherhof Wurmwiese. The total unidentified radioactivity amounted to a maximum of 1.8% AR at DAT-35 in soil Laacherhof AXXa, 1.0% AR at DAT-35 in soil Dollendorf II and 2.4% AR at DAT-14 in soil Laacherhof Wurmwiese.

III. CONCLUSIONS

[thiadiazole-5-^{14}C]flufenacet was rapidly degraded in soil under aerobic conditions in the dark in the laboratory.

Formation of carbon dioxide was observed up to 5.6% AR in soil Laacherhof AXXa, 6.5% AR in soil Dollendorf II and 4.5% AR in soil Laacherhof Wurmwiese.

Besides carbon dioxide, one major degradation product was detected. Trifluoroacetic acid was identified with maximum amounts of 74.1% AR at DAT-121 in soil Laacherhof AXXa, 81.5% AR at DAT-91 in soil Dollendorf II and 74.8% AR at DAT-91 in soil Laacherhof Wurmwiese, respectively.

Formation of non-extractable residues up to a maximum of 18.6% AR in soil Laacherhof AXXa, 11.5% AR in soil Dollendorf II and 18.6% AR in soil Laacherhof Wurmwiese, declining at study end in all soils was observed.

The formation of carbon dioxide indicates the potential for mineralization of the test item and its transformation products. Therefore, flufenacet is not expected to have a potential for accumulation in the environment.

The results received were in good agreement with the proposed aerobic soil degradation pathway of flufenacet known from studies using the [phenyl-UL-^{14}C] and the [thiadiazole-2-^{14}C]label.

CA 7.1.1.2 Anaerobic degradation

Anaerobic soil degradation studies were not submitted for Annex I listing and have therefore not been summarized in the Baseline Dossier.

The route of degradation of flufenacet in soil under anaerobic conditions in the dark in the laboratory is now newly addressed by two studies, which are submitted within this Supplemental Dossier for the flufenacet renewal of approval. A summary of the route of degradation of flufenacet in soil is given in section CA 7.1.1 and Figure 7.1.1- 1.

Report:	**KCA 7.1.1.2 /01; [redacted], N. C.; [redacted], D. M.; 1995**
Title:	Anaerobic Soil Metabolism of [phenyl-U-^{14}C]FOE 5043
Report No:	MR106645
Document No:	M-002162-01-1
Guidelines:	• OECD Test Guideline No. 307 • OCSPP Test Guideline No. 835.4100/4200
GLP:	Yes

Executive Summary

The degradation of [phenyl-UL-^{14}C]flufenacet under anaerobic conditions was investigated in one soil in the dark in the laboratory for 180 days at 21 ± 1 °C, applying an aerobic incubation phase of 30 days (soil moisture 75% of 1/3 bar water holding capacity) before start of the anaerobic incubation phase (total study period 210 days).

Soil	Source	Texture (USDA)	pH [1]	OC [2] [%]
Howe	Indiana, USA	sandy loam	6.2	0.3

[1] pH in water
[2] calculated from organic matter (OM) by OC = OM/1.724

The study application rate was 103.0 µg/100 g soil (dry weight), equal to 1.03 mg flufenacet/kg soil (dry weight).

During the aerobic incubation phase, test systems were processed and analyzed 0, 7, 15 and 30 days after treatment (DAT) in triplicate (DAT-0) or in duplicate (DAT-7 to DAT-30). During the anaerobic incubation phase, duplicate test systems were processed and analyzed at DAT-45, DAT- 60, DAT-97, DAT -153 and DAT -210, corresponding to 15, 30, 67, 123 and 180 days after soil flooding (DASF).

In the following those parts of the study are summarized which were performed to elucidate the route of degradation in soil under anaerobic conditions. Parts concerning evaluation of rate of degradation are reported in section CA 7.1.2.1.3 (study KCA 7.1.2.1.3 /01) of this document.

Mean material balances ranged from 91.3% of applied radioactivity (% AR) to 105.0% AR.

The maximum amount of carbon dioxide was 1.4% AR at DAT-30 (end of aerobic incubation phase). Formation of volatile organic compounds was not significant, values being ≤ 0.1% AR at all sampling intervals.

Total extractable residues decreased steadily from 99.9% AR at DAT-0 (study start) to 89.7% AR at DAT-30 during aerobic incubation phase and further to 56.8% AR at DAT-210 during anaerobic incubation phase.

Non-extractable residues (NER) increased from 0.1% AR at DAT-0 to 8.4% AR at DAT-30 during the aerobic incubation phase and further to a maximum of 32.6% AR at DAT-210 during the anaerobic incubation phase.

The amount of flufenacet decreased from 99.4% AR at DAT-0 to 69.0% AR at DAT-30 during the aerobic incubation phase and further to 39.0% AR at DAT-210 during the anaerobic incubation phase.

Two major degradation products were identified during the study: FOE oxalate (max. aerobic: 11.2% AR at DAT-30; anaerobic: 14.5% AR at DAT-60) and FOE sulfonic acid (max. aerobic and anaerobic: 6.6% AR at DAT-30).

I. MATERIALS AND METHODS

A. MATERIALS

1. Test Item

[phenyl-UL-^{14}C]flufenacet	
Batch No	C-584
Specific activity	6.77 MBq/mg (≙ 66.5 mCi/mmol)
Radiochemical purity	99.2% (TLC analyses of application solution before and after application to soil)

2. Test Soils

The soil (Table 7.1.1.2-1) was sampled freshly from a field and placed inside two 5-gallon (approx. 19 L) buckets which were kept under outdoor conditions The soil was initially planted with soybeans to maintain a viable microbial population, but was overrun with weeds just prior to the start of the study. Immediately prior to starting the study, approximately 10 kg of the top soil (5-6 in approx. 12-15 cm) was sampled and plant parts were removed. The moist soil was sieved to a particle size of ≤ 2 mm and air-dried. The soil was taken from agricultural use area representing one of the common agricultural soils of this region.

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

Parameter	Soil	
Geographic location - city - state - country	 Howe Indiana USA	
GPS Coordinates	no information available	
Site description	The soil was placed into 5-gallon buckets (approx. 19 L) and planted with soybeans which were overrun with weeds prior to start of the study.	
Soil taxonomic classification (USDA)	loamy-Skeletal, mixed, mesic Typic Argiudoll	
Soil series	no information available	
Texture class (USDA) Sand [%] [50 µm – 2 mm] Silt [%] [2 µm – 50 µm] Clay [%] [< 2 µm]	sandy loam 73.5 19.1 7.5	
pH - in water (soil/water 1/1)	6.2	
Organic matter [%]	0.6	
Organic carbon [%] [1]	0.3	
Microbial biomass [2] [mg microbial carbon/kg soil] DAT-0 DAT-30	 83 101	
Microbial mass / activity during aerobic and anaerobic phases [2]	Phospholipid fatty acid assay [3] [cells/ g soil] flow through/static incubation	Plasmalogens[4] [total detected, pmol] flow through/static incubation
- DAT-0	2.9×10^8	n.d.
- DAT-30	2.6×10^8	n.d.
- DAT-37 (DASF-7)	8.4×10^8/ n.a.	189282/ n.a.
- DAT-125 (DASF-95)	5.2×10^8/ n.a.	25810/ n.a.
- DAT-210 (DASF-180)	3.5×10^8 / 3.2×10^8	n.a. / n.a.
- DAT-233 (DASF-203)	2.6×10^8 / 1.9×10^8	11756 / 13810
Cation Exchange Capacity [meq/100 g]	6.5	
Moisture at 1/3 bar (pF 2.5) [%]	13.1	
Bulk density (disturbed) [g/cm³]	1.37	

n.a. = not analyzed, n.d. = not detected
GPS: global positioning system
USDA: United States Department of Agriculture
DAT: days after treatment
DASF. Days after soil flooding

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

[2] Biomass samples were treated with 1 mL of application solvent

[3] Microbial biomass was estimated using the phospholipid fatty acid assay (PLFA). A microbial population level of 2 x 10^6 cells/mL water and 2.0 x 10^7 cells/g dry soil is generally accepted as potentially adequate to support passive biodegradation

[4] The proportion of organisms that form plasmalogen lipids (e.g. clostridia) increases with the shift to anaerobic metabolism

B. STUDY DESIGN

1. Experimental Conditions

Static test systems were used during the aerobic incubation phase, consisting of Erlenmeyer flasks and equipped with solid trap attachments for collection of carbon dioxide and volatile organic compounds. 100 g of the sieved soil (dry weight equivalents) were weighed into each flask.

After the aerobic incubation phase the trap attachments of the remaining test systems were removed and the soil of each flask was flooded with 100 mL of rain-water (approx. 2 cm above soil level). The rain-water was enriched with glucose (5 mg/mL) to enhance soil microbial growth and facilitate attainment of anaerobic conditions. Afterwards, flow-through systems were established by equipping the flasks with double-valve glass stoppers and connect them to the liquid traps for volatiles. The head-space on each flask was flushed with nitrogen for 5 minutes. Anaerobic conditions were maintained by continuously purging the headspace of each flask with nitrogen into trapping solutions for volatiles.

To provide material balance in the event losses were observed, static incubation systems were established additionally by sealing the flasks with glass stoppers after the nitrogen flush. The headspace of the static test systems was purged weekly and monthly into air-tight plastic bags.

The study application rate (SAR) was based on a single field application rate of flufenacet of 0.8 lbs/acre (approx. 896 g/ha), resulting in a SAR of 103.0 µg/100 g soil (dry weight), equal to 1.03 mg /kg soil (dry weight).

The application solution was prepared in acetonitrile/water (1:3, *v/v*). 1 mL of the application solution was applied drop wise onto the soil surface of the respective test systems using a pipette. The flasks were shaken after each application, at 300 µL increments, to aid in the dispersal of the treatment solution. After application the soil moisture was adjusted to 75% of 1/3 bar water holding capacity and the test vessels were closed with the trap attachments.

The test systems were incubated under aerobic conditions in the dark for 30 days at 21±1 °C in a walk-in climatic chamber. During the anaerobic incubation phase of 180 days the flow-through test systems were placed in an incubator at 21±1 °C. The flow-through test systems were divided into four shelves, with at least 10 test systems per shelf. The static test systems were placed into a separate incubator at 21±1 °C.

2. Sampling

Nine sampling intervals were distributed over the entire incubation period of 210 days, four sampling intervals during the aerobic incubation phase and five during the anaerobic incubation phase.

During the aerobic incubation phase, test systems were processed and analyzed 0, 7, 15 and 30 days after treatment (DAT) in triplicate (DAT-0) or in duplicate (DAT-7 to DAT-30). During the anaerobic incubation phase, duplicate test systems were processed and analyzed at DAT-45, DAT- 60, DAT-97, DAT -153 and DAT -210, corresponding to 15, 30, 67, 123 and 180 days after soil flooding (DASF).

Microbial soil biomass was determined at DAT-0 and DAT-30 of the aerobic incubation phase. Phospholipid fatty acids assays were performed at DAT-0 and DAT-30 of the aerobic incubation phase and at DAT-37, -125, -210 and -233 of the anaerobic incubation phase. Additionally, the samples were analyzed for plasmalogens at DAT-37, -125 and -233 of the anaerobic incubation phase to provide evidence for the presence of anaerobic soil microorganisms.

3. Analytical Procedures

At each sampling interval of the aerobic incubation phase the trap attachments were removed from the test systems and the soil was extracted three times at ambient temperature using in sequence acetonitrile, acetonitrile/water (7:3, *v/v*) and acetonitrile/water (1:1, *v/v*) with 0.1 N HCl. The acidic extracts were partitioned three times, with acetonitrile/methylene chloride (1:2, *v/v*) using approx. twice the volume of the soil extract.

At each sampling interval of the anaerobic incubation phase, the flaks were disconnected from the flow-through system and the water was separated from soil by filtration to allow for separate analysis. Afterwards, the soil was extracted as described for the aerobic incubation phase. The redox potential, dissolved oxygen content, and pH of untreated control samples were determined at DAST-0, -7, -15, -30, -67, -123, and -180.

The soil extracts and, if applicable, the water were characterized by liquid scintillation counting as well as by HPLC/radiodetection and/or TLC/radiodetection. The water was additionally partitioned into organic solvents to allow for TLC/radiodetection analysis. All sample extracts were analyzed at sufficient concentrations to detect amounts ≥1.0% AR. The amount of volatiles and non-extractable residues was determined by liquid scintillation counting and/or combustion/liquid scintillation counting, respectively.

The identity of the test item and its degradation products was elucidated by thermospray HPLC-MS and GC/MS analysis, either directly or after derivatization.

II. RESULTS AND DISCUSSION

A. EXTRACTION AND QUANTITATION OF RADIOACTIVITY IN SOIL SAMPLES

Table 7.1.1.2- 2 summarizes the degradation of [phenyl-UL-^{14}C]flufenacet and the formation and degradation of its degradation products as a function of time.

Table 7.1.1.2- 2: Degradation of flufenacet in Soil Howe under Aerobic and Anaerobic Conditions
(expressed as percent of applied radioactivity; mean value of triplicates (DAT-0) or duplicates)

	DAT	0	7	15	30 [1]	45 [2]	60 [2]	97 [2]	153 [3]	210 [3]
Compound	**DASF**	**N/A**			**0 [1]**	**15**	**30**	**67**	**123**	**180**
flufenacet		99.4	82.2	78.7	69.0	60.3	55.6	52.0	44.2	39.0
FOE oxalate		n.d.	4.9	9.8	11.2	12.2	14.5	10.9	11.4	9.9
FOE sulfonic acid		n.d.	2.1	4.7	6.6	6.1	5.3	4.7	5.0	4.5
FOE thioglycolate sulfoxide		n.d.	0.9	2.7	2.6	0.5	n.d.	n.d.	n.d.	n.d.
FOE alcohol		0.4	0.3	n.d.	n.d.	0.3	n.d.	0.6	1.4	0.9
FOE thioglycolate/ FOE methylsulfone [4]		n.d.	n.d.	n.d.	n.d.	1.1	1.7	1.5	1.3	1.4
Unidentified Radioactivity [5]		0.0	0.2	0.1	0.2	0.2	0.0	0.2	0.7	1.1
Total Extractable Residues		99.9	90.6	96.1	89.7	80.7	77.0	70.0	64.0	56.8
Carbon dioxide		n.a.	0.3	0.9	1.4	1.3	1.3	1.4	1.5	1.8
Volatile Organic Compounds		n.a	n.d.	n.d.	n.d.	n.a	n.a	n.a	<0.1	<0.1
Non-extractable Residues		0.1	5.0	8.0	8.4	10.2	15.8	22.9	27.2	32.6
Material Balance		**100.0**	**95.9**	**105.0**	**99.5**	**92.2**	**94.1**	**94.3**	**92.7**	**91.3**

DAT: days after treatment
DASF: days after soil flooding
n.a.: not analyzed
n.d.: not detected

[1] The results from DAT-30 samples (end of aerobic incubation phase), were also taken for DASF-0.

[2] The results for DAT-45-, -60 and -97 were derived from flow-through test systems

[3] The results for DAT-153 and -210 were derived from static test systems, to establish the material balance.

[4] The mass spectral analysis of the isolated FOE thioglycolate fraction revealed, that this fraction contained also FOE methylsulfone.

[5] Minor degradation products were summed up to unidentified radioactivity, the maximum amount of a single degradation product was < 1.0% AR at any sampling interval.

B. MATERIAL BALANCE

The amount of dosed test item was determined at DAT-0 in triplicate analysis and was set to 100% AR for all samples. Mean material balances ranged from 95.9 to 105.0% AR during the aerobic incubation phase and from 91.3 to 94.1% AR during the anaerobic incubation phase.

The complete material balance found at all sampling intervals (mean of duplicates) demonstrated that no significant portion of radioactivity dissipated from the vessels or was lost during processing of these samples.

C. EXTRACTABLE AND NON-EXTRACTABLE RESIDUES

Total extractable residues decreased steadily from 99.9% AR at DAT-0 (study start) to 89.7% AR at DAT-30 during aerobic incubation phase and further to 56.8% AR at DAT-210 during anaerobic incubation phase.

The formation of non-extractable residues increased from 0.1% AR at DAT-0 to 8.4% AR at DAT-30 during the aerobic incubation phase and further to 32.6% AR at DAT-210 during the anaerobic incubation phase. See also Table 7.1.1.2- 2 for details.

D. VOLATILIZATION

The maximum amount of carbon dioxide formed in the test systems during the aerobic incubation phase was 1.4% AR. Formation of volatile organic compounds during the aerobic and anaerobic incubation phases was insignificant as demonstrated by values of ≤ 0.1% AR at all sampling intervals. See also Table 7.1.1.2- 2 for details.

E. DEGRADATION OF TEST ITEM

The amount of [phenyl-UL-^{14}C]flufenacet in the entire system decreased from 99.4% AR at DAT-0 to 69.0% AR at DAT-30 during the aerobic incubation phase and further to 39.0% AR at DAT-210 during the anaerobic incubation phase. See also Table 7.1.1.2- 2 for details.

Two major degradation products were identified: FOE oxalate (max. aerobic: 11.2% AR at DAT-30; anaerobic: 14.5% AR at DAT-60) and FOE sulfonic acid (max. aerobic and anaerobic: 6.6% AR at DAT-30). Additionally, the known degradation products FOE thioglycolate, FOE thioglycolate sulfoxide, FOE alcohol and FOE methylsulfone were detected with max. amounts of 2.7% AR during aerobic and/or anaerobic incubation phases. The total unidentified radioactivity amounted to a maximum of 1.1% AR at DAT-210.

III. CONCLUSIONS

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

Formation of carbon dioxide was observed up to 1.4% AR in the tested soil during the aerobic incubation phase. Two major degradation products were identified: FOE oxalate (max. aerobic: 11.2%; anaerobic: 14.5% AR) and FOE sulfonic acid (max. aerobic and anaerobic: 6.6% AR). Formation of non-extractable residues (max. aerobic: 8.4% AR at DAT-30; anaerobic: 32.6% AR at DAT-210) was observed in parallel. All major degradation products are known from the aerobic route of degradation of [phenyl-UL-^{14}C]flufenacet in soil, thus, no additional degradation products were formed during the anaerobic phase of the study.

The results indicate that flufenacet is not expected to have a potential for accumulation in the environment.

*****

Report:	**KCA 7.1.1.2 /02; [redacted], O.; 2012**
Title:	Amendment No. 2 to [thiadiazole-5-14C]FOE 5043: Anaerobic Degradation/Metabolism in Two European Soils
Report No:	MEF-11/908
Document No:	M-437443-03-1
Guidelines:	• OECD Test Guideline No. 307 • OCSPP Test Guideline No. 835.4100/4200
GLP:	Yes

Executive Summary

The degradation of [thiadiazole-5-^{14}C]flufenacet under anaerobic conditions was investigated in two soils in the dark in the laboratory for 120 days at 19.7 °C, applying an aerobic incubation phase of 15 days (soil moisture 55 ± 5% of the maximum water holding capacity) before start of the anaerobic incubation phase (total study period 135 days):

Soil	Source	Texture (USDA)	pH [1]	OC [%]
Hoefchen am Hohenseh	Burscheid, Germany	silt loam	6.1	2.0
Dollendorf II	Blankenheim, Germany	loam	7.0	4.6

[1] pH in 0.01 M $CaCl_2$

The study application rate (SAR) was 151.2 µg/100 g soil (dry weight), equal to 1.5 mg flufenacet/kg soil (dry weight).

During the aerobic incubation phase, duplicate test systems were processed and analyzed 0 and 15 days after treatment (DAT). During the anaerobic incubation phase, duplicate test systems were processed and analyzed at DAT-15, DAT-17, DAT-21, DAT-29, DAT-35, DAT-48, DAT-77, DAT-105 and DAT-135, corresponding to 0, 2, 6, 14, 20, 33, 62, 90 and 120 days after soil flooding (DASF).

In the following those parts of the study are summarized which were performed to elucidate the route of degradation in soil under anaerobic conditions. Parts concerning evaluation of rate of degradation are reported in section CA 7.1.2.1.3 (study KCA 7.1.2.1.3 /02) of this document.

Overall mean material balance was 96.2 and 96.5 of applied radioactivity (% AR) for soil Hoefchen am Hohenseh and Dollendorf II, respectively.

The following maximum amounts of carbon dioxide were detected at DAT-15 (end of aerobic incubation phase): 1.6% AR in soil Hoefchen am Hohenseh and 1.9% AR in soil Dollendorf II. Formation of volatile organic compounds was not significant, values being ≤ 0.1% AR at all sampling intervals in both soils.

Total extractable residues decreased from DAT-0 to DAT-15 during the aerobic incubation phase from 96.4 to 78.1% AR in soil Hoefchen am Hohenseh and from 93.1 to 85.0% AR in soil Dollendorf II. During the anaerobic incubation phase from DAT-15 (DASF-0) to DAT-135 (DASF-120) total extractable residues decreased from 86.6 to 68.3% AR in soil Hoefchen am Hohenseh and from 88.5 to 59.4% AR in soil Dollendorf II.

Non-extractable residues (NER) increased from DAT-0 to DAT-15 during the aerobic incubation phase from 0.8 to 16.9% AR in soil Hoefchen am Hohenseh and from 3.7 to 10.1% AR in soil Dollendorf II. During the anaerobic incubation phase NER increased further towards end of the study (DAT-135) to 24.5 and 31.6% AR in soil Hoefchen am Hohenseh and Dollendorf II, respectively.

The amount of flufenacet in the entire test system decreased from DAT-0 to DAT-15 during the aerobic incubation phase from 96.4 to 30.8% AR at DAT-15 in soil Hoefchen am Hohenseh and from 93.1 to 44.2% AR in soil Dollendorf II. During the anaerobic incubation phase the amount of flufenacet in the entire test system decreased further towards end of the study (DAT-135) to 6.4 and 3.1% AR in soil Hoefchen am Hohenseh and Dollendorf II, respectively.

Three major degradation products were identified during the study: FOE-thiadone (max. aerobic: 5.9% AR at DAT-15; anaerobic: 13.6% AR at DAT-77), FOE 5043-trifluoroethanesulfonic acid (max. aerobic: 6.0% AR at DAT-15; anaerobic 5.1% AR at DAT-15) and trifluoroacetic acid (max. aerobic: 37.5% AR at DAT-15; anaerobic: 53.2% AR at DAT-105).

I. MATERIALS AND METHODS

A. MATERIALS

1. Test Item

[thiadiazole-5-^{14}C]flufenacet	
CAS No	142459-58-3
Specific activity	1.54 MBq/mg
Radiochemical purity	> 98% HPLC with radioactivity detector and TLC, scan

2. Test Soils

The soil (Table 7.1.1.2- 3) was 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.

Table 7.1.1.2- 3: Physico-chemical properties of test soil

Parameter	Soil		Soil	
	Hoefchen am Hohenseh		Dollendorf II	
Geographic location				
- city	Burscheid		Blankenheim	
- state	North-Rhine Westphalia		North-Rhine Westphalia	
- country	Germany		Germany	
GPS Coordinates	N 51° 04.0' E 007° 06.3'		N 50° 22.9' E 006° 43.0'	
Soil taxonomic classification (USDA)	loamy, mixed, mesic Typic Argudalfs		N/A	
Soil series	no information available			
Texture class (USDA)	silt loam		loam	
Sand [%] [50 µm – 2 mm]	22		48	
Silt [%] [2 µm – 50 µm]	62		28	
Clay [%] [< 2 µm]	16		24	
pH				
- in $CaCl_2$ (soil/$CaCl_2$ 1/2)	6.1		7.0	
- in water (soil/water 1/1)	6.3		7.1	
- in KCl	5.8		6.7	
Organic matter [1] [%]	3.4		7.9	
Organic carbon [%]	2.0		4.6	
Cation Exchange Capacity [meq/100 g]	11.1		19.5	
Water Holding Capacity				
maximum [g H2O ad 100 g soil DW]	54.8		79.1	
at 0.33 bar (pF 2.5) [%]	20.9		35.1	
Bulk density (disturbed) [g/cm³]	1.09		1.03	
Microbial biomass [2]	[mg microbial carbon/kg dry soil]			
	BIO -	BIO +	BIO -	BIO +
DAT-0	1089	1075	3789	3788
DAT-15	972	998	3612	3519
Anaerobic Plate Count Assay[2]	[CFU / g soil in 10^{-4} Dilution]			
	BIO -	BIO +	BIO -	BIO +
DAT-135	7.33×10^4	1.30×10^5	3.30×10^3	1.33×10^4

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

[2] BIO- samples were left untreated, BIO+ samples were applied with solvent of application solution

DAT: days after treatment GPS: global positioning system

DW: dry weight USDA: United States Department of Agriculture

B. STUDY DESIGN

1. Experimental Conditions

Static test systems were used, consisting of Erlenmeyer flasks filled with soil and equipped with solid trap attachments for collection of carbon dioxide and volatile organic compounds during the aerobic incubation period. 100 g of the sieved soil (dry weight equivalents) were weighed into each flask and the soil moisture was adjusted to 55 ± 5% maximum water holding capacity by addition of de-ionized water. The untreated test systems were equilibrated to study conditions for 4 days prior to application.

After the aerobic incubation phase the trap attachments of the remaining test systems were removed and the soil of each flask was flooded with approx. 150 mL of oxygen-depleted, de-ionized water

(approx. 3 cm above soil level). Afterwards, the flasks were equipped with sealable double-valve glass stoppers, flushed with argon for 1 minute and connected to air-tight gas sampling bags, which had been flushed with nitrogen gas before. The valves were set to connect flask headspace and gas sampling bag, but closing the system from the outer atmosphere.

The study application rate (SAR) was based on a single field application rate of flufenacet of 600 g/ha, resulting in a nominal SAR 160 µg/100 g soil (dry weight), equal to 1.6 mg/kg soil (dry weight). The actual SAR was 151.2 µg/100 g soil (dry weight), equal to 1.5 mg flufenacet/kg soil (dry weight).

The application solution was prepared in methanol/water (1:1, *v/v*). 369 µL of the application solution were applied drop wise onto the soil surface of the respective test systems using a pipette. After application, the test vessels were closed with the trap attachments (except DAT-0 samples).

The test systems were incubated in the dark for the total study period of 135 days at 19.7 °C in a walk-in climatic chamber. After the aerobic incubation phase of 15 days, the test systems were additionally placed in inert gas flooded boxes within the walk-in climatic chamber for the anaerobic incubation phase of 120 days.

2. Sampling

Eleven sampling intervals were distributed over the entire incubation period of 135 days, two sampling intervals during the aerobic incubation phase and nine during the anaerobic incubation phase.

During the aerobic incubation phase, duplicate test systems were processed and analyzed 0 and 15 days after treatment (DAT). During the anaerobic incubation phase, duplicate test systems were processed and analyzed at DAT-15, DAT-17, DAT-21, DAT-29, DAT-35, DAT-48, DAT-77, DAT-105 and DAT-135, corresponding to 0, 2, 6, 14, 20, 33, 62, 90 and 120 days after soil flooding (DASF).

Determinations of microbial biomass were performed at DAT-0 and DAT-15 of the aerobic incubation phase. Anaerobic plate count assays were performed at DAT-135 of the anaerobic incubation phase.

3. Analytical Procedures

At each sampling interval of the aerobic phase, the trap attachments were removed from the test systems and the soil was extracted three times at ambient temperature using acetonitrile/water (1:1, *v/v*), followed by two microwave-accelerated extractions: first with acetonitrile/water (1:1, *v/v*) at 70 °C and second with methanol at 50 °C. After each extraction step, supernatant and soil were separated by centrifugation and decantation.

At each sampling interval of the anaerobic phase, the test systems were connected to a combustion oven unit to determine the volatiles present in the headspace of the test systems and the gas sampling bags. Afterwards, the oxygen content, redox potential and pH of the water was determined as well as the redox potential and pH of the soil. The water was separated from the soil by decantation and centrifugation to allow for separate analysis. Afterwards, the soil was extracted as described for the aerobic incubation phase.

The soil extracts and, if applicable, the water were characterized by liquid scintillation counting as well as by HPLC/radiodetection and TLC/radiodetection. The limit of detection (LOD) for both chromatographic methods was 0.3% AR. The amount of volatiles and non-extractable residues was determined by liquid scintillation counting and/or combustion/liquid scintillation counting, respectively.

The identity of the test item and its degradation products was elucidated by HPLC-MS and/or HPLC-MS/MS including accurate mass determination.

II. RESULTS AND DISCUSSION

A. EXTRACTION AND QUANTITATION OF RADIOACTIVITY IN SOIL SAMPLES

Table 7.1.1.2- 4 and Table 7.1.1.2- 5 summarizes the degradation of [thiadiazole-5-^{14}C]flufenacet and the formation and degradation of its degradation products as a function of time.

Table 7.1.1.2- 4: **Degradation of flufenacet in Soil Hoefchen am Hohensch (Entire System) under Anaerobic Conditions** (expressed as percent of applied radioactivity, mean value of duplicates)

Compound	DAT	0	15 [1]	15 [2]	17	21	29	35	48	77	105	135
	DASF	N/A		0	2	6	14	20	33	62	90	120
flufenacet		96.4	30.8	42.8	38.8	33.3	25.5	22.4	18.2	13.0	9.7	6.4
FOE-thiadone		n.d.	5.9	4.8	8.5	10.5	11.6	12.7	13.1	13.6	12.2	10.6
FOE 5043-trifluoro-ethanesulfonic acid		n.d.	2.5	5.1	5.0	4.0	4.4	2.8	4.2	2.1	2.2	2.3
trifluoroacetic acid		n.d.	37.5	31.4	32.8	36.5	43.5	42.3	42.1	47.3	46.0	47.9
Unid./Diff. Radioactivity		n.d.	1.3	2.5	1.2	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.8
Total Extractable Residues		96.4	78.1	86.6	86.4	84.4	82.3	80.3	77.6	76.0	70.1	68.3
Carbon dioxide		n.a.	1.6	1.5	1.6	1.6	1.6	1.6	1.6	1.6	1.7	1.6
Volatile Organic Compounds		n.a.	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1
Non-extractable Residues		0.8	16.9	10.2	9.5	10.9	12.5	13.9	16.0	19.1	21.4	24.5
Material Balance		**97.2**	**96.5**	**98.3**	**97.5**	**96.9**	**96.4**	**95.9**	**95.2**	**96.6**	**93.3**	**94.4**

DAT: days after treatment
DASF: days after soil flooding
n.a.: not analyzed
n.d.: not detected
[1] before soil flooding (aerobic incubation phase)
[2] after soil flooding (anaerobic incubation phase)

Table 7.1.1.2- 5: Degradation of flufenacet in Soil Dollendorf II (Entire System) under Anaerobic Conditions (expressed as percent of applied radioactivity; mean value of duplicates)

Compound	DAT	0	15 [1]	15 [2]	17	21	29	35	48	77 [3]	105	135
	DASF	N/A		0	2	6	14	20	33	62 [3]	90	120
flufenacet		93.1	44.2	35.4	27.0	23.3	18.2	15.9	10.6	12.1	4.5	3.1
FOE-thiadone		n.d.	4.3	7.1	11.3	12.4	11.5	11.9	8.7	7.7	5.2	2.7
FOE 5043-trifluoro-ethanesulfonic acid		n.d.	6.0	3.2	1.7	1.1	0.7	< LOD	0.8	0.7	LOD	1.2
trifluoroacetic acid		n.d.	28.0	40.4	46.5	48.7	53.2	51.3	52.7	47.3	53.2	51.5
Unid./Diff. Radioactivity		n.d.	2.4	2.4	1.1	1.0	n.d.	n.d.	< LOD	< LOD	n.d.	0.7
Total Extractable Residues		93.1	85.0	88.5	87.7	86.7	83.6	79.8	73.8	68.9	63.7	59.4
Carbon dioxide		n.a.	1.9	1.8	1.9	1.9	1.9	1.9	1.9	1.9	1.9	1.9
Volatile Organic Compounds		n.a.	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1
Non-extractable Residues		3.7	10.1	8.6	8.8	10.1	12.6	15.5	19.4	24.5	27.9	31.6
Material Balance		**96.9**	**97.0**	**98.9**	**98.4**	**98.8**	**98.0**	**97.2**	**95.1**	**95.4**	**93.6**	**92.9**

DAT: days after treatment DASF: days after soil flooding

n.a.: not analyzed n.d.: not detected

[1] before soil flooding (aerobic incubation phase)

[2] after soil flooding (anaerobic incubation phase)

[3] Only one replicate was considered, as the material balance of the other replicate was not in the acceptable range between 90 and 110% AR.

B. MATERIAL BALANCE

The amount of dosed test item was determined at DAT-0 before, during and after the application and was set to 100% AR for all samples. The total radioactivity recovery (mean of duplicates) of all sampling intervals ranged from 93.3 to 98.3% AR in soil Hoefchen am Hohenseh (overall mean 96.2% AR, RSD 1.4%) and from 92.9 to 98.9% AR in soil Dollendorf II (overall mean 96.5% AR, RSD 2.0%). See also Table 7.1.1.2- 4 and Table 7.1.1.2- 5.

The complete material balance found at all sampling intervals demonstrated that no significant portion of radioactivity dissipated from the vessels or was lost during processing of theses samples.

C. EXTRACTABLE AND NON-EXTRACTABLE RESIDUES

Total extractable residues decreased from DAT-0 to DAT-15 during the aerobic incubation phase from 96.4 to 78.1% AR in soil Hoefchen am Hohenseh and from 93.1 to 85.0% AR in soil Dollendorf II. During the anaerobic incubation phase from DAT-15 (DASF-0) to DAT-135 (DASF-120) total extractable residues decreased from 86.6 to 68.3% AR in soil Hoefchen am Hohenseh and from 88.5 to 59.4% AR in soil Dollendorf II.

Non-extractable residues (NER) increased from DAT-0 to DAT-15 during the aerobic incubation phase from 0.8 to 16.9% AR in soil Hoefchen am Hohenseh and from 3.7 to 10.1% AR in soil

Dollendorf II. During the anaerobic incubation phase NER increased further towards end of the study (DAT-135) to 24.5 and 31.6% AR in soil Hoefchen am Hohenseh and Dollendorf II, respectively. See also Table 7.1.1.2- 4 and Table 7.1.1.2- 5.

D. VOLATILIZATION

The following maximum amounts of carbon dioxide were detected at DAT-15 (end of aerobic incubation phase): 1.6% AR in soil Hoefchen am Hohenseh and 1.9% AR in soil Dollendorf II. Formation of volatile organic compounds was not significant, values being ≤ 0.1% AR at all sampling intervals in both soils. See also Table 7.1.1.2- 4 and Table 7.1.1.2- 5.

E. DEGRADATION OF TEST ITEM

The amount of flufenacet in the entire test system decreased from DAT-0 to DAT-15 during the aerobic incubation phase from 96.4 to 30.8% AR at DAT-15 in soil Hoefchen am Hohenseh and from 93.1 to 44.2% AR in soil Dollendorf II. During the anaerobic incubation phase the amount of flufenacet in the entire test system decreased further towards end of the study (DAT-135) to 6.4 and 3.1% AR in soil Hoefchen am Hohenseh and Dollendorf II, respectively.

Three major degradation products were identified during the study: FOE-thiadone, FOE 5043-trifluoroethanesulfonic acid and trifluoroacetic acid. FOE-thiadone was identified in soil Hoefchen am Hohenseh with maximum amounts of 5.9% AR at DAT-15 (aerobic) and 13.6% AR at DAT-77 (anaerobic) as well as in soil Dollendorf II with maximum amounts of 4.3% AR at DAT-15 (aerobic) and 12.4% AR at DAT-21(anaerobic). FOE 5043-trifluoroethanesulfonic acid was identified in soil Hoefchen am Hohenseh with maximum amounts of 2.5% AR at DAT-15 (aerobic) and 5.1% AR at DAT-15 (anaerobic) as well as in soil Dollendorf II with maximum amounts of 6.0% AR at DAT-15 (aerobic) and 3.2% AR at DAT-15 and DAT-105 (anaerobic). Trifluoroacetic acid was identified in soil Hoefchen am Hohenseh with maximum amounts of 37.5% AR at DAT-15 (aerobic) and 47.9% AR at DAT-135 (anaerobic) as well as in soil Dollendorf II with maximum amounts of 28.0% AR at DAT-15 (aerobic) and 53.2% AR at DAT-15 and DAT-105 (anaerobic). The total unidentified radioactivity amounted to a maximum of 2.5% AR at DAT-15 (aerobic and anaerobic) in both soils.

III. CONCLUSIONS

[thiadiazole-5-^{14}C]flufenacet was degraded in soil under aerobic and anaerobic conditions in the dark in the laboratory.

Formation of carbon dioxide was observed up to 1.6% AR in soil Hoefchen am Hohenseh and 1.9% AR in soil Dollendorf II during the aerobic incubation phase.

Three major degradation products were identified during the study: FOE-thiadone (max. aerobic: 5.9% AR at DAT-15; anaerobic: 13.6% AR at DAT-77), FOE 5043-trifluoroethanesulfonic acid (max. aerobic: 6.0% AR at DAT-15; anaerobic 5.1% AR at DAT-) and trifluoroacetic acid (max. aerobic: 37.5% AR at DAT-15; anaerobic: 53.2% AR at DAT-105). Formation of non-extractable residues was observed in parallel over the entire incubation period up to 24.5% AR in soil Hoefchen am Hohenseh and up to 31.6% AR in soil Dollendorf II. All major degradation products are known from the aerobic route of degradation of [thiadiazole-5-^{14}C]flufenacet in soil, thus, no additional degradation products were formed during the anaerobic phase of the study.

The results indicate that flufenacet is not expected to have a potential for accumulation in the environment.

CA 7.1.1.3 Soil photolysis

The route of degradation of flufenacet in soil under photolytic conditions was evaluated during the Annex I Inclusion and was accepted by the European Commission (7469/VI/98-Final – 3rd July 2003). The following studies are included in the Baseline Dossier:

Annex Point / Reference No	Author(s)	Year	Document No
KCA 7.1.1.3/01	[redacted], A. M.; [redacted], B. A.	1995	M-002145-01-1

An additional study has been performed for FOE-thiadone on request of the US Environmental Protection Agency (EPA) and is submitted within this Supplemental Dossier for the flufenacet renewal of approval. A summary of the route of degradation of flufenacet in soil is given in section CA 7.1.1 and Figure 7.1.1- 1.

Report:	**KCA 7.1.1.3 /02; [redacted] N. R.; [redacted], A. M.; 2001**
Title:	Soil photolysis of thiadone on loamy sand (a metabolite of FOE 5043)
Report No:	108721
Document No:	M-106297-01-1
Guidelines:	• EPA Ref: Subdivision N 161-3, Soil Photolysis Study
GLP:	Yes

Executive Summary

The photolytic route and rate of degradation of [thiadiazole-2-^{14}C]FOE-thiadone were studied in one soil under exposure to simulated sunlight in the laboratory for 14 days at 20 ± 1 °C at soil moisture of approx. 75% of 1/3 bar water holding capacity:

Soil	Source	Texture (USDA)	pH	OC [%]
Janeswill	Iowa, USA	loamy sand	7.2	1.11

A study application rate of approximately 3.2 mg per kg soil dry weight was applied.

Duplicate test systems of irradiated samples were processed and analyzed 0, 0.5, 1, 2, 3, 5, 7, 10 and 14 days after treatment (DAT). In addition, dark control samples were incubated, processed and analyzed in parallel.

The radiation intensity, spectral distribution and exposure time under experimental conditions would match natural sunlight exposure during the month of June in Painesville, Ohio.

Mean material balances ranged from 93.1 to 102.1% of applied radioactivity [% AR] for all samples and averaged 97.7 and 97.9% AR for irradiated and dark control samples, respectively.

The maximum amount of carbon dioxide was 57.8 and 57.6% AR at DAT-14 in irradiated and dark control samples, respectively. The maximum amount of volatile organic compounds was 4.7 and 2.5% AR at DAT-14 in irradiated and dark control samples, respectively.

Extractable residues decreased from study start (DAT-0) to study end (DAT-14) from 101.6 to 14.5% AR in irradiated samples and from 101.6 to 17.3% AR in dark control samples.

Non-extractable residues were formed until study termination (DAT-14) up to 19.4 and 15.7% AR in irradiated and dark control samples, respectively.

The amount of FOE-thiadone in the soil extracts decreased from DAT-0 to DAT-14 from 96.7 to 7.2% AR in irradiated samples and from 96.7 to 13.3% AR in dark control samples.

Besides carbon dioxide, one degradation product was identified in both, irradiated and dark control, samples: FOE-thiadone propionic acid conjugate (max. 6.1% AR irradiated, 12.0% AR dark control). However, this degradation product would occur only in minor amounts < 1% AR in degradation studies of the parent flufenacet, as FOE-thiadone itself was detected with max. amounts of 5.9% AR in aerobic soil degradation studies.

The experimental DT50 values of FOE-thiadone in irradiated and dark control samples were calculated using single first order kinetics, resulting in half-lives of 3.7 and 4.7 days for irradiated and dark control samples, respectively.

It is concluded that the route and rate of degradation of FOE-thiadone is driven by microbial degradation under typical conditions in the environment and photodegradation plays only a minor role in the overall fate of FOE-thiadone.

I. MATERIALS AND METHODS

A. MATERIALS

1. Test Item

[thiadiazole-2-^{14}C]FOE-thiadone	
Registry No:	84352-75-0
Specific Activity:	10.88 MBq/mg (50 mCi/mmol; 652,680 dpm/µg)
Radiochemical Purity:	95.3%
Chemical Purity:	99.3%

2. Test Soils

One soil was used (see Table 7.1.1.3- 1), which was sampled freshly from the field and sieved to a particle size of < 2 mm.

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

Parameter		Results / Units
Soil Designation		Iowa loamy sand (EFS113)
Geographic Location		
City		Janesville
State		Iowa
Country		USA
Soil Taxonomic Classification (USDA)		Two soils in close proximity: 1. Sparta Loamy fine Sand 2. Dickinson fine Sandy Loam
Soil Series		no information available
Textural Class (USDA)		loamy sand
Sand	[50 µm – 2 mm]	79.2%
Silt	[2 µm – 50 µm]	12.0%
Clay	[< 2 µm]	8.8%
pH		7.2
Organic Carbon [1]		1.11%
Organic Matter		1.91%
Cation Exchange Capacity [meq/100 g]		5.6
Water Holding Capacity at 1/3 bar (pF 2.5)		9.9%
Bulk Density (disturbed) [g/cm³]		1.34
Microbial Viability [2] [CFU x 10^6/g soil DW]		
DAT-0		9.7 (bacteria) / 0.12 (fungi)
DAT-14		1.3 (bacteria) / 0.13 (fungi)

CFU: colony forming units DW: dry weight
DAT: days after treatment USDA: United States Department of Agriculture
[1] Calculated as OC [%] = OM [%] / 1.724
[2] Test systems for determination of the microbial viability were applied with 250 µL application solution.

B. STUDY DESIGN

1. Experimental Conditions

Static test systems were used, consisting of flint glass sample jars filled with soil and equipped with opaque screw caps fitted with Teflon liners. For the irradiated samples the tops of the sample jar caps were previously cut out and a quartz disk was attached with glue. The Teflon liners were also cut out to leave an O-ring gasket. For collection of volatiles four separate flow-through test systems (two dark controls and two irradiated) were prepared in 16-oz jars. The lids of these jars were also fitted with quartz disks drilled with two 1/8-in holes. The jars were connected to a small pump, which pumped moisturized laboratory air through each jar. The air stream from each jar was passed through traps for adsorption of volatile organic compounds (VOC) and carbon dioxide.

For preparation of the test systems, 5 g dry weight equivalents of the sieved soil with a soil moisture of 75% field capacity (FC) at 1/3 bar were weighed into the jars. For preparation of the separate test systems for collection of volatiles, 15 g dry weight equivalents of the sieved soil with a soil moisture of 75% field capacity (FC) at 1/3 bar were weighed into the separate jars.

The study application rate (SAR) of FOE-thiadone was approximately 3.2 mg per kg soil dry weight, based on one-half the application rate used for the soil photolysis study of flufenacet (KCA 7.1.1.3/01). Thus, the SAR was equal to 16.9 µg [thiadiazole-2-^{14}C]FOE-thiadone per test system.

The application solution was prepared in acetonitrile/water (1:10, *v/v*). 250 µL of the application solution were applied drop wise onto the soil surface of the respective test systems using a gas-tight syringe. After application, the DAT-0 samples were immediately processed. The remaining test systems were sealed and incubated either under dark or irradiated conditions.

The separate test systems for collection of volatiles were applied with 3 x 250 µL application solution and connected to the flow-through system.

The irradiated test systems were incubated using a 12-hour light / 12-hour dark cycle for 14 days at 20 ± 1°C in a solar simulator 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 continuously determined using a radiometer. The radiation intensity, spectral distribution and exposure time under experimental conditions would match natural sunlight exposure during the month of June in Painesville, Ohio.

The dark control test systems were incubated in the dark for 14 days at 20 ± 1°C and a soil moisture of 75% FC at 1/3 bar in an environmental chamber.

2. Sampling

Nine sampling intervals were distributed over the entire incubation period of 14 days.

Duplicate samples were processed and analyzed 0, 0.5, 1, 2, 3, 5, 7, 10 and 14 days after treatment (DAT) for both irradiated and dark samples.

Trapping solutions for adsorption carbon dioxide were sampled and replaced at DAT-0.5, 1, 2, 3, 4, 5, 6, 7, 8, 10 and 14 . Trapping solutions for adsorption volatile organic compounds were sampled and replaced at DAT-3, 7, 10 and 14.

Microbial viability of the soil was determined at DAT-0 and DAT-14.

3. Analytical Procedures

At each sampling interval, duplicate non-irradiated and irradiated test systems were removed from the environmental chamber or photolysis apparatus.

The entire soil of each jar was extracted once with acetonitrile followed by an acidic extraction with acetonitrile/water (1:1, *v/v*) containing 0.1 N HCl. After each extraction step, extracts were separate from soil by filtration. The acidic extracts were additionally partitioned three times with ACN/DCM (1/2, *v/v*).

Soil extracts were characterized by liquid scintillation counting (LSC) and HPLC/radiodetection (organic extracts only). The limit of detection (LOD) for the HPLC/radiodetection method was 0.3% AR for the acetonitrile extracts and 3% AR for the acidic extracts. The amount of volatiles and non-extractable residues was determined by liquid scintillation counting and combustion/ liquid scintillation counting, respectively.

The identity of the test item and its degradation product was elucidated by HPLC-MS.

The degradation kinetics of the test item was determined using single first order kinetics. Input datasets were the mean residual amounts found at each sampling interval. DT50 values were calculated from the resulting parameters.

II. RESULTS AND DISCUSSION

A. EXTRACTION AND QUANTITATION OF RADIOACTIVITY IN SOIL SAMPLES

Table 7.1.1.3- 2 summarizes the degradation of [thiadiazole-2-^{14}C]FOE-thiadone and the formation and degradation of its degradation products as a function of time.

Table 7.1.1.3- 2: Degradation of FOE-thiadone in Soil under Photolytic Conditions
(expressed as percent of applied radioactivity; mean value of duplicates)

Compound	Mean	DAT 0	0.5	1	2	3	5	7	10	14
FOE-thiadone	irradiated	96.7	79.2	77.3	52.3	48.2	35.2	21.6	12.5	7.2
	dark	96.7	83.6	78.1	65.7	59.8	41.1	28.9	18.3	13.3
FOE-thiadone propionic acid conjugate	irradiated	n.d.	0.6	0.9	2.3	4.7	3.8	5.4	6.1	2.9
	dark	n.d.	0.2	0.4	1.3	3.6	7.7	12.0	8.6	1.2
Reg #1 (fortification impurity)	irradiated	0.5	0.2	n.d.	0.5	n.d.	n.d.	0.9	n.d.	n.d.
	dark	0.5	1.0	0.9	0.7	0.7	1.0	0.5	0.4	n.d.
Reg #2 (fortification impurity)	irradiated	1.2	0.9	1.1	1.1	1.1	0.9	0.8	0.8	1.1
	dark	1.2	1.3	0.9	1.2	1.0	0.9	0.9	0.7	0.8
Unidentified Radioactivity [1]	irradiated	3.2	0.1	n.d.	n.d.	1.2	1.6	2.3	3.5	3.3
	dark	3.2	0.2	n.d.	0.4	0.4	1.0	1.2	1.5	1.1
Total Extractable Residues	irradiated	101.6	81.0	79.3	56.2	55.2	41.5	31.0	22.9	14.5
	dark	101.6	86.3	80.3	69.2	65.5	51.7	43.5	29.5	17.3
Carbon dioxide	irradiated	n.a.	6.0	11.2	23.4	27.9	38.8	43.8	53.5	57.8
	dark	n.a.	5.9	11.2	18.4	25.0	34.7	43.0	53.2	60.1
Volatile Organic Compounds	irradiated	n.a.	n.a.	n.a.	n.a.	1.0	1.0	2.8	3.9	4.7
	dark	n.a.	n.a.	n.a.	n.a.	0.8	0.8	1.7	2.0	2.5
Non-Extractable Residues	irradiated	0.5	6.8	6.3	14.4	16.4	14.5	20.9	21.2	19.4
	dark	0.5	2.9	4.6	6.8	8.9	13.9	14.4	17.1	15.7
Material Balances	irradiated	**102.1**	**93.8**	**96.8**	**94.0**	**100.5**	**95.8**	**98.5**	**101.5**	**96.4**
	dark	**102.1**	**95.1**	**96.1**	**94.2**	**99.4**	**100.3**	**100.9**	**99.8**	**93.1**

DAT: days after treatment n.d.: not detected n.a.: not analyzed
[1] All individual areas of radioactivity were less than 2% of the applied radioactivity

B. MATERIAL BALANCE

Mean material balances ranged from 93.1 to 102.1% of applied radioactivity [% AR] for all samples and averaged 97.7 and 97.9 % AR for irradiated and dark control samples, respectively.

The complete material balance found at all sampling intervals demonstrated that no significant portion of radioactivity dissipated from the vessels or was lost during processing of theses samples.

C. EXTRACTABLE AND NON-EXTRACTABLE RESIDUES

Extractable residues decreased from study start (DAT-0) to study end (DAT-14) from 101.6 to 14.5% AR in irradiated samples and from 101.6 to 17.3% AR in dark control samples. Non-extractable residues were formed until study termination (DAT-14) up to 19.4 and 15.7% AR in irradiated and dark control samples, respectively.

D. VOLATILIZATION

The maximum amount of carbon dioxide was 57.8 and 57.6% AR at DAT-14 in irradiated and dark control samples, respectively.

The maximum amount of volatile organic compounds was 4.7 and 2.5% AR at DAT-14 in irradiated and dark control samples, respectively.

E. DEGRADATION OF TEST ITEM

The amount of FOE-thiadone in the soil extracts decreased from DAT-0 to DAT-14 from 96.7 to 7.2% AR in irradiated samples and from 96.7 to 12.3% AR in dark control samples, thus not indicating a significant difference in the rate of degradation.

Besides carbon dioxide, one degradation product was identified in both, irradiated and dark control, samples: FOE-thiadone propionic acid conjugate (max. 6.1% AR irradiated; 12.0% AR dark control).

The experimental half-lives of FOE-thiadone in irradiated and dark samples were calculated using single first order (SFO) kinetics (see Table 7.1.1.3- 3).

Table 7.1.1.3- 3: Photodegradation Kinetics of FOE-thiadone in Soil

Test System	Kinetic Model	DT_{50} [days]	R^2
Irradiated	SFO	3.7	0.9904
Dark	SFO	4.7	0.9858

III. CONCLUSIONS

FOE-thiadone was rapidly degraded in soil both under exposure to simulated sunlight as well as under dark conditions in the laboratory. The experimental half-lives in irradiated and dark control samples were calculated as 3.7 and 4.7 days, respectively.

Besides carbon dioxide, one degradation product was identified in both, irradiated and dark control, samples: FOE-thiadone propionic acid conjugate (max. 6.1% AR irradiated; 12.0% AR dark control). However, this degradation product would occur only in minor amounts < 1% AR in degradation studies of the parent flufenacet, as FOE-thiadone itself was detected with max. amounts of 5.9% AR in aerobic soil degradation studies.

It is concluded that the route and rate of degradation of FOE-thiadone is driven by microbial degradation under typical conditions in the environment and photodegradation plays only a minor role in the overall fate of FOE-thiadone.

CA 7.1.2 Rate of degradation in soil

Flufenacet was rapidly degraded in soil under aerobic and anaerobic conditions in the laboratory as well as under field conditions. The kinetic models and DT_{50} values in soil of flufenacet and its major degradation products used for modeling purpose and trigger evaluation (best-fit) as well as the formation fractions in soil for major degradation products are summarized in sections CA 7.1.2.1 and CA 7.1.2.2.

Modeling input values for the calculation of predicted environmental concentrations (PECs) of flufenacet and its major degradation products in soil (PEC_{soil}), groundwater (PEC_{gw}) and surface water (PEC_{sw}) were derived from studies and kinetic evaluations according to FOCUS kinetics (2005, 2006, 2011) [2, 3, 4] summarized in sections CA 7.1.1, CA 7.1.2 and CA 7.2, and are submitted within this Supplemental Dossier for the flufenacet renewal of approval. The DT_{50} values and maximum occurrences / formation fractions in soil and aquatic systems of flufenacet and its major degradation products used as modeling input values for the calculation of PECs are summarized in Table 7.1.2- 1 to Table 7.1.2- 3.

Table 7.1.2- 1: DT_{50} values and maximum occurrences in soil of flufenacet and its major degradation products used as modeling input values for calculation of PEC_{soil}

Compound	Modeling Input Parameter	Endpoint	Comment
flufenacet	DT_{50} in soil [days]	32.2	worst case, lab., non-normalized
FOE oxalate	DT_{50} in soil [days]	20.7	worst case, lab., non-normalized
	maximum occurrence in soil [%]	26.5	lab. aerobic soil
FOE sulfonic acid	DT_{50} in soil [days]	258.4	worst case, lab., non-normalized
	maximum occurrence in soil [%]	26.3	lab. aerobic soil
FOE methylsulfone	DT_{50} in soil [days]	163.0	worst case, lab., non-normalized
	maximum occurrence in soil [%]	6.6	lab. aerobic soil
FOE-thiadone	DT_{50} in soil [days]	2.9	worst case, lab., non-normalized
	maximum occurrence in soil [%]	5.9	lab. aerobic soil
FOE 5043-trifluoro-ethanesulfonic acid	DT_{50} in soil [days]	22.5	worst case, lab., non-normalized
	maximum occurrence in soil [%]	6.0	lab. aerobic soil
trifluoroacetic acid	DT_{50} in soil [days]	1000	worst case, lab., non-normalized
	maximum occurrence in soil [%]	81.5	lab. aerobic soil

---

[2] FOCUS kinetics (2005): "Guidance Document on Estimating Persistence and Degradation Kinetics from Environmental Fate Studies on Pesticides in EU Registration", Report of the FOCUS Work Group on Degradation Kinetics, EC Document Reference SANCO 10058/2005, version 1.0.

[3] FOCUS kinetics (2006): "Guidance Document on Estimating Persistence and Degradation Kinetics from Environmental Fate Studies on Pesticides in EU Registration", Report of the FOCUS Work Group on Degradation Kinetics, EC Document Reference Sanco/10058/2005 version 2.0.

[4] FOCUS (2011): Generic Guidance for Estimating Persistence and Degradation Kinetics from Environmental Fate Studies on Pesticides in EU Registration, version 1.0.

Table 7.1.2- 2: DT_{50} values and formation fraction / maximum occurrences in soil of flufenacet and its major degradation products used as modeling input values for calculation of PEC_{gw}

Compound	Modeling Input Parameter	Endpoint	Comment
flufenacet	DT_{50} in soil [days]	18.3	geomean, lab., normalized
FOE oxalate	DT_{50} in soil [days]	13.7	geomean, lab normalized
	FF flufenacet → FOE oxalate	0.414	mean, lab.
FOE sulfonic acid	DT_{50} in soil [days]	20.5	median, field, normalized
	FF flufenacet → FOE sulfonic acid	0.192	mean, lab.
FOE methylsulfone	DT_{50} in soil [days]	67.7	geomean, lab., normalized
	FF flufenacet → FOE methylsulfone	0.066	mean, lab.
FOE-thiadone	DT_{50} in soil [days]	1.6	geomean, lab., normalized
	FF flufenacet → FOE-thiadone	0.570	mean, lab.
FOE 5043-trifluoro-ethanesulfonic acid	DT_{50} in soil [days]	9.1	geomean, lab., normalized
	FF FOE-thiadone → FOE 5043-trifluoro-ethanesulfonic acid	0.469	mean, lab.
trifluoroacetic acid	DT_{50} in soil [days]	1000	default, worst case
	FF flufenacet → trifluoroacetic acid	0.430	mean, lab.
	FF FOE-thiadone → trifluoroacetic acid	0.531	mean, lab.

FF: formation fraction

Table 7.1.2- 3: DT_{50} values and maximum occurrences in soil and aquatic systems of flufenacet and its major degradation products used as modeling input values for calculation of PEC_{sw}

Compound	Modeling Input Parameter	Endpoint	Comment
flufenacet	DT_{50} in soil [days]	18.3	geomean, lab., normalized
	DT_{50} in water [days]	49.6	degradation total system
	DT_{50} in sediment [days]	1000	worst case default
	max. occurrence in sediment [%]	32.4	lab., water/sediment study
FOE oxalate	DT_{50} in soil [days]	13.7	geomean, lab normalized
	max. occurrence in soil [%]	26.5	lab. aerobic soil
	DT_{50} in water [days]	1000	worst case
	DT_{50} in sediment [days]	1000	worst case
	max. occurrence in total system [%]	0	no major degradation product in water/sediment studies
	max. occurrence in sediment [%]	0	no major degradation product in sediment
	max. occurrence in water [%]	0	no major degradation product in water
FOE sulfonic acid	DT_{50} in soil [days]	20.5	median, field, normalized
	max. occurrence in soil [%]	26.3	lab. aerobic soil
	DT_{50} in water [days]	1000	worst case
	DT_{50} in sediment [days]	1000	worst case
	max. occurrence in total system [%]	0	no major degradation product in water/sediment studies
	max. occurrence in sediment [%]	0	no major degradation product in sediment
	max. occurrence in water [%]	0	no major degradation product in water

Table 7.1.2- 3 (continued)

Compound	Modeling Input Parameter	Endpoint	Comment
FOE methylsulfide	DT_{50} in soil [days]	1000	worst case default
	max. occurrence in soil [%]	0	no major soil degradation product
	DT_{50} in water [days]	1000	worst case
	DT_{50} in sediment [days]	1000	worst case
	max. occurrence in total system [%]	11.4	total system
	max. occurrence in sediment [%]	3.5	water/sediment study
	max. occurrence in water [%]	8.0	water/sediment study
FOE methylsulfone	DT_{50} in soil [days]	67.7	geomean, lab., normalized
	max. occurrence in soil [%]	6.6	lab. aerobic soil
	DT_{50} in water [days]	1000	worst case
	DT_{50} in sediment [days]	1000	worst case
	max. occurrence in total system [%]	0	no major degradation product in water/sediment studies
	max. occurrence in sediment [%]	0	no major degradation product in sediment
	max. occurrence in water [%]	0	no major degradation product in water
FOE-thiadone	DT_{50} in soil [days]	1.6	geomean, lab., normalized
	max. occurrence in soil [%]	5.9	lab. aerobic soil
	DT_{50} in water [days]	1000	worst case
	DT_{50} in sediment [days]	1000	worst case
	max. occurrence in total system [%]	84.3	total system
	max. occurrence in sediment [%]	3.8	water/sediment study
	max. occurrence in water [%]	81.8	water/sediment study
FOE 5043-trifluoro-ethanesulfonic acid (TFESA)	DT_{50} in soil [days]	9.1	geomean, lab., normalized
	max. occurrence in soil [%]	6.0	lab. aerobic soil
	DT_{50} in water [days]	1000	worst case
	DT_{50} in sediment [days]	1000	worst case
	max. occurrence in total system [%]	0	no major degradation product in water/sediment studies
	max. occurrence in sediment [%]	0	no major degradation product in sediment
	max. occurrence in water [%]	0	no major degradation product in water
trifluoroacetic acid (TFA)	DT_{50} in soil [days]	1000	default, worst case
	max. occurrence in soil [%]	81.5	lab. aerobic soil
	DT_{50} in water [days]	1000	worst case
	DT_{50} in sediment [days]	1000	worst case
	max. occurrence in total system [%]	0	no major degradation product in water/sediment studies
	max. occurrence in sediment [%]	0	no major degradation product in sediment
	max. occurrence in water [%]	0	no major degradation product in water

CA 7.1.2.1 Laboratory studies

The degradation rates of flufenacet and its major degradation products in soil were studied using three different radiolabel positions, [phenyl-UL-^{14}C], [thiadiazole-2-^{14}C] and [thiadiazole-5-^{14}C], as well as unlabeled test items. The studies have been performed in a number of soils in the dark in the laboratory at temperatures 20 ± 2 °C and different soil moistures. The kinetic models and DT_{50} values used for modeling purpose (non-normalized) and trigger evaluation (best fit) as well as formation fractions for major degradation products are summarized in Table 7.1.2.1-1 to Table 7.1.2.1-14.

Furthermore, a supportive study concerning the evolution of the microbial biomass in biometer flask systems during degradation studies in soil under aerobic conditions in the dark in the laboratory was evaluated during the Annex I Inclusion and was accepted by the European Commission (7469/VI/98-Final – 3rd July 2003). The following study is included in the Baseline Dossier:

Annex Point / Reference No	Author(s)	Year	Document No
KCA 7.1.2.1/01	[redacted]	1995	M-002164-01-1

Table 7.1.2.1- 1: Summary of DT_{50} and DT_{90} values for degradation of flufenacet in aerobic soils 20 °C for trigger evaluation

Soil	Texture (USDA)	Annex Point / Reference No	Kinetic Model [1]	DT_{50} [days]	DT_{90} [days]
Howe Indiana	sandy loam	KCA 7.1.2.1.1/01	SFO	33.8 [2]	n.d.
Howe Indiana	sandy loam	KCA 7.1.2.1.1/02	SFO	63.6 [3]	n.d.
BBA 2.2	loamy sand	KCA 7.1.2.1.1/03	1.5st order	25.5	132
Laacherhof AIII	silt loam		1.5st order	10.1	52.6
Hoefchen im Tal	silt loam		1.5st order	27.1	90.0
Laacherhof AXXa	sandy loam	KCA 7.1.2.1.1 /04	SFO	7	34
Hoefchen am Hohensch.	silt loam	KCA 7.1.2.1.1 /05	DFOP	14.7	44.7
Laacherhof AXXa	loamy sand	KCA 7.1.2.1.1 /06	SFO	18.5	61.6
Dollendorf	clay loam		DFOP	15.4	46.4
Wurmwiese	loam		SFO	13.5	44.8

[1] SFO: single first order, DFOP: double first order in parallel
[2] Cut-off of the soil residue data after DAT-28, due to collapse of the microbial activity
[3] Cut-off of the soil residue data after DAT-32, due to collapse of the microbial activity
n.d.: not determined

Table 7.1.2.1- 2: Summary of DT_{50} values for degradation of flufenacet in aerobic soils 20 °C for modeling purpose (non-normalized)

Soil	Texture (USDA)	Annex Point / Reference No	Kinetic Model [1]	DT_{50} [days]
Howe Indiana	sandy loam	KCA 7.1.2.1.1 /07	SFO	32.2
Howe Indiana	sandy loam	KCA 7.1.2.1.1 /09	SFO	55.0 [2]
BBA 2.2	loamy sand		SFO	31.9
Laacherhof AIII	silt loam	KCA 7.1.2.1.1 /07	SFO	15.2
Hoefchen im Tal	silt loam		SFO	20.4
Laacherhof AXXa	sandy loam	KCA 7.1.2.1.1 /07	SFO	7.4
Hoefchen am Hohenseh	silt loam	KCA 7.1.2.1.1 /08	SFO	15.8
Laacherhof AXXa	loamy sand		SFO	19.9
Dollendorf	clay loam	KCA 7.1.2.1.1 /08	SFO	16.3
Wurmwiese	loam		SFO	14.9

[1] SFO: single first order
[2] Outlier not considered for selection of DT_{50} for PEC_{soil} calculation.

Table 7.1.2.1- 3: Summary of DT_{50} and DT_{90} values for degradation of FOE oxalate in aerobic soils 20 °C for trigger evaluation

Soil	Texture (USDA)	Annex Point / Reference No	Kinetic Model [1]	DT_{50} [days]	DT_{90} [days]
Howe Indiana	sandy loam	KCA 7.1.2.1.2 /11	SFO*-SFO	19.6	65.0
BBA 2.2	loamy sand		FOMC*-SFO	11.9	39.6
Laacherhof AIII	silt loam	KCA 7.1.2.1.2 /11	SFO*-SFO	23.4	44.5
Hoefchen im Tal	silt loam		FOMC*-SFO	13.4	77.7

[1] SFO-SFO: single first order (parent) – single first order (degradation product)
FOMC-SFO: first order multiple compartment (parent) – single first order (degradation product)
* Kinetic parameters of FOE oxalate degradation were derived based on the pathway fit using the best-fit kinetics selected from the parent only fits.

Table 7.1.2.1- 4: Summary of DT_{50} values for degradation of FOE oxalate in aerobic soils 20 °C for modeling purpose (non-normalized)

Soil	Texture (USDA)	Annex Point / Reference No	Kinetic Model [1]	DT_{50} [days]
Howe Indiana	sandy loam	KCA 7.1.2.1.2 /14	SFO - SFO	6.9
BBA 2.2	loamy sand		SFO - SFO	20.7
Laacherhof AIII	silt loam	KCA 7.1.2.1.2 /14	SFO - SFO	19.4
Hoefchen im Tal	silt loam		SFO - SFO	13.1

[1] SFO-SFO: single first order (parent) – single first order (degradation product)

Table 7.1.2.1- 5: Summary of DT_{50} and DT_{90} values for degradation of FOE sulfonic acid in aerobic soils 20 °C for trigger evaluation

Soil	Texture (USDA)	Annex Point / Reference No	Kinetic Model [1]	DT_{50} [days]	DT_{90} [days]
BBA 2.1	sand	KCA 7.1.2.1.2 /01	linear	266.9	n.d.
BBA 2.2	loamy sand		linear	189.2	n.d.
Laacherhof AIII	silt loam		linear	247.3	n.d.
Laacherhof AXXa	sandy loam	KCA 7.1.2.1.2 /08	SFO	61.8	205
Laacherhof AIII	silt loam		SFO	60.2	200
Laacherhof AXXa	loamy sand	KCA 7.1.2.1.2 /07	SFO	73.4	243.8
Dollendorf II	loam		SFO	6.7	22.3
Hoefchen am Hohenseh	silt loam		DFOP	24.0	105.8
Wurmwiese	sandy loam		SFO	49.8	165.3
Hanscheider Hof	loam	KCA 7.1.2.1.2/10	SFO	27.3	90.7
Frankenforst	silt loam		SFO	21.8	72.4
LUFA 2.3	sandy loam		SFO	63.9	212
LUFA 6S	clay		SFO	11.9	39.4

[1] SFO: single first order, DFOP: double first order in parallel
n.d. not determined

Table 7.1.2.1- 6: Summary of DT_{50} values for degradation of FOE sulfonic acid in aerobic soils at 20 °C for modeling purpose (non-normalized)

Soil	Texture (USDA)	Annex Point / Reference No	Kinetic Model [1]	DT_{50} [days]
Howe Indiana	sandy loam	KCA 7.1.2.1.2 /14	SFO - SFO	> 1000 [3]
BBA 2.2	loamy sand	KCA 7.1.2.1.2 /14	SFO - SFO	> 1000 [3]
Laacherhof AIII	silt loam		SFO - SFO	> 1000 [3]
Hoefchen im Tal	silt loam		SFO - SFO	> 1000 [3]
BBA 2.1	sand	KCA 7.1.2.1.2 /16	SFO	258.4
BBA 2.2	loamy sand		SFO	180.8
Laacherhof AIII	silt loam		SFO	234.9
Laacherhof AXXa	sandy loam	KCA 7.1.2.1.2 /16	SFO	62.3
Laacherhof AIII	silt loam		SFO	60.3
Laacherhof AXXa	loamy sand	KCA 7.1.2.1.2 /07	SFO	73.4
Dollendorf II	loam		SFO	6.7
Hoefchen am Hohenseh	silt loam		SFO [2]	28.6
Wurmwiese	sandy loam		SFO	49.8
Hanscheider Hof	loam	KCA 7.1.2.1.2/10	SFO	27.3
Frankenforst	silt loam		SFO	21.8
LUFA 2.3	sandy loam		SFO	63.9
LUFA 6S	clay		SFO	11.9

[1] SFO-SFO: single first order (parent) – single first order (degradation product)
SFO: single first order
[2] Taken from original report M-461413-02-1.
[3] DT_{50} > 1000 not considered for further evaluation: non-reliable DT_{50} estimation due to slow metabolite formation and limited decay observed until end of experimental study.

Table 7.1.2.1- 7: Summary of DT_{50} and DT_{90} values for degradation of FOE methylsulfone in aerobic soils at 20 °C for trigger evaluation

Soil	Texture (USDA)	Annex Point / Reference No	Kinetic Model [1]	DT_{50} [days]	DT_{90} [days]
Laacherhof AXXa	loamy sand	KCA 7.1.2.1.2 /06	SFO	43.1	143.3
Dollendorf II	loam		SFO	23.3	77.4
Hoefchen am Hohenseh	silt loam		DFOP	40.9	149.1
Laacherhof Wurmwiese	sandy loam		SFO	96.1	319.4
Hanscheider Hof	loam	KCA 7.1.2.1.2 /09	SFO	82.5	274
Frankenforst	silt loam		SFO	64.0	213
LUFA 2.3	sandy loam		SFO	147.0	488
LUFA 6S	clay		SFO	163.0	542

[1] SFO: single first order, DFOP: double first order in parallel

Table 7.1.2.1- 8: Summary of DT_{50} values for degradation of FOE methylsulfone in aerobic soils 20 °C for modeling purpose (non-normalized)

Soil	Texture (USDA)	Annex Point / Reference No	Kinetic Model [1]	DT_{50} [days]
BBA 2.2	loamy sand	KCA 7.1.2.1.2 /14	SFO - SFO	> 1000 [2]
Laacherhof AIII	silt loam		SFO - SFO	82.7
Hoefchen im Tal	silt loam		SFO - SFO	> 1000 [2]
Laacherhof AXXa	loamy sand	KCA 7.1.2.1.2 /17	SFO	43.1
Dollendorf II	loam		SFO	23.3
Hoefchen am Hohensch	silt loam		SFO	43.8
Wurmwiese	sandy loam		SFO	96.1
Hanscheider Hof	loam	KCA 7.1.2.1.2 /09	SFO	82.5
Frankenforst	silt loam		SFO	64.0
LUFA 2.3	sandy loam		SFO	147.0
LUFA 6S	clay		SFO	163.0

[1] SFO-SFO: single first order (parent) – single first order (degradation product)
SFO: single first order

[2] DT_{50} > 1000 not considered for further evaluation: non-reliable DT_{50} estimation due to slow metabolite formation and limited decay observed until end of experimental study.

Table 7.1.2.1- 9: Summary of DT_{50} and DT_{90} values for degradation of FOE-thiadone in aerobic soils 20 °C for trigger evaluation

Soil	Texture (USDA)	Annex Point / Reference No	Kinetic Model [1]	DT_{50} [days]	DT_{90} [days]
Iowa	loamy sand	KCA 7.1.2.1.2 /03	SFO	2.5	n.d.
Indiana	sandy loam		SFO	2.0	n.d.
Nebraska	silt loam		SFO	2.8	n.d.

[1] SFO: single first order
n.d.: not determined

Table 7.1.2.1- 10: Summary of DT_{50} values for degradation of FOE-thiadone in aerobic soils 20 °C for modeling purpose (non-normalized)

Soil	Texture (USDA)	Annex Point / Reference No	Kinetic Model [1]	DT_{50} [days]
Iowa	loamy sand	KCA 7.1.2.1.2 /15	SFO	2.0
Indiana	sandy loam		SFO	1.4
Nebraska	silt loam		SFO	2.9
Hoefchen Am Hohenseh	silt loam	KCA 7.1.2.1.2 /13	SFO - SFO	1.1
Laacherhof AXXa	loamy sand		SFO - SFO	1.4
Dollendorf II	clay loam		SFO - SFO	2.8
Laacherhof Wurmwiese	loam		SFO - SFO	2.0

[1] SFO: single first order
SFO-SFO: single first order (parent) – single first order (degradation product)

Table 7.1.2.1- 11: Summary of DT_{50} and DT_{90} values for degradation of FOE 5043-trifluoroethanesulfonic acid in aerobic soils for trigger evaluation

Soil	Texture (USDA)	Annex Point / Reference No	Kinetic Model [1]	DT_{50} [days]	DT_{90} [days]
Hoefchen am Hohenseh	silt loam	KCA 7.1.2.1.2 /12	SFO*-SFO	9.1	30.2
Laacherhof AXXa	loamy sand	KCA 7.1.2.1.2 /12	SFO*-SFO	4.5	14.9
Dollendorf II	clay loam		SFO*-SFO	22.5 [2]	74.7 [2]
Wurmwiese	loam		- [3]	-	-

[1] SFO: single first order
[2] Worst case estimate based on decline fits (steady degradation product formation is not considered in the evaluation).
[3] No valid trigger value could be estimated based on both pathway fit and decline fit.
[*] Kinetic parameters of FOE 5043-trifluoroethanesulfonic acid degradation were derived based on the pathway fit using the best-fit kinetics selected from the parent only fits.

Table 7.1.2.1- 12: Summary of DT_{50} values for degradation of FOE 5043-trifluoroethanesulfonic acid in aerobic soils at 20 °C for modeling purpose (non-normalized)

Soil	Texture (USDA)	Annex Point / Reference No	Kinetic Model [1]	DT_{50} [days]
Hoefchen am Hohenseh	silt loam	KCA 7.1.2.1.2 /13	SFO - SFO	9.1
Laacherhof AXXa	loamy sand		SFO - SFO	4.5
Dollendorf II	clay loam		SFO - SFO	22.5 [2]
Wurmwiese	loam		SFO - SFO	7.6 [2]

[1] SFO-SFO: single first order (parent) – single first order (degradation product)
[2] Conservative estimates based on decline fits - steady degradation product formation is not considered.

Table 7.1.2.1- 13: Summary of DT_{50} and DT_{90} values for degradation of trifluoroacetic acid in aerobic soils at 20 °C for trigger evaluation

Soil	Texture (USDA)	Annex Point / Reference No	Kinetic Model [1]	DT_{50} [days]	DT_{90} [days]
Laacherhof AXXa	sandy loam	KCA 7.1.2.1.2 /04	SFO	> 1000	> 1000
Dollendorf II	clay loam		SFO	> 1000	> 1000
Laacherhof Wurmwiese	sandy loam		SFO	> 1000	> 1000
Hoefchen am Hohenseh	silt loam		SFO	> 1000	> 1000

[1] SFO: single first order

Table 7.1.2.1- 14: Summary of DT_{50} values for degradation of trifluoroacetic acid in aerobic soils at 20 °C for modeling purpose (non-normalized)

Soil	Texture (USDA)	Annex Point / Reference No	Kinetic Model [1]	DT_{50} [days]
Hoefchen am Hohenseh	silt loam	KCA 7.1.2.1.2 /13	SFO - SFO	> 1000
Laacherhof AXXa	loamy sand		SFO - SFO	> 1000
Dollendorf II	clay loam		SFO - SFO	> 1000
Wurmwiese	loam		SFO - SFO	> 1000

[1] SFO-SFO: single first order (parent) – single first order (degradation product)

CA 7.1.2.1.1 Aerobic degradation of the active substance

The rate of degradation flufenacet in soil under aerobic conditions in the dark in the laboratory was evaluated during the Annex I inclusion and was accepted by the European Commission (7469/VI/98-Final – 3rd July 2003). The following studies are included in the Baseline Dossier:

Annex Point / Reference No	Author(s)	Year	Document No
KCA 7.1.2.1.1/01	[redacted], N. C[redacted], D. M.	1994	M-002166-01-1
KCA 7.1.2.1.1/02	[redacted], N. C[redacted], D. M.	1994	M-002165-01-1
KCA 7.1.2.1.1/03	[redacted], V.; [redacted], S.; [redacted], M.	1995	M-002146-01-1

Three additional studies have been performed for flufenacet and are submitted within this Supplemental Dossier for the flufenacet renewal of approval. Furthermore, updated kinetic evaluations of the degradation behavior of flufenacet in soil under aerobic conditions in the dark in the laboratory have been performed according to FOCUS kinetics (2005, 2006, 2011) [2, 3, 4] to derive kinetic parameters suitable for modeling purpose and environmental risk assessment. A summary of the degradation rates of flufenacet and its major degradation products in soil in the laboratory is given in section CA 7.1.2.1.

Report:	**KCA 7.1.2.1.1 /04; [redacted], E.; 1999**
Title:	Aerobic Degradation of Flufenacet in Lysimeter Soil Laacherhof AXXa
Report No:	MR-388/99
Document No:	M-009592-01-1
Guidelines:	• BBA Guideline Part IV, 4-1 • SETAC Procedures for Assessing the Environmental Fate and Ecotoxicity of Pesticides • Commission Directive 95/36/EC amending Council Directive 91/414/EEC

GLP:	Yes

Executive Summary

The degradation of [phenyl-UL-^{14}C]flufenacet was investigated in one soil under aerobic conditions in the dark in the laboratory for 56 days at 20 °C and soil moisture of 50% of the maximum water holding capacity:

Soil	Source	Texture (USDA)	pH [1]	OC [%]
Laacherhof AXXa	Monheim, Germany	sandy loam	6.1	1.41

[1] in 0.01 M $CaCl_2$

The study application rate was 63 µg/100 g soil (dry weight), equal to 0.63 mg flufenacet/kg soil (dry weight).

Duplicate test systems were processed and analyzed 0.1, 1, 3, 7, 14, 28, 42 and 56 days after treatment.

Mean material balances ranged from 94.8 to 99.5% of applied radioactivity (% AR).

The maximum amount of carbon dioxide was 19.5% AR at DAT-56 (study end). Formation of volatile organic compounds was not significant, values being ≤ 0.1% AR for all sampling intervals.

Extractable residues decreased from 93.6% AR at DAT-0.1 to 20.0% AR at DAT-56.

Non-extractable residues increased from 5.9% AR at DAT-0.1 to 56.7% AR at DAT-42 and slightly decreased to 55.2% AR at DAT-56.

The amount of flufenacet decreased from 92.3% AR at DAT-0 to 4.9% AR at DAT-56.

Only carbon dioxide was identified as major degradation product.

The experimental data were kinetically evaluated according to 1.5st order kinetic model in order to derive half-lives (best fit) for flufenacet. The calculated half-life was 7 days in soil Laacherhof AXXa.

I. MATERIALS AND METHODS

A. MATERIALS

1. Test Item

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

CAS No	142459-58-3
Batch No	94-38
Specific activity	2.0 MBq/mg
Radiochemical purity	> 95% HPLC/radiodetection, 96% TLC/radiodetection

2. Test Soils

The soils (Table 7.1.2.1.1- 1) were sampled freshly from the field and sieved to a particle size of ≤ 2 mm. The soils were taken from an agricultural area and its soil properties met the guideline requirements.

Table 7.1.2.1.1- 1: Physico-chemical properties of test soils

Parameter		Results / Units
Soil Designation		Laacherhof AXXa
Geographic Location		
City		Monheim
State		North-Rhine Westphalia
Country		Germany
GPS Coordinates		N 51° 04.0' E 007° 06.3'
Soil Taxonomic Classification (USDA)		sandy, mixed, mesic typic Cambudolls
Soil Series		no information available
Textural Class (USDA)		sandy loam
Sand [%]	[50 µm – 2 mm]	71.77
Silt [%]	[2 µm – 50 µm]	16.47
Clay [%]	[< 2 µm]	11.76
pH		
- in $CaCl_2$		6.1
- in water		7.0
Organic Carbon [%]		1.41
Organic Matter [%] [1]		2.42
Cation Exchange Capacity [meq/100 g]		9.61
Water Holding Capacity maximum [g H_2O *ad* 100 g soil DW]		34.4
Particle Density (disturbed) [g/mL]		2.5
Microbial Biomass [mg microbial carbon / kg soil DW]		
DAT$_0$ (replicate A / B)		667 / 702
DAT-56 (replicate A / B) [2]		392 / 356

DAT: days after treatment DW: dry weight
USDA: United States Department of Agriculture
[1] calculated as: OM [%] = OC [%] * 1.724
[2] The biomass samples of DAT-56 were applied with the application solvent: 475 µL ACN/water (1:7, *v/v*)

B. STUDY DESIGN

1. Experimental Conditions

Static test systems were used, consisting of Erlenmeyer flasks filled with soil and equipped with solid trap attachments for collection of carbon dioxide and volatile organic compounds.

100 g of the sieved soil (dry weight equivalents) were weighed into each flask and the soil moisture was adjusted to 50% maximum water holding capacity by addition of de-ionized water. The untreated test systems were closed with quartz wool stoppers and equilibrated to study conditions for 7 days prior to application.

The study application rate (SAR) was based on a single field application rate of flufenacet of 480 g/ha, resulting in a nominal study application rate 64 µg/100 g soil (dry weight), equal to 1.6 mg /kg soil

(dry weight). The actual SAR was 62.51 µg/100 g soil (dry weight), equal to 0.6 mg flufenacet/kg soil (dry weight).

The application solution was prepared in acetonitrile/water (1:7, *v/v*). 475 µL of the application solution were applied drop wise onto the soil surface of the respective test systems using a microliter syringe. After application, the organic solvent contained in the application solution was allowed to evaporate for about 10 min and the soil moisture was re-adjusted to the initial value of 50% MWHC using de-ionized water. Afterwards, all the test vessels were closed with the trap attachments (except DAT-0 samples).

The test systems (except DAT-0) were incubated under aerobic conditions in the dark for 56 days at 20 °C and a soil moisture of 50% 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 56 days. Duplicate test systems were processed and analyzed 0.1, 1, 3, 7, 14, 28, 42 and 56 days after treatment (DAT).

Microbial soil biomass was determined at DAT-0 and DAT-56.

3. Analytical Procedures

At each sampling interval, the trap attachments were removed from the test systems and the entire soil of each test system was extracted three times at ambient temperature using acetonitrile. After each extraction step supernatant and soil were separated by centrifugation and the clear supernatant was decanted through a paper filter.

Soil extracts were characterized by liquid scintillation counting and TLC/radiodetection. The limit of detection (LOD) for the HPLC/radiodetection method was approx. 1% AR. The amount of volatiles and non-extractable residues (exhaustive extracted soil plus paper filters) was determined by liquid scintillation counting and combustion/ liquid scintillation counting, respectively.

The identity of the test item was confirmed by HPLC/radiodetection and co-chromatography with reference items.

4. Kinetic Evaluation

The degradation kinetics of the test item was determined using the software Microsoft Excel and the single first order kinetic model. For the best fit evaluation the software Timme/Frehse Program 2.0 and a 1.5st order kinetic model was used. Model input datasets were the residual amounts of flufenacet found in each replicate test system at each sampling interval. For the best fit evaluation residue data from DAT-0.1 were not considered. DT50 and DT90 values were calculated from the resulting kinetic parameters.

II. RESULTS AND DISCUSSION

A. EXTRACTION AND QUANTITATION OF RADIOACTIVITY IN SOIL SAMPLES

Table 7.1.2.1.1- 2 summarizes the degradation of [phenyl-UL-^{14}C]flufenacet as a function of time.

Table 7.1.2.1.1- 2: Degradation of flufenacet in Soil Laacherhof AXXa under Aerobic Conditions
(expressed as percent of applied radioactivity; mean value of duplicates)

Compartment	DAT							
	0 [1]	0.1	3	7	14	28	42	56
flufenacet	92.3	88.0	58.1	46.7	25.6	14.4	5.3	4.9
Unknown Z2 [2]	2.9	1.0	0.7	0.4	0.7	0.3	0.3	0.4
Unknown Z3 [2]	1.5	1.1	0.9	0.8	2.2	2.6	2.7	2.5
Origin [3]	1.9	2.5	7.1	10.7	11.1	13.6	12.0	10.8
Unid./Diff. Radioactivity	1.4	1.0	4.2	0.9	3.7	0.6	1.5	1.4
Total Extractable Residues	n.d.	93.6	71.0	59.5	43.3	31.5	21.8	20.0
Carbon dioxide	n.d.	n.a.	1.6	3.2	6.0	11.8	17.0	19.5
Volatile Organic Compounds	n.d.	n.a.	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1
Non-extractable Residues	n.d.	5.9	24.5	35.3	46.2	52.1	56.7	55.2
Material Balance	**n.d.**	**99.5**	**97.1**	**98.1**	**95.5**	**95.4**	**95.5**	**94.8**

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

[1] Results of purity and homogeneity control of application

[2] Fortification impurities

[3] Degradation products contained in the origin zone were already described in earlier studies.

B. MATERIAL BALANCE

Mean material balances ranged from 94.8 to 99.5% of applied radioactivity [% AR].

The complete material balance found at all sampling intervals demonstrated that no significant portion of radioactivity dissipated from the vessels or was lost during processing of theses samples.

C. EXTRACTABLE AND NON-EXTRACTABLE RESIDUES

Extractable residues decreased from 93.6% AR at DAT-0.1 to 20.0% AR at DAT-56.

Non-extractable residues increased from 5.9% AR at DAT-0.1 to 56.7% AR at DAT-42 and slightly decreased to 55.2% AR at DAT-56.

D. VOLATILIZATION

The maximum amount of carbon dioxide was 19.5% AR at DAT-56 (study end). Formation of volatile organic compounds was not significant, values being ≤ 0.1% AR for all sampling intervals.

E. DEGRADATION OF TEST ITEM

The amount of flufenacet decreased from 92.3% AR at DAT-0 to 4.9% AR at DAT-56.

Only carbon dioxide was identified as major degradation product. The two minor compounds, detected in the TLC chromatograms with max. amounts of 2.9% AR at any sampling interval, were already detected in the purity controls of application and thus, are fortification impurities.

The experimental data were kinetically evaluated according to the 1.5st first order kinetic model in order to derive the best fit half-life for flufenacet (see Table 7.1.2.1.1- 3).

Table 7.1.2.1.1- 3: 1.5st Order degradation kinetics of flufenacet in soil under aerobic conditions for trigger evaluation

Soil	DT_{50}[1] [d]	DT_{90} [d]	Modeling Likelihood
Laacherhof AXXa	7	34	0.9908

[1] The input of 0.1 days into the modeling program was not possible. Therefore, that interval was excluded for the calculations.

III. CONCLUSIONS

[phenyl-UL-^{14}C]flufenacet was rapidly degraded in soil under aerobic conditions in the dark in the laboratory. The calculated best fit half-life was 7 days.

Only carbon dioxide was identified as major degradation product with amounts of up to 19.5% AR at study end.

*****

Report:	**KCA 7.1.2.1.1 /05; [redacted], E. M.; 2013**
Title:	Amendment No 1 - [thiadiazole-5-^{14}C]flufenacet: Aerobic Degradation / Metabolism in One European Soil
Report No:	MEF-11/937
Document No:	M-439105-02-1
Guidelines:	• OECD Test Guideline No. 307 • OCSPP Test Guideline No. 835.4100/4200
GLP:	Yes

Executive Summary

The degradation data as reported in study KCA 7.1.1.1 /04 were kinetically evaluated according to FOCUS (2005)[2] as part of the study to derive best fits for trigger endpoint determination. The experimental data could be well described by a double first order in parallel kinetic model for the testes soil. The calculated half-life of flufenacet under aerobic conditions was 14.7 days.

It is concluded that flufenacet has no potential for accumulation in the environment.

I. MATERIALS AND METHODS

Details on the study conduct and its results are summarized under KCA 7.1.1.1 /04.

The residue data for the test item were evaluated according to the FOCUS guidance document [2] on degradation kinetics using the software KinGUI 2 to derive the DT_{50} and DT_{90} values for flufenacet.

Model input datasets were the residual amounts of flufenacet 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. See Table 7.1.2.1.1- 4 for input values.

For the determination of the degradation kinetics following procedure was followed:

- Values between LOD and LOQ were set to the measured values.
- All single values < LOD or non-detected (n.d.) were set to 50% HPLC 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, single first order (SFO), first order multi compartment (FOMC), and double first order in parallel (DFOP), 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).

II. RESULTS AND DISCUSSION

Table 7.1.2.1.1- 4 summarizes the degradation of [thiadiazole-5-^{14}C]flufenacet as a function of time.

Table 7.1.2.1.1- 4: Degradation of flufenacet in Soil Hoefchen am Hohensch under Aerobic Conditions
(expressed as percent of applied radioactivity; single values)

Replicate	DAT									
	0 [1]	2	4	7	10	14	35	60	87	120
A	99.1	93.3	87.4	74.8	61.8	52.8	13.4	4.1	1.7	0.9
B	100.4	91.2	88.3	76.3	66.3	56.8	14.2	3.4	1.6	0.9

[1] Material balances at DAT-0 were 99.5% AR for replicate A and 100.9% AR for replicate B

The chi² error values of the fits of all investigated kinetic models were below 9 and the visual assessment of the regression curves gave good results. The degradation of flufenacet followed DFOP kinetics in soil Hoefchen am Hohensch (silt loam), according to the lowest chi² error value.

The amount of flufenacet was declining rapidly during the test period of 120 days. The half-life of flufenacet in the tested soil was 14.7 days under aerobic conditions in the dark in the laboratory.

Table 7.1.2.1.1- 5: Best-fit degradation kinetics of flufenacet in soil under aerobic conditions for trigger evaluation according to FOCUS

Kinetic Model [1]	DT_{50} [d]	DT_{90} [d]	Chi^2 Error [%]	Visual Assessment [2]
DFOP	14.7	44.7	3.79	+

[1] DFOP = double first order in parallel
[2] Visual assessment: +=good

III. CONCLUSIONS

Flufenacet was rapidly degraded in degraded in soil under aerobic conditions in the dark in the laboratory. Its calculated best-fit half-life was 14.7 days in the tested soil.

It is concluded that flufenacet has no potential for accumulation in the environment.

*****

Report:	**KCA 7.1.2.1.1 /06; [redacted], E. M.; 2013**
Title:	Amendment No 1 to: [thiadiazole-5-^{14}C]flufenacet: Aerobic Degradation / Metabolism in Three European Soils
Report No:	MEF-11/938
Document No:	M-440348-02-1
Guidelines:	• OECD Test Guideline No. 307 • OCSPP Test Guideline No. 835.4100/4200
GLP:	Yes

Executive Summary

The degradation data as reported in study KCA 7.1.1.1 /05 were kinetically evaluated according to FOCUS (2005) [2] as part of the study to derive best fits for trigger endpoint determination. The experimental data could be well described by a single first order kinetic model for soils Laacherhof AXXa (loamy sand) and Laacherhof Wurmwiese (loam) as well as by a double first order in parallel kinetic model for soil Dollendorf II (clay loam). The calculated half-lives of flufenacet under aerobic conditions were between 18.5, 15.4 and 13.5 days for soil Laacherhof AXXa, Dollendorf II and Laacherhof Wurmwiese, respectively.

It is concluded that flufenacet has no potential for accumulation in the environment.

I. MATERIALS AND METHODS

Details on the study conduct and its results are summarized under KCA 7.1.1.1 /05.

The data for the test item were evaluated according to the FOCUS guidance document [2] on degradation kinetics using the software KinGUI 2 to derive the DT_{50} and DT_{90} values of flufenacet.

Model input datasets were the residual amounts of flufenacet found in each replicate test system at each sampling interval (see Table 7.1.2.1.1- 6 to Table 7.1.2.1.1- 8). 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 following procedure was followed:

- Values between LOD and LOQ were set to the measured values.
- All single values < LOD or non-detected (n.d.) were set to 50% HPLC 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- single first order (SFO), first order multi compartment (FOMC), and double first order in parallel (DFOP)- were tested in order to determine the best fit kinetic model. The best-fit kinetic model was selected on the basis of the chi^2 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).

II. RESULTS AND DISCUSSION

Table 7.1.2.1.1- 6 to Table 7.1.2.1.1- 8 summarizes the degradation of [thiadiazole-5-^{14}C]flufenacet as a function of time.

Table 7.1.2.1.1- 6: Degradation of flufenacet in Soil Laacherhof AXXa under Aerobic Conditions
(expressed as percent of applied radioactivity; single values)

Replicate	DAT										
	0 [1]	1	2	4	7	10	14	35	63	91	121
A	98.9	97.9	92.3	89.7	80.6	70.7	60.2	29.0	5.1	3.0	1.6
B	98.5	96.2	91.3	90.0	82.2	70.5	59.6	22.4	10.0	3.3	1.3

[1] Material balances at DAT-0 were 99.3% AR for replicate A and 98.9% AR for replicate B

Table 7.1.2.1.1- 7: Degradation of flufenacet in Soil Dollendorf II under Aerobic Conditions
(expressed as percent of applied radioactivity; single values)

Replicate	DAT										
	0 [1]	1	2	4	7	10	14	35	63	91	121
A	101.2	97.7	88.0	86.9	75.1	62.7	57.6	15.9	2.4	0.9	1.0
B	98.6	96.0	88.4	88.5	78.9	67.5	54.3	14.8	2.6	1.5	0.9

[1] Material balances at DAT-0 were 102.4% AR for replicate A and 99.6% AR for replicate B

Table 7.1.2.1.1- 8: Degradation of flufenacet in Soil Laacherhof Wurmwiese under Aerobic Conditions
(expressed as percent of applied radioactivity; single values)

Replicate	DAT										
	0 [1]	1	2	4	7	10	14	35	63	91	121
A	97.4	96.8	89.5	87.5	74.6	64.3	46.5	13.8	3.4	1.3	1.2
B	99.9	96.8	91.4	85.0	74.2	62.6	48.3	12.8	3.8	1.4	0.8

[1] Material balances at DAT-0 were 98.1% AR for replicate A and 100.6% AR for replicate B

The chi^2 error values of the fits of all investigated kinetic models were below 11 and the visual assessment of the regression curves gave good results. The degradation of flufenacet followed single first order (SFO) kinetics in soils Laacherhof AXXa and Laacherhof Wurmwiese and double first order in parallel (DFOP) kinetics in soil Dollendorf II, according to the lowest chi^2 error value.

The amount of flufenacet was declining rapidly during the test period of 121 days. The half-lives for flufenacet were 18.5 days in soil Laacherhof AXXa, 15.4 days in soil Dollendorf II and 13.5 days in soil Laacherhof Wurmwiese under aerobic conditions in the dark in the laboratory.

Table 7.1.2.1.1- 9: Best-fit degradation kinetics of flufenacet in soils under aerobic conditions for trigger evaluation according to FOCUS

Soil (Soil Type)	Kinetic Model [1]	DT_{50} [d]	DT_{90} [d]	chi^2 error [%]	Visual Assessment [2]
Laacherhof AXXa (loamy sand)	SFO	18.5	61.6	2.58	+
Dollendorf II (clay loam)	DFOP	15.4	46.4	3.94	+
Laacherhof Wurmwiese (loam)	SFO	13.5	44.8	3.44	+

[1] SFO = single first order; DFOP = double first order in parallel
[2] Visual assessment: + good

III. CONCLUSIONS

Flufenacet was rapidly degraded in soil under aerobic conditions in the dark in the laboratory. Its calculated half-lives were 18.5 days in soil Laacherhof AXXa, 15.4 days in soil Dollendorf II and 13.5 days in soil Laacherhof Wurmwiese.

It is concluded that flufenacet has no potential for accumulation in the environment.

*****

Report:	**KCA 7.1.2.1.1 /07; [redacted], G.; [redacted], S.; 2014**
Title:	Kinetic Evaluation of the Degradation of [phenyl-UL-^{14}C]flufenacet and its Degradation Products under Aerobic Soil Conditions in Laboratory According to FOCUS Kinetics Using the KinGUI 2 Tool
Report No:	EnSa-12-0575
Document No:	M-477878-01-1
Guidelines:	• FOCUS kinetics (2006, 2011) [3, 4]
GLP:	no

Executive Summary

A kinetic analysis of soil residue data from three aerobic soil degradation studies M-002166-01-1 (Baseline Dossier, KCA 7.1.2.1.1/01), M-002146-01-1 (Baseline Dossier, KCA 7.1.2.1.1/03) and M-009592-01-1 (Supplemental Dossier, KCA 7.1.2.1.1 /04) was performed with the software KinGUI 2 according to FOCUS kinetics (2006, 2011) [3, 4] to derive half-lives for flufenacet and its degradation products FOE oxalate, FOE sulfonic acid and FOE methylsulfone as well as formation fraction for the degradation products, which are suitable for modeling purpose. Only the results for flufenacet are described here.

The single first order was the most appropriate kinetic model to describe the degradation of flufenacet for modeling purpose in the five tested soils (1 × loamy sand, 2 × silt loam, 2 × sandy loam) under aerobic conditions in the dark in the laboratory at 20 ± 2 °C and soil moistures ranging from 40% of the maximum water holding capacity (MWHC) to 75% of the field capacity (FC) at 1/3 bar.

The calculated half-lives of flufenacet for modeling purposes were 31.9 days, 15.2 days, 20.4 days (all 20 ± 1 °C, 40% MWHC), 32.2 days (21 ± 1 °C, 75% FC at 1/3 bar) and 7.4 days (20 ± 1 °C, 50% MWHC).

I. METHODS

Soil residue data from the aerobic soil degradation studies M-002166-01-1 (Baseline Dossier, KCA 7.1.2.1.1/01) [5], M-002146-01-1 (Baseline Dossier, KCA 7.1.2.1.1/03) and M-009592-01-1 Supplemental Dossier, KCA 7.1.2.1.1 /04) were used. In these studies, the degradation of flufenacet was studied in a total of 5 soils (1 × loamy sand, 2 × silt loam, 2 × sandy loam) under aerobic conditions in the dark in the laboratory at 20 ± 2 °C and soil moistures ranging from 40% MWHC to 75% FC at 1/3 bar (for details see Table 7.1.2.1.1- 10 below).

The kinetic analysis was performed according to FOCUS kinetics (2006, 2011) [3, 4] using the software KinGUI 2 with four different kinetic models: single first order (SFO), first order multi-compartment (FOMC), hockey-stick (HS, DFOS = double first order sequential) and double first order parallel (DFOP). Model input datasets were the residual amounts of flufenacet 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. 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 occurred. The most appropriate kinetic model was selected on the basis of a detailed statistical analysis including visual assessment of the goodness of the fits, chi^2-scaled error criterion, t-test significance, correlation analysis and standard deviation. The DT_{50} values were calculated from the resulting kinetic parameters.

II. RESULTS

The single first order (SFO) was the most appropriate kinetic model to describe the degradation of flufenacet for modeling purpose in the five tested soils under aerobic conditions. (Table 7.1.2.1.1- 10) summarizes the results of the kinetic analysis.

Table 7.1.2.1.1- 10: Kinetic parameters for the degradation of flufenacet in soil under aerobic conditions for modeling purpose according to FOCUS

Soil	Kinetic Model [1]	DT_{50} [days]	chi^2 error [%]	t-test	Visual Assessment [2]
Howe, Indiana [3]	SFO	32.2	2.4	<< 0.001	+
BBA 2.2 [4]	SFO	31.9	8.5	<< 0.001	o
Laacherhof AIII [5]	SFO	15.2	8.9	<< 0.001	+
Hoefchen im Tal [6]	SFO	20.4	5.5	<< 0.001	+
Laacherhof AXXa [7]	SFO	7.4 [a)]	11.2	< 0.001	o

[1] SFO: single first order
[2] visual assessment: + = good, o = acceptable
[3] sandy loam , 21 ± 1 °C, 75% FC 1/3 bar (KCA 7.1.2.1.1/01)
Cut-off of the soil residue data after DAT-28, due to collapse of the microbial activity
[4] loamy sand, 20 ± 1 °C, 40% MWHC (KCA 7.1.2.1.1/03)
[5] silt loam , 20 ± 1 °C, 40% MWHC (KCA 7.1.2.1.1/03)
[6] silt loam, 20 ± 1 °C, 40% MWHC (KCA 7.1.2.1.1/03)
[7] sandy loam, 20 °C, 50% MWHC (KCA 7.1.2.1.1 /04)
[a)] taken from parent only fit

[5] Soil residue data of the study M-002166-01-1 were cut off after DAT-28, due to a breakdown of the microbial activity.

III. CONCLUSIONS

The calculated half-lives of flufenacet for modeling purpose in soil under aerobic conditions in the dark in the laboratory ranged from 7.4 to 32.2 days in all tested soils.

The results are included in the summary of the degradation rates of flufenacet and its major degradation products in soil in the laboratory given in section CA 7.1.2.1.

*****

Report:	**KCA 7.1.2.1.1 /09; [redacted], G.; [redacted], S.; 2014**
Title:	Kinetic Evaluation of the Degradation of [thiadiazole-2-^{14}C]flufenacet and its Degradation Products under Aerobic Soil Conditions in Laboratory According to FOCUS Kinetics Using the KinGUI 2 Tool
Report No:	EnSa-12-0576
Document No:	M-477885-01-1
Guidelines:	• FOCUS kinetics (2006, 2011) [3,4]
GLP:	no

Executive Summary

A kinetic analysis of soil residue data from the aerobic soil degradation study M-002165-01-1 (Baseline Dossier, KCA 7.1.2.1.1/02) was performed with the software KinGUI 2 according to FOCUS kinetics (2006, 2011) [3,4] to derive half-lives for flufenacet and its degradation product FOE-thiadone as well as formation fractions for the degradation product, which are suitable for modeling purpose. No reliable half-life or formation fraction could be derived from the soil residue data for FOE-thiadone. Therefore, only the results for flufenacet are summarized in this dossier.

The single first order was the most appropriate kinetic model for modeling purpose for the degradation of flufenacet in the tested soil under aerobic conditions in the dark in the laboratory at 21 ± 1 °C and soil moisture of 75% of the field capacity (FC) at 1/3 bar.

The calculated half-life of flufenacet was 55.0 days.

I. METHODS

Soil residue data from the aerobic soil degradation study M-002165-01-1 [6] ((Baseline Dossier, KCA 7.1.2.1.1/02) were used. In this study, the degradation of flufenacet was studied in one soil (sandy loam) under aerobic conditions in the dark in the laboratory at 21 ± 1 °C and soil moisture of 75% FC at 1/3 bar (for details see Table 7.1.2.1.1- 11 below).

The kinetic analysis was performed according to FOCUS kinetics (2006, 2011) [3, 4] using the software KinGUI 2 with four different kinetic models: single first order (SFO), first order multi-compartment (FOMC), hockey-stick (HS, DFOS = double first order sequential) and double first order parallel (DFOP). Model input datasets were the residual amounts of flufenacet 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. 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 x LOD. If they became < LOD / n.d. for a second time the curve was cut off until a subsequent value > LOQ occurred. The most appropriate kinetic model was selected on the basis of a detailed statistical analysis including visual assessment of the goodness of

6 Soil residue data of the study M-002165-01-1 were cut off after DAT-32, due to a breakdown of the microbial activity.

the fits, chi^2-scaled error criterion, t-test significance, correlation analysis and standard deviation. The DT_{50} values were calculated from the resulting kinetic parameters.

II. RESULTS

The single first order (SFO) was the most appropriate kinetic model to describe the degradation of flufenacet for modeling purpose in the tested soil. Table 7.1.2.1.1- 11 summarizes the results of the kinetic analysis.

Table 7.1.2.1.1- 11: Kinetic parameters for the degradation of flufenacet in soil under aerobic conditions for modeling purpose according to FOCUS

Soil	Kinetic Model [1]	DT_{50} [days]	chi^2 error [%]	t-test	Visual Assessment [2]
Howe, Indiana [3]	SFO	55.0	2.8	0.003	o

[1] SFO: single first order
[2] visual assessment: o = acceptable
[3] sandy loam, 21 ± 1 °C, 75% FC 1/3 bar (KCA 7.1.2.1.1/02)
Cut-off of the soil residue data after DAT-32, due to collapse of the microbial activity

III. CONCLUSIONS

The calculated half-life of flufenacet for modeling purpose in soil under aerobic conditions in the dark in the laboratory was 55.0 days in the tested soil.

The results are included in the summary of the degradation rates of flufenacet in soil in the laboratory given in section CA 7.1.2.1.

*****

Report:	**KCA 7.1.2.1.1/08; [redacted], G.; [redacted], S.; 2014**
Title:	Kinetic Evaluation of the Degradation of [thiadiazole-5-^{14}C]flufenacet and its Degradation Products under Aerobic Soil Conditions in Laboratory According to FOCUS Kinetics Using the KinGUI 2 Tool
Report No:	EnSa-12-0577
Document No:	M-477835-01-1
Guidelines:	• FOCUS kinetics (2006, 11) [3, 4]
GLP:	no

Executive Summary

A kinetic analysis of soil residue data from two aerobic soil degradation studies M-439105-02-1 (Supplemental Dossier, KCA 7.1.2.1.1 /05) and M-440348-02-1 (Supplemental Dossier, KCA 7.1.2.1.1 /06) was performed with the software KinGUI 2 according to FOCUS kinetics (2006, 2011) [3, 4] to derive half-lives for flufenacet and its degradation products FOE-thiadone, FOE 5043-trifluoroethanesulfonic acid and trifluoroacetic acid as well as formation fractions for the degradation products, which are suitable for modeling purpose. Only the results for flufenacet are described here.

The single first order was the most appropriate kinetic model to describe the degradation of flufenacet for modeling purpose in a total of four tested soils (silt loam, loamy sand, clay loam and loam) under aerobic conditions in the dark in the laboratory at 20 ± 2 °C and soil moisture of 55% of the maximum water holding capacity (MWHC).

The calculated half-lives of flufenacet for modeling purposes were 15.8 days (19.7 ± 0.1 °C, 55% MWHC), 19.9 days, 16.3 days and 14.9 days (all 19.8 ± 0.2 °C, 55% MWHC).

I. METHODS

Soil residue data from the aerobic soil degradation studies M-439105-02-1 (Supplemental Dossier, KCA 7.1.2.1.1 /05) and M-440348-02-1 (Supplemental Dossier, KCA 7.1.2.1.1 /06) were used. In these studies, the degradation of flufenacet was studied in a total of 4 soils (silt loam, loamy sand, clay loam and loam) under aerobic conditions in the dark in the laboratory at 20 ± 2 °C and soil moisture of 55% MWHC (for details see Table 7.1.2.1.1- 12 below).

The kinetic analysis was performed according to FOCUS kinetics (2006, 2011)[3, 4] using the software KinGUI 2 with four different kinetic models: single first order (SFO), first order multi-compartment (FOMC), hockey-stick (HS, DFOS = double first order sequential) and double first order parallel (DFOP). Model input datasets were the residual amounts of flufenacet 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. 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 x LOD. If they became < LOD / n.d. for a second time the curve was cut off until a subsequent value > LOQ occurred. The most appropriate kinetic model was selected on the basis of a detailed statistical analysis including visual assessment of the goodness of the fits, chi^2-scaled error criterion, t-test significance, correlation analysis and standard deviation. The DT_{50} values were calculated from the resulting kinetic parameters.

II. RESULTS

The single first order (SFO) was the most appropriate kinetic model to describe the degradation of flufenacet for modeling purpose in the 4 tested soils. Table 7.1.2.1.1- 12 summarizes the results of the kinetic analysis.

Table 7.1.2.1.1- 12: Kinetic parameters for the degradation of flufenacet in soil under aerobic conditions for modeling purpose according to FOCUS

Soil	Kinetic Model [1]	DT_{50} [days]	chi^2 error [%]	t-test	Visual Assessment [2]
Hoefchen Am Hohenseh [3]	SFO	15.8	4.8	< 2e-16	+
Laacherhof AXXa [4]	SFO	19.9	3.0	< 2e-16	+
Dollendorf II [5]	SFO	16.3	4.7	< 2e-16	+
Laacherhof Wurmwiese [6]	SFO	14.9	4.3	< 2e-16	+

[1] SFO: single first order
[2] visual assessment: + = good
[3] silt loam, 19.7 ± 0.1 °C, 55% MWHC (KCA 7.1.2.1.1 /05)
[4] loamy sand, 19.8 ± 0.2 °C, 55% MWHC (KCA 7.1.2.1.1 /06)
[5] clay loam, 19.8 ± 0.2 °C, 55% MWHC (KCA 7.1.2.1.1 /06)
[6] loam, 19.8 ± 0.2 °C, 55% MWHC (KCA 7.1.2.1.1 /06)

III. CONCLUSIONS

The calculated half-lives of flufenacet for modeling purpose in soil under aerobic conditions in the dark in the laboratory ranged from 14.9 to 19.9 days in the tested soils.

The results are included in the summary of the degradation rates of flufenacet and its major degradation products in soil in the laboratory given in section CA 7.1.2.1.

CA 7.1.2.1.2 Aerobic degradation of metabolites, breakdown and reaction products

The rates of degradation of the major degradation products FOE oxalate and FOE sulfonic acid in soil under aerobic conditions in the dark in the laboratory were evaluated during the Annex I Inclusion and were accepted by the European Commission (7469/VI/98-Final – 3rd July 2003). The following studies are included in the Baseline Dossier:

Annex Point / Reference No	Author(s)	Year	Document No
KCA 7.1.2.1.2 /01	[redacted], E.	1996	M-004098-01-2
KCA 7.1.2.1.2 /02	[redacted], E.	1995	M-004479-02-1

Within the additional route studies of flufenacet (Supplemental Dossier, KCA 7.1.1.1 /04 and KCA 7.1.1.1 /05) three new major degradation products were identified, FOE-thiadone, FOE 5043-trifluoroethanesulfonic acid and trifluoroacetic acid, which are also newly addressed in this Supplemental Dossier. Furthermore, all former route studies of flufenacet were re-evaluated regarding the new identification trigger based on regulation (EC) no. 1107/2009 and SANCO/11802/2010. Thus, the degradation product FOE methylsulfone is newly addressed as soil degradation product in this Supplemental Dossier because it was formed above the new identification triggers in aerobic soil degradation study M-002146-01-1 (Baseline Dossier, KCA 7.1.1.1/03). Thus, eight additional studies have been performed for major degradation products in total and are submitted within this Supplemental Dossier for the flufenacet renewal of approval using [phenyl-UL-^{14}C]-labeled and unlabeled FOE sulfonic acid, unlabeled FOE methylsulfone, [thiadiazole-2-^{14}C]-labeled FOE-thiadone and [1-^{14}C]-labeled trifluoroacetic acid.

Furthermore, updated kinetic evaluations of the degradation behaviors of major degradation products in soil under aerobic conditions in the dark in the laboratory have been performed according to FOCUS kinetics (2006, 2011) [3,4] to derive kinetic parameters suitable for trigger evaluation, modeling purpose and environmental risk assessment. A summary of the degradation rates of flufenacet and its major degradation products in soil in the laboratory is given in section CA 7.1.2.1.

Report:	**KCA 7.1.2.1.2 /08; [redacted], E.; 2003**
Title:	Time-dependent sorption of FOE5043-sulfonic acid in soil
Report No:	MEF-229/03
Document No:	M-111445-01-1
Guidelines:	• None (Supportive study to Annex II, Fate and Behavior in the Environment, 7171/VI/94-EN, Section 7.1.2)
GLP:	yes

Executive Summary

The objective of the study was to clarify why simulation runs overestimate the groundwater concentrations (PEC_{GW}) of FOE sulfonic acid, as significant lower experimental concentrations of FOE sulfonic acid were detected in the leachates of lysimeter studies [KCA 7.1.4.2 /01, KCA 7.1.4.2 /05]. Possible explanations might be a time-dependent sorption behavior of FOE sulfonic acid or a faster degradation of FOE sulfonic acid under aerobic conditions in soil than observed in a former laboratory study [KCA 7.1.2.1.2 /01].

The time dependent sorption and degradation of [phenyl-UL-^{14}C]FOE sulfonic acid was investigated in two soils under aerobic conditions in the dark in the laboratory for 100 days at 20 °C and soil moisture of 40% of the maximum water holding capacity:

Soil	Source	Texture (USDA)	pH [1]	OC [%]
Laacherhof AXXa	Monheim, Germany	sandy loam	6.3	1.47
Laacherhof AIII	Monheim, Germany	silt loam	6.7	0.88

[1] in 0.01 M $CaCl_2$

The study application rate was 12.3 µg/100 g soil (dry weight), equal to 0.123 mg FOE sulfonic acid /kg soil (dry weight).

Duplicate test systems were processed and analyzed 0, 3, 7, 14, 28, 56 and 100 days after treatment.

In the following those parts of the study are summarized which were performed to determine the rate of degradation in soil. Parts concerning the evaluation of the time dependent sorption are reported in section CA 7.1.3.2 (study KCA 7.1.3.2 /01) of this document.

As the study design was not intended to determine total material balances, e.g. no volatiles were determined, the recovery of radioactivity decreased to approx. 60% of the applied radioactivity [% AR] in soil Laacherhof AXXa and to approx. 56% AR in soil Laacherhof AIII.

Extractable residues decreased from DAT-0 to DAT-100 from 97.9 to 29.4% AR in soil Laacherhof AXXa and from 97.8 to 27.8% AR in soil Laacherhof AIII.

Non-extractable residues increased from DAT-0 to DAT-100 from 2.1 to 30.7% AR in soil Laacherhof AXXa and from 2.2 to 28.4% AR in soil Laacherhof AIII.

The amount of FOE sulfonic acid decreased from DAT-0 to DAT-100 from 12.23 to 3.46 µg in soil Laacherhof AXXa and from 12.4 to 3.34 µg in soil Laacherhof AIII.

The experimental data were kinetically evaluated according to the Single First Order kinetic model in order to derive half-lives for FOE sulfonic acid. The calculated half-life was 62 and 60 days in soil Laacherhof AXXa and Laacherhof AIII, respectively. These half-lives are significantly shorter than those found in an earlier study [KCA 7.1.2.1.2/01], where only weak degradation of FOE sulfonic acid was found in three soils after 100 days (DT_{50} between 189 and 270 days). However, in that former study it was recognized that the soil moisture during test was too low and that an approx. 3-fold higher application rate was used.

These results clearly indicate that not a time-dependent sorption behavior of FOE sulfonic acid , but rather shorter half-lives under aerobic condition in soil are the most plausible reason for measuring much lower peak concentrations of test item in the leachates of the lysimeter studies than that expected by modeling calculations with the earlier input parameters (longer half-lives).

I. MATERIALS AND METHODS

A. MATERIALS

1. Test Item

[phenyl-UL-^{14}C]FOE5043-sulfonic acid ammonium salt (report name [1]: FOE sulfonic acid)

Batch No	#C-606B
Specific activity	2.66 MBq/mg
Radiochemical purity	> 98% HPLC with radioactivity-detector

2. Test Soils

The soils (Table 7.1.1.1- 3) 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 areas representing different geographical origins and different soil properties as required by the guidelines.

Table 7.1.2.1.2- 1: Physico-chemical properties of test soils

Parameter	Results / Units	
Soil Designation	Laacherhof AXXa	Laacherhof AIII°
Geographic Location		
City	Monheim	Monheim
State	North-Rhine Westphalia	North-Rhine Westphalia
Country	Germany	Germany
Soil Taxonomic Classification (USDA)	sandy, mixed, mesic typic Cambudolls	loamy, mixed, mesic typic Agrudalfs
Soil Series	no information available	
Textural Class (USDA)	sandy loam	silt loam
Sand [%] [50 µm – 2 mm]	72.4	36.9
Silt [%] [2 µm – 50 µm]	22.6	51.1
Clay [%] [< 2 µm]	5.0	12.0
pH		
- in $CaCl_2$ (soil/$CaCl_2$ 1/2)	6.3	6.8
- in water (soil/water 1/1)	6.9	7.6
- in KCl	6.3	7.2
Organic Carbon [%]	1.47	0.88
Organic Matter [%] *	2.53	1.51
Cation Exchange Capacity [meq/100 g]	10.3	9.8
Water Holding Capacity maximum [g H_2O *ad* 100 g soil DW]	34.42	36.40
Bulk Density (disturbed) [g/cm^3]	2.5	2.55
Microbial Biomass [mg microbial carbon / kg soil DW]		
DAT-0	242	275
DAT-100	209	195

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

DAT: days after treatment DW: dry weight

USDA: United States Department of Agriculture

B. STUDY DESIGN

1. Experimental Conditions

Static test systems were used, consisting of centrifuge tubes filled with soil and closed with cotton wool.

100 g of the sieved soil (dry weight equivalents) were weighed into each tube and the soil moisture was adjusted to 40% of the maximum water holding capacity (MWHC) by addition of de-ionized

water. The untreated test systems were closed with cotton wool and equilibrated to study conditions for at least 1 week days prior to application.

The study application rate (SAR) was orientated on the lowest concentration of FOE sulfonic acid used in the former batch equilibrium study (KCA 7.1.3.1.2 /01), i.e. 0.04 µg/mL FOE sulfonic acid x 20 mL / 6 g soil (DW) = 0.133 µg / g soil (DW).

The application solution was prepared in acetonitrile/water (1:20, v/v). 73 µL of the application solution were applied drop wise onto the soil surface of the respective test systems using a pipette. After application the soil moisture was re-adjusted to the initial value of 40% MWHC using de-ionized water and the test vessels were closed with cotton wool.

The test systems (except DAT-0) were incubated under aerobic conditions in the dark for 100 days at 20 °C and a soil moisture of 40% of the maximum water holding capacity in a walk-in climatic chamber.

2. Sampling

Seven sampling intervals were distributed over the entire incubation period of 100 days. Duplicate test systems were processed and analyzed 0, 3, 7, 14, 28, 56 and 100 days after treatment (DAT).

Microbial soil biomass was determined at DAT-0 and DAT-100.

3. Analytical Procedures

At each sampling interval, a so-called batch equilibrium shaking test was performed firstly to determine the time-dependent sorption of FOE sulfonic acid. Therefore, the soils were supplemented with 100 mL 0.01 M $CaCl_2$ solution (soil/solution ratio = 1:1) and agitated for 24 h in the dark at 20 °C. Afterwards, supernatant and soil were separated by centrifugation and decantation.

Following, the soils were extracted four times at ambient temperature using 0.01 M $CaCl_2$ solution (1x), acetonitrile/water (1 x, 1:1, v/v) or acetonitrile containing 0.01 M HCl (2x). After each extraction step, supernatant and soil were separated by centrifugation and decantation.

The desorption solution of the batch equilibrium shaking test as well as the $CaCl_2$ extract and the combined organic soil extracts were characterized separately by liquid scintillation counting and TLC/radiodetection. The limit of detection (LOD) for the TLC/radiodetection method was 0.5% AR. The amount of non-extractable residues was determined by combustion/ liquid scintillation counting.

The identity of the test item was elucidated by HPLC-MS(/MS) and assigned by comparison of the R_f values with those of reference items.

4. Kinetic Evaluation

The degradation kinetics of the test item was determined using the software ModelManager and the Single First Order kinetic model. Model input datasets were the residual amounts of FOE sulfonic acid found in each replicate test system at each sampling interval. DT50 and DT90 values were calculated from the resulting kinetic parameters.

II. RESULTS AND DISCUSSION

A. EXTRACTION AND QUANTITATION OF RADIOACTIVITY IN SOIL SAMPLES

Table 7.1.2.1.2- 2 to Table 7.1.2.1.2- 5 summarizes the degradation of [phenyl-UL-^{14}C]FOE sulfonic acid as a function of time.

Table 7.1.2.1.2- 2: Distribution of Radioactivity in Soil Laacherhof AXXa under Aerobic Conditions
(expressed in as percent of applied radioactivity; mean value of duplicates)

Compartment	DAT 0	3	7	14	28	56	100
Carbon dioxide	not analyzed						
Volatile Organic Compounds							
Total Extractable Residues	97.9	96.9	93.4	87.2	74.6	58.6	29.4
Non-extractable Residues	2.1	3.0	5.0	7.2	13.5	20.2	30.7
Material Balance	**100.0**	**99.9**	**98.4**	**94.4**	**88.1**	**78.8**	**60.1**

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

Table 7.1.2.1.2- 3: Degradation of FOE sulfonic acid in Soil Laacherhof AXXa under Aerobic Conditions
(expressed in µg; single values and mean values)

Compound (replicate)	DAT 0	3	7	14	28	56	100
FOE sulfonic acid (A1)	12.2	12.2	11.9	11.1	9.3	7.1	3.5
(A2)	12.3	12.2	11.7	11.0	9.5	7.5	3.5
mean	**12.2**	**12.2**	**11.8**	**11.0**	**9.4**	**7.3**	**3.5**

DAT: days after treatment

Table 7.1.2.1.2- 4: Distribution of Radioactivity in Soil Laacherhof AIII under Aerobic Conditions
(expressed in as percent of applied radioactivity; mean value of duplicates)

Compound	DAT 0	3	7	14	28	56	100
Carbon dioxide	not analyzed						
Organic Volatiles							
Total Extractable Residues	97.8	94.4	90.6	86.1	74.1	55.9	27.8
Non-extractable Residues	2.2	3.4	5.2	6.5	11.9	18.4	28.4
Material Balance	**100.0**	**97.9**	**95.8**	**92.6**	**86.1**	**74.3**	**56.2**

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

Table 7.1.2.1.2- 5: Degradation of FOE sulfonic acid in Soil Laacherhof AIII under Aerobic Conditions
(expressed in µg; single values and mean values)

Compound (replicate)		DAT 0	3	7	14	28	56	100
FOE sulfonic acid	(A1)	12.6	12.2	11.9	11.2	9.7	7.2	3.4
	(A2)	12.2	11.9	11.6	11.0	9.4	6.9	3.3
	mean	**12.4**	**12.1**	**11.7**	**11.1**	**9.6**	**7.1**	**3.3**

DAT: days after treatment

B. MATERIAL BALANCE

As the study design was not intended to determine total material balances, e.g. no volatiles were determined, the recovered radioactivity decreased to approx. 60% of the applied radioactivity [% AR] in soil Laacherhof AXXa and to approx. 56% AR in soil Laacherhof AIII; see also Table 7.1.2.1.2- 2 and Table 7.1.2.1.2- 4.

C. EXTRACTABLE AND NON-EXTRACTABLE RESIDUES

Extractable residues decreased from DAT-0 to DAT-100 from 97.9 to 29.4% AR in soil Laacherhof AXXa and from 97.8 to 27.8% AR in soil Laacherhof AIII.

Non-extractable residues increased from DAT-0 to DAT-100 from 2.1 to 30.7% AR in soil Laacherhof AXXa and from 2.2 to 28.4% AR in soil Laacherhof AIII. See also Table 7.1.2.1.2- 2 and Table 7.1.2.1.2- 4.

D. VOLATILIZATION

No volatiles were determined within this study.

E. DEGRADATION OF TEST ITEM

The amount of [phenyl-UL-^{14}C]FOE sulfonic acid decreased from DAT-0 to DAT-100 from 12.23 to 3.46 µg in soil Laacherhof AXXa and from 12.4 to 3.34 µg in soil Laacherhof AIII.

The experimental data were kinetically evaluated according to the Single First Order kinetic model in order to derive half-lives for FOE sulfonic acid.

Table 7.1.2.1.2- 6: Single First Order degradation kinetics of FOE sulfonic acid in soil under aerobic conditions for trigger evaluation

Soil	DT_{50} [d]	DT_{90} [d]	k [d^{-1}]	Correlation Coefficient (R^2)
Laacherhof AXXa	61.8	205	0.0112	0.985
Laacherhof AIII	60.2	200	0.0115	0.986

III. CONCLUSIONS

[phenyl-UL-^{14}C]FOE sulfonic acid was well degraded in soil under aerobic conditions in the dark in the laboratory. The calculated half-lives were between 60 and 62 days in the tested soils.

It is concluded that FOE sulfonic acid has no potential for accumulation in the environment.

These half-lives are significantly shorter than those found in an earlier study (KCA 7.1.2.1.2 /01), where only weak degradation of FOE sulfonic acid was found in three soils after 100 days (DT_{50} between189 and 270 days). However, in that former study it was recognized that the soil moisture during test was too low and that an approx. 3-fold higher application rate was used.

Thus, these results clearly indicate that not a time-dependent sorption behavior of FOE sulfonic acid, but rather shorter half-lives under aerobic condition in soil are the most plausible reason for measuring much lower peak concentrations of test item in the leachates of the lysimeter studies than that expected by modeling calculations with the earlier input parameters (longer half-lives).

*****

Report:	**KCA 7.1.2.1.2 /07; [redacted], E.-M., 2013**
Title:	Amendment No 1 - FOE sulfonic acid: Aerobic Degradation in Four European Soils
Report No:	EnSa-13-0442
Document No:	M-461413-02-1
Guidelines:	• OECD Test Guideline No. 307
GLP:	yes

Executive Summary

The degradation rate of FOE sulfonic acid, a soil degradation product of flufenacet was studied in four soils under aerobic conditions in the dark in the laboratory for up to 120 days at 19.6 °C and 54.9% of the maximum water holding capacity:

Soil	Source	Texture (USDA)	pH *	OC [%]
Laacherhof AXXa	Monheim, Germany	loamy sand	6.2	1.7
Dollendorf II	Blankenheim, Germany	loam	7.0	4.6
Hoefchen am Hohenseh	Burscheid, Germany	silt loam	6.1	2.0
Wurmwiese	Monheim, Germany	sandy loam	5.0	1.8

* pH value was derived from aqueous 0.01 M $CaCl_2$ suspension

A study application rate of 344 µg per kg soil dry weight was applied based on a single field application rate of flufenacet of 600 g per hectare and a maximum formation of FOE sulfonic acid of 26.3% in a flufenacet aerobic soil degradation study.

The amount of FOE sulfonic acid in the soil extracts decreased from study start (DAT-0) to study end from 103.2 to 33.9% of applied amount [% AA] (DAT-120) in soil Laacherhof AXXa, from 94.8 to 2.6% AA (DAT-37) in soil Dollendorf II, from 104.6 to 3.3% AA (DAT-120) in soil Hoefchen am Hohenseh and from 102.1 to 25.3% AA (DAT-120) in soil Wurmwiese.

The experimental data could be well described by a single first order kinetic model for soils Laacherhof AXXa, Dollendorf II and Wurmwiese and by a double first order in parallel kinetic model for soil Hoefchen am Hohenseh. The half-life of FOE sulfonic acid under aerobic conditions was 73.4, 6.7, 24.0 and 49.8 days in Laacherhof AXXa, Dollendorf II, Hoefchen am Hohenseh and Wurmwiese, respectively.

It is concluded that FOE sulfonic acid has no potential for accumulation in the environment.

I. MATERIALS AND METHODS

A. MATERIALS

1. Test Item

unlabeled AE 0841914 (FOE5043-sulfonic acid sodium salt; report name: FOE sulfonic acid)

Certificate of Analysis:	AZ 17486
Batch Code:	AE 0841914 00 1 C86 001
Chemical Purity:	86% (w/w) with ^{19}F-NMR

2. Test Soils

Four soils were used (see Table 7.1.2.1.2- 7). 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 were used for the previous 5 years. The soils were sampled freshly from the fields (upper horizon of 0 to 20 cm) and sieved to a particle size of ≤ 2 mm. Soil collection and handling were in accordance to ISO 10381-6.

Table 7.1.2.1.2- 7: Physico-chemical properties of test soils

Parameter	Results / Units			
Soil Designation	Laacherhof AXXa	Dollendorf II	Hoefchen am Hohenseh	Laacherhof Wurmwiese
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)	loamy sand	loam	silt loam	sandy loam
Sand [%] [50 µm – 2 mm]	84	48	22	60
Silt [%] [2 µm – 50 µm]	10	28	62	26
Clay [%] [< 2 µm]	6	24	16	14
pH				
- in $CaCl_2$ (soil/$CaCl_2$ 1/2)	6.2	7.0	6.1	5.0
- in water (soil/water 1/1)	6.3	7.1	6.3	5.2
- in water (saturated paste)	6.4	7.1	6.3	6.3
- in KCl	6.0	6.7	5.8	4.7
Organic Carbon	1.7	4.6	2.0	1.8
Organic Matter [1]	2.9	7.9	3.4	3.1
Cation Exchange Capacity [meq/100 g]	9.2	19.9	11.1	10.4
Water Holding Capacity				
maximum [g H_2O *ad* 100 g soil DW]	48.5	79.1	54.8	56.3
at 0.1 bar (pF 2.0) [%]	12.9	45.4	33.1	19.8
Bulk Density (disturbed) [g/cm³]	1.19	1.03	1.09	1.17
Microbial Biomass [mg microbial carbon per kg soil DW] [2]				
DAT-0 (BIO-)	924	3883	1100	770
DAT-60 (BIO- / BIO+)	510/517	2116/2057	657/623	476/498
DAT-120 (BIO- / BIO+)	412/399	n.d./n.d. [3]	472/510	367/362

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

[1] Calculated as OM [%] = OC [%] x 1.724

[2] BIO- samples were left untreated, BIO+ samples were applied with solvent of application solution (400 µL methanol/water 1/1 (*v/v*)).

[3] Due to strong degradation of the test item in soil "Dollendorf II" until DAT-37, the study was terminated for this soil after this time point. Microbial biomass measurements at DAT-120 of this soil were discarded.

B. STUDY DESIGN

1. Experimental Conditions

The static test system for degradation in soil under aerobic conditions consisted of Erlenmeyer glass flasks (volume e.g. 300 mL). Each flask was closed with a polyurethane (PU) foam plug allowing free oxygen exchange.

For preparation of the test systems, 100 g dry weight equivalents of the sieved soils were weighed into each flask. Soil moisture was adjusted to 55 ± 5% of the maximum water holding capacity (MWHC) for the individual test systems by addition of de-ionized water, taking into account the water content of the application solution. The flasks were then closed with PU foam plugs and equilibrated to study conditions for 3 days prior to application.

The study application rate (SAR) was based on a single field application rate of flufenacet of 600 g per hectare and a maximum formation of 26.3% of FOE sulfonic acid in aerobic soil metabolism study M-002146-01-1 (Baseline Dossier, KCA 7.1.1.1/03), resulting in a nominal SAR of 344 µg FOE sulfonic acid per kg soil dry weight.

The test item was applied drop wise onto the soil surface of the respective test systems in 400 µL methanol/water 1/1 (*v/v*) using a pipette. After application, the test vessels (except DAT-0 samples) were closed with PU foam plugs.

The test systems were incubated in the dark for 120 days at 19.6 °C and soil moisture of 54.9% MWHC in a walk-in climatic chamber.

2. Sampling

Ten sampling intervals were distributed over the entire incubation period of 120 days. Duplicate samples were processed and analyzed 0, 1[7], 3[7], 7, 14, 21, 37, 58[8], 86[8] and 120[8] days after treatment (DAT). Microbial soil biomass was determined at start, middle and end of the study (DAT-0, DAT-60 and DAT-120[8]).

At each sampling interval, concurrent recovery samples were prepared freshly by fortification of a representative soil (Laacherhof AXXa) with the test item at LOQ level (corresponding to 5% of the nominal SAR) and application rate level (corresponding to 100% of the nominal SAR). Duplicate samples were prepared and processed in parallel to the degradation samples of the respective sampling interval for each fortification level.

3. Analytical Procedures

The entire soil of each test system was extracted three times at ambient temperature using a mechanical shaker and acetonitrile/water 1/1 (*v/v*). Furthermore, two accelerated extraction steps using a microwave with a magnetic stirrer were performed, first with acetonitrile/water 1/1 (*v/v*) at 70 °C and second with methanol/water 1/1 (*v/v*) at 50 °C. After each extraction step, extract and soil were separated by centrifugation approx. 10 minutes at 4200 x g) and decantation. All soil extracts were combined, made up to a final volume of 400 mL with acetonitrile/water (1/1, *v/v*) and mixed thoroughly.

Aliquots of the combined soil extract were analyzed by HPLC-MS/MS in selected reaction monitoring mode using matrix-matched external multi-point calibration curves. Concurrent recovery samples were processed and analyzed analogously. The limit of detection (LOD) and limit of quantitation (LOQ) for HPLC-MS/MS analysis of the combined soil extracts corresponded to 1 and 5% of the nominal SAR, respectively.

The HPLC-MS/MS method was validated with regard to linearity, accuracy and precision. The mass selective detector was operated in the positive electrospray ionization selected reaction monitoring mode, tuned for the mass transitions of parent and significant product ions. The linearity range of the mass spectrometer was tested in pure extraction solvent and in blank soil matrix solutions (matrix-

[7] only soils Dollendorf II and Höfchen am Hohenseh 4a
[8] except soil Dollendorf II

matched), covering a range from 1 to 150% of the nominal SAR. Based on these results, an external multi-point calibration curve was established for quantitation using standard solutions in blank soil matrix of soil Laacherhof AXXa (matrix-matched), as the observed matrix effects were in the same order of magnitude for all investigated soils.

The accuracy and precision of the method was assessed on the basis of the recovery rates determined for each soil after fortification with the test item at LOQ level (corresponding to 5% of the nominal SAR) and at application rate level (corresponding to 100% of the nominal SAR). The fortified samples were processed and analyzed as described for the degradation samples. Blank soil matrix solutions were used to determine the background abundance of the test item in the respective soils.

4. Kinetic Evaluation

The degradation kinetics of the test item was determined according to FOCUS kinetics (2006) [3] using the software KinGUI 2 with three different kinetic models: single first order, first order multi compartment and double first order in parallel. 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. The best-fit kinetic model was selected on the basis of the chi^2 scaled error criterion and on the basis of a visual assessment of the goodness of the fits. DT_{50} and DT_{90} values were calculated from the resulting kinetic parameters.

II. RESULTS AND DISCUSSION

A. DATA

Table 7.1.2.1.2- 8: Degradation of FOE sulfonic acid in soils under aerobic conditions
(expressed as % AA)

Soil	Replicate	DAT 0	1	3	7	14	21	37	58	86	120
Laacherhof AXXa	A	103.2	n.a.	n.a.	93.0	90.2	85.7	70.9	58.1	44.4	33.9
	B	103.2	n.a.	n.a.	94.1	88.9	84.5	70.6	58.0	46.0	34.0
	Mean	**103.2**	**n.a.**	**n.a.**	**93.5**	**89.5**	85.1	70.7	58.1	45.2	33.9
Dollendorf II	A	93.7	90.3	67.4	39.2	31.2	6.9	3.7	n.a.	n.a.	n.a.
	B	95.9	92.6	63.5	47.6	22.6	16.0	1.5	n.a.	n.a.	n.a.
	Mean	**94.8**	**91.5**	**65.4**	**43.4**	**26.9**	11.5	2.6	n.a.	n.a.	n.a.
Hoefchen am Hohenseh	A	104.2	100.9	94.4	69.9	56.4	60.7	46.3	28.2	12.9	3.6
	B	104.9	101.8	95.1	75.7	66.4	60.4	46.9	25.5	15.2	3.1
	Mean	**104.6**	**101.3**	**94.8**	**72.7**	**61.4**	60.5	46.6	26.8	14.0	3.3
Wurmwiese	A	102.9	n.a.	n.a.	92.5	86.4	78.6	58.2	43.1	29.3	25.1
	B	101.4	n.a.	n.a.	92.1	85.5	78.1	56.2	42.6	29.6	25.6
	Mean	**102.1**	**n.a.**	**n.a.**	**92.3**	**85.9**	78.4	57.2	42.9	29.5	25.3

DAT: days after treatment n.a.: not analyzed

B. METHOD VALIDATION

The HPLC-MS/MS method was successfully validated prior to application of the degradation samples.

The correlation coefficient (R^2) of the external multi-point calibration curve was 0.9999. The recovery rates ranged from 95.5 to 104.0% of applied amount [% AA] for all soils and both fortification levels. The relative standard deviations for each recovery set ranged from 1.2 to 2.4%, showing a good repeatability of this method. Background abundance in blank soil matrix was far below 30% of the

LOQ in all soils and no interference by other matrix components occurred. The combination of the selective MS/MS detection method used with the preceding HPLC separation leads to a high specificity of the method.

In addition, the extraction efficiency was demonstrated by concurrent recovery samples at each sampling interval. The overall mean concurrent recovery was 104.7% AA (range from 95.9 to 117.4% AA).

C. DEGRADATION OF TEST ITEM

The amount of FOE sulfonic acid in the soil extracts decreased from study start (DAT-0) to study end (DAT-120) from 103.2 to 33.9% of applied amount [% AA] in soil Laacherhof AXXa, from 94.8 to 2.6% AA in soil Dollendorf II, from 104.6 to 3.3% AA in soil Hoefchen am Hohenseh and from 102.1 to 25.3% AA in soil Wurmwiese.

The degradation of FOE sulfonic acid followed single first order kinetics in soils Laacherhof AXXa, Dollendorf II and Wurmwiese and double first order in parallel kinetics in soil Hoefchen am Hohenseh according to the lowest chi^2 error values and visual assessments. Table 7.1.2.1.2- 9 summarizes the best-fit results of the DT_{50} and DT_{90} calculations.

Table 7.1.2.1.2- 9: Best-fit degradation kinetics of FOE sulfonic acid in soils under aerobic conditions for trigger evaluation according to FOCUS

Soil	Best-Fit Kinetic Model [1]	DT_{50} [days]	DT_{90} [days]	chi^2 error [%]	Visual Assessment [2]
Laacherhof AXXa	SFO	73.4	243.8	1.3	+
Dollendorf II	SFO	6.7	22.3	5.6	+
Hoefchen am Hohenseh	DFOP	24.0	105.8	5.7	+
Wurmwiese	SFO	49.8	165.3	3.7	+

[1] SFO: single first order, DFOP: double first order in parallel
[2] visual assessment: + = good

III. CONCLUSIONS

FOE sulfonic acid, a soil degradation product of flufenacet was well degraded in soil under aerobic conditions in the dark in the laboratory. The calculated best-fit half-lives were between 6.7 and 73.4 days in the tested soils.

It is concluded that FOE sulfonic acid has no potential for accumulation in the environment.

*****

Report:	**KCA 7.1.2.1.2/10; [redacted], K.; [redacted], T.; 2013**
Title:	FOE sulfonic acid: Degradation in Four Aerobic Soils
Report No:	EnSa-13-0618
Document No:	M-467862-01-1
Guidelines:	• OECD Test Guideline No. 307
GLP:	yes

Executive Summary

The degradation rate of FOE sulfonic acid, a soil degradation product of flufenacet was studied in four soils under aerobic conditions in the dark in the laboratory for up to 120 days at 19.9 °C and 55.0% of the maximum water holding capacity:

Soil	Source	Texture (USDA)	pH [1]	OC [%]
Hanscheider Hof	Burscheid, Germany	loam	5.6	2.8
Frankenforst	Vinxel, Germany	silt loam	6.8	1.8
LUFA 2.3	Offenbach, Germany	sandy loam	6.8	1.1
LUFA 6S	Siebeldingen, Germany	clay	7.0	1.9

[1] pH in 0.01 M $CaCl_2$

A study application rate of 419 µg per kg soil dry weight was applied based on a single field application rate of flufenacet of 600 g per hectare and a maximum formation of FOE sulfonic acid of 26.3% in a flufenacet aerobic soil degradation study.

The amount of FOE sulfonic acid in the soil extracts decreased from study start (DAT-0) to study end from 102.9 to 4.7% (DAT-91) of applied amount [% AA] in soil Hanscheider Hof, from 105.0 to <LOD (DAT-91) in soil Frankenforst, from 100.2 to 27.5% AA (DAT-120) in soil LUFA 2.3 and from 98.5 to 3.0% AA (DAT-120) in soil LUFA 6S.

The experimental data could be well described by a single first-order kinetic model for all soils. The half-life of FOE sulfonic acid under aerobic conditions was 27.3, 21.8, 63.9 and 11.9 days in soil Hanscheider Hof, Frankenforst, LUFA 2.3 and LUFA 6S, respectively.

It is concluded that FOE sulfonic acid has no potential for accumulation in the environment.

I. MATERIALS AND METHODS

A. MATERIALS

1. Test Item

unlabeled AE 0841914 (FOE5043-sulfonic acid sodium salt, report name [1]: FOE sulfonic acid)
Certificate of Analysis: AZ 17542
Batch Code: AE 0841914-01-02
Chemical Purity: 87.6% (w/w) with ^{19}F-NMR

2. Test Soils

Four soils were used (see Table 7.1.2.1.2- 10). 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 were used for the previous 5 years. The soils were sampled freshly from the fields (upper horizon of 0 to 20 cm) and sieved to a particle size of ≤ 2 mm. Soil collection and handling were in accordance to ISO 10381-6.

Table 7.1.2.1.2- 10: Physico-chemical properties of test soils

Parameter	Results / Units			
Soil Designation	Hanscheider Hof	Frankenforst	LUFA 2.3	LUFA 6S
Geographic Location				
City	Burscheid	Vinxel	Offenbach	Siebeldingen
State	North-Rhine Westphalia	North-Rhine Westphalia	Hesse	Rhineland-Palatinate
Country	Germany	Germany	Germany	Germany
Soil Taxonomic Classification (USDA)	loamy-skeletal, mixed, semiactive, mesic Dystric Eutrudept	no information available	no information available	no information available
Soil Series	no information available			
Textural Class (USDA)	loam	silt loam	sandy loam	clay
Sand [%] [50 µm – 2 mm]	42	30	63	35
Silt [%] [2 µm – 50 µm]	45	51	27	23
Clay [%] [< 2 µm]	13	19	10	42
pH				
- in $CaCl_2$ (soil/$CaCl_2$ 1/2)	5.6	6.8	6.8	7.0
- in water (soil/water 1/1)	5.8	7.0	7.1	7.2
- in water (saturated paste)	5.8	6.9	7.1	7.1
- in KCl	5.3	6.3	6.7	6.6
Organic Carbon	2.8	1.8	1.1	1.9
Organic Matter [1]	4.8	3.1	1.9	3.3
Cation Exchange Capacity [meq/100 g]	10.8	15.4	8.9	21.5
Water Holding Capacity				
maximum [g H_2O *ad* 100 g soil DW]	64.4	56.7	39.3	48.3
at 0.1 bar (pF 2.0) [%]	30.1	30.5	17.8	32.8
Bulk Density (disturbed) [g/cm³]	1.04	1.15	1.28	1.22
Microbial Biomass [mg microbial carbon per kg soil DW]				
DAT-0 (BIO-)	870	1065	398	957
DAT-58 (BIO- / BIO+)	813/787	999/1024	736/671	1305/1019
DAT-120 (BIO- / BIO+)	601/566	800/757	227/242	984/875

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

[1] Calculated as OM [%] = OC [%] x 1.724

[2] BIO- samples were applied with 200 µL water, BIO+ samples were applied with solvent of application solution (400 µL methanol/water 1/1 (*v/v*)).

B. STUDY DESIGN

1. Experimental Conditions

The static test system for degradation in soil under aerobic conditions consisted of Erlenmeyer glass flasks (volume e.g. 300 mL). Each flask was closed with a polyurethane (PU) foam plug allowing free oxygen exchange.

For preparation of the test systems, 100 g dry weight equivalents of the sieved soils were weighed into each flask. Soil moisture was adjusted to 55 ± 5% of the maximum water holding capacity (MWHC) for the individual test systems by addition of de-ionized water. The flasks were then closed with PU foam plugs and equilibrated to study conditions for 3 days prior to application.

The study application rate (SAR) was based on a single field application rate of flufenacet of 600 g per hectare and a maximum formation of 26.3% of FOE sulfonic acid in aerobic soil metabolism study M-002146-01-1 (Baseline Dossier, KCA 7.1.1.1/03), resulting in a nominal SAR of 344 µg FOE sulfonic acid per kg soil dry weight. The actual SAR was 419 µg FOE sulfonic acid per kg soil dry weight

The test item was applied drop wise onto the soil surface of the respective test systems in 400 µL methanol/water 1/1 (*v/v*) using a pipette. After application, the test vessels (except DAT-0 samples) were closed with PU foam plugs.

The test systems were incubated in the dark for 120 days at 19.9 °C and soil moisture of 55.0% MWHC in a walk-in climatic chamber.

2. Sampling

Nine sampling intervals were distributed over the entire incubation period of 120 days. Duplicate samples were processed and analyzed 0, 2, 4, 7, 14, 30, 58, 91 and 120 [9] days after treatment (DAT). Microbial soil biomass was determined at start, middle and end of the study (DAT-0, DAT-58 and DAT-120).

At each sampling interval, concurrent recovery samples were prepared freshly by fortification of a representative soil (LUFA 2.3) with the test item at LOQ level (corresponding to 5% of the nominal SAR) and application rate level (corresponding to 100% of the nominal SAR). Duplicate samples were prepared and processed in parallel to the degradation samples of the respective sampling interval for each fortification level.

3. Analytical Procedures

The entire soil of each test system was extracted three times at ambient temperature using a mechanical shaker and acetonitrile/water 1/1 (*v/v*). Furthermore, two accelerated extraction steps using a microwave with a magnetic stirrer were performed, first with acetonitrile/water 1/1 (*v/v*) at 70 °C and second with methanol/water 1/1 (*v/v*) at 50 °C. After each extraction step, extract and soil were separated by centrifugation (approx. 10 minutes at 3480 x g) and decantation. All soil extracts were combined, fortified with internal standard solution, made up to a final volume of 400 mL with acetonitrile/water (1/1, *v/v*) and mixed thoroughly. The nominal concentration of the stable-labeled reference item used as internal standard corresponded to 10% of the nominal SAR after addition to the combined soil extracts (test item equivalents).

Aliquots of the combined soil extract were analyzed by HPLC-MS/MS in selected reaction monitoring mode using calibration curves in acetonitrile/water 1/1 (*v/v*) and a stable-labeled reference item as

[9] Only soils LUFA 2.3 and LUFA 6S

internal standard. Concurrent recovery samples were processed and analyzed analogously. The limit of detection (LOD) and limit of quantitation (LOQ) for HPLC-MS/MS analysis of the combined soil extracts corresponded to 1 and 5% of the nominal SAR, respectively.

The HPLC-MS/MS method was validated with regard to linearity, accuracy and precision. The mass selective detector was operated in the positive electrospray ionization selected reaction monitoring mode, tuned for the mass transitions of parent and significant product ions.

The linearity range of the mass spectrometer was tested in pure solvent. A multi-point calibration curve was established by plotting the nominal test item concentration versus the corresponding detector responses of the test item and the stable-labeled reference item used as internal standard, covering a range from 1 to 150% of the nominal SAR.

The accuracy and precision of the method was assessed on the basis of the recovery rates determined for each soil after fortification with the test item at LOQ level (corresponding to 5% of the nominal SAR) and at application rate level (corresponding to 100% of the nominal SAR). The fortified samples were processed and analyzed as described for the degradation samples. Blank soil matrix solutions were used to determine the background abundance of the test item in the respective soils.

4. Kinetic Evaluation

The degradation kinetics of the test item was determined according to FOCUS kinetics (2006) [3] using the software KinGUI 2 with three different kinetic models: single first order, first order multi compartment and double first order in parallel. 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. The best-fit kinetic model was selected on the basis of the chi^2 scaled error criterion and on the basis of a visual assessment of the goodness of the fits. DT_{50} and DT_{90} values were calculated from the resulting kinetic parameters.

II. RESULTS AND DISCUSSION

A. DATA

Table 7.1.2.1.2- 11: Degradation of FOE sulfonic acid in soils under aerobic conditions
(expressed as percentage of applied amount [% AA])

Soil	Replicate	DAT 0	2	4	7	14	30	58	91	120
Hanscheider Hof	A	101.3	98.3	92.2	88.6	76.5	53.3	22.4	4.7	n.a.
	B	104.4	102.0	98.3	85.9	76.2	51.8	23.1	4.5	n.a.
	Mean	**102.9**	**100.1**	**95.3**	**87.2**	**76.3**	**52.5**	**23.3**	**4.7**	
Frankenforst	A	103.1	97.8	84.2	73.9	66.3	45.1	14.2	< LOD	n.a.
	B	106.9	98.3	85.4	71.4	69.5	45.6	13.6	< LOD	n.a.
	Mean	**105.0**	**98.1**	**84.8**	**72.6**	**67.9**	**45.3**	**13.9**	**< LOD**	
LUFA 2.3	A	102.5	99.6	94.8	91.5	87.7	72.8	53.3	36.4	27.4
	B	98.0	100.1	95.4	89.3	89.0	73.6	52.7	37.5	27.6
	Mean	**100.2**	**99.8**	**95.1**	**90.4**	**88.3**	**73.2**	**53.0**	**36.9**	**27.5**
LUFA 6S	A	98.9	91.4	86.6	80.1	76.8	64.2	37.7	13.8	2.5
	B	98.0	97.4	92.7	77.8	79.4	64.5	37.2	11.7	3.6
	Mean	**98.5**	**94.5**	**89.6**	**78.9**	**78.1**	**64.4**	**37.5**	**12.7**	**3.0**

DAT: days after treatment n.a.: not analyzed

B. METHOD VALIDATION

The HPLC-MS/MS method was successfully validated prior to application of the degradation samples.

For quantitation multi-point calibration curves with a stable-labeled reference item as internal standard were established using standard solutions in pure solvent, with correlation coefficients (R^2) ranging from 0.9992 to 0.9999. The recovery rates ranged from 93.6 to 112.1% of applied amount [% AA] for all soils and both fortification levels. The relative standard deviations for each recovery set ranged from 1.1 to 3.1%, showing a good repeatability of this method. Background abundance in blank soil matrix was far below 30% of the LOQ in all soils and no interference by other matrix components occurred. The combination of the selective MS/MS detection method used with the preceding HPLC separation leads to a high specificity of the method.

In addition, the extraction efficiency was demonstrated by concurrent recovery samples at each sampling interval. The overall mean concurrent recovery was 101.3% AA, range from 95.9 to 109.5% AA).

C. DEGRADATION OF TEST ITEM

The amount of FOE sulfonic acid in the soil extracts decreased from study start (DAT-0) to study end from 102.9 to 4.7% (DAT-91) of applied amount [% AA] in soil Hanscheider Hof, from 105.0 to <LOD (DAT-91) in soil Frankenforst, from 100.2 to 27.5% AA (DAT-120) in soil LUFA 2.3 and from 98.5 to 3.0% AA (DAT-120) in soil LUFA 6S.

The degradation of FOE sulfonic acid followed single first order kinetics in all soils according to the lowest chi2 error values and visual assessments. Table 7.1.2.1.2- 12 summarizes the best-fit results of the DT50 and DT90 calculations.

Table 7.1.2.1.2- 12: Best-fit degradation kinetics of FOE sulfonic acid in soils under aerobic conditions for trigger evaluation according to FOCUS

Soil	Best-Fit Kinetic Model [1]	DT_{50} [days]	DT_{90} [days]	chi^2 error [%]	Visual Assessment [2]
Hanscheider Hof	SFO	27.3	90.7	3.2	+
Frankenforst	SFO	21.8	72.4	6.4	+
LUFA 2.3	SFO	63.9	212	1.5	+
LUFA 6S	SFO	11.9	39.4	6.5	+

[1] SFO: single first order, DFOP: double first order in parallel
[2] visual assessment: + = good

III. CONCLUSIONS

FOE sulfonic acid, a soil degradation product of flufenacet was well degraded in soil under aerobic conditions in the dark in the laboratory. The calculated best-fit half-lives were between 11.9 and 63.9 days in the tested soils.

It is concluded that FOE sulfonic acid has no potential for accumulation in the environment.

*****

Report:	**KCA 7.1.2.1.2 /06; [redacted], M.; 2012**
Title:	FOE methylsulfone: Aerobic Degradation in Four European Soils
Report No:	S11-03808
Document No:	M-443658-01-1
Guidelines:	• OECD Test Guideline No. 307
GLP:	yes

Executive Summary

The degradation rate of FOE methylsulfone, a soil degradation product of flufenacet was studied in four soils under aerobic conditions in the dark in the laboratory for up to 120 days at 19.7 °C and 55 ± 5% of the maximum water holding capacity:

Soil	Source	Texture (USDA)	pH [1]	OC [%]
Laacherhof AXXa	Monheim, Germany	loamy sand	6.2	1.7
Dollendorf II	Blankenheim, Germany	loam	7.0	4.6
Hoefchen am Hohenseh	Burscheid, Germany	silt loam	6.1	2.0
Laacherhof Wurmwiese	Monheim, Germany	sandy loam	5.0	1.8

[1] pH in 0.01 M $CaCl_2$

A study application rate of 81.7 µg per kg soil dry weight was applied based on a single field application rate of flufenacet of 600 g per hectare and a maximum formation of FOE methylsulfone of 6.6% in a flufenacet aerobic soil degradation study.

The amount of FOE methylsulfone in the soil extracts decreased from study start (DAT-0) to study end from 94.0 to 11.4 % (DAT-120) of applied amount (% AA) in soil Laacherhof AXXa, from 102.5 to 5.8% AA (DAT-92) in soil Dollendorf II, from 106.4 to 14.2% AA (DAT-120) in soil Hoefchen am Hohenseh and from 102.7 to 39.4% AA (DAT-120) in soil Laacherhof Wurmwiese.

The experimental data could be well described by a single first order kinetic model for soils Laacherhof AXXa, Dollendorf II and Laacherhof Wurmwiese and by a double first order in parallel kinetic model for soil Hoefchen am Hohenseh. The half-life of FOE methylsulfone under aerobic conditions was 43.1, 23.3, 40.9 and 96.1 days in soil Laacherhof AXXa, Dollendorf II, Hoefchen am Hohenseh and Laacherhof Wurmwiese, respectively.

It is concluded that FOE methylsulfone has no potential for accumulation in the environment.

I. MATERIALS AND METHODS

A. MATERIALS

1. Test Item

unlabeled FOE methylsulfone
Certificate of Analysis: AZ 15999
Batch Code: BCS-CO62475-01-01
Chemical Purity: 97.2% (w/w)

2. Test Soils

Four soils were used (see Table 7.1.2.1.2- 13). 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 were used for the previous 5 years. The soils were sampled freshly from the fields (upper horizon of 0 to 20 cm) and sieved to a particle size of ≤ 2 mm.

Table 7.1.2.1.2- 13: Physico-chemical properties of test soils

Parameter	Results / Units			
Soil Designation	Laacherhof AXXa	Dollendorf II	Hoefchen am Hohenseh	Laacherhof Wurmwiese
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
GPS Coordinates	N 51° 04.647' E 006° 53.517'	N 50° 22.899' E 006° 43.001'	N 51° 04.001' E 007° 06.327'	N 51° 04.857' E 006° 55.251'
Soil Taxonomic Classification (USDA)	sandy, mixed, mesic typic Cambudolls	fine-loamy, mixed, active, frigid Typic Eutrudept	loamy, mixed, mesic, Typic Argudalf	loamy, mixed, mesic Typic Argudalfs
Soil Series	no information available			
Textural Class (USDA)	loamy sand	loam	silt loam	sandy loam
Sand [%] [50 µm – 2 mm]	84	48	22	60
Silt [%] [2 µm – 50 µm]	10	28	62	26
Clay [%] [< 2 µm]	6	24	16	14
pH				
- in $CaCl_2$ (soil/$CaCl_2$ 1/2)	6.3	7.1	6.3	5.2
- in water (soil/water 1/1)	6.4	7.1	6.3	6.3
- in water (saturated paste)	6.0	6.7	5.8	4.7
- in KCl	6.2	7.0	6.1	5.0
Organic Carbon	1.7	4.6	2.0	1.8
Organic Matter [1]	2.9	7.9	3.4	3.1
Cation Exchange Capacity [meq/100 g]	9.2	19.5	11.1	10.4
Water Holding Capacity				
maximum [g H_2O *ad* 100 g soil DW]	48.5	79.1	54.8	56.3
at 0.33 bar (pF 2.5) [%]	10.8	35.1	20.9	15.6
Bulk Density (disturbed) [g/cm^3]	1.19	1.03	1.09	1.17
Microbial Biomass [mg microbial carbon per 100 g soil DW] [2]				
DAT-0 (BIO-)	204.4	447.4	229.9	196.3
DAT-58 (BIO- / BIO+)	182.0/175.6	447.4/446.9	186.5/198.8	131.0/153.4
DAT-121 (BIO- / BIO+)	138.6/123.2	421.7/405.2	141.4/166.9	100.8/103.9

DAT: days after treatment
DW: dry weight
USDA: United States Department of Agriculture
GPS: global positioning system
[1] Calculated as OM [%] = OC [%] x 1.724
[2] BIO- samples were left untreated, BIO+ samples were applied with solvent of application solution (198 µL methanol/water 1/1 (*v/v*)).

B. STUDY DESIGN

1. Experimental Conditions

The static test system for degradation in soil under aerobic conditions consisted of Erlenmeyer glass flasks (volume e.g. 300 mL or 250 mL). Each flask was closed with cotton wool allowing free oxygen exchange.

For preparation of the test systems, 100 g dry weight equivalents of the sieved soils were weighed into each flask. Soil moisture was adjusted to 55 ± 5% of the maximum water holding capacity (MWHC) for the individual test systems by addition of de-ionized water. The flasks were then closed with cotton wool and equilibrated to study conditions for 5 days prior to application.

The study application rate (SAR) was based on a single field application rate of flufenacet of 600 g per hectare and a maximum formation of 6.6% of FOE methylsulfone in aerobic soil metabolism study M-002146-01-1 (Baseline Dossier, KCA 7.1.1.1/03), resulting in a nominal SAR of 79.4 µg FOE methylsulfone per kg soil dry weight. The actual SAR was 81.7 µg FOE methylsulfone per kg soil dry weight

The test item was applied drop wise onto the soil surface of the respective test systems in 198 µL methanol/water 1/1 (*v/v*) using a pipette. After application, the test vessels (except DAT-0 samples) were closed with cotton wool.

The test systems were incubated in the dark for 120 days at 19.7 °C and soil moisture of 55 ± 5% MWHC in a walk-in climatic chamber.

2. Sampling

Ten sampling intervals were distributed over the entire incubation period of 120 days. Duplicate samples were processed and analyzed at 0, 1, 2, 6, 13, 27, 61, 70 [10], 92 and 120 days after treatment (DAT). Microbial soil biomass was determined after arrival of the soil at the test facility and at start, middle and end of the study (post-handling, DAT-0, DAT-58 and DAT-120).

At each sampling interval, concurrent recovery samples were prepared freshly by fortification of a representative soil (Laacherhof AXXa) with the test item at LOQ level (corresponding to 5% of the nominal SAR) and 22-fold LOQ level (corresponding to approx. 110% of the nominal SAR). Duplicate samples were prepared and processed in parallel to the degradation samples of the respective sampling interval for each fortification level.

3. Analytical Procedures

The entire soil of each test system was extracted three times at ambient temperature using a mechanical shaker and acetonitrile/water 4/1 (*v/v*). Furthermore, two accelerated extraction steps using a microwave were performed, first with acetonitrile/water 4/1 (*v/v*) at 62 °C and second with methanol/water 4/1 (*v/v*) at 50 °C. After each extraction step, extract and soil were separated by centrifugation and decantation. All soil extracts were combined, mixed thoroughly and the volume was determined.

Aliquots of the combined soil extract were analyzed by HPLC-MS/MS in selected reaction monitoring mode using matrix-matched external multi-point calibration curves. Concurrent recovery samples were processed and analyzed analogously. The limit of detection (LOD) and limit of quantitation

[10] only soil Laacherhof Wurmwiese

(LOQ) for HPLC-MS/MS analysis of the combined soil extracts corresponded to 1 and 5% of the nominal SAR, respectively.

The HPLC-MS/MS method was validated with regard to linearity, accuracy and precision. The mass selective detector was operated in the positive electrospray ionization selected reaction monitoring mode, tuned for the mass transitions of parent and significant product ions.

The linearity range of the mass spectrometer was tested in pure extraction solvent and in blank soil matrix solutions (matrix-matched), covering a range from 1 to 200% of the nominal SAR. Matrix effects between 0 and 13% were observed in the tested soils; therefore, external multi-point calibration curves were established using the respective matrix matched standard solution for each soil.

The accuracy and precision of the method was assessed on the basis of the recovery rates determined for each soil after fortification with the test item at LOQ level (corresponding to 5% of the nominal SAR) and at 22 x LOQ level (corresponding to 110% of the nominal SAR). The fortified samples were processed and analyzed as described for the degradation samples. Blank soil matrix solutions were used to determine the background abundance of the test item in the respective soils.

4. Kinetic Evaluation

The degradation kinetics of the test item was determined according to FOCUS kinetics (2006) [3] using the software KinGUI 2 with three different kinetic models: single first order, first order multi compartment and double first order in parallel. 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. The best-fit kinetic model was selected on the basis of the chi^2 scaled error criterion and on the basis of a visual assessment of the goodness of the fits. DT_{50} and DT_{90} values were calculated from the resulting kinetic parameters.

II. RESULTS AND DISCUSSION

A. DATA

Table 7.1.2.1.2- 14: Degradation of FOE methylsulfone in soils under aerobic conditions (expressed as % AA)

Soil	Replicate	DAT									
		0	**1**	**2**	**6**	**13**	**27**	**61**	**70**	**92**	**120**
Laacherhof AXXa	A	92.7	95.8	94.7	90.3	83.6	69.5	35.6	n.a.	21.3	12.5
	B	95.3	99.0	103.7	88.5	82.3	67.1	38.4	n.a.	20.7	10.3
	Mean	**94.0**	**97.4**	**99.2**	**89.4**	**82.9**	**68.3**	**37.0**		**21.0**	**11.4**
Dollendorf II	A	107.6	100.1	105.8	88.6	73.7	48.1	12.2	n.a.	4.5	n.a.
	B	97.4	98.5	99.0	87.8	73.1	49.9	13.7	n.a.	7.0	n.a.
	Mean	**102.5**	**99.3**	**102.4**	**88.2**	**73.4**	**49.0**	**13.8**		**5.8**	
Hoefchen am Hohenseh	A	101.3	103.3	96.1	93.9	77.7	66.0	40.9	n.a.	29.5	13.0
	B	111.5	109.4	94.1	89.0	81.6	70.4	41.0	n.a.	20.8	15.4
	Mean	**106.4**	**106.4**	**95.1**	**91.4**	**79.7**	**68.2**	**41.0**		**25.2**	**14.2**
Laacherhof Wurmwiese	A	102.6	100.4	95.8	102.6	89.4	79.7	72.2	68.2	55.9	37.5
	B	102.7	105.9	102.2	95.8	89.2	76.1	71.5	54.3	51.7	41.4
	Mean	**102.7**	**103.1**	**99.0**	**99.2**	**89.3**	**77.9**	**71.8**	**61.3**	**53.8**	**39.4**

DAT: days after treatment   n.a.: not analyzed

B. METHOD VALIDATION

The HPLC-MS/MS method was successfully validated prior to application of the degradation samples.

The correlation coefficient (R^2) of the external, multi-point calibration curves were between 0.9971 and 0.9997. The recovery rates ranged from 89.1 to 108.2% of applied amount [% AA] for all soils and both fortification levels. The relative standard deviations for each recovery set ranged from 1.8 to 3.3%, showing a good repeatability of this method. Background abundance in blank soil matrix was far below 20% of the LOQ in all soils and no interference by other matrix components occurred. The combination of the selective MS/MS detection method used with the preceding HPLC separation leads to a high specificity of the method.

In addition, the extraction efficiency was demonstrated by concurrent recovery samples at each sampling interval. The overall mean concurrent recovery ranged from 90.3 to 116.4% AA.

C. DEGRADATION OF TEST ITEM

The amount of FOE methylsulfone in the soil extracts decreased from study start (DAT-0) to study end from 94.0 to 11.4% of applied amount [% AA] (DAT-120) in soil Laacherhof AXXa, from 102.5 to 5.8% AA (DAT-92) in soil Dollendorf II, from 106.4 to 14.2% AA (DAT-120) in soil Hoefchen am Hohenseh and from 102.7 to 39.4% AA (DAT-120) in soil Laacherhof Wurmwiese.

The degradation of FOE methylsulfone followed single first order kinetics in soils Laacherhof AXXa, Dollendorf II and Laacherhof Wurmwiese and double first order in parallel kinetics in soil Hoefchen am Hohenseh according to the lowest chi² error values and visual assessments. Table 7.1.2.1.2- 15 summarizes the best-fit results of the DT_{50} and DT_{90} calculations.

Table 7.1.2.1.2- 15: Best-fit degradation kinetics of FOE methylsulfone in soils under aerobic conditions for trigger evaluation according to FOCUS

Soil	Best-Fit Kinetic Model [1]	DT_{50} [days]	DT_{90} [days]	chi² error [%]	Visual Assessment [2]
Laacherhof AXXa	SFO	43.1	143.3	3.4	+
Dollendorf II	SFO	23.3	77.4	3.0	+
Hoefchen am Hohenseh	DFOP	40.9	149.1	2.9	+
Laacherhof Wurmwiese	SFO	96.1	319.4	3.3	+

[1] SFO: single first order, DFOP: double first order in parallel
[2] visual assessment: + = good

III. CONCLUSIONS

FOE methylsulfone, a soil degradation product of flufenacet was well degraded in soil under aerobic conditions in the dark in the laboratory. The calculated best-fit half-lives were between 23.3 and 96.1 days in the tested soils.

It is concluded that FOE methylsulfone has no potential for accumulation in the environment.

*****

Report:	**KCA 7.1.2.1.2 /09; [redacted], K.; [redacted], T.; 2013**
Title:	FOE methylsulfone: Degradation in Four Aerobic Soils
Report No:	EnSa-13-0617
Document No:	M-467858-01-1
Guidelines:	• OECD Test Guideline No. 307
GLP:	yes

Executive Summary

The degradation rate of FOE methylsulfone, a soil degradation product of flufenacet was studied in four soils under aerobic conditions in the dark in the laboratory for up to 120 days at 19.9 °C and 54.4% of the maximum water holding capacity:

Soil	Source	Texture (USDA)	pH [1]	OC [%]
Hanscheider Hof	Burscheid, Germany	loam	5.6	2.8
Frankenforst	Vinxel, Germany	silt loam	6.8	1.8
LUFA 2.3	Offenbach, Germany	sandy loam	6.8	1.1
LUFA 6S	Siebeldingen, Germany	clay	7.0	1.9

[1] pH in 0.01 M $CaCl_2$

A study application rate of 79 µg per kg soil dry weight was applied based on a single field application rate of flufenacet of 600 g per hectare and a maximum formation of FOE methylsulfone of 6.6% in a flufenacet aerobic soil degradation study.

The amount of FOE methylsulfone in the soil extracts decreased from study start (DAT-0) to DAT-120 from 96.8 to 37.0 of applied amount [% AA] in soil Hanscheider Hof, from 95.8 to 26.6% AA in soil Frankenforst, from 96.7 to 56.9% AA in soil LUFA 2.3 and from 100.2 to 58.9% AA (DAT-120) in soil LUFA 6S.

The experimental data could be well described by a single first order kinetic model for all soils. The half-life of FOE methylsulfone under aerobic conditions was 82.5, 64.0, 147 and 163 days in soil Hanscheider Hof, Frankenforst, LUFA 2.3 and LUFA 6S, respectively.

It is concluded that FOE sulfonic acid has no potential for accumulation in the environment.

I. MATERIALS AND METHODS

A. MATERIALS

1. Test Item

unlabeled FOE methylsulfone
Certificate of Analysis: AZ 18125
Batch Code: BCS-CO62475-01-01
Chemical Purity: 97.2% (w/w)

2. Test Soils

Four soils were used (see Table 7.1.2.1.2- 16). 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 were used for the previous 5 years. The soils were sampled freshly from

the fields (upper horizon of 0 to 20 cm) and sieved to a particle size of ≤ 2 mm. Soil collection and handling were in accordance to ISO 10381-6.

Table 7.1.2.1.2- 16: Physico-chemical properties of test soils

Parameter	Results / Units			
Soil Designation	Hanscheider Hof	Frankenforst	LUFA 2.3	LUFA 6S
Geographic Location				
City	Burscheid	Winxel	Offenbach-Hesse	Siebeldingen
State	North-Rhine Westphalia	North-Rhine Westphalia	Hesse	Rhineland-Palatinate
Country	Germany	Germany	Germany	Germany
Soil Taxonomic Classification (USDA)	loamy-skeletal, mixed, semiactive, mesic Dystric Eutrudept	no information available	no information available	no information available
Soil Series	no information available			
Textural Class (USDA)	loam	silt loam	sandy loam	clay
Sand [%] [50 µm – 2 mm]	42	30	63	35
Silt [%] [2 µm – 50 µm]	45	51	27	23
Clay [%] [< 2 µm]	13	19	10	42
pH				
- in $CaCl_2$ (soil/$CaCl_2$ 1/2)	5.6	6.8	6.8	7.0
- in water (soil/water 1/1)	5.8	7.0	7.1	7.2
- in water (saturated paste)	5.8	6.9	7.1	7.1
- in KCl	5.3	6.3	6.7	6.6
Organic Carbon	2.8	1.8	1.1	1.9
Organic Matter [1]	4.8	3.1	1.9	3.3
Cation Exchange Capacity [meq/100 g]	10.8	15.4	8.9	21.5
Water Holding Capacity				
maximum [g H_2O /a 100 g soil DW]	64.4	56.7	39.3	48.3
at 0.1 bar (pF 2.0) [%]	30.1	30.5	17.8	32.8
Bulk Density (disturbed) [g/cm³]	1.04	1.15	1.28	1.22
Microbial Biomass [mg microbial carbon per kg soil DW] [2]				
DAT-0 (BIO-)	764	1055	269	871
DAT-59 (BIO- / BIO+)	659/679 [3]	827/627	270/276	976/871
DAT-120 (BIO- / BIO+)	621/575	790/761	268/245	943/878

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

[1] Calculated as OM [%] = OC [%] x 1.724

[2] BIO- samples were applied with 200 µL water, BIO+ samples were applied with solvent of application solution (400 µL methanol/water 1/1 (v/v)).

[3] Due to a deviation during the measurement, the BIO+ sample of soil Hanscheider Hof was reanalyzed at DAT-63.

B. STUDY DESIGN

1. Experimental Conditions

The static test system for degradation in soil under aerobic conditions consisted of Erlenmeyer glass flasks (volume e.g. 300 mL). Each flask was closed with a polyurethane (PU) foam plug allowing free oxygen exchange.

For preparation of the test systems, 100 g dry weight equivalents of the sieved soils were weighed into each flask. Soil moisture was adjusted to 55 ± 5% of the maximum water holding capacity (MWHC) for the individual test systems by addition of de-ionized water. The flasks were then closed with PU foam plugs and equilibrated to study conditions for 4 days prior to application.

The study application rate (SAR) was based on a single field application rate of flufenacet of 600 g per hectare and a maximum formation of 6.6% of FOE methylsulfone in aerobic soil metabolism study M-002146-01-1 (Baseline Dossier, KCA 7.1.1.1/03), resulting in a nominal SAR of 79 µg FOE methylsulfone per kg soil dry weight. The actual SAR was 79 µg FOE methylsulfone per kg soil dry weight.

The test item was applied drop wise onto the soil surface of the respective test systems in 400 µL methanol/water 1/1 (*v/v*) using a pipette. After application, the test vessels (except DAT-0 samples) were closed with PU foam plugs.

The test systems were incubated in the dark for 120 days at 19.9 °C and soil moisture of 54.4% MWHC in a walk-in climatic chamber.

2. Sampling

Eight sampling intervals were distributed over the entire incubation period of 120 days. Duplicate samples were processed and analyzed 0, 3, 7, 14, 30, 59, 93 and 120 days after treatment (DAT). Microbial soil biomass was determined at start, middle and end of the study (DAT-0, DAT-59 and DAT-120).

At each sampling interval, concurrent recovery samples were prepared freshly by fortification of a representative soil (LUFA 2.3) with the test item at LOQ level (corresponding to 5% of the nominal SAR) and application rate level (corresponding to 100% of the nominal SAR). Duplicate samples were prepared and processed in parallel to the degradation samples of the respective sampling interval for each fortification level.

3. Analytical Procedures

The entire soil of each test system was extracted three times at ambient temperature using a mechanical shaker and acetonitrile/water 4/1 (*v/v*). Furthermore, two accelerated extraction steps using a microwave with a magnetic stirrer were performed, first with acetonitrile/water 4/1 (*v/v*) at 70 °C and second with methanol/water 1/1 (*v/v*) at 50 °C. After each extraction step, extract and soil were separated by centrifugation (approx. 10 minutes at 3480 x g) and decantation. All soil extracts were combined, fortified with internal standard solution, made up to a final volume of 400 mL with acetonitrile/water (4/1, *v/v*) and mixed thoroughly. The nominal concentration of the stable-labeled reference item used as internal standard corresponded to 10% of the nominal SAR after addition to the combined soil extracts (test item equivalents).

Aliquots of the combined soil extract were analyzed by HPLC-MS/MS in selected reaction monitoring mode using calibration curves in acetonitrile/water 1/1 (*v/v*) and a stable-labeled reference item as internal standard. Concurrent recovery samples were processed and analyzed analogously. The limit of

detection (LOD) and limit of quantitation (LOQ) for HPLC-MS/MS analysis of the combined soil extracts corresponded to 1 and 5% of the nominal SAR, respectively.

The HPLC-MS/MS method was validated with regard to linearity, accuracy and precision. The mass selective detector was operated in the positive electrospray ionization selected reaction monitoring mode, tuned for the mass transitions of parent and significant product ions.

The linearity range of the mass spectrometer was tested in pure solvent. A multi-point calibration curve was established by plotting the nominal test item concentration versus the corresponding detector responses of the test item and the stable-labeled reference item used as internal standard, covering a range from 1 to 150% of the nominal SAR.

The accuracy and precision of the method was assessed on the basis of the recovery rates determined for each soil after fortification with the test item at LOQ level (corresponding to 5% of the nominal SAR) and at application rate level (corresponding to 100% of the nominal SAR). The fortified samples were processed and analyzed as described for the degradation samples. Blank soil matrix solutions were used to determine the background abundance of the test item in the respective soils.

4. Kinetic Evaluation

The degradation kinetics of the test item was determined according to FOCUS kinetics (2006) [3] using the software KinGUI 2 with three different kinetic models: single first order, first order multi compartment and double first order in parallel. 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. The best-fit kinetic model was selected on the basis of the chi^2 scaled error criterion and on the basis of a visual assessment of the goodness of the fits. DT_{50} and DT_{90} values were calculated from the resulting kinetic parameters.

II. RESULTS AND DISCUSSION

A. DATA

Table 7.1.2.1.2-17: Degradation of FOE methylsulfone in soils under aerobic conditions
(expressed in percent of applied amount [% AA])

Soil	Replicate	DAT 0	3	7	14	30	59	93	120
Hanscheider Hof	A	95.4	101.9	91.9	88.9	80.7	59.3	43.3	34.4
	B	98.2	95.0	90.6	87.6	81.2	59.4	45.5	37.1
	Mean	**96.8**	**98.3**	**91.3**	**88.3**	**81.0**	**59.4**	**44.6**	**37.0**
Frankenforst	A	98.8	100.0	95.7	84.2	75.2	52.7	33.4	26.3
	B	92.9	99.1	93.6	84.6	76.4	55.9	34.7	26.8
	Mean	**95.8**	**99.5**	**94.6**	**84.4**	**75.8**	**54.3**	**34.1**	**26.6**
LUFA 2.3	A	95.6	99.1	94.2	85.6	84.9	72.6	62.0	56.8
	B	97.9	99.0	93.1	87.8	80.6	70.4	61.9	56.9
	Mean	**96.7**	**99.0**	**93.7**	**86.7**	**82.7**	**71.5**	**62.0**	**56.9**
LUFA 6S	A	100.7	95.8	92.5	87.8	86.5	74.9	66.4	58.9
	B	99.6	99.6	93.7	88.6	84.9	77.3	65.0	59.0
	Mean	**100.2**	**97.7**	**93.1**	**88.2**	**85.7**	**76.1**	**65.7**	**58.9**

DAT: days after treatment

B. METHOD VALIDATION

The HPLC-MS/MS method was successfully validated prior to application of the degradation samples.

For quantitation multi-point calibration curves with a stable-labeled reference item as internal standard were established using standard solutions in pure solvent, with correlation coefficients (R^2) ranging from 0.9997 to 1.0000. The recovery rates ranged from 91.4 to 107.0% of applied amount [% AA] for all soils and both fortification levels. The relative standard deviations for each recovery set ranged from 0.9 to 4.6%, showing a good repeatability of this method. Background abundance in blank soil matrix was far below 30% of the LOQ in all soils and no interference by other matrix components occurred. The combination of the selective MS/MS detection method used with the preceding HPLC separation leads to a high specificity of the method.

In addition, the extraction efficiency was demonstrated by concurrent recovery samples at each sampling interval. The overall mean concurrent recovery was 99.6% AA (range from 95.3 to 102.7% AA).

C. DEGRADATION OF TEST ITEM

The amount of FOE methylsulfone in the soil extracts decreased from study start (DAT-0) to DAT-120 from 96.8 to 37.0 of applied amount [% AA] in soil Hanscheider Hof, from 95.8 to 26.6% AA in soil Frankenforst, from 96.7 to 56.9% AA in soil LUFA 2.3 and from 100.2 to 58.9% AA (DAT-120) in soil LUFA 6S.

The degradation of FOE methylsulfone followed single first order kinetics in all soils according to the lowest chi^2 error values and visual assessments. Table 7.1.2.1.2- 18 summarizes the best-fit results of the DT_{50} and DT_{90} calculations.

Table 7.1.2.1.2- 18: Best-fit degradation kinetics of FOE methylsulfone in soils under aerobic conditions for trigger evaluation according to FOCUS

Soil	Best-Fit Kinetic Model [1]	DT_{50} [days]	DT_{90} [days]	chi^2 error [%]	Visual Assessment [2]
Hanscheider Hof	SFO	82.5	274	2.1	+
Frankenforst	SFO	64.0	213	2.9	+
LUFA 2.3	SFO	147.0	488	2.1	+
LUFA 6S	SFO	163.0	542	1.7	+

[1] SFO: single first order, DPOP: double first order in parallel
[2] visual assessment: + = good

III. CONCLUSIONS

FOE methylsulfone, a soil degradation product of flufenacet was moderately degraded in soil under aerobic conditions in the dark in the laboratory. The calculated best-fit half-lives were between 64.0 and 163 days in the tested soils.

It is concluded that FOE methylsulfone has no potential for accumulation in the environment.

*****

Report:	**KCA 7.1.2.1.2 /03; [redacted], N. R.; [redacted], A. M.; 1999**
Title:	Rate of Aerobic Soil Degradation for Thiadone (a Metabolite of FOE 5043) - Amended Report
Report No:	F3042108
Document No:	M-009828-01-1
Guidelines:	• EPA Ref: Subdivision N, 162-1 (Supplemental)
GLP:	yes

Executive Summary

The degradation of [thiadiazole-2-^{14}C]FOE-thiadone was investigated in three soils under aerobic conditions in the dark in the laboratory for 14 days at 20 ±1 °C and a soil moisture of approx. 75% of the water holding capacity at 1/3 bar:

Soil	Source	Texture (USDA)	pH	OC [1] [%]
Iowa (EFS115)	Iowa, USA	loamy sand	7.2	1.1
Indiana (EFS117)	Indiana, USA	sandy loam	6.4	0.8
Nebraska (EFS118)	Nebraska, USA	silt loam	7.7	1.0

[1] Calculated from organic matter as OC [%] = OM [%] / 1.724

The study application rate was 25 µg/50 g soil (dry weight) (≙ 0.5 ppm), equal to 0.5 mg FOE-thiadone/kg soil (dry weight).

Duplicate test systems were processed and analyzed 0, 0.25, 1, 2, 3, 5, 7 and 10 days after treatment (loamy sand); 0, 0.5, 1, 2, 3, 4, 7, and 10 days after treatment (sandy loam) as well as 0, 1, 2, 3, 5, 6, 10 and 14 days after treatment (silt loam).

Overall mean material balance was 95.7% of applied radioactivity (% AR) for soil Iowa, 96.4% AR for soil Indiana and 94.9% AR for soil Nebraska.

The following maximum amounts of carbon dioxide were detected at end of the study: 65.6% AR in soil Iowa, 82.1% AR in soil Indiana and 71.8% AR in soil Nebraska. Volatile organic compounds were formed to a maximum of 4.0% AR at all sampling intervals in all soils.

Extractable residues decreased steadily from 102.6% AR at DAT-0 to 9.6% AR at DAT-10 in soil Iowa, from 99.0% AR at DAT-0 to 6.2% AR at DAT-10 in soil Indiana and from 97.0% AR at DAT-0 to 5.5% AR at DAT-14 in soil Nebraska.

Non-extractable residues (NER) increased from 1.1% AR at DAT-0 to 20.1% AR at DAT-7 and slightly decreased to 19.5% AR at DAT-10 in soil Iowa. In soil Indiana NER increased from 0.6% AR at DAT-0 to 8.4% AR at DAT-5 and slightly decreased to 7.6% AR at DAT-10. In soil Nebraska NER increased from 1.4% AR at DAT-0 to 14.7% AR from DAT-7 onwards.

The amount of FOE-thiadone decreased from 98.3% AR at DAT-0 to 6.6% AR at DAT-10 in soil Iowa, from 94.8% AR at DAT-0 to 3.0% AR at DAT-10 in soil Indiana and from 93.5% AR at DAT-0 to 3.3% AR at DAT-14 in soil Nebraska.

The experimental data were kinetically evaluated according to the first order kinetic model in order to derive half-lives for FOE-thiadone. The calculated half-lives were between 2.0 and 2.8 days in the tested soils.

Besides carbon dioxide, one degradation product was identified. FOE-thiadone propionic acid conjugate was detected with maximum amounts of 10.2% AR at DAT-2 in soil Iowa, 7.0% AR at DAT-2 in soil Indiana and 1.3% AR at DAT-1 in soil Nebraska. This degradation product and declined rapidly to 0.1% or less of the applied radioactivity by DAT-10 to 14 of the study for all of the soils. However, this degradation product would occur only in minor amounts < 1% AR in degradation studies of the parent flufenacet, as FOE-thiadone itself was detected with max. amounts of 5.9% AR in aerobic soil degradation studies.

It is concluded that flufenacet has no potential for accumulation in the environment.

I. MATERIALS AND METHODS

A. MATERIALS

1. Test Item

[thiadiazole-2-^{14}C]FOE-thiadone	
Lot No	97B064-130(C-784)
Specific activity	10.88 MBq/mg (50 mCi/mmol ≙ 0.294 mCi/mg)
Radiochemical purity	> 97.7%

2. Test Soils

The soils (Table 7.1.1.1- 3) were sampled from the field and sieved to a particle size of ≤ 2 mm. The soils were taken from agricultural areas representing different geographical origins and different soil properties as required by the guidelines.

Table 7.1.2.1.2- 19: Physico-chemical properties of test soils

Parameter	Results / Units		
Soil Designation	Iowa (EFS115)	Indiana (EFS117)	Nebraska (EFS118)
Geographic Location			
City	Janesville	Howe	Minden
State	Iowa	Indiana	Nebraska
Country	USA	USA	USA
Soil Taxonomic Classification (USDA)	Two soils in close proximity: 1. sandy, mixed, mesic Entic Hapludolls 2. coarse-loamy, mixed, mesic Typic Hapludolls	loamy-skeletal, mixed, mesic Typic Haplustolls	1. Coly silt loam: fine-silty, mixed (calcareous), mesic Typic Ustorthents 2. Kenesaw silt loam: coarse-silty, mixed, mesic Typic Haplustolls
Soil Series	no information available		
Textural Class (USDA)	loamy sand	sandy loam	silt loam
Sand [%] [50 µm – 2 mm]	79.2	63.6	25.6
Silt [%] [2 µm – 50 µm]	12.0	25.6	55.6
Clay [%] [< 2 µm]	8.8	10.8	18.8
pH	7.2	6.5	7.7
Organic Carbon [%]	1.1	0.8	1.0
Organic Matter [%] [1]	1.91	1.28	1.66
Cation Exchange Capacity [meq/100 g]	5.64	15.12	6.44
Water Holding Capacity			
at 15 bar	4.06	3.87	9.16
at 0.3 bar (pF 2.5) [%]	9.92	13.27	24.19
Bulk Density (disturbed) [g/cm³]	1.34	1.62	1.37
Microbial Biomass [cfu/g] [2]			
DAT-0 (fungi / bacteria)	3.8×10^4 / 1.2×10^7	4.8×10^4 / 9.1×10^6	1.0×10^5 / 1.0×10^7
DAT-14 (fungi / bacteria)	6.0×10^4 / 1.1×10^7	2.8×10^4 / 1.2×10^7	1.1×10^5 / 6.0×10^7

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

[2] cfu = colony forming units per g of soil

DAT: days after treatment USDA: United States Department of Agriculture

DW: dry weight

B. STUDY DESIGN

1. Experimental Conditions

Flow through test systems were used, consisting of 250 mL centrifuge bottles filled with soil, which were placed in desiccators equipped with inlet and outlet tubes. A primary carbon dioxide trap was placed in the desiccators with the soil samples and three additional traps for collection of carbon dioxide and volatile organic compounds were connected in series to the outlet tube of each desiccator. A small pump was used to draw air through the apparatus.

50 g of the sieved soil (dry weight equivalents) were weighed into each bottle. The untreated test systems were equilibrated to study conditions for 1 week prior to application.

The study application rate (SAR) was 25 µg/50 g soil (dry weight) (≙ 0.5 ppm), equal to 0.5 mg FOE-thiadone/kg soil (dry weight). Calculation of the nominal SAR was based on one-half the assumed maximum single field application rate of parent flufenacet of 0.8 lbs/acre (≙ approx. 896 g/ha) and a theoretically conversion of 100% flufenacet (M = 363 g/mol) to FOE-thiadone (M=170 g/mol).

The application solution was prepared by isotopic dilution of [thiadiazole-2-^{14}C]FOE-thiadone with unlabeled FOE-thiadone. Therefore, [thiadiazole-2-^{14}C]FOE-thiadone was dissolved in acetone and fortified with unlabeled FOE-thiadone in acetonitrile, the volumetric flask were made up to volume with acetone (final solution acetonitrile /acetone 1:8, *v/v*). 100 µL of the application solution were applied drop wise onto the soil surface of the respective test systems using a gas-tight syringe. After application the test vessels were connected to the flow through system (except DAT-0 samples).

The test systems were incubated under aerobic conditions in the dark for 14 days at 20 ± 1 °C and a soil moisture of approx. 75% of the water holding capacity at 1/3 bar in a walk-in climatic chamber.

2. Sampling

Eight sampling intervals were distributed over the entire incubation period of 10 or 14 days. The following sampling schedule was used for analysis of soil samples for each of the three soils:

Iowa (EFS115): 0, 0.25, 1, 2, 3, 5, 7 and 10 days after treatment (DAT). Duplicates were analyzed for the following time points: DAT-0, 1, 2, 3, and 5. The traps for carbon dioxide were changed and analyzed at DAT-0.25, 1, 2, 3, 4, 5, 7 and 10. The traps for volatile organic compounds were changed and analyzed at DAT-3, 4 and 10. Microbial soil biomass was determined at DAT-0 and DAT-10.

Indiana (EFS117): DAT-0, 0.5, 1, 2, 3, 5, 7 and 10. Duplicates were analyzed for the following time points: DAT-0, 0.5, 1, 3, and 5. The traps for carbon dioxide were changed and analyzed at DAT-0.25, 0.5, 1, 2, 3, 4, 5, 7 and 10. The traps for volatile organic compounds were changed and analyzed at DAT-3, 4 and 10. Microbial soil biomass was determined at DAT-0 and DAT-10.

Nebraska (EFS118): DAT-0, 1, 2, 3, 5, 7, 10 and 14. Duplicates were analyzed for the following time points: DAT-0, 1, 3, 5 and 7. The traps for carbon dioxide were changed and analyzed at DAT-1, 2, 3, 4, 5, 7, 10 and 14. The traps for volatile organic compounds were changed and analyzed at DAT-3, 5, 7, 10 and 14. Microbial soil biomass was determined at DAT-0 and DAT-14.

3. Analytical Procedures

At each sampling interval, the soils were extracted at ambient temperature using acetonitrile (1 x) and acetonitrile/water with 0.1 N HCl (1 x 1:1, *v/v*). After each extraction step, supernatant and soil were separated by filtration. The acidic extracts were additionally partitioned three times with ACN/DCM (1:2, *v/v*).

The aqueous and organic soil extracts were analyzed by liquid scintillation counting and the organic extracts were further characterized by HPLC/radiodetection. The instrumental limit of detection (LOD) for the HPLC/radiodetection method was 300 dpm (5 Bq), sufficient sample volume was injected to detect residue levels at approximately 1.5 and 8.5% of the injected radioactivity for the ACN and ACN: 0.1 N HC1 extracts, respectively. The amount of volatiles and non-extractable residues was determined by liquid scintillation counting and combustion/ liquid scintillation counting, respectively.

The identity of the test item and its degradation products was confirmed by co-chromatography with reference items using HPLC/radiodetection.

4. Kinetic Evaluation

The degradation kinetics of the test item was determined using a first order kinetic model. Model input datasets were the residual amounts of FOE-thiadone found at each sampling interval. DT_{50} and DT_{90} values were calculated from the resulting kinetic parameters.

II. RESULTS AND DISCUSSION

A. EXTRACTION AND QUANTITATION OF RADIOACTIVITY IN SOIL SAMPLES

Table 7.1.2.1.2- 20 to Table 7.1.2.1.2- 22 summarizes the degradation of [thiadiazole-2-^{14}C]FOE-thiadone and the formation and degradation of its degradation products as a function of time.

Table 7.1.2.1.2- 20: Degradation of FOE-thiadone in Soil Iowa under Aerobic Conditions
(expressed as percent of applied radioactivity; single values)

Compound	DAT							
	0 [1]	**0.25**	**1** [1]	**2** [1]	**3** [1]	**5** [1]	**7**	**10**
FOE-thiadone	98.3	81.2	57.5	36.6	26.6	16.1	8.9	6.6
FOE-thiadone propionic acid conjugate	n.d.	1.3	7.5	10.2	7.5	3.1	1.2	0.1
Reg #1 [2]	0.6	0.7	0.3	n.d.	n.d.	0.2	n.d.	n.d.
Reg #4 [2]	0.7	1.3	0.9	1.0	1.8	1.4	1.5	0.9
Unid./Diff. Radioactivity	3.0	2.3	2.5	2.6	1.5	2.0	3.2	2.0
Total Extractable Residues	102.6	86.8	68.7	50.4	37.4	22.8	14.8	9.6
Carbon dioxide	n.a.	2.6	13.9	27.2	36.6	48.9	57.0	63.2
Volatile Organic Compounds	n.a.	n.a.	n.a.	n.a.	1.9	1.9	1.9	2.3
Non-extractable Residues	1.1	7.3	12.9	14.9	19.7	19.7	20.1	19.5
Material Balance	**103.7**	**96.7**	**95.5**	**92.5**	**95.6**	**93.3**	**93.8**	**94.6**

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

[1] Mean values of duplicates

[2] Fortification impurities

[3] All individual areas of radioactivity were less than 2% of the applied radioactivity.

Table 7.1.2.1.2- 21: Degradation of FOE-thiadone in Soil Indiana under Aerobic Conditions
(expressed as percent of applied radioactivity; single values)

Compound	DAT							
	0 [1]	0.5 [1]	1 [1]	2	3 [1]	5 [1]	7	10
FOE-thiadone	94.8	69.1	54.3	29.0	16.7	8.9	4.6	3.0
FOE-thiadone propionic acid conjugate	n.d.	0.8	4.1	7.0	4.9	2.6	n.d.	0.1
Reg #1 [2]	0.5	n.d.	n.d.	n.d.	0.3	0.6	0.3	n.d.
Reg #4 [2]	1.6	1.3	1.4	1.3	1.8	1.8	1.5	1.8
Unid./Diff. Radioactivity [3]	2.1	2.1	2.5	3.1	1.4	2.9	3.4	1.3
Total Extractable Residues	99.0	73.3	62.3	40.4	25.1	16.8	9.8	6.2
Carbon dioxide	n.a.	13.9	21.5	50.3	59.1	69.1	76.9	82.1
Volatile Organic Compounds	n.a.	n.a.	n.a.	n.a.	3.0	3.0	3.0	4.0
Non-extractable Residues	0.6	5.9	6.9	7.4	8.2	8.4	7.3	7.6
Material Balance	**99.6**	**93.1**	**90.7**	**98.1**	**95.4**	**97.3**	**97.0**	**99.9**

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

[1] Mean values of duplicates

[2] Fortification impurities

[3] All individual areas of radioactivity -were less than 2% of the applied radioactivity.

Table 7.1.2.1.2- 22: Degradation of FOE-thiadone in Soil Nebraska under Aerobic Conditions
(expressed as percent of applied radioactivity; single values)

Compound	DAT							
	0 [1]	1 [1]	2	3 [1]	5 [1]	7 [1]	10	14
FOE-thiadone	93.5	79.2	62.7	52.2	28.9	16.2	7.7	3.3
FOE-thiadone propionic acid conjugate	0.2	1.3	1.1	1.0	0.7	0.2	n.d.	n.d.
Reg #1 [2]	0.7	0.5	n.d.	n.d.	n.d.	n.d.	0.1	n.d.
Reg #4 [2]	1.9	1.4	1.2	0.6	0.5	0.7	0.6	0.3
Unid./Diff. Radioactivity [3]	0.7	1.6	1.4	1.1	1.4	1.8	1.7	1.9
Total Extractable Residues	97.0	84.0	66.4	54.9	31.5	18.9	10.1	5.5
Carbon dioxide	n.a.	8.1	18.9	27.7	43.9	56.1	66.0	71.8
Volatile Organic Compounds	n.a.	n.a.	n.a.	1.5	2.4	2.8	3.1	3.3
Non-extractable Residues	1.4	6.5	9.4	10.0	13.8	14.7	14.7	14.7
Material Balance	**98.4**	**98.6**	**94.7**	**94.1**	**91.6**	**92.5**	**93.9**	**95.3**

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

[1] Mean values of duplicates

[2] Fortification impurities

[3] All individual areas of radioactivity -were less than 2% of the applied radioactivity.

B. MATERIAL BALANCE

The amount of dosed test item was determined at DAT-0 before, during and after the application and was set to 100% AR for all samples. The total radioactivity recovery (mean of duplicates) of all sampling intervals ranged from 92.5 to 103.7% AR in soil Iowa (overall mean 95.7% AR), from 90.7 to 99.9% AR in soil Indiana (overall mean 96.4% AR) and from 91.6 to 98.6% AR in soil Nebraska (overall mean 94.9% AR), see also Table 7.1.2.1.2- 20 to Table 7.1.2.1.2- 22.

The complete material balance found at all sampling intervals (mean of duplicates) in all soils demonstrated that no significant portion of radioactivity dissipated from the vessels or was lost during processing of theses samples.

C. EXTRACTABLE AND NON-EXTRACTABLE RESIDUES

Extractable residues decreased steadily from 102.6% AR at DAT-0 to 9.6% AR at DAT-10 in soil Iowa, from 99.0% AR at DAT-0 to 6.2% AR at DAT-10 in soil Indiana and from 97.0% AR at DAT-0 to 5.5% AR at DAT-14 in soil Nebraska.

The formation of non-extractable residues (NER) increased from 1.1% AR at DAT-0 to 20.1% AR at DAT-7 and slightly decreased to 19.5% AR at DAT-10 in soil Iowa. In soil Indiana NER increased from 0.6% AR at DAT-0 to 8.4% AR at DAT-5 and slightly decreased to 7.6% AR at DAT-10. In soil Nebraska NER increased from 1.4% AR at DAT-0 to 14.7% AR from DAT-7 onwards. See also Table 7.1.2.1.2- 20 to Table 7.1.2.1.2- 22 for details.

D. VOLATILIZATION

The maximum amount of carbon dioxide formed in the test systems was 65.5% AR in soil Iowa, 82.1% AR in soil Indiana and 71.8% AR in soil Nebraska.

The maximum amount of volatile organic compounds formed in the test systems was 2.3% AR in soil Iowa, 4.0% AR in soil Indiana and 3.3% AR in soil Nebraska. See also Table 7.1.2.1.2- 20 to Table 7.1.2.1.2- 22 for details.

E. DEGRADATION OF TEST ITEM

The amount of FOE-thiadone in the combined soil extracts decreased from 98.3% AR at DAT-0 to 6.6% AR at DAT-10 in soil Iowa, from 94.8% AR at DAT-0 to 3.0% AR at DAT-10 in soil Indiana and from 93.5% AR at DAT-0 to 3.3% AR at DAT-14 in soil Nebraska.

Besides carbon dioxide, one degradation product was identified. FOE-thiadone propionic acid conjugate was detected with maximum amounts of 10.2% AR at DAT-2 in soil Iowa, 7.0% AR at DAT-2 in soil Indiana and 1.3% AR at DAT-1 in soil Nebraska.

The total unidentified radioactivity amounted to a maximum of 2% AR at each sampling interval and for each soil.

The experimental data were kinetically evaluated according to a first order kinetic model in order to derive half-lives for FOE-thiadone.

Table 7.1.2.1.2- 23: Single First Order degradation kinetics of FOE-thiadone in soil under aerobic conditions for trigger evaluation

Soil	DT_{50} [d]	Correlation Coefficient (R^2)
Iowa	2.5	0.9512
Indiana	2.0	0.9490
Nebraska	2.8	0.9971

III. CONCLUSIONS

[thiadiazole-2-^{14}C]FOE-thiadone was rapidly degraded in soil under aerobic conditions in the dark in the laboratory with half-lives between 2.0 and 2.8 days.

Formation of carbon dioxide was observed up to 65.5% AR in soil Iowa, 82.1% AR in soil Indiana and 71.8% AR in soil Nebraska.

Besides carbon dioxide, one degradation product was identified. FOE-thiadone propionic acid conjugate was detected with maximum amounts of 10.2% AR at DAT-2 in soil Iowa, 7.0% AR at DAT-2 in soil Indiana and 1.3% AR at DAT-1 in soil Nebraska. This degradation product and declined rapidly to 0.1% or less of the applied radioactivity by DAT-10 to 14 of the study for all of the soils. However, this degradation product would occur only in minor amounts < 1% AR in degradation studies of the parent flufenacet, as FOE-thiadone itself was detected with max. amounts of 5.9% AR in aerobic soil degradation studies.

Formation of non-extractable residues up to a maximum of 20.1% AR in soil Iowa, 8.4% AR in soil Indiana and 14.7% AR in soil Nebraska was observed.

The high formation of carbon dioxide demonstrates the potential for mineralization of the test item and its transformation products. Therefore, FOE-thiadone is not expected to have a potential for accumulation in the environment.

*****

Report:	**KCA 7.1.2.1.2/04; [redacted], N.; 2012**
Title:	[1-^{14}C]trifluoroacetate : Aerobic Degradation in Four European Soils
Report No:	EnSa-12-0393
Document No:	M-439283-01-1
Guidelines:	• OECD Test Guideline No. 307 • US EPA OCSPP Test Guidelines 835.4100
GLP:	yes

Executive Summary

The degradation of [1-^{14}C]trifluoroacetate (report name: trifluoroacetic acid) was investigated in four soils under aerobic conditions in the dark in the laboratory for 120 days at 20.0 °C and a soil moisture of 55 ± 5% of the maximum water holding capacity:

Soil	Source	Texture (USDA)	pH[1]	OC [%]
Laacherhof AXXa	Monheim, Germany	sandy loam	6.2	1.6
Dollendorf II	Blankenheim, Germany	clay loam	7.3	5.5
Laacherhof Wurmwiese	Monheim, Germany	sandy loam	5.1	1.9
Hoefchen am Hohenseh	Burscheid, Germany	silt loam	6.4	2.4

[1] in 0.01 M $CaCl_2$

The study application rate was 20.0 µg/100 g soil (dry weight), equal to 0.2 mg trifluoroacetate/kg soil (dry weight).

Duplicate test systems were processed and analyzed 0, 3, 7, 14, 28, 43, 59, 92 and 120 days after treatment.

Overall mean material balance was 100.4% of applied radioactivity (% AR) for soil Laacherhof AXXa, 100.5% AR for soil Dollendorf II, 100.0% AR for soil Laacherhof Wurmwiese and 101.2% AR for soil Hoefchen am Hohenseh.

Volatiles were detected with amounts ≤ 0.1% AR at every sampling interval in all four soils.

Extractable residues stayed constant between 95.9 and 102.1% AR over the entire incubation period of 120 days in all four soils.

Non-extractable residues (NER) were detected with amounts ≤ 2% AR at every sampling interval in all four soils.

The test item was virtually not degraded within the tested incubation period of 120 days in the dark in the laboratory in all four soils.

The degradation data were kinetically evaluated according to FOCUS (2005) [2] to derive best fits for trigger endpoint determination. The experimental data could be well described by a single first order kinetic model for all soils. The calculated half-lives of trifluoroacetic acid under aerobic conditions were > 1000 days in all four soils.

I. MATERIALS AND METHODS

A. MATERIALS

1. Test Item

[1-^{14}C]trifluoroacetate (sodium salt; report name [1]: trifluoroacetic acid)
CAS No 2923-18-4
Specific activity 3.48 MBq/mg
Radiochemical purity > 98% HPLC with radioactivity-detector

2. Test Soils

The soils (Table 7.1.1.1- 3) 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 areas representing different geographical origins and different soil properties as required by the guidelines.

Table 7.1.2.1.2- 24: Physico-chemical properties of test soils

Parameter	Results / Units			
Soil Designation	Laacherhof AXXa	Dollendorf II	Laacherhof Wurmwiese	Hoefchen am Hohenseh
Geographic Location				
City	Monheim	Blankenheim	Monheim	Burscheid
State	North-Rhine Westphalia	North-Rhine Westphalia	North-Rhine Westphalia	North-Rhine Westphalia
Country	Germany	Germany	Germany	Germany
GPS Coordinates	N 51° 04.65' E 006° 53.52'	N 50° 22.90' E 006° 43.00'	N 51° 04.86' E 006° 55.25'	N 51° 04.01' E 007° 06.33'
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)	sandy loam	clay loam	sandy loam	silt loam
Sand [%] [50 µm – 2 mm]	77	29	57	25
Silt [%] [2 µm – 50 µm]	14	40	26	60
Clay [%] [< 2 µm]	9	31	17	15
pH				
- in $CaCl_2$ (soil/$CaCl_2$ 1/2)	6.2	7.3	5.1	6.4
- in water (soil/water 1/1)	6.5	7.5	5.4	6.7
- in water (saturated paste)	6.3	7.4	5.2	6.5
- in KCl	6.0	7.1	4.7	6.1
Organic Carbon [%]	1.6	5.5	1.9	2.4
Organic Matter [%] [1]	2.8	9.5	3.3	4.1
Cation Exchange Capacity [meq/100 g]	8.1	21.2	10.0	13.6
Water Holding Capacity				
maximum [g H_2O *ad* 100 g soil DW]	4.69	84.9	57.6	62.0
at 0.33 bar (pF 2.5) [%]	12.2	34.9	18.2	26.3
Bulk Density (disturbed) [g/cm³]	1.26	0.97	1.13	1.08
Microbial Biomass [mg microbial carbon / kg soil DW] [2]				
DAT-0	536	2930	423	833
DAT-59	589	3344	459	844
DAT-120	248	1412	424	387

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

DAT: days after treatment
DW: dry weight
GPS: global positioning system
USDA: United States Department of Agriculture

B. STUDY DESIGN

1. Experimental Conditions

Static test systems were used, consisting of Erlenmeyer flasks filled with soil and equipped with solid trap attachments for collection of carbon dioxide and volatile organic compounds.

100 g of the sieved soil (dry weight equivalents) were weighed into each flask and the soil moisture was adjusted to 55 ± 5% maximum water holding capacity by addition of de-ionized water. The untreated test systems were equilibrated to study conditions for approx. 3 days (over the weekend) prior to application.

The study application rate (SAR) was based on an assumed single field application rate of the parent of 250 g/ha, a maximum formation of trifluoroacetate of 25% and a relative molar mass of trifluoroacetate of 0.3, resulting in a nominal study application rate 20.0 µg/100 g soil (dry weight), equal to 0.2 mg/kg soil (dry weight). The actual SAR was 20.9 µg/100 g soil (dry weight), equal to 0.2 mg trifluoroacetate/kg soil (dry weight).

The application solution was prepared in water. 1000 µL of the application solution were applied drop wise onto the soil surface of the respective test systems using a pipette. After application the test vessels were closed with the trap attachments (except DAT-0 samples).

The test systems were incubated under aerobic conditions in the dark for 120 days at 20.0 °C and soil moisture of 55 ± 5% of the maximum water holding capacity in a walk-in climatic chamber.

2. Sampling

Nine sampling intervals were distributed over the entire incubation period of 120 days. Duplicate test systems were processed and analyzed 0, 3, 7, 14, 28, 43, 59, 92 and 120 days after treatment (DAT).

Microbial soil biomass was determined at DAT-0, DAT-59 and DAT-120.

3. Analytical Procedures

At each sampling interval, the trap attachments were removed from the test systems and the soils were extracted three times at ambient temperature using acetonitrile/water (1:1, *v/v*), followed by a microwave-accelerated extraction with acetonitrile/water (1:1, *v/v*) at 70 °C. After each extraction step, supernatant and soil were separated by centrifugation and decantation.

Soil extracts were characterized by liquid scintillation counting and TLC/radiodetection. The limit of detection (LOD) for the HPLC/radiodetection method was < 1% AR. The amount of volatiles and non-extractable residues was determined by liquid scintillation counting and combustion/liquid scintillation counting, respectively.

The identity of the test item and its degradation products was elucidated by HPLC-MS(/MS) including accurate mass determination.

4. Kinetic Evaluation

The data for the test item were evaluated according to the FOCUS guidance document [3] on degradation kinetics using the software KinGUI 2 to derive the DT_{50} and DT_{90} values of trifluoroacetic acid.

Model input datasets were the residual amounts of trifluoroacetic acid found in each replicate test system at each sampling interval (see Table 7.1.2.1.1- 6 to Table 7.1.2.1.1- 8). 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 following procedure was followed:

- Values between LOD and LOQ were set to the measured values.
- All single values < LOD or non-detected (n.d.) were set to 50% HPLC 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- single first order (SFO), first order multi compartment (FOMC), and double first order in parallel (DFOP)- were tested in order to determine the best fit kinetic model. The best-fit kinetic model was selected on the basis of the chi^2 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).

II. RESULTS AND DISCUSSION

A. EXTRACTION AND QUANTITATION OF RADIOACTIVITY IN SOIL SAMPLES

Table 7.1.2.1.2- 25 to Table 7.1.2.1.2- 28 summarizes the degradation of [1-^{14}C]trifluoroacetate and the formation and degradation of its degradation products as a function of time.

Table 7.1.2.1.2- 25: Degradation of trifluoroacetic acid in soil Laacherhof AXXa under aerobic conditions
(expressed as percent of applied radioactivity; mean value of duplicates)

Compound		DAT 0	3	7	14	28	43	59	92	120
trifluoroacetic acid [1]	replicate A	97.8	99.8	100.9	99.9	97.7	100.2	101.3	101.7	98.0
	replicate 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
Unid./Diff. Radioactivity		n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Total Extractable Residues		97.7	99.7	100.5	100.2	97.5	99.9	101.3	101.4	98.6
Carbon dioxide		n.a.	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1
Volatile Organic Compounds		n.a.	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1
Non-extractable Residues		0.6	0.6	0.8	0.6	0.7	0.9	0.8	0.7	0.8
Material Balance [2]		**98.2**	**100.4**	**101.3**	**101.0**	**98.2**	**100.9**	**102.1**	**102.1**	**99.4**

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

[1] single values of replicates and mean values of duplicates

[2] Material balances at DAT-0 were 98.4% AR for replicate A and 98.1% AR for replicate B

Table 7.1.2.1.2- 26: Degradation of trifluoroacetic acid in soil Dollendorf II under aerobic conditions
(expressed as percent of applied radioactivity; mean value of duplicates)

Compound		DAT 0	3	7	14	28	43	59	92	120
trifluoroacetic acid [1]	replicate A	98.5	98.6	100.5	99.4	96.0	99.1	100.5	100.3	96.1
	replicate 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
Unid./Diff. Radioactivity		n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Total Extractable Residues		98.4	99.8	100.2	99.4	96.4	99.4	100.0	100.2	96.4
Carbon dioxide		n.a.	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1
Volatile Organic Compounds		n.a.	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1
Non-extractable Residues		1.3	1.2	1.3	1.3	1.4	1.7	1.8	1.7	2.0
Material Balance [2]		**99.7**	**101.0**	**101.6**	**100.8**	**97.8**	**101.1**	**101.8**	**101.9**	**98.5**

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

[1] single values of replicates and mean values of duplicates

[2] Material balances at DAT-0 were 99.8% AR for replicate A and 99.7% AR for replicate B

Table 7.1.2.1.2- 27: Degradation of trifluoroacetic acid in soil Laacherhof Wurmwiese under aerobic conditions (expressed as percent of applied radioactivity; mean value of duplicates)

Compound		DAT 0	3	7	14	28	43	59	92	120
trifluoroacetic acid [1]	replicate A	98.4	99.9	99.6	99.6	96.3	99.9	100.6	100.0	97.0
	replicate 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
Unid./Diff. Radioactivity		n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Total Extractable Residues		98.7	99.7	99.7	99.2	95.9	99.6	99.7	99.7	97.6
Carbon dioxide		n.a.	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1
Volatile Organic Compounds		n.a.	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1
Non-extractable Residues		1.0	1.1	1.0	1.0	1.1	1.2	1.2	1.1	1.3
Material Balance [2]		**99.7**	**100.9**	**100.8**	**100.3**	**97.0**	**100.9**	**100.9**	**100.8**	**99.0**

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

[1] single values of replicates and mean values of duplicates

[2] Material balances at DAT-0 were 99.5% AR for replicate A and 99.9% AR for replicate B

Table 7.1.2.1.2- 28: Degradation of trifluoroacetic acid in soil Hoefchen am Hohenseh under aerobic conditions (expressed as percent of applied radioactivity; mean value of duplicates)

Compound		DAT 0	3	7	14	28	43	59	92	120
trifluoroacetic acid [1]	replicate A	99.1	101.3	101.1	100.0	97.1	100.3	102.5	102.5	97.9
	replicate B	99.3	100.0	100.4	100.0	96.9	100.6	101.0	101.7	98.7
	mean	99.1	100.7	100.7	100.0	97.0	100.5	101.7	102.1	98.3
Unid./Diff. Radioactivity		n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Total Extractable Residues		99.2	100.7	100.7	100.0	97.0	100.5	101.7	102.1	98.3
Carbon dioxide		n.a.	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1
Volatile Organic Compounds		n.a.	0.1	0.1	0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1
Non-extractable Residues		0.9	1.0	1.0	0.9	1.1	1.3	1.3	1.3	1.2
Material Balance [2]		**100.1**	**101.8**	**101.8**	**101.0**	**98.2**	**101.8**	**103.1**	**103.4**	**99.5**

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

[1] single values of replicates and mean values of duplicates

[2] Material balances at DAT-0 were 100.0% AR for replicate A and 100.2% AR for replicate B

B. MATERIAL BALANCE

The amount of dosed test item was determined at DAT-0 before, during and after the application and was set to 100% AR for all samples. The total radioactivity recovery (mean of duplicates) of all sampling intervals ranged from 98.2 to 102.1% AR in soil Laacherhof AXXa (overall mean 100.4% AR, RSD 1.4%), from 97.8 to 101.9% AR in soil Dollendorf II (overall mean 100.5% AR, RSD 1.4%), from 97.0 to 100.9% AR in soil Laacherhof Wurmwiese (overall mean 100.0% AR, RSD 1.2%) and from 98.2 to 103.4% AR in soil Hoefchen am Hohenseh (overall mean 101.2% AR, RSD 1.6%), see also Table 7.1.2.1.2- 25 to Table 7.1.2.1.2- 28.

The complete material balance found at all sampling intervals (mean of duplicates) in all soils demonstrated that no significant portion of radioactivity dissipated from the vessels or was lost during processing of theses samples.

C. EXTRACTABLE AND NON-EXTRACTABLE RESIDUES

Extractable residues stayed constant between 95.9 and 102.1% AR over the entire incubation period of 120 days in all four soils.

Non-extractable residues (NER) were detected with amounts ≤ 2% AR at every sampling interval in all four soils. See also Table 7.1.2.1.2- 25 to Table 7.1.2.1.2- 28 for details.

D. VOLATILIZATION

Volatiles were detected with amounts ≤ 0.1% AR at every sampling interval in all four soils. See also Table 7.1.2.1.2- 25 to Table 7.1.2.1.2- 28 for details.

E. DEGRADATION OF TEST ITEM

The test item was virtually not degraded within the tested incubation period of 120 days in the dark in the laboratory in all four soils. See also Table 7.1.2.1.2- 25 to Table 7.1.2.1.2- 28 for details.

The chi^2 error values of the fits of all investigated kinetic models were ≤ 1.2 and the visual assessment of the regression curves gave good results. The degradation of trifluoroacetic acid followed single first order (SFO) kinetics in all soils, according to the lowest chi^2 error value.

The half-lives for trifluoroacetic acid were > 1000 days in all soils under aerobic conditions in the dark in the laboratory.

Table 7.1.2.1.2- 29: Best-fit degradation kinetics of trifluoroacetic acid in soils under aerobic conditions for trigger evaluation according to FOCUS

Soil (Soil Type)	Kinetic Model [1]	DT_{50} [d]	DT_{90} [d]	chi^2 error [%]	Visual Assessment [2]
Laacherhof AXXa (sandy loam)	SFO	> 1000	> 1000	1.0	+
Dollendorf II (clay loam)	SFO	> 1000	> 1000	1.1	+
Laacherhof Wurmwiese (sandy loam)	SFO	> 1000	> 1000	1.2	+
Hoefchen am Hohenseh (silt loam)	SFO	> 1000	> 1000	1.0	+

[1] SFO = single first order; DFOP = double first order in parallel

[2] Visual assessment: + good

III. CONCLUSIONS

[1-^{14}C]trifluoroacetate (report name: trifluoroacetic acid) was virtually not degraded in soil under aerobic conditions in the dark in the laboratory during the incubation time of 120 days.

No significant amounts of volatiles or non-extractable residues were formed during the study course.

The calculated half-lives of trifluoroacetic acid were > 1000 days in all soils.

*****

Report:	**KCA 7.1.2.1.2 /05; [redacted], N.; 2012**
Title:	[1-^{14}C]trifluoroacetate: Concentration Dependent Mineralization Under Aerobic Conditions
Report No:	EnSa-12-0445
Document No:	M-441101-01-1
Guidelines:	• OECD Test Guideline No. 307 • US EPA OCSPP Test Guidelines 835.4100
GLP:	yes

Executive Summary

The concentration dependent mineralization of [1-^{14}C]trifluoroacetate (report name: trifluoroacetic acid) was investigated in four soils under aerobic conditions in the dark in the laboratory for 120 days at 20.0 °C and a soil moisture of 55 ± 5% of the maximum water holding capacity.

Soil	Source	Texture (USDA)	pH [1]	OC [%]
Laacherhof AXXa	Monheim, Germany	sandy loam	6.2	1.6
Dollendorf II	Blankenheim, Germany	clay loam	7.3	5.5
Laacherhof Wurmwiese	Monheim, Germany	sandy loam	5.1	1.9
Hoefchen am Hohenseh	Burscheid, Germany	silt loam	6.4	2.4

[1] in 0.01 M $CaCl_2$

Three study application rates were tested:

- 20.0 µg/100 g soil (dry weight), equal to 0.2 mg trifluoroacetate/kg soil (dry weight)
- 1.0 µg/100 g soil (dry weight), equal to 0.01 mg trifluoroacetate/kg soil (dry weight)
- 0.1 µg/100 g soil (dry weight), equal to 0.001 mg trifluoroacetate/kg soil (dry weight)

For each study application rate duplicate test systems were analyzed for the amount of carbon dioxide 30, 59 and 120 days after treatment.

No significant mineralization (≥ 1% of applied radioactivity [% AR]) of the test item could be detected at any study application rate within the tested incubation period of 120 days in the dark in the laboratory in all four soils.

I. MATERIALS AND METHODS

A. MATERIALS

1. Test Item

[1-^{14}C]trifluoroacetate (sodium salt; report name [1]: trifluoroacetic acid)

CAS No	2923-18-4
Specific activity	3.48 MBq/mg
Radiochemical purity	> 98% HPLC with radioactivity-detector

2. Test Soils

The soils (Table 7.1.2.1.2- 30) 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 areas representing different geographical origins and different soil properties as required by the guidelines.

Table 7.1.2.1.2- 30: Physico-chemical properties of test soils

Parameter	Results / Units			
Soil Designation	Laacherhof AXXa	Dollendorf II	Laacherhof Wurmwiese	Hoefchen am Hohenseh
Geographic Location				
City	Monheim	Blankenheim	Monheim	Burscheid
State	North-Rhine Westphalia	North-Rhine Westphalia	North-Rhine Westphalia	North-Rhine Westphalia
Country	Germany	Germany	Germany	Germany
GPS Coordinates	N 51° 04.65' E 006° 53.52'	N 50° 22.90' E 006° 43.00'	N 51° 04.86' E 006° 55.25'	N 51° 04.01' E 007° 06.33'
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)	sandy loam	clay loam	sandy loam	silt loam
Sand [%] [50 µm – 2 mm]	77	29	57	25
Silt [%] [2 µm – 50 µm]	14	40	26	60
Clay [%] [< 2 µm]	9	31	17	15
pH				
- in $CaCl_2$ (soil/$CaCl_2$ 1/2)	6.2	7.3	5.1	6.4
- in water (soil/water 1/1)	6.5	7.5	5.4	6.7
- in water (saturated paste)	6.3	7.4	5.2	6.5
- in KCl	6.0	7.1	4.7	6.1
Organic Carbon [%]	1.6	5.5	1.9	2.4
Organic Matter [%] [1]	2.8	9.5	3.3	4.1
Cation Exchange Capacity [meq/100 g]	8.1	21.2	10.0	13.6
Water Holding Capacity				
maximum [g H_2O *ad* 100 g soil DW]	4.69	84.9	57.6	62.0
at 0.33 bar (pF 2.5) [%]	12.2	34.9	18.2	26.3
Bulk Density (disturbed) [g/cm³]	1.26	0.97	1.13	1.08
Microbial Biomass [mg microbial carbon / kg soil DW]				
DAT-0	642	3145	598	1016
DAT-59	484	2798	316	696
DAT-120	323	1931	173	499

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

DAT: days after treatment
DW: dry weight
GPS: global positioning system
USDA: United States Department of Agriculture

B. STUDY DESIGN

1. Experimental Conditions

Static test systems were used, consisting of Erlenmeyer flasks filled with soil and equipped with solid trap attachments for collection of carbon dioxide and volatile organic compounds.

100 g of the sieved soil (dry weight equivalents) were weighed into each flask and the soil moisture was adjusted to 55 ± 5% maximum water holding capacity by addition of de-ionized water. The untreated test systems were equilibrated to study conditions for approx. 3 days (over the weekend) prior to application.

The highest study application rate (SAR) was equal to the SAR used in a standard aerobic soil degradation study [KCA 7.1.2.1.2 /04]: 20.0 µg/100 g soil (dry weight), equal to 0.2 mg trifluoroacetate/kg soil (dry weight). For the investigation of a concentration dependency of mineralization two lower doses were tested in addition: 1.0 µg/100 g soil (dry weight), equal to 0.01 mg trifluoroacetate/kg soil (dry weight) and 0.1 µg/100 g soil (dry weight), equal to 0.001 mg trifluoroacetate/kg soil (dry weight).

The application solutions were prepared in water. 1000 µL of the respective application solutions were applied drop wise onto the soil surface of the respective test systems using a pipette. After application the test vessels were closed with the trap attachments.

The test systems were incubated under aerobic conditions in the dark for 120 days at 20.0 °C and soil moisture of 55 ± 5% of the maximum water holding capacity in a walk-in climatic chamber.

2. Sampling

Three sampling intervals were distributed over the entire incubation period of 120 days. For each study application rate duplicate test systems were analyzed for the amount of carbon dioxide 30, 59 and 120 days after treatment. At DAT-0 the amount of applied test item was determined.

Microbial soil biomass was determined at DAT-0, DAT-59 and DAT-120.

3. Analytical Procedures

At each sampling interval, the trap attachments were collected from the respective test systems and processed. Prior to opening a test system, volatiles still present in the headspace of the test systems were purged into the trap attachments. Afterwards, the amount of volatiles was determined by liquid scintillation counting. The soil was not further investigated.

The identity of the test item and its degradation products was elucidated by HPLC-MS(/MS) including accurate mass determination.

II. RESULTS AND DISCUSSION

A. EXTRACTION AND QUANTITATION OF RADIOACTIVITY IN SOIL SAMPLES

Table 7.1.2.1.2- 31 to Table 7.1.2.1.2- 34 summarizes the mineralization of [1-^{14}C]trifluoroacetate as a function of time.

Table 7.1.2.1.2- 31: Mineralization of trifluoroacetic acid in Soil Laacherhof AXXa under Aerobic Conditions (expressed as percent of applied radioactivity; mean value of duplicates)

		SAR								
		20.0 µg			1.0 µg			0.1 µg		
Compound (Replicate)		DAT-30	DAT-59	DAT-120	DAT-30	DAT-59	DAT-120	DAT-30	DAT-59	DAT-120
Carbon dioxide	A	0.0061	0.0073	0.0074	0.0093	0.0085	0.0109	0	0.179	0.123
	B	0.0062	0.0074	0.0072	0.0060	0.0147	0.0155	0.025	0.221	0.109

DAT: days after treatment

Table 7.1.2.1.2- 32: Mineralization of trifluoroacetic acid in Soil Dollendorf II under Aerobic Conditions (expressed as percent of applied radioactivity; mean value of duplicates)

		SAR								
		20.0 µg			1.0 µg			0.1 µg		
Compound (Replicate)		DAT-30	DAT-59	DAT-120	DAT-30	DAT-59	DAT-120	DAT-30	DAT-59	DAT-120
Carbon dioxide	A	0.0067	0.0075	0.0072	0.0139	0.0101	0.0425	0.042	0.227	0.230
	B	0.0068	0.0079	0.0076	0.0196	0.0153	0.0158	0.006	0.048	0.129

DAT: days after treatment

Table 7.1.2.1.2- 33: Mineralization of trifluoroacetic acid in Soil Laacherhof Wurmwiese under Aerobic Conditions (expressed as percent of applied radioactivity; mean value of duplicates)

		SAR								
		20.0 µg			1.0 µg			0.1 µg		
Compound (Replicate)		DAT-30	DAT-59	DAT-120	DAT-30	DAT-59	DAT-120	DAT-30	DAT-59	DAT-120
Carbon dioxide	A	0.0064	0.0073	0.0083	0.0076	0.0134	0.0155	0.039	0.017	0.348
	B	0.0069	0.0076	0.0080	0.0065	0.0123	0.0194	0	0.045	0.095

DAT: days after treatment

Table 7.1.2.1.2- 34: Mineralization of trifluoroacetic acid in Soil Hoefchen am Hohenseh under Aerobic Conditions (expressed as percent of applied radioactivity; mean value of duplicates)

		SAR								
		20.0 µg			1.0 µg			0.1 µg		
Compound (Replicate)		DAT-30	DAT-59	DAT-120	DAT-30	DAT-59	DAT-120	DAT-30	DAT-59	DAT-120
Carbon dioxide	A	0.0068	0.0074	0.0070	0.0769	0.0115	0.0202	0.115	0.087	0.154
	B	0.0066	0.0075	0.0072	0.0112	0.0071	0.0234	0.070	0.163	0.109

DAT: days after treatment

B. MATERIAL BALANCE

No material balances were established within this study.

C. EXTRACTABLE AND NON-EXTRACTABLE RESIDUES

Extractable and non-extractable residues were not determined within this study.

D. VOLATILIZATION

Carbon dioxide was detected with amounts ≤ 1% AR at every sampling interval in all four soils. See also Table 7.1.2.1.2- 31 to Table 7.1.2.1.2- 34 for details. Volatile organic compounds were not determined within this study.

III. CONCLUSIONS

No significant mineralization (≥ 1% of applied radioactivity [% AR]) of the test item [1-^{14}C]trifluoroacetate was observed at any study application rate within the tested incubation period of 120 days in the dark in the laboratory in all four soils.

*****

Report:	**KCA 7.1.2.1.2 /11; [redacted], G.; [redacted], K.; 2014**
Title:	Trigger evaluation for the Degradation of Flufenacet - Degradation Product FOE oxalate under Aerobic Soil Conditions in Laboratory According to FOCUS Kinetics Using the KinGUI 2 Tool
Report No:	EnSa-13-1009
Document No:	M-478440-01-1
Guidelines:	• FOCUS kinetics (2006, 2011) [3, 4]
GLP:	no

Executive Summary

A kinetic analysis of residue data from two aerobic soil degradation studies M-002166-01-1(Baseline Dossier, KCA 7.1.2.1.1/01) and M-002146-01-1 (Baseline Dossier, KCA 7.1.2.1.1/03) was performed with the software KinGUI 2 according to FOCUS kinetics (2006, 2011) [3, 4] to derive half-lives for FOE oxalate, a degradation product of flufenacet, which are suitable for trigger evaluation.

Single first order (SFO) was the most appropriate kinetic model to describe the degradation of FOE oxalate for trigger evaluation in the four tested soils (1 × loamy sand, 2 × silt loam, 1 × sandy loam) under aerobic conditions in the dark in the laboratory at 20 ± 2 °C and soil moistures ranging from 40% of the maximum water holding capacity (MWHC) to 75% of the field capacity (FC) at 1/3 bar.

The calculated half-lives of FOE oxalate for trigger evaluation were 11.9, 13.4, and 23.4 days (all 20 ± 1 °C, 40% MWHC), and 19.6 days (21 ± 1 °C, 75% FC at 1/3 bar).

I. METHODS

Soil residue data from the two aerobic soil degradation studies M-002166-01-1(Baseline Dossier, KCA 7.1.2.1.1/01) and M-002146-01-1 (Baseline Dossier, KCA 7.1.2.1.1/03) were used. In these studies the degradation of FOE oxalate was studied in a total of four soils (1 × loamy sand, 2 × silt loam, 1 × sandy loam) under aerobic conditions in the dark in the laboratory at 20 ± 2 °C and soil moistures ranging from 40% of the maximum water holding capacity (MWHC) to 75% of the field capacity (FC) at 1/3 bar.

The kinetic analysis was performed according to FOCUS kinetics (2006, 2011) [3, 4] using the software KinGUI 2 with four different kinetic models: single first order (SFO), first order multi-compartment (FOMC), hockey-stick (HS, DFOS = double first order sequential) and double first order parallel

(DFOP). Model input datasets were the residual amounts of flufenacet and FOE oxalate found in each replicate test system at each sampling interval.

The soil residue data for the parent were pre-processed as follows: 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. 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 occurred.

The soil residue data for the degradation product were pre-processed as follows: amounts of degradation products detected at DAT-0 were set to 0. Thereafter (in the formation phase of a degradation product), values < LOD or non-detected (n.d.) were also set to 0, except for the last data point before the first detectable amount of the respective degradation product. If this data point was ≠ DAT-0, it was included in the fit by setting values < LOD or non-detected (n.d.) to 0.5 × LOD. Values between LOD and LOQ were set to the measured values. In the decline phase of a degradation product 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 occurred.

The most appropriate kinetic model was selected on the basis of a detailed statistical analysis including visual assessment of the goodness of the fits, chi^2-scaled error criterion, t-test significance, correlation analysis and standard deviation. Kinetic parameters of FOE oxalate degradation were derived based on the pathway fits (flufenacet and FOE oxalate) using the best-fit kinetics selected from the parent only fits.

II. RESULTS

The single first order (SFO) was the most appropriate kinetic model to describe the degradation of FOE oxalate for trigger evaluation in all tested soils under aerobic conditions. Table 7.1.2.1.2- 35 summarizes the results of the kinetic analysis for the trigger evaluation.

Table 7.1.2.1.2- 35: Kinetic parameters for the degradation of FOE oxalate in soil under aerobic conditions for trigger evaluation according to FOCUS

Soil	Kinetic Model [1]	DT_{50} [days]	DT_{90} [days]	chi^2 error [%]	t-test	Visual Assessment [2]
Howe, Indiana [3]	SFO*-SFO	19.6	65.0	6.2	0.020	+
BBA 2.2 [4]	FOMC*-SFO	11.9	39.6	23.3	<0.001	+
Laacherhof AIII [5]	FOMC*-SFO	23.4	77.7	16.0	<0.001	+
Hoefchen im Tal [6]	SFO*-SFO	13.4	44.5	10.4	<0.001	+

[1] SFO/FOMC-SFO: single first order / first order multi-compartment (parent - flufenacet)* – single first order (FOE oxalate)
[2] visual assessment: + = good
[3] sandy loam, 21 ± 1 °C, 75% FC 1/3 bar (KCA 7.1.2.1.1/01)
Cut-off of the soil residue data after DAT-28 due to collapse of the microbial activity
[4] loamy sand, 20 ± 1 °C, 40% MWHC (KCA 7.1.2.1.1/03)
[5] silt loam, 20 ± 1 °C, 40% MWHC (KCA 7.1.2.1.1/03
[6] silt loam, 20 ± 1 °C, 40% MWHC (KCA 7.1.2.1.1/03
[*] Kinetic parameters of FOE oxalate degradation were derived based on the pathway fit using the best-fit kinetics selected from the parent only fits.

III. CONCLUSIONS

The calculated half-lives of FOE oxalate for trigger evaluation in soil under aerobic conditions in the dark in the laboratory ranged from 11.9 to 23.4 days in all tested soils.

The results are included in the summary of the route and rate of degradation of flufenacet and its major degradation products in soil given in section CA 7.1.2.1.

*****

Report:	**KCA 7.1.2.1.2 /12; [redacted], G.; [redacted], K.; 2014**
Title:	Trigger evaluation for the Degradation of flufenacet Degradation Product FOE 5043-trifluoroethanesulfonic acid under Aerobic Soil Conditions in Laboratory According to FOCUS Kinetics Using the KinGUI 2 Tool
Report No:	EnSa-13-1010
Document No:	M-478444-01-1
Guidelines:	• FOCUS kinetics (2006, 2011) [3, 4]
GLP:	no

Executive Summary

A kinetic analysis of residue data from two aerobic soil degradation studies M-439105-02-1 (Supplemental Dossier, KCA 7.1.2.1.1 /05) and M-440348-02-1 (Supplemental Dossier, KCA 7.1.2.1.1 /06) was performed with the software KinGUI 2 according to FOCUS kinetics (2006, 2011) [3, 4] to derive half-lives for FOE 5043-trifluoroethanesulfonic acid, a degradation product of flufenacet, which are suitable for trigger evaluation.

Single first order (SFO) was the most appropriate kinetic model to describe the degradation of FOE 5043-trifluoroethanesulfonic acid for the trigger evaluation in three of the four tested soils (silt loam, loamy sand, clay loam) under aerobic conditions in the dark in the laboratory at 20 ± 2 °C and soil moisture of 55 ± 5% of the maximum water holding capacity (MWHC) - for one soil no valid half-life could be derived for FOE 5043-trifluoroethanesulfonic acid.

The calculated half-lives of FOE 5043-trifluoroethanesulfonic acid for trigger evaluation were 9.1, 4.5 and 22.5 days[11].

I. METHODS

Soil residue data from the two aerobic soil degradation studies M-439105-02-1 (Supplemental Dossier, KCA 7.1.2.1.1 /05) and M-440348-02-1 (Supplemental Dossier, KCA 7.1.2.1.1 /06) were used. In these studies, the degradation of FOE 5043-trifluoroethanesulfonic acid was studied in a total of four soils (silt loam, loamy sand, clay loam, loam) under aerobic conditions in the dark in the laboratory at 20 ± 2 °C and soil moistures of 55 ± 5% of maximum water holding capacity (MWHC).

The kinetic analysis was performed according to FOCUS kinetics (2006, 2011) [3, 4] using the software KinGUI 2 with four different kinetic models: single first order (SFO), first order multi-compartment (FOMC), hockey-stick (HS, DFOS = double first order sequential) and double first order parallel (DFOP). Model input datasets were the residual amounts of flufenacet and FOE 5043-trifluoro-ethanesulfonic acid found in each replicate test system at each sampling interval.

[11] Worst case estimate based on decline fit (steady degradation product formation is not considered in the evaluation).

The soil residue data for the parent were pre-processed as follows: 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. 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 occurred.

The soil residue data for the degradation product were pre-processed as follows: amounts of degradation products detected at DAT-0 were set to 0. Thereafter (in the formation phase of a degradation product), values < LOD or non-detected (n.d.) were also set to 0, except for the last data point before the first detectable amount of the respective degradation product. If this data point was ≠ DAT-0, it was included in the fit by setting values < LOD or non-detected (n.d.) to 0.5 × LOD. Values between LOD and LOQ were set to the measured values. In the decline phase of a degradation product 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 occurred.

The most appropriate kinetic model was selected on the basis of a detailed statistical analysis including visual assessment of the goodness of the fits, chi²-scaled error criterion, t-test significance, correlation analysis and standard deviation. Kinetic parameters of FOE oxalate degradation were derived based on the pathway fits (flufenacet and FOE 5043-trifluoroethanesulfonic acid) using the best-fit kinetics selected from the parent only fits.

II. RESULTS

The single first order (SFO) was the most appropriate kinetic model to describe the degradation of FOE 5043-trifluoroethanesulfonic acid for trigger evaluation in three of four tested soils under aerobic conditions -from one soil no valid half-life could be derived. Table 7.1.2.1.2- 36 summarizes the results of the kinetic analysis for the trigger evaluation.

Table 7.1.2.1.2- 36: Kinetic parameters for the degradation of FOE 5043-trifluoroethanesulfonic acid in soil under aerobic conditions for trigger evaluation according to FOCUS

Soil	Kinetic Model [1]	DT_{50} [days]	DT_{90} [days]	chi² error [%]	t-test	Visual Assessment [2]
Hoefchen Am Hohenseh [3]	SFO*-SFO	9.1	30.2	5.8	<0.001	+
Laacherhof AXXa [4]	SFO*-SFO	4.5	14.9	18.3	<0.001	o
Dollendorf II [5]	SFO*-SFO	22.5 [7]	74.7	24.1	0.004	+
Laacherhof Wurmwiese [6]	- [8]	- [8]	- [8]	- [8]	- [8]	- [8]

[1] SFO-SFO: single first order (parent - flufenacet) - single first order (FOE 5043-trifluoroethanesulfonic acid)
[2] visual assessment: + = good, o = medium/acceptable
[3] silt loam, 19.7 ± 0,1 °C, 55% MWHC (KCA 7.1.2.1.1 /05)
[4] loamy sand, 19.8 ± 0,2 °C, 55% MWHC (KCA 7.1.2.1.1 /06)
[5] clay loam, 19.8 ± 0.2 °C, 55% MWHC (KCA 7.1.2.1.1 /06)
[6] sandy loam, 19.8 ± 0.2 °C, 55% MWHC (KCA 7.1.2.1.1 /06)
[7] Worst case estimate based on decline fits (steady degradation product formation is not considered in the evaluation).
[8] No valid trigger value could be estimated based on both pathway fit and decline fit.
[*] Kinetic parameters of FOE 5043-trifluoroethanesulfonic acid degradation were derived based on the pathway fit using the best-fit kinetics selected from the parent only fits.

III. CONCLUSIONS

The calculated half-lives of FOE 5043-trifluoroethanesulfonic acid for trigger evaluation in soil under aerobic conditions in the dark in the laboratory ranged from 4.5 and 22.5 days in three of four tested soils. In one soil no valid half-life could be derived for FOE 5043-trifluoroethanesulfonic acid.

The results are included in the summary of the route and rate of degradation of flufenacet and its major degradation products in soil given in section CA 7.1.2.1.

*****

Report:	**KCA 7.1.2.1.2 /14; [redacted], G.; [redacted], S.; 2014**
Title:	Kinetic Evaluation of the Degradation of [phenyl-UL-^{14}C]flufenacet and its Degradation Products under Aerobic Soil Conditions in Laboratory According to FOCUS Kinetics Using the KinGUI 2 Tool
Report No:	EnSa-12-0575
Document No:	M-477878-01-1
Guidelines:	• FOCUS kinetics (2006, 2011) [3, 4]
GLP:	no

Executive Summary

A kinetic analysis of soil residue data from three aerobic soil degradation studies M-002166-01-1 (Baseline Dossier, KCA 7.1.2.1.1/01), M-002146-01-1 (Baseline Dossier, KCA 7.1.2.1.1/03) and M-009592-01-1 (Supplemental Dossier, KCA 7.1.2.1.1 /04) was performed with the software KinGUI 2 according to FOCUS kinetics (2006, 2011) [3, 4] to derive half-lives for flufenacet and its degradation products FOE oxalate, FOE sulfonic acid and FOE methylsulfone as well as formation fraction for the degradation products, which are suitable for modeling purpose. Only the results for the degradation products are described here; therefore, study M-009592-01-1 (Supplemental Dossier, KCA 7.1.2.1.1 /04) is not considered, as it only contains soil residue data for flufenacet.

The single first order kinetic model was used to describe the degradation of FOE oxalate, FOE sulfonic acid and FOE methylsulfone for modeling purpose in the four tested soils under aerobic conditions in the dark in the laboratory at 20 ± 2 °C and soil moistures ranging from 40% of the maximum water holding capacity (MWHC) to 75% of the field capacity (FC) at 1/3 bar.

The calculated half-lives of FOE oxalate were 6.9 days, 20.7 days, 13.1 days (all 20 ± 1 °C, 40% MWHC) and 19.4 days (21 ± 1 °C, 75% FC at 1/3 bar). The formation fractions of FOE oxalate formed from flufenacet were calculated as 0.448, 0.375, 0.350 (all 20 ± 1 °C, 40% MWHC) and 0.484 (21 ± 1 °C, 75% FC at 1/3 bar).

For FOE sulfonic acid no reliable half-lives could be derived from the soil residue data. However, the formation fractions for FOE sulfonic acid formed from flufenacet could be determined for all of the tested soils and were calculated as 0.257, 0.259, 0.143 (all 20 ± 1 °C, 40% MWHC) and 0.108 (21 ± 1 °C, 75% FC at 1/3 bar).

Formation of FOE methylsulfone was not observed in study M-002166-01-1 (Baseline Dossier, KCA 7.1.2.1.1/01) and thus, no degradation data could be derived from this study. The half-life of FOE methylsulfone could be determined only in one of the tested soil (Laacherhof AIII) of study M-002146-01-1 (Baseline Dossier, KCA 7.1.2.1.1/03) and was calculated as 82.7 days. However, the formation fractions for FOE methylsulfone formed from flufenacet could be determined for all of the tested soils and were calculated as 0.061, 0.087 and 0.051 (all 20 ± 1 °C, 40% MWHC).

I. METHODS

Soil residue data from the aerobic soil degradation studies M-002166-01-1 (Baseline Dossier, KCA 7.1.2.1.1/01) and M-002146-01-1 (Baseline Dossier, KCA 7.1.2.1.1/03) were used. In these studies, the degradation of flufenacet was studied in four soils (1 × loamy sand, 2 × silt loam, 1 × sandy loam) under aerobic conditions in the dark in the laboratory at 20 ± 2 °C and soil moistures ranging from 40% MWHC to 75% FC at 1/3 bar (for details see Table 7.1.2.1.2- 37 to Table 7.1.2.1.2- 39 below).

The kinetic analysis was performed according to FOCUS kinetics (2006, 2011) [3, 4] using the software KinGUI 2 and the single first order (SFO) kinetic model. Model input datasets were the amounts of degradation products found in each replicate test system at each sampling interval. Amounts of degradation products detected at DAT-0 were set to 0, thereafter values < LOD or non-detected (n.d.) were also set to 0, except for the last data point before the first detectable amount of the respective degradation product. If this data point was ≠ DAT-0, it was included in the fit by setting values < LOD or non-detected (n.d.) to 0.5 × LOD. Values between LOD and LOQ were set to the measured values. In the decline phase of a degradation product 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 occurred. The DT_{50} values and formation fractions were calculated from the resulting kinetic parameters.

II. RESULTS

The single first order (SFO) kinetic model was used to describe the degradation of FOE oxalate, FOE sulfonic acid and FOE methylsulfone for modeling purpose in the four tested soils. Table 7.1.2.1.2- 37 to Table 7.1.2.1.2- 39 summarizes the results of the kinetic analysis.

Table 7.1.2.1.2- 37: Kinetic parameters for degradation of FOE oxalate in soils under aerobic conditions for modeling purpose according to FOCUS

Soil	FF	Kinetic Model [1]	DT_{50} [days]	chi² error [%]	t-test	Visual Assessment [2]
Howe, Indiana [3]	0.484	SFO - SFO	19.4	6.2	0.017	+
BBA 2.2 [4]	0.448	SFO - SFO	6.9	25.2	0.006	o
Laacherhof AIII [5]	0.375	SFO - SFO	20.7	13.1	<< 0.001	o
Hoefchen im Tal [6]	0.350	SFO - SFO	13.1	10.6	<< 0.001	+

FF formation fraction from flufenacet
[1] SFO-SFO: single first order (parent) – single first order (degradation product)
[2] visual assessment: + = good fit, o = acceptable fit
[3] sandy loam, 21 ± 1 °C, 75% of the field capacity at 1/3 bar (KCA 7.1.2.1.1/01)
[4] loamy sand, 20 ± 1 °C, 40% MWHC (KCA 7.1.2.1.1/03)
[5] silt loam, 20 ± 1 °C, 40% MWHC (KCA 7.1.2.1.1/03
[6] silt loam, 20 ± 1 °C, 40% MWHC (KCA 7.1.2.1.1/03

Table 7.1.2.1.2- 38: Kinetic parameters for degradation of FOE sulfonic acid in soils under aerobic conditions for modeling purpose according to FOCUS

Soil	FF	Kinetic Model [1]	DT_{50} [days]	chi^2 error [%]	t-test	Visual Assessment [2]
Howe, Indiana [3]	0.108	SFO - SFO	> 1000	6.3	n.a. [a)]	+
BBA 2.2 [4]	0.257	SFO - SFO	> 1000	15.4	0.500	+
Laacherhof AIII 5	0.259	SFO - SFO	> 1000	9.5	0.500	+
Hoefchen im Tal [6]	0.143	SFO - SFO	> 1000	6.6	n.a. [a)]	+

FF formation fraction from flufenacet
[1] SFO-SFO: single first order (parent) – single first order (degradation product)
[2] visual assessment: + = good fit
[3] sandy loam, 21 ± 1 °C, 75% of the field capacity at 1/3 bar (KCA 7.1.2.1.1/01)
[4] loamy sand, 20 ± 1 °C, 40% MWHC (KCA 7.1.2.1.1/03)
[5] silt loam, 20 ± 1 °C, 40% MWHC (KCA 7.1.2.1.1/03
[6] silt loam, 20 ± 1 °C, 40% MWHC (KCA 7.1.2.1.1/03
[a)] n.a. = not available; not calculated by KinGUI due to statistical reasons

Table 7.1.2.1.2- 39: Kinetic parameters for degradation of FOE methylsulfone in soils under aerobic conditions for modeling purpose according to FOCUS

Soil	FF	Kinetic Model [1]	DT_{50} [days]	chi^2 error [%]	t-test	Visual Assessment [2]
BBA 2.2 [3]	0.061	SFO - SFO	> 1000	27.8	0.500	+
Laacherhof AIII [4]	0.087	SFO - SFO	82.7	15.4	0.005	+
Hoefchen im Tal [5]	0.051	SFO - SFO	>1000	16.1	0.500	+

FF formation fraction from flufenacet
[1] SFO-SFO: single first order (parent) – single first order (degradation product)
[2] visual assessment: + = good fit
[3] loamy sand, 20 ± 1 °C, 40% MWHC (KCA 7.1.2.1.1/03)
[4] silt loam, 20 ± 1 °C, 40% MWHC (KCA 7.1.2.1.1/03)
[5] silt loam, 20 ± 1 °C, 40% MWHC (KCA 7.1.2.1.1/03)

III. CONCLUSIONS

The calculated half-lives of FOE oxalate for modeling purpose in soil under aerobic conditions in the dark in the laboratory ranged from 6.9 to 20.7 days in the tested soils. The formation fractions of FOE oxalate formed from flufenacet ranged from 0.350 to 0.484.

For FOE sulfonic acid no reliable half-lives could be derived from the soil residue data. However, the formation fractions for FOE sulfonic acid formed from flufenacet could be determined for all of the tested soils and ranged from 0.108 to 0.2596.

The half-life of FOE methylsulfone for modeling purpose in soil under aerobic conditions in the dark in the laboratory could only be determined in one of the tested soils and was calculated as 82.7 days. The formation fractions for FOE methylsulfone formed from flufenacet could be determined for all of the tested soils of study M-002146-01-1 (Baseline Dossier, KCA 7.1.2.1.1/03)and ranged from 0.051 to 0.087.

The results are included in the summary of the degradation rates of flufenacet and its major degradation products in soil in the laboratory given in section CA 7.1.2.1.

*****

Report:	**KCA 7.1.2.1.2 /16; [redacted], G.; [redacted], S.; 2014**
Title:	Kinetic Evaluation of the Degradation of Flufenacet Degradation Product FOE sulfonic acid under Aerobic Soil Conditions in Laboratory According to FOCUS Kinetics Using the KinGUI 2 Tool
Report No:	EnSa-12-0580
Document No:	M-477844-01-1
Guidelines:	• FOCUS kinetics (2006, 11) [3, 4]
GLP:	no

Executive Summary

A kinetic analysis of soil residue data from two aerobic soil degradation studies M-004098-01-2 (Baseline Dossier, KCA 7.1.2.1.2 /01) and M-111445-01-1 (Supplemental Dossier, KCA 7.1.2.1.2 /08) was performed with the software KinGUI 2 according to FOCUS kinetics (2006, 2011) [3, 4] to derive half-lives of FOE sulfonic acid, which are suitable for modeling purpose.

The single first order kinetic model was used for modeling purpose to describe the degradation of FOE sulfonic acid in a total of five tested soils under aerobic conditions in the dark in the laboratory at 20 ± 2 °C and soil moistures ranging from 29% to 44% of the maximum water holding capacity (MWHC).

The calculated half-lives of FOE sulfonic acid were 258.4 days (20 ± 2 °C, 31% MWHC,), 180.8 days (20 ± 2 °C, 29% MWHC), 234.9 days (20 ± 2 °C, 44% MWHC), 62.3 days and 60.3 days (both 20 ± 2 °C, 40% MWHC).

I. METHODS

Soil residue data from the aerobic soil degradation studies M-004098-01-2 (Baseline Dossier, KCA 7.1.2.1.2 /01) and M-111445-01-1 (Supplemental Dossier, KCA 7.1.2.1.2 /08) were used. In these studies, the degradation of FOE sulfonic acid was studied in a total of five soils (1 × sand, 1 × loamy sand, 2 × silt loam, 1 × sandy loam) under aerobic conditions in the dark in the laboratory at 20 ± 2 °C and soil moisture ranging from 29% MWHC to 44% MWHC.

The kinetic analysis was performed according to FOCUS kinetics (2006, 2011) [3, 4] using the software KinGUI 2 with four different kinetic models: single first order (SFO), first order multi-compartment (FOMC), hockey-stick (HS, DFOS = double first order sequential) and double first order parallel (DFOP). Model input datasets were the residual amounts of FOE sulfonic acid 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. 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 occurred. The most appropriate kinetic model was selected on the basis of a detailed statistical analysis including visual assessment of the goodness of the fits, chi²-scaled error criterion, t-test significance, correlation analysis and standard deviation. The DT_{50} values were calculated from the resulting kinetic parameters.

II. RESULTS

The single first order (SFO) kinetic model was used for modeling purpose to describe the degradation of FOE sulfonic acid in the five tested soils. Table 7.1.2.1.2- 40 summarizes the results of the kinetic analysis.

Table 7.1.2.1.2- 40: Kinetic parameters for degradation of FOE sulfonic acid in soil under aerobic conditions for modeling purpose according to FOCUS

Soil	Kinetic Model [1]	DT_{50} [days]	chi^2 error [%]	t-test	Visual Assessment [2]
BBA 2.1 [3]	SFO	258.4	4.38	<= 0.001	+
BBA 2.2 [4]	SFO	180.8	4.64	<= 0.001	o
Laacherhof AIII [5]	SFO	234.9	11.24	<= 0.001	o
Laacherhof AXXa [6]	SFO	62.3	3.05	<= 0.001	+
Laacherhof AIII [7]	SFO	60.3	3.03	<= 0.001	+

[1] SFO: single first order
[2] visual assessment: + = good, o = acceptable
[3] sand, 20 ± 2 °C, 31% MWHC (KCA 7.1.2.1.2 /01)
[4] loamy sand, 20 ± 2 °C, 29% MWHC (KCA 7.1.2.1.2 /01)
[5] silt loam, 20 ± 2 °C, 44% MWHC (KCA 7.1.2.1.2 /01)
[6] sandy loam, 20 ± 2 °C, 40% MWHC (KCA 7.1.2.1.2 /08)
[7] silt loam, 20 ± 2 °C, 40% MWHC (KCA 7.1.2.1.2 /08)

III. CONCLUSIONS

The calculated half-lives for modeling purpose for the degradation of FOE sulfonic acid in soil under aerobic conditions in the dark in the laboratory ranged from 60.3 to 258.4 days in the tested soils.

The results are included in the summary of the degradation rates of flufenacet and its major degradation products in soil in the laboratory given in section 7.1.2.1.

*****

Report:	**KCA 7.1.2.1.2 /17; [redacted], G.; [redacted], S.; 2014**
Title:	Kinetic Evaluation of the Degradation of Flufenacet Degradation Product FOE methylsulfone under Aerobic Soil Conditions in Laboratory According to FOCUS Kinetics Using the KinGUI 2 Tool
Report No:	EnSa-12-0578
Document No:	M-477839-01-1
Guidelines:	• FOCUS kinetics (2006, 11) [3, 4]
GLP:	no

Executive Summary

A kinetic analysis of soil residue data from the aerobic soil degradation study M-443658-01-1 (Supplemental Dossier, KCA 7.1.2.1.2 /06) was performed with the software KinGUI 2 according to FOCUS kinetics (2006, 2011) [3, 4] to derive half-lives of FOE methylsulfone, which are suitable for modeling purpose.

The single first order kinetic model was used for modeling purpose to describe the degradation of FOE methylsulfone in a total of 4 tested soils under aerobic conditions in the dark in the laboratory at 20 ± 2 °C and soil moisture of 55 ± 5% of the maximum water holding capacity (MWHC).

The calculated half-lives of FOE methylsulfone were 43.1, 23.3, 43.8 and 96.1 days (all 20 ± 2 °C, 55 ± 5% MWHC).

I. METHODS

Soil residue data from the aerobic soil degradation study M-443658-01-1 (Supplemental Dossier, KCA 7.1.2.1.2 /06) were used. In this study, the degradation of FOE methylsulfone was studied in a total of four soils (loamy sand, loam, silt loam and sandy loam) under aerobic conditions in the dark in the laboratory at 20 ± 2 °C and soil moisture of 55 ± 5% MWHC.

The kinetic analysis was performed according to FOCUS kinetics (2006, 2011) [3,4] using the software KinGUI 2 with four different kinetic models: single first order (SFO), first order multi-compartment (FOMC), hockey-stick (HS, DFOS = double first order sequential) and double first order parallel (DFOP). Model input datasets were the residual amounts of FOE methylsulfone 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. 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 occurred. The most appropriate kinetic model was selected on the basis of a detailed statistical analysis including visual assessment of the goodness of the fits, chi^2-scaled error criterion, t-test significance, correlation analysis and standard deviation. The DT_{50} values were calculated from the resulting kinetic parameters.

II. RESULTS

The single first order (SFO) kinetic model was used for modeling purpose to describe the degradation of FOE methylsulfone in the four tested soils. Table 7.1.2.1.2- 41 summarizes the results of the kinetic analysis.

Table 7.1.2.1.2- 41: Kinetic parameters for degradation of FOE methylsulfone in soil under aerobic conditions for modeling purpose according to FOCUS

Soil	Kinetic Model [1]	DT_{50} [days]	chi^2 error [%]	t-test	Visual Assessment [2]
Laacherhof AXXa [3]	SFO	43.1	3.4	<< 0.001	+
Dollendorf II [4]	SFO	23.3	3.0	<< 0.001	+
Hoefchen am Hohensch [5]	SFO	43.8	3.6	<< 0.001	+
Laacherhof Wurmwiese [6]	SFO	96.1	3.3	<< 0.001	+

[1] SFO: single first order
[2] visual assessment: + = good
[3] loamy sand
[4] loam
[5] silt loam
[6] sandy loam

III. CONCLUSIONS

The calculated half-lives for modeling purpose for the degradation of FOE methylsulfone in soil under aerobic conditions in the dark in the laboratory ranged from 23.3 to 96.1 days in the tested soils.

The results are included in the summary of the degradation rates of flufenacet and its major degradation products in soil in the laboratory given in section CA 7.1.2.1.

*****

Report:	**KCA 7.1.2.1.2 /15; [redacted], G.; [redacted], S.; 2014**
Title:	Kinetic Evaluation of the Degradation of Flufenacet Degradation Product FOE-thiadone under Aerobic Soil Conditions in Laboratory According to FOCUS Kinetics Using the KinGUI 2 Tool
Report No:	EnSa-12-0579
Document No:	M-477840-01-1
Guidelines:	• FOCUS kinetics (2006, 11) [3, 4]
GLP:	no

Executive Summary

A kinetic analysis of soil residue data from the aerobic soil degradation study M-009828-01-1 (Supplemental Dossier, KCA 7.1.2.1.2 /03) was performed with the software KinGUI 2 according to FOCUS kinetics (2006, 2011) [3, 4] to derive half-lives of FOE-thiadone, which are suitable for modeling purpose.

The single first order kinetic model was used for modeling purpose to describe the degradation of FOE-thiadone in a total of three tested soils under aerobic conditions in the dark in the laboratory at 20 ± 1 °C and soil moisture of 75% of the field capacity (FC) at 1/3 bar.

The calculated half-lives of FOE-thiadone were 2.0, 1.4 and 2.9 days (all 20 ± 1 °C, 75% FC at 1/3 bar).

I. METHODS

Soil residue data from the aerobic soil degradation study M-009828-01-1 (Supplemental Dossier, KCA 7.1.2.1.2 /03) were used. In this study, the degradation of FOE-thiadone was studied in a total of three soils (loamy sand, sandy loam, silt loam) under aerobic conditions in the dark in the laboratory at 20 ± 1 °C and soil moisture of 75% FC at 1/3 bar.

The kinetic analysis was performed according to FOCUS kinetics (2006, 2011) [3, 4] using the software KinGUI 2 with four different kinetic models: single first order (SFO), first order multi-compartment (FOMC), hockey-stick (HS, DFOS = double first order sequential) and double first order parallel (DFOP). Model input datasets were the residual amounts of FOE-thiadone found in each replicate test system at each sampling interval. As there was evidence in the study that the transient degradation product FOE-thiadone propionic acid conjugate is in equilibrium with FOE-thiadone under neutral conditions, a worst case assumption for the degradation of FOE-thiadone was made, and the sum of the residual amounts of FOE-thiadone and FOE-thiadone propionic acid conjugate found in each replicate test system at each sampling interval were used as model input datasets. 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. 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 occurred. The most appropriate kinetic model was selected on the basis of a detailed statistical analysis including visual assessment of the goodness of the fits, chi^2-scaled error criterion, t-test significance, correlation analysis and standard deviation. The DT_{50} values were calculated from the resulting kinetic parameters.

II. RESULTS

The single first order (SFO) kinetic model was used for modeling purpose to describe the degradation of FOE-thiadone in the three tested soils. Table 7.1.2.1.2- 42 summarizes the results of the kinetic analysis.

Table 7.1.2.1.2- 42: Kinetic parameters for degradation of FOE-thiadone in soil under aerobic conditions for modeling purpose according to FOCUS

Soil	Kinetic Model [1]	DT_{50} [2] [days]	chi^2 error [%]	t-test	Visual Assessment [3]
Iowa [4]	SFO	2.0	6.7	< 0.001	o
Indiana [5]	SFO	1.4	5.7	< 0.001	o
Nebraska [6]	SFO	2.9	3.7	< 0.001	o

[1] SFO: single first order
[2] worst case assumption; sum of residue values of FOE-thiadone and thiadone propionic acid conjugate
[3] visual assessment: o = acceptable
[4] loamy sand
[5] sandy loam
[6] silt loam

III. CONCLUSIONS

The calculated half-lives for modeling purpose for the degradation of FOE-thiadone in soil under aerobic conditions in the dark in the laboratory ranged from 1.4 days to 2.9 days in the tested soils.

The results are included in the summary of the degradation rates of flufenacet and its major degradation products in soil in the laboratory given in section CA 7.1.2.1.

*****

Report:	**KCA 7.1.2.1.2/13; [redacted], G.; [redacted], S.; 2014**
Title:	Kinetic Evaluation of the Degradation of [thiadiazole-5-^{14}C]flufenacet and its Degradation Products under Aerobic Soil Conditions in Laboratory According to FOCUS Kinetics Using the KinGUI 2 Tool
Report No:	EnSa-12-0577
Document No:	M-477835-01-1
Guidelines:	• FOCUS kinetics (2006, 11) [2, 4]
GLP:	no

Executive Summary

A kinetic analysis of soil residue data from two aerobic soil degradation studies M-439105-02-1 (Supplemental Dossier, KCA 7.1.2.1.1/05) and M-440348-01-1 (Supplemental Dossier, KCA 7.1.2.1.1/06) was performed with the software KinGUI 2 according to FOCUS kinetics (2006, 2011) [3, 4] to derive half-lives for flufenacet and its degradation products FOE-thiadone, FOE 5043-trifluoroethanesulfonic acid and trifluoroacetic acid as well as formation fractions for the degradation products, which are suitable for modeling purpose. Only the results for the degradation products are described here.

The single first order kinetic model was used for modeling purpose to describe the degradation of the three degradation products in a total of four tested soils (silt loam, loamy sand, clay loam and loam) under aerobic conditions in the dark in the laboratory at 20 ± 2 °C and soil moisture of 55% of the maximum water holding capacity (MWHC).

The calculated half-lives of FOE-thiadone were 1.1 days (19.7 ± 0.1 °C, 55% MWHC), 1.4 days, 2.8 days and 2.0 days (all 19.8 ± 0.2 °C, 55% MWHC). The formation fractions of FOE-thiadone formed from flufenacet were calculated as 0.913 (19.7 ± 0.1 °C, 55% MWHC), 0.524, 0.438 and 0.405 (all 19.8 ± 0.2 °C, 55% MWHC).

The calculated half-lives of FOE 5043-trifluoroethanesulfonic acid were 9.1 days (19.7 ± 0.1 °C, 55% MWHC), 4.5 days, 22.5 days[12] and 7.6 days[12] (all 19.8 ± 0.2 °C, 55% MWHC). The formation fractions of FOE 5043-trifluoroethanesulfonic acid formed from FOE-thiadone were calculated as 0.264 (19.7 ± 0.1 °C, 55% MWHC), 0.534, 0.422 and 0.655 (all 19.8 ± 0.2 °C, 55% MWHC).

The calculated half-lives of trifluoroacetic acid were >1000 days in all tested soils (19.7 ± 0.1 °C and 19.8 ± 0.2 °C, 55% MWHC). The formation fractions of trifluoroacetic acid formed from flufenacet were calculated as 0.087 (19.7 ± 0.1 °C, 55% MWHC), 0.476, 0.562 and 0.596 (all 19.8 ± 0.2 °C, 55% MWHC). The formation fractions of trifluoroacetic acid formed from FOE-thiadone were calculated as 0.736 (19.7 ± 0.1 °C, 55% MWHC), 0.466, 0.578 and 0.345 (all 19.8 ± 0.2 °C, 55% MWHC).

I. METHODS

Soil residue data from the aerobic soil degradation studies M-439105-02-1 (Supplemental Dossier, KCA 7.1.2.1.1 /05) and M-440348-02-1 (Supplemental Dossier, KCA 7.1.2.1.1 /06) were used. In these studies, the degradation of flufenacet was studied in a total of four soils (silt loam, loamy sand, clay loam and loam) under aerobic conditions in the dark in the laboratory at 20 ± 2 °C and soil moisture of 55% MWHC (for details see Table 7.1.2.1.2- 43 to Table 7.1.2.1.2- 45 below).

The kinetic analysis was performed according to FOCUS kinetics (2006, 2011)[3,4] using the software KinGUI 2 with four different kinetic models: single first order (SFO), first order multi-compartment (FOMC), hockey-stick (HS, DFOS = double first order sequential) and double first order parallel (DFOP). Model input datasets were the residual amounts of the degradation products found in each replicate test system at each sampling interval. Amounts of degradation products detected at DAT-0 were set to 0; thereafter values < LOD or non-detected (n.d.) were also set to 0, except for the last data point before the first detectable amount of the respective degradation product. If this data point was ≠ DAT-0, it was included in the fit by setting values < LOD or non-detected (n.d.) to 0.5 x LOD. Values between LOD and LOQ were set to the measured values. In the decline phase of a degradation product all single values < LOD or non-detected (n.d.) were set to 0.5 x LOD. If they became < LOD / n.d. for a second time the curve was cut off until a subsequent value > LOQ occurred. The DT50 values and formation fractions were calculated from the resulting kinetic parameters.

II. RESULTS

The single first order (SFO) kinetic model was used for modeling purpose to describe the degradation of FOE-thiadone, FOE 5043-trifluoroethanesulfonic acid and trifluoroacetic acid in the four tested soils. Table 7.1.2.1.2- 43 to Table 7.1.2.1.2- 45 summarizes the results of the kinetic analysis.

[12] Due to poor chi^2 error additional decline fits (based on conservative estimates of the true DT_{50} as the steady metabolite formation is not considered in the evaluation) were conducted for FOE5043-trifluoroethanesulfonic acid residues in the soils Dollendorf II and Laacherhof Wurmwiese.

Table 7.1.2.1.2- 43: Kinetic parameters for degradation of FOE-thiadone in soils under aerobic conditions for modeling purpose according to FOCUS

Soil	FF	Kinetic Model [1]	DT_{50} [days]	chi^2 error [%]	t-test	Visual Assessment [2]
Hoefchen Am Hohenseh [3]	0.913	SFO - SFO	1.1	16.4	1.34e-09	+
Laacherhof AXXa [4]	0.524	SFO - SFO	1.4	15.6	8.30e-08	+
Dollendorf II [5]	0.438	SFO - SFO	2.8	16.4	7.93e-07	+
Laacherhof Wurmwiese [6]	0.405	SFO - SFO	2.0	14.7	1.97e-08	+

FF formation fraction from flufenacet
[1] SFO-SFO: single first order (parent) – single first order (degradation product)
[2] Visual assessment: + = good
[3] silt loam, 19.7 ± 0.1 °C, 55% MWHC (KCA 7.1.2.1.1 /05)
[4] loamy sand, 19.8 ± 0.2 °C, 55% MWHC (KCA 7.1.2.1.1 /06)
[5] clay loam, 19.8 ± 0.2 °C, 55% MWHC (KCA 7.1.2.1.1 /06)
[6] loam, 19.8 ± 0.2 °C, 55% MWHC (KCA 7.1.2.1.1 /06)

Table 7.1.2.1.2- 44: Kinetic parameters for degradation of FOE 5043-trifluoroethanesulfonic acid in soils under aerobic conditions for modeling purpose according to FOCUS

Soil	FF	Kinetic Model [1]	DT_{50} [days]	chi^2 error [%]	t-test	Visual Assessment [2]
Hoefchen Am Hohenseh [3]	0.264	SFO - SFO	9.1	5.8	< 2e-16	+
Laacherhof AXXa [4]	0.534	SFO - SFO	4.5	18.3	2.67e-09	+
Dollendorf II [5]	0.422	SFO - SFO	22.5 *)	24.1	0.0035	+
Laacherhof Wurmwiese [6]	0.655	SFO - SFO	17.6 *)	39.8	0.0415	o

FF: formation fraction from FOE-thiadone
[1] SFO-SFO: single first order (parent) – single first order (degradation product)
[2] Visual assessment: + = good, o = acceptable
[3] silt loam, 19.7 ± 0.1 °C, 55% MWHC (KCA 7.1.2.1.1 /05)
[4] loamy sand, 19.8 ± 0.2 °C, 55% MWHC (KCA 7.1.2.1.1 /06)
[5] clay loam, 19.8 ± 0.2 °C, 55% MWHC (KCA 7.1.2.1.1 /06)
[6] loam, 19.8 ± 0.2 °C, 55% MWHC (KCA 7.1.2.1.1 /06)
*) Conservative estimates based on decline fits, steady degradation product formation is not considered.

Table 7.1.2.1.2- 45: Kinetic parameters for degradation of trifluoroacetic acid in soils under aerobic conditions for modeling purpose according to FOCUS

Soil	FF [a), b)]	Kinetic Model [1]	DT_{50} [days]	chi^2 error [%]	t-test	Visual Assessment [2]
Hoefchen Am Hohenseh [3]	0.087 [a)] 0.736 [b)]	SFO - SFO	> 1000	9.2	0.5	+
Laacherhof AXXa [4]	0.476 [a)] 0.466 [b)]	SFO - SFO	> 1000	10.3	0.5	
Dollendorf II [5]	0.562 [a)] 0.578 [b)]	SFO - SFO	> 1000	9.5	0.5	+
Laacherhof Wurmwiese [6]	0.596 [a)] 0.345 [b)]	SFO – SFO	1000	9.4	0.5	+

FF: formation fraction; [a)] from flufenacet; [b)] from FOE-thiadone
[1] SFO-SFO: single first order (parent) – single first order (degradation product)
[2] Visual assessment: + = good
[3] silt loam, 19.7 ± 0.1 °C, 55% MWHC (KCA 7.1.2.1.1/05)
[4] loamy sand, 19.8 ± 0.2 °C, 55% MWHC (KCA 7.1.2.1.1 /06)
[5] clay loam, 19.8 ± 0.2 °C, 55% MWHC (KCA 7.1.2.1.1 /06)
[6] loam, 19.8 ± 0.2 °C, 55% MWHC (KCA 7.1.2.1.1/06)

III. CONCLUSIONS

The calculated half-lives of FOE-thiadone for modeling purpose in soil under aerobic conditions in the dark in the laboratory ranged from 1.1 to 2.8 days in the tested soils. The formation fractions of FOE-thiadone formed from flufenacet ranged from 0.405 to 0.913.

The calculated half-lives of FOE 5043-trifluoroethanesulfonic acid for modeling purpose in soil under aerobic conditions in the dark in the laboratory ranged from 4.5 to 22.5 days in the tested soils. The formation fractions of FOE 5043-trifluoroethanesulfonic acid formed from FOE-thiadone ranged from 0.264 to 0.655.

The calculated half-lives of trifluoroacetic acid for modeling purpose in soil under aerobic conditions in the dark in the laboratory were >1000 days in all tested soils. The formation fractions of trifluoroacetic acid formed from flufenacet ranged from 0.087 to 0.596. The formation fractions of trifluoroacetic acid formed from FOE-thiadone ranged from 0.345 to 0.736.

The results are included in the summary of the degradation rates of flufenacet and its major degradation products in soil in the laboratory given in section CA 7.1.2.1.

CA 7.1.2.1.3 Anaerobic degradation of the active substance

Anaerobic soil degradation studies were not submitted for Annex I listing and have therefore not been summarized in the Baseline Dossier.
The rate of degradation of flufenacet in soil under anaerobic conditions in the dark in the laboratory is now newly addressed by two studies, which are submitted within this Supplemental Dossier for the flufenacet renewal of approval. Furthermore, kinetic evaluations of the degradation behavior of flufenacet in soil under anaerobic conditions in the dark in the laboratory have been performed according to FOCUS kinetics (2006, 2011) [3, 4] to derive kinetic parameters suitable for trigger evaluation, modeling purpose and environmental risk assessment.

Report:	**KCA 7.1.2.1.3 /01; [redacted], N. C.; [redacted], D. M.; 1995**
Title:	Anaerobic Soil Metabolism of [Phenyl-U-^{14}C]FOE 5043
Report No:	MR106645
Document No:	M-002162-01-1
Guidelines:	• OECD Test Guideline No. 307 • OCSPP Test Guideline No. 835.4100/4200
GLP:	yes

Executive Summary

The degradation data as reported in study KCA 7.1.1.2 /01 were kinetically evaluated as part of the study to derive trigger endpoints.

The calculated half-life of flufenacet under anaerobic conditions was 240 days, assuming first order kinetics.

I. MATERIALS AND METHODS

Details on the study conduct and its results are summarized under KCA 7.1.1.2 /01.

The residue data for the test item from the anaerobic study phase were evaluated using first order kinetics. Model input datasets were the residual amounts of flufenacet found at each sampling interval of the anaerobic study phase. See Table 7.1.1.2- 2 for input values.

II. RESULTS AND DISCUSSION

The amount of flufenacet was declining during the aerobic as well as during the anaerobic incubation phase. The half-life of flufenacet in the tested soil was 240 days under anaerobic conditions in the dark in the laboratory. The correlation coefficient (r^2) for the fit was 0.95.

Table 7.1.2.1.3- 1: Degradation kinetics of flufenacet in soil under anaerobic conditions for trigger evaluation

Kinetic Model	DT_{50} [d]	r^2
SFO	240	0.9536

SFO = single first order

III. CONCLUSIONS

Flufenacet was degraded in soil under aerobic and anaerobic conditions in the dark in the laboratory. Its calculated half-life under anaerobic conditions was 240 days in the tested soil.

*****

Report:	**KCA 7.1.2.1.3 /02; [redacted], O.; 2012**
Title:	Amendment No. 2 to [thiadiazole-5-^{14}C]BOE 5043: Anaerobic Degradation/Metabolism in Two European Soils
Report No:	MEF-11/908
Document No:	M-437443-03-1
Guidelines:	• OECD Test Guideline No. 307 • OCSPP Test Guideline No. 835.4100/4200
GLP:	yes

Executive Summary

The degradation data as reported in study KCA 7.1.1.2 /02 were kinetically evaluated according to FOCUS (2005) [2] as part of the study to derive best fits for trigger endpoint determination. The experimental data could be well described by a double first order in parallel kinetic model for both soils. The calculated half-lives of flufenacet under anaerobic conditions were 23 days in soil Hoefchen am Hohenseh and 15 days in soil Dollendorf II.

It is concluded that flufenacet has no potential for accumulation in the environment.

I. MATERIALS AND METHODS

Details on the study conduct and its results are summarized under KCA 7.1.1.2 /02.

The residue data for the test item from the anaerobic study phase were evaluated according to the FOCUS guidance document [3] on degradation kinetics using the software KinGUI 2 to derive the DT_{50} and DT_{90} values for flufenacet.

Model input datasets were the residual amounts of flufenacet found in each replicate test system at each sampling interval of the anaerobic study phase. 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. See Table 7.1.2.1.1- 4 for input values.

For the determination of the degradation kinetics following procedure was followed:

- Values between LOD and LOQ were set to the measured values.
- All single values < LOD or non-detected (n.d.) were set to 50% HPLC 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, single first order (SFO), first order multi compartment (FOMC), and double first order in parallel (DFOP), were tested in order to determine the best fit kinetic model. The best-fit kinetic model was selected on the basis of the chi^2 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).

II. RESULTS AND DISCUSSION

Table 7.1.2.1.3- 2 and Table 7.1.2.1.3- 3 summarize the degradation of [thiadiazole-5-^{14}C]flufenacet as a function of time.

Table 7.1.2.1.3- 2: Degradation of flufenacet in Soil Hoefchen am Hohenseh under Anaerobic Conditions
(expressed as percent of applied radioactivity; single values)

Replicate	DAT	0 [1]	15 [2]	15 [3]	17	21	29	35	48	77	105	135
	DASF	N/A		0	2	6	14	20	33	62	90	120
A		97.0	29.6	43.7	38.9	34.3	25.4	21.6	19.0	12.9	10.2	6.5
B		95.8	32.1	41.9	38.7	32.4	25.6	23.3	17.5	13.0	9.3	6.2

[1] Material balances at DAT-0 were 97.8% AR for replicate A and 96.7% AR for replicate B

[2] before soil flooding (aerobic incubation phase)

[3] after soil flooding (anaerobic incubation phase)

Table 7.1.2.1.3- 3: Degradation of flufenacet in Soil Dollendorf II under Anaerobic Conditions
(expressed as percent of applied radioactivity; single values)

Replicate	DAT	0 [1]	15 [2]	15 [3]	17	21	29	35	48	77	105	135
	DASF	N/A		0	2	6	14	20	33	62	90	120
A		92.9	42.5	34.6	28.9	22.8	17.6	17.8	10.9	3.1 [4]	4.4	3.1
B		93.3	45.8	36.1	25.1	23.7	18.7	13.9	10.3	12.1	4.5	3.1

[1] Material balances at DAT-0 were 96.7% AR for replicate A and 97.0% AR for replicate B

[2] before soil flooding (aerobic incubation phase)

[3] after soil flooding (anaerobic incubation phase)

[4] Material balance of replicate A at DAT-77was not in the acceptable range between 90 and 110% AR – thus, results are not considered for kinetic evaluation

The chi^2 error values of the fits of all investigated kinetic models were ≤ 10 and the visual assessment of the regression curves gave acceptable or good results (see Table 7.1.2.1.3- 4 for details). The degradation of flufenacet followed DFOP kinetics in both soils, according to the lowest chi^2 error values.

The amount of flufenacet was declining during the aerobic as well as during the anaerobic incubation phase. The half-lives of flufenacet under anaerobic conditions in the dark in the laboratory were 23 and 15 days in soil Hoefchen am Hohenseh and Dollendorf II, respectively.

Table 7.1.2.1.3- 4: Degradation kinetics of flufenacet in soil under anaerobic conditions for trigger evaluation

Soil (Soil Type)	Kinetic Model [1]	DT_{50} [d]	DT_{90} [d]	chi^2 error [%]	Visual Assessment [2]
Hoefchen am Hohenseh (silt loam)	DFOP	23	161	0.9	+
Dollendorf II (loam)	DFOP	15	111	9.2	+

[1] DFOP = double first order in parallel

[2] Visual assessment: + good

III. CONCLUSIONS

Flufenacet was degraded in soil under aerobic and anaerobic conditions in the dark in the laboratory. Its calculated half-lives under anaerobic conditions were 23 and 15 days in the tested soils Hoefchen am Hohenseh and Dollendorf II.

*****

Report:	**KCA 7.1.2.1.3 /03; [redacted], G.; [redacted], S.; 2014**
Title:	Kinetic Evaluation of the Degradation of Flufenacet and its Degradation Products under Anaerobic Soil Conditions in Laboratory According to FOCUS Kinetics Using the KinGUI 2 Tool
Report No:	EnSa-13-0971
Document No:	M-478213-02-1
Guidelines:	• FOCUS kinetics (2006, 2011) [3, 4]
GLP:	no

Executive Summary

A kinetic analysis of soil residue data from two anaerobic soil degradation studies M-002162-01-1 (Supplemental Dossier; KCA 7.1.2.1.3 /01) and M-437443-02-1 (Supplemental Dossier; KCA 7.1.2.1.3 /02) was performed with the software KinGUI 2 according to FOCUS kinetics (2006, 2011) [3, 4] to derive half-lives for flufenacet and its degradation products FOE oxalate, FOE sulfonic acid, FOE-thiadone, FOE 5043-trifluoroethanesulfonic acid and trifluoroacetic acid as well as formation fractions for the degradation products, which are suitable for modeling purposes. Additionally, a kinetic analysis of this data was performed to derive half-lives for flufenacet and its degradation products for trigger evaluation. Only the results for flufenacet are described here.

The single first order or the double first order parallel were the most appropriate kinetic models to describe the degradation of flufenacet for modeling purposes in the three tested soils under anaerobic conditions in the dark in the laboratory at 20 ± 2 °C.

The double first order parallel was the most appropriate kinetic model to describe the degradation of flufenacet for trigger evaluation in the three tested soils under anaerobic conditions in the dark in the laboratory at 20 ± 2 °C.

The calculated half-lives of flufenacet for modeling purposes were 224.9 days, 41.6 days[13] and 59.7 days[13] (all 20 ± 2 °C, flooded soil conditions).

The calculated half-lives of flufenacet for trigger evaluation were 229.6 days, 15.0 days and 22.7 days (all 20 ± 2 °C, flooded soil conditions).

I. METHODS

Soil residue data from the anaerobic soil degradation studies M-002162-01-1 (Supplemental Dossier; KCA 7.1.2.1.3 /01) and M-437443-02-1 (Supplemental Dossier; KCA 7.1.2.1.3 /02) were used. In these studies, the degradation of flufenacet was studied in a total of three soils (sandy loam, loam and silt loam) under anaerobic conditions in the dark in the laboratory at 20 ± 2 °C.

The kinetic analysis was performed according to FOCUS kinetics (2006, 2011) [3, 4] using the software KinGUI 2 with four different kinetic models: single first order (SFO), first order multi-compartment (FOMC), hockey-stick (HS, DFOS = double first order sequential) and double first order parallel (DFOP). Model input datasets were the residual amounts of flufenacet found in each replicate test

[13] Calculated from DFOP slow rate

system at each sampling interval after soil flooding. 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 occurred. The most appropriate kinetic model was selected on the basis of a detailed statistical analysis including visual assessment of the goodness of the fits, chi2-scaled error criterion, t-test significance, correlation analysis and standard deviation. The DT50 values were calculated from the resulting kinetic parameters.

II. RESULTS

The single first order or double first order parallel were the most appropriate kinetic models to describe the degradation of flufenacet for modeling purposes in all tested soils. Table 7.1.2.1.3- 5 summarizes the results of the kinetic analysis.

Table 7.1.2.1.3- 5: Kinetic parameters for the degradation of flufenacet in soil under anaerobic conditions for modeling purpose according to FOCUS

Soil	Kinetic Model [1]	DT_{50} [days]	chi^2 error [%]	t-test	Visual Assessment [2]
Howe, Indiana [3]	SFO	224.9	3.6	< 0.001	o
Dollendorf II [4]	DFOP	41.6	9.5	k_1: 0.002 k_2: < 0.001	+
Hoefchen am Hohenseh [5]	DFOP	59.7 [6]	1.1	k_1: < 0.001 k_2: < 0.001	+

[1] SFO: single first order, DFOP double first order parallel
[2] VA = visual assessment: + = good, o = acceptable
[3] sandy loam
[4] loam
[5] silt loam
[6] calculated from DFOP slow rate

The double first order parallel was the most appropriate kinetic model to describe the degradation of flufenacet for trigger evaluation in all tested soils. Table 7.1.2.1.3- 6 summarizes the results of the kinetic analysis.

Table 7.1.2.1.3- 6: Kinetic parameters for the degradation of flufenacet in soil under anaerobic conditions for trigger evaluation according to FOCUS

Soil	Kinetic Model [1]	DT_{50} [days]	DT_{90} [days]	chi^2 error [%]	t-test	Visual Assessment [2]
Howe, Indiana [3]	DFOP	229.6	895.6	1.0	k_1: 0.011 k_2: < 0.001	+
Dollendorf II [4]	DFOP	15.0	111.1	9.2	k_1: 0.049 k_2: < 0.001	+
Hoefchen am Hohenseh [5]	DFOP	22.7	156.9	1.1	k_1: < 0.001 k_2: < 0.001	+

[1] SFO: single first order, DFOP double first order parallel
[2] VA = visual assessment: + = good
[3] sandy loam
[4] loam
[5] silt loam

III. CONCLUSIONS

The calculated half-lives of flufenacet for modeling purposes in soil under anaerobic conditions in the dark in the laboratory ranged from 41.6 to 224.9 days in all tested soils.

The calculated half-lives of flufenacet for trigger evaluation in soil under anaerobic conditions in the dark in the laboratory ranged from 15.0 and 229.6 days in all tested soils.

The results are included in the summary of the degradation rates of flufenacet and its major degradation products in soil in the laboratory given in section section CA 7.1.2.1.

CA 7.1.2.1.4 Anaerobic degradation of metabolites, breakdown and reaction products

No separate anaerobic soil degradation studies were conducted for major degradation products of flufenacet.
However, when studying the route and rate of degradation of flufenacet in soil under anaerobic conditions in the dark in the laboratory (see section CA 7.1.2.1.3) in both studies an aerobic incubation phase of approx. one half-life of flufenacet was applied before start of the anaerobic incubation phase.
Thus, both studies were kinetically evaluated with respect to the degradation behavior of FOE oxalate, FOE sulfonic acid, FOE-thiadone, FOE 5043-trifluoroethanesulfonic acid and trifluoroacetic acid in soil under anaerobic conditions in the dark in the laboratory according to FOCUS kinetics (2006, 2011)[3, 4] to derive kinetic parameters suitable for trigger evaluation, modeling purpose and environmental risk assessment.

*****

Report:	**KCA 7.1.2.1.4 /01; [redacted], G.; [redacted], S.; 2014**
Title:	Kinetic Evaluation of the Degradation of Flufenacet and its Degradation Products under Anaerobic Soil Conditions in Laboratory According to FOCUS Kinetics Using the KinGUI 2 Tool
Report No:	EnSa-13-0971
Document No:	M-478213-02-1
Guidelines:	• FOCUS kinetics (2006, 2011)[3, 4]
GLP:	no

Executive Summary

A kinetic analysis of soil residue data from two anaerobic soil degradation studies M-002162-01-1 (Supplemental Dossier; KCA 7.1.2.1.3 /01) and M-437443-02-1 (Supplemental Dossier; KCA 7.1.2.1.3 /02) was performed with the software KinGUI 2 according to FOCUS kinetics (2006, 2011)[3, 4] to derive half-lives for flufenacet and its degradation products FOE oxalate, FOE sulfonic acid, FOE-thiadone, FOE 5043-trifluoroethanesulfonic acid and trifluoroacetic acid as well as formation fractions for the degradation products, which are suitable for modeling purpose. Additionally, a kinetic analysis of this data was performed to derive half-lives for flufenacet and its degradation products for trigger evaluation. Only the results for the degradation products are described here.

The single first order kinetic model was used to describe the degradation of all five degradation products for modeling purposes as well as for trigger evaluation in one [14] or in two[15] tested soils under anaerobic conditions (flooded soil conditions) in the dark in the laboratory at 20 ± 2 °C.

The calculated half-lives of the degradation products for modeling purposes were: 48.8 days for FOE oxalate, 352.2 days for FOE sulfonic acid, 33.9 and 97.0 days for FOE-thiadone, 1.8 and 16.4 days for FOE 5043-trifluoroethanesulfonic acid and 471.2 and 762.7 days for trifluoroacetic acid. The formation fractions of the degradation products formed from flufenacet were calculated as 1.0 for FOE oxalate, as 1.1×10^{-6} for FOE sulfonic acid, as 0.425 for FOE-thiadone (both soils), and as 0.575 for trifluoroacetic acid (both soils). The formation fractions of the degradation products formed from FOE-thiadone were calculated as 1.0 (both soils) for FOE 5043-trifluoroethanesulfonic acid and as 6.3×10^{-7} and 3.9×10^{-7} for trifluoroacetic acid.

The calculated half-lives of the degradation products for trigger evaluation were: 142.8 days for FOE oxalate, 352.3 days for FOE sulfonic acid, 33.9 and 97.0 days for FOE-thiadone, 1.8 and 16.4 days for FOE 5043-trifluoroethanesulfonic acid and 471.2 and 762.7 days for trifluoroacetic acid.

I. METHODS

Soil residue data from the anaerobic soil degradation studies M-002162-01-1 (Supplemental Dossier; KCA 7.1.2.1.3 /01) and M-437443-02-1 (Supplemental Dossier; KCA 7.1.2.1.3 /02) were used. In these studies, the degradation of flufenacet was studied in one [14] or in two [15] soils (sandy loam, loam and silt loam) under anaerobic conditions in the dark in the laboratory at 20 ± 2 °C.

The kinetic analysis was performed according to FOCUS kinetics (2006, 2011) [3, 4] using the software KinGUI 2 with four different kinetic models: single first order (SFO), first order multi-compartment (FOMC), hockey-stick (HS, DFOS = double first order sequential) and double first order parallel (DFOP). Model input datasets were the residual amounts of the degradation products found in each replicate test system at each sampling interval. 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 occurred. The most appropriate kinetic model was selected on the basis of a detailed statistical analysis including visual assessment of the goodness of the fits, chi^2-scaled error criterion, t-test significance, correlation analysis and standard deviation. The DT_{50} values were calculated from the resulting kinetic parameters.

II. RESULTS

The single first order kinetic model was used to describe the degradation of the five degradation products for modeling purposes as well as for trigger evaluation one[14] or in two[15] tested soils under anaerobic conditions.

Table 7.1.2.1.4- 1, Table 7.1.2.1.4- 3, Table 7.1.2.1.4- 5, Table 7.1.2.1.4- 7 and Table 7.1.2.1.4- 9 summarize the results of the kinetic analysis for modeling purposes. Table 7.1.2.1.4- 2, Table 7.1.2.1.4- 4, Table 7.1.2.1.4- 6, Table 7.1.2.1.4- 8 and Table 7.1.2.1.4- 10 summarize the results of the kinetic analysis for trigger evaluation.

[14] [phenyl-UL-14C]flufenacet: formation of degradation products FOE oxalate and FOE sulfonic acid

[15] [thiadiazole-5-^{14}C] flufenacet: formation of degradation products FOE-thiadone, FOE 5043-trifluoro-ethanesulfonic acid and trifluoroacetic acid.

Table 7.1.2.1.4- 1: Kinetic parameters for the degradation of FOE oxalate in soil under anaerobic conditions for modeling purpose according to FOCUS

Soil	FF	Kinetic Model [1]	DT_{50} [days]	chi^2 error [%]	t-test	VA [2]
Howe, Indiana [3]	1.0 [a]	SFO - SFO	48.8	7.9	< 0.001	+

FF = formation fraction
[1] SFO: single first order, DFOP double first order parallel
[2] VA = visual assessment: + = good, o = acceptable, - = poor fit
[3] sandy loam

Table 7.1.2.1.4- 2: Kinetic parameters for the degradation of FOE oxalate in soil under anaerobic conditions for trigger evaluation according to FOCUS

Soil	Kinetic Model [1]	DT_{50} [days]	DT_{90} [days]	chi^2 error [%]	t-test	VA [2]
Howe, Indiana [3]	DFOP - SFO	142.8	474.4	6.7	0.081	o

[1] SFO: single first order, DFOP double first order parallel
[2] VA = visual assessment: + = good, o = acceptable, - = poor fit
[3] sandy loam

Table 7.1.2.1.4- 3: Kinetic parameters for the degradation of FOE sulfonic acid in soil under anaerobic conditions for modeling purpose according to FOCUS

Soil	FF	Kinetic Model [1]	DT_{50} [days]	chi^2 error [%]	t-test	VA [2]
Howe, Indiana [3]	1.1×10^{-7} [a]	SFO - SFO	352.2	6.6	0.011	o

FF = formation fraction
[1] SFO: single first order, DFOP double first order parallel
[2] VA = visual assessment: + = good, o = acceptable, - = poor fit
[3] sandy loam

Table 7.1.2.1.4- 4: Kinetic parameters for the degradation of FOE sulfonic acid in soil under anaerobic conditions for trigger evaluation according to FOCUS

Soil	Kinetic Model [1]	DT_{50} [days]	DT_{90} [days]	chi^2 error [%]	t-test	VA [2]
Howe, Indiana [3]	DFOP - SFO	352.3	> 1000	6.6	0.295	o

[1] SFO: single first order, DFOP double first order parallel
[2] VA = visual assessment: + = good, o = acceptable, - = poor fit
[3] sandy loam

Table 7.1.2.1.4- 5: Kinetic parameters for the degradation of FOE-thiadone in soil under anaerobic conditions for modeling purpose according to FOCUS

Soil	FF	Kinetic Model [1]	DT_{50} [days]	chi^2 error [%]	t-test	VA [2]
Dollendorf II [3]	0.425 [a]	DFOP - SFO	33.9	5.6	< 0.001	+
Hoefchen am Hohenseh [4]	0.425 [a]	DFOP - SFO	97.0	5.0	< 0.001	+

FF = formation fraction
[1] SFO: single first order, DFOP double first order parallel
[2] VA = visual assessment: + = good, o = acceptable, - = poor fit
[3] loam
[4] silt loam

Table 7.1.2.1.4- 6: Kinetic parameters for the degradation of FOE-thiadone in soil under anaerobic conditions for trigger evaluation according to FOCUS

Soil	Kinetic Model [1]	DT_{50} [days]	DT_{90} [days]	chi^2 error [%]	t-test	VA [2]
Dollendorf II [3]	DFOP - SFO	33.9	112.6	5.6	< 0.001	+
Hoefchen am Hohenseh [4]	DFOP - SFO	97.0	322.3	5.0	< 0.001	+

[1] SFO: single first order, DFOP double first order parallel
[2] VA = visual assessment: + = good, o = acceptable, - = poor fit
[3] loam
[4] silt loam

Table 7.1.2.1.4- 7: Kinetic parameters for the degradation of FOE 5043-trifluoroethanesulfonic acid in soil under anaerobic conditions for modeling purpose according to FOCUS

Soil	FF	Kinetic Model [1]	DT_{50} [days]	chi^2 error [%]	t-test	VA [2]
Dollendorf II [3]	1.000 [a]	DFOP - SFO	1.8	30.6	< 0.001	o
Hoefchen am Hohenseh [4]	1.000 [a]	DFOP - SFO	16.4	22.2	< 0.001	-

FF = formation fraction
[1] SFO: single first order, DFOP double first order parallel
[2] VA = visual assessment: + = good, o = acceptable, - = poor fit
[3] loam
[4] silt loam
[a] formed from FOE-thiadone

Table 7.1.2.1.4- 8: Kinetic parameters for the degradation of FOE 5043-trifluoroethanesulfonic acid in soil under anaerobic conditions for trigger evaluation according to FOCUS

Soil	Kinetic Model [1]	DT_{50} [days]	DT_{90} [days]	chi^2 error [%]	t-test	VA [2]
Dollendorf II [3]	DFOP - SFO	1.8	6.0	30.6	< 0.001	o
Hoefchen am Hohenseh [4]	DFOP - SFO	16.4	54.4	22.2	< 0.001	-

[1] SFO: single first order, DFOP double first order parallel
[2] VA = visual assessment: + = good, o = acceptable, - = poor fit
[3] loam
[4] silt loam

Table 7.1.2.1.4- 9: Kinetic parameters for the degradation of trifluoroacetic acid in soil under anaerobic conditions for modeling purpose according to FOCUS

Soil	FF	Kinetic Model [1]	DT_{50} [days]	chi^2 error [%]	t-test	VA [2]
Dollendorf II [3]	0.575 [a] 6.3×10^{-7} [b]	DFOP - SFO	471.2	3.8	0.004	o
Hoefchen am Hohenseh [4]	0.575 [a] 3.9×10^{-7} [b]	DFOP - SFO	762.7	2.9	0.026	+

FF = formation fraction
[1] SFO: single first order, DFOP double first order parallel
[2] VA = visual assessment: + = good, o = acceptable, - = poor fit
[3] loam
[4] silt loam
[a] formed from flufenacet
[b] formed from FOE-thiadone

Table 7.1.2.1.4- 10: Kinetic parameters for the degradation of trifluoroacetic acid in soil under anaerobic conditions for trigger evaluation according to FOCUS

Soil	Kinetic Model [1]	DT_{50} [days]	DT_{90} [days]	chi^2 error [%]	t-test	VA [2]
Dollendorf II [3]	DFOP - SFO	471.2	> 1000	3.8	0.004	o
Hoefchen am Hohenseh [4]	DFOP - SFO	762.7	> 1000	2.9	0.026	+

[1] SFO: single first order, DFOP double first order parallel
[2] VA = visual assessment: + = good, o = acceptable, - = poor fit
[3] loam
[4] silt loam

III. CONCLUSIONS

The calculated half-lives for the degradation products for modeling purposes in soil under anaerobic conditions in the dark in the laboratory were: 48.8 days for FOE oxalate, 352.2 days for FOE sulfonic acid, 33.9 and 97.0 days for FOE-thiadone, 1.8 and 16.4 days for FOE 5043-trifluoroethanesulfonic acid and 471.2 and 762.7 days for trifluoroacetic acid.

The formation fractions of the degradation products formed from flufenacet were calculated as 1.0 for FOE oxalate, as 1.1×10^{-6} for FOE sulfonic acid, as 0.425 for FOE-thiadone (both soils), and as 0.575 for trifluoroacetic acid (both soils). The formation fractions of the degradation products formed from FOE-thiadone were calculated as 1.0 (both soils) for FOE 5043-trifluoroethanesulfonic acid and as 6.3×10^{-7} and 3.9×10^{-7} for trifluoroacetic acid.

The calculated half-lives for the degradation products for trigger evaluation in soil under anaerobic conditions in the dark in the laboratory were: 142.8 days for FOE oxalate, 352.3 days for FOE sulfonic acid, 33.9 and 97.0 days for FOE-thiadone, 1.8 and 16.4 days for FOE 5043-trifluoroethanesulfonic acid and 471.2 and 762.7 days for trifluoroacetic acid.

The results are included in the summary of the degradation rates of flufenacet and its major degradation products in soil in the laboratory given in section CA 7.1.2.1.

CA 7.1.2.2 Field studies

The dissipation and degradation of flufenacet was investigated in 16 field trials conducted at 10 different sites in Germany, Spain and Italy (10 trials in northern Europe, and 6 trials in southern Europe). The half-lives for the degradation of flufenacet and its major degradation product FOE sulfonic acid in soil under field conditions for modeling purpose are summarized in Table 7.1.2.2- 1.

Table 7.1.2.2- 1: Overall summary of DT_{50} values for degradation of flufenacet and its major degradation product FOE sulfonic acid in soils under field conditions for modeling purpose (normalized to 20 °C and 100% field capacity)

Compound	DT_{50} [1] [days]
flufenacet	22.3
FOE sulfonic acid	21.7

[1] geometric mean

CA 7.1.2.2.1 Soil dissipation studies

The dissipation and degradation of flufenacet in soil under field conditions and the freezer storage of flufenacet and its degradation products were evaluated during the Annex I inclusion using unlabeled flufenacet formulated as WG 60 and was accepted by the European Commission (7469/VI/98-Final – 3rd July 2003). The following studies are included in the Baseline Dossier:

Annex Point / Reference No	Author(s)	Year	Document No
KCA 7.1.2.2.1 /01	[redacted], H.	1995	M-002175-01-2
KCA 7.1.2.2.1 /02	[redacted] H.	1995	M-002171-01-2
KCA 7.1.2.2.1 /03	[redacted] H.	1995	M-002169-01-2
KCA 7.1.2.2.1 /04	[redacted], H.	1995	M-002172-01-2
KCA 7.1.2.2.2 /01	[redacted] H.; [redacted], D. L.; [redacted], P. S.	1995	M-002201-01-1
KCA 7.1.2.2.2 /02	[redacted], H.; [redacted], D. L	1995	M-002199-01-1

No additional studies are submitted within this Supplemental Dossier for the flufenacet renewal of approval. However, updated kinetic evaluations of the degradation behaviors of flufenacet and its major degradation product FOE sulfonic acid in soil under field conditions have been performed according to FOCUS kinetics (2006) to derive kinetic parameters suitable for modeling purpose and environmental risk assessment. A summary of degradation rates of flufenacet and its major degradation products in soil under field conditions is given in section CA 7.1.2.2.

Report:	**KCA 7.1.2.2.1 /05; [redacted], K.; 2008**
Title:	Kinetic evaluation of the dissipation of flufenacet and its metabolite flufenacet - sulfonic acid in soil based on field studies
Report No:	MEF-08/266
Document No:	M-306683-01-1
Guidelines:	• FOCUS kinetics (2006) [3]
GLP:	no

Executive Summary

A kinetic analysis of soil residue data from the field dissipation studies M-002175-01-2 (Baseline Dossier, KCA 7.1.2.2.1 /01), M-002171-01-2 (Baseline Dossier, KCA 7.1.2.2.1 /02), M-002169-01-2 (Baseline Dossier, KCA 7.1.2.2.1 /03), M-002172-01-2 (Baseline Dossier, KCA 7.1.2.2.1 /04) was performed with the software KinGUI 2 according to FOCUS kinetics (2005) [2] to derive normalized half-lives (20 °C and 100% field capacity) for flufenacet and its major degradation product FOE sulfonic acid, which are suitable for modeling purpose.

Because FOE sulfonic acid is relatively mobile an inverse modeling approach was taken to separately account for leaching under field conditions. The single first order was the kinetic model used to describe the degradation of flufenacet and FOE sulfonic acid for modeling purpose under field conditions with application rates of 240, 480 and 600 g/ha and normalized to 20 °C and 100% field capacity.

The normalized half-lives ranged from 6.0 to 51.1 days (geometric mean 22.3 d) for flufenacet and from 14.1 to 41.4 days (geometric mean 21.7 d) for FOE sulfonic acid.

I. METHODS

Soil residue data from the field dissipation studies M-002175-01-2 (Baseline Dossier, KCA 7.1.2.2.1 /01), M-002171-01-2 (Baseline Dossier, KCA 7.1.2.2.1 /02), M-002169-01-2 (Baseline Dossier, KCA 7.1.2.2.1 /03), M-002172-01-2 (Baseline Dossier, KCA 7.1.2.2.1 /04) were used. In these studies, the degradation of flufenacet was studied at sites Breitenfelde (Germany), Kirchlauter (Germany), Monheim (Germany), Burscheid (Germany), Fresne-L'Archeveque (France), Fresne-L'Archeveque (France), Laudun (France), St. Etienne du Gres (France), Saussay La Campagne (France), Fresne-L'Archeveque (France), Ravenna (Italy) and S. Romualdo (Italy) under field conditions covering a period of at least 231 days up to 303 days after treatment. 14 trials were applied in spring and two in autumn, using application rates of 240, 480 and 600 g/ha. Thereof, seven trials were applied on bare soil and nine trials were cropped with maize, sunflower, winter wheat and soybean. For the cropped trials application was performed from pre-emergence to early post-emergence.

The mathematical evaluation of the experimental data was done with the optimization code PEST and the transport model PEARL. The kinetic analysis was performed according to FOCUS kinetics (2005) [2], thus, in principle, four kinetic models are to be considered: The single first-order (SFO), first-order multiple-compartment (FOMC), the hockey-stick model (HS) and the double-first-order in parallel (DFOP). However, as FOE sulfonic acid is relatively mobile an inverse modeling approach was taken to separately account for leaching. Due to the application of this inverse modeling with an exposure model (PEARL) the kinetic model considered is exclusively Single First Order. No weighting of the data was performed in the kinetic analysis. In inverse modeling a model is made to best fit a given set of observations by varying the values of a given set of model input parameters. The parameters to be fitted here were restricted to the following kinetic parameters: the half-lives (DT_{50}) of flufenacet and FOE sulfonic acid, the formation fraction of FOE sulfonic acid and the mass applied. This is equivalent to the parameter set optimized in a normal evaluation with a compartment model as described in FOCUS. Because of the low level of measured FOE sulfonic acid residues it was not

possible to fit its half-life and formation fraction simultaneously. Thus, independent information was used from former laboratory studies (Baseline Dossier, KCA 7.1.1.1/03) to fix the formation fraction to 0.26 and thereby to improve the reliability of the calculated half-life. Additionally, the conservative nature of the finally selected estimates was assessed by comparison with independent data from two lysimeter experiments. For this purpose the experimental conditions at the lysimeters were closely reproduced, combined with the kinetic parameters derived here and implemented in PEARL

All DT_{50} used by PEARL are referenced with respect to temperature and soil moisture which were set to 20 °C and 100% FC (field capacity). The dependence of degradation on temperature was considered using a molar activation energy of 65.4 kJ mol-1 (corresponding to Q10 = 2.58).

Field residue data were pre-processed as follows: at DAT-0 values < LOD in deep horizons were set to 0. Values between LOD and LOQ were set to 0.5 x (LOD + LOQ). Values < LOD were set to 0.5 x LOD for samples after, before or deeper as a value < LOD, or for samples between values > LOQ. The curve was cut off after the first non-detect (< LOD), if no later value > LOQ followed. As an additional conservatism, all depths were considered for FOE sulfonic acid during practically the whole experimental period (from the second sampling on for the 10 - 20 cm soil layer and from the third on for the 20 - 30 cm soil layer), i.e. all values < LOD were set to 0.5 LOD irrespective of the fact that below or after all values are also < LOD. By this procedure residues can hardly be underestimated, but are likely to be overestimated. Finally the concentrations for each depth increment were summed to represent to concentration in a 10 cm thick soil layer containing all mass found in the 0 - 30 cm layer and were used for the kinetic evaluation. As a last step this concentration was transformed to mass per area in 0 - 30 cm using the same estimated site specific bulk density employed for the inverse modeling. This last transformation was made because the mass per area down to a given soil depth is a direct output of PEARL and thus technically simplifies the inverse modeling.

Because daily soil temperature and moisture data which are necessary to normalize the degradation parameters were not measured on-field corresponding values were generated by employing a suitable simulation model. Necessary driving variables for such a model are rainfall and potential evapotranspiration. In the field dissipation studies, rainfall and temperature data are reported as weekly, ten day or monthly sums and averages. Because continuous daily weather data are required for a normalized evaluation, the MARS weather database [16] was employed to provide the daily variation of these variables. The weather data given in the field dissipation studies were used to calibrate the MARS data.

II. RESULTS

Single first order (SFO) was used as kinetic model to describe the degradation of flufenacet and FOE sulfonic acid for modeling purpose at all sites. The fixed formation fraction of FOE sulfonic acid did hardly change the results for flufenacet but produces much more reliable and consistent results for FOE sulfonic acid. Additionally, this formation fraction is similar to the mean value of 0.18 obtained from the fitting to the field data. The conservative nature of the finally selected estimates was assessed by comparison with independent data from two lysimeter experiments, demonstrating that the measured maximum annual concentrations of FOE sulfonic acid in the leachate were substantially lower than the calculated ones in both cases. Thus the half-lives obtained from the field studies enable a much more realistic, but still conservative assessment of the predicted environmental concentrations of FOE sulfonic acid. Table 7.1.2.2.1- 1 summarizes the results of the kinetic analysis.

[16] MARS, Interpolated meteorological data -JRC/MARS Database. European Commission, Joint Research Center (JRC). Ispra, 2004.

Table 7.1.2.2.1- 1: SFO of flufenacet ($DT50_{FFA}$) and FOE sulfonic acid ($DT50_{FOE\ SA}$) referenced to 20 °C and 100% field capacity

Trial number	Site	Texture (0 – 30 cm depth)	DT_{50} flufenacet [days]	DT_{50} flufenacet [days]
30159/0	Breitenfelde (Germany)	sandy loam	17.1	17.7
30162/0	Kirchlauter (Germany)	sandy loam	33.3	19.8
30163/9	Monheim (Germany)	sandy loam	31.8	20.5
30164/7	Burscheid (Germany)	silt loam	11.4	n.a.
30248/1	Fresne-L'Archeveque (France)	silt loam	31.4	18.1
30250/3	Fresne-L'Archeveque (France)	silt loam	32.9	20.8
30251/1	Laudun (France)	loam	24.7	n.a.
30253/8	St. Etienne du Gres (France)	loam	37.6	19.6
30254/6	Saussay La Campagne (France)	silt loam	6.0	n.a.
30455/7	Fresne-L'Archeveque (France)	silt loam	7.1	n.a.
30499/9	Burscheid (Germany)	silt loam	8.5	29.8
30500/6	Monheim (Germany)	sandy loam	14.7	n.a.
40163/3	Laudun (France)	clay loam	45.3	21.8
40164/1	St. Etienne du Gres (France)	silt loam	41.0	25.0
40494/2	Ravenna (Italy)	silt loam	36.2	41.4
40495/0	S. Romualdo (Italy)	silty clay	51.1	14.1
Geometric mean			**22.3**	**21.7**

n.a.: not applicable

III. CONCLUSIONS

The calculated normalized half-lives (20 °C and 100% field capacity) for modeling purpose for the degradation in soil under field conditions ranged from 6.0 to 51.1 days (geometric mean 22.3 d) for flufenacet and from 14.1 to 41.4 days (geometric mean 21.7 d) for FOE sulfonic acid.

CA 7.1.2.2.2 Soil accumulation studies

The accumulation potential of flufenacet was evaluated during the Annex I Inclusion. Due to the short dissipation times, soil accumulation testing is not required for flufenacet.

CA 7.1.3 Adsorption and desorption in soil

CA 7.1.3.1 Adsorption and desorption

The adsorption and desorption behavior in soil of flufenacet and its major degradation products were studied in a number of soils in batch equilibrium experiments using either ^{14}C-labeled or unlabeled test items. Adsorption and desorption isotherms were calculated by linear regression analysis of the adsorption or desorption data according to the Freundlich equation. Additionally, an aged sorption (time dependent sorption) study for FOE sulfonic acid was conducted to get a more thorough understanding of its adsorption behavior in soil.
The calculated adsorption constants and correlation coefficients of flufenacet and its major degradation products are listed in Table 7.1.3.1- 2 to Table 7.1.3.1- 6 an overall summary is given Table 7.1.3.1- 1.

Table 7.1.3.1- 1: Overall summary of adsorption constants $K_{OC(ads)}$ in soils of flufenacet and its major degradation products

Compound	$K_{OC(ads)}$ [1] [mL/g]
flufenacet	215.2
FOE oxalate	11.0
FOE sulfonic acid	10.3
FOE methylsulfone	74.1
FOE thiadone	43.7
FOE 5043 trifluoroethanesulfonic acid	0
trifluoroacetic acid	0

[1] arithmetic mean

Table 7.1.3.1- 2: Overall summary of adsorption constants and correlation coefficients in soils of flufenacet

Soil	Texture (USDA)	pH	Annex Point / Reference No	$K_{F(ads)}$ [mL/g]	1/n	$K_{OC(ads)}$ [mL/g]
# 307, Stanley, KS	silt loam	5.9	KCA 7.1.3.1.1 /01	3.2	0.84 [1]	190 [1]
# 396, Vero Beach, FL	sand	5.0		0.97 [2]	0.98 [1, 2]	588 [1, 2]
# 318, Hagerstown, MD	clay loam	6.4		2.7	0.90 [1]	211 [1]
# 395, Howe, IN	loamy sand	6.4		1.6 [2]	0.87 [1, 2]	696 [1, 2]
# 3253, Lysimeter soil, Monheim, Germany	sandy loam	6.4		4.8	0.89 [1]	354 [1]
Harriston Loam, Harriston, Ontario	loam	7.1	KCA 7.1.3.1.1 /02	4.0	0.96	113
Brantford Silt Clay, St. George, Onatrio	silt loam	7.3		4.0	0.86	144
Ibaraki Ushiku, Japan	sandy loam	5.6	KCA 7.1.3.1.1 /04	6.92	0.85	160.8 [3]
Hokkaido Kamikawa, Japan	loam	4.9		8.96	0.96	426.5
Laacherhof AXXa	loamy sand	5.8	KCA 7.1.3.1.1 /03	3.56	0.93	161.6
Hoefchen am Hohenseh	silt loam	6.5		3.28	0.93	205.0
Hanscheiderhof	silt loam	5.3		5.10	0.93	188.9
Dollendorf II	loam	7.4		7.30	0.90	178.5
Wurmwiese	sandy loam	5.1		3.32	0.98	195.2
			arithmetic mean	4.7	0.92	215.2

[1] as reported in the review report by the European Commission (7469/VI/98-Final – 3rd July 2003)
[2] not considered for arithmetic mean as less than 20% of the test item were adsorbed
[3] not considered for arithmetic mean as it is a volcanic ash soil, not representative for European agricultural soils

Table 7.1.3.1- 3: Overall summary of adsorption constants and correlation coefficients in soils of FOE oxalate

Soil	Texture (USDA)	pH	Annex Point / Reference No	$K_{F(ads)}$ [mL/g]	1/n [1]	$K_{OC(ads)}$ [1] [mL/g]
Winder Vero Beach, FL	sand	5.8	KCA 7.1.3.1.2 /01	0.06 [2]	1.42 [1, 2]	23 [1, 2]
Shipshe, Howe, IN	sandy loam	6.3		0.10	0.93 [1]	13 [1]
Drummer, Champaign, IL	silty clay loam	6.6		0.15	0.82 [1]	7 [1]
Oska-Martin Stilwell, KS	silty clay	6.0		0.16	0.98 [1]	13 [1]
			arithmetic mean	0.14	0.91	11.0

[1] as reported in the review report by the European Commission (7469/VI/98-Final – 3rd July 2003)
[2] not considered for arithmetic mean as organic carbon content < 0.3%

Table 7.1.3.1- 4: Overall summary of adsorption constants and correlation coefficients in soils of FOE sulfonic acid

Soil	Texture (USDA)	pH	Annex Point / Reference No	$K_{F(ads)}$ [mL/g]	1/n [-]	$K_{OC(ads)}$ [mL/g]
Winder Vero Beach, FL	sand	5.8	KCA 7.1.3.1.2 /01	0.05 [2]	0.86 [1, 2]	19 [1, 2]
Shipshe, Howe, IN	sandy loam	6.3		0.11	1.00 [1]	15 [1]
Drummer, Champaign, IL	silty clay loam	6.6		0.20	0.93 [1]	10 [1]
Oska-Martin Stilwell, KS	silty clay	6.0		0.07	1.08 [1]	6 [1]
Laacherhof AXXa	sandy loam	6.3	KCA 7.1.3.2 /01	0.12 [3]	- [3]	8 [3]
Laacherhof AIII	silt loam	6.8		0.12 [3]	- [3]	13 [3]
			arithmetic mean	0.12	1.04	10.4

[1] as reported in the review report by the European Commission (7469/VI/98-Final – 3rd July 2003)
[2] not considered for arithmetic mean as organic carbon content < 0.3%
[3] time-dependent sorption study with only one test concentration; therefore, no Freundlich equation was established and K_d and $K_{d, OC}$ values are reported.

Table 7.1.3.1- 5: Overall summary of adsorption constants and correlation coefficients in soils of FOE methylsulfone

Soil	Texture (USDA)	pH	Annex Point / Reference No	$K_{F(ads)}$ [mL/g]	1/n [-]	$K_{OC(ads)}$ [mL/g]
Wurmwiese	loam	5.3	KCA 7.1.3.1.2 /03	0.66	0.89	37.4
Hoefchen am Hohenseh	silt loam	6.6		1.28	0.89	52.9
Dollendorf II	clay loam	7.3		1.57	0.90	33.2
Guadalupe	sandy loam	6.7		0.53	0.91	75.0
Springfield	silt loam	6.6		2.92	0.86	171.8
			arithmetic mean	1.39	0.89	74.1

Table 7.1.3.1- 6: Overall summary of adsorption constants and correlation coefficients in soils of FOE-thiadone

Soil	Texture (USDA)	pH	Annex Point / Reference No	$K_{F(ads)}$ [mL/g]	1/n [-]	$K_{OC(ads)}$ [mL/g]
Winder Vero Beach, FL	sand	5.8	KCA 7.1.3.1.2 /01	0.12 [2]	0.78 [1,2]	43 [1, 2]
Shipshe, Howe, IN	sandy loam	6.3		0.33	0.81 [1]	44 [1]
Drummer, Champaign, IL	silty clay loam	6.6		0.61	0.67 [1]	29 [1]
Oska-Martin Stilwell, KS	Silty clay	6.0		0.71	0.80 [1]	58 [1]
			arithmetic mean	0.55	0.76	43.7

[1] as reported in the review report by the European Commission (7469/VI/98-Final – 3rd July 2003)
[2] not considered for arithmetic mean as organic carbon content < 0.3%

CA 7.1.3.1.1 Adsorption and desorption of the active substance

The adsorption and desorption behavior of flufenacet in soil in batch equilibrium experiments was evaluated during the Annex I Inclusion and was accepted by the European Commission (7469/VI/98-Final – 3rd July 2003). The following studies are included in the Baseline Dossier:

Annex Point / Reference No	Author(s)	Year	Document No
KCA 7.1.3.1.1 /01	[redacted], I. V.; [redacted], S.	1992	M-002202-01-1
KCA 7.1.3.1.1 /02	[redacted], K. P.; [redacted], W.	1994	M-002186-01-1

Two additional studies have been performed for flufenacet and are submitted within this Supplemental Dossier for the flufenacet renewal of approval.

Report:	**KCA 7.1.3.1.1 /04; [redacted], H. P.; 2010**
Title:	[phenyl-UL-^{14}C]flufenacet: Adsorption on Two Japanese Soils
Report No:	MEF-10/534
Document No:	M-387572-01-1
Guidelines:	• Japanese MAFF New Test Guidelines 12 Nousan 8147 • OECD Test Guideline No. 106
GLP:	yes

Executive Summary

The adsorption/desorption behavior of [phenyl-UL-^{14}C]flufenacet was studied in two different soils in the dark in the laboratory at 25 ± 1 °C using the batch equilibrium method:

Soil	Source	Texture (USDA)	pH	OC [%]
Ibaraki Ushiku	Ushiku, Ibaraki, Japan	sandy loam	5.6	4.3
Hokkaido Kamikawa	Hokkaido, Kamikawa, Japan	loam	4.9	2.1

The adsorption phase of the study was carried out using air-dried soils pre-equilibrated in aqueous 0.01 M $CaCl_2$ solution with a soil-to-solution ratio of 1.5:10 (3 g soil DW/20 mL solution). Flufenacet was applied at nominal concentrations of 1.0, 0.3, 0.1, 0.03 and 0.01 mg/L in aqueous 0.01 M $CaCl_2$. The adsorption step was carried out for 24 hours under continuous agitation.

Flufenacet was sufficient stable throughout the study. The parental mass balances were 103.8 and 104.8 % of applied radioactivity [% AR] for soil Ibaraki Ushiku and Hokkaido Kamikawa, respectively.

Mean material balances were 98.0 and 96.9% AR for soil Ibaraki Ushiku and Hokkaido Kamikawa, respectively.

The adsorption constants $KF_{(ads)}$ of flufenacet ranged from 6.916 to 8.956 mL/g (arithmetic mean: 7.936 mL/g); the respective normalized adsorption constants $KOC_{(ads)}$ ranged from 160.8 to 426.5 mL/g (arithmetic mean: 293.6 mL/g). The Freundlich exponents 1/n were in the range of 0.8479 to 0.9583 (arithmetic mean: 0.9031), indicating that the concentration of the test item affects its adsorption behavior in the examined concentration range.

According to Briggs [17], flufenacet can be classified as low mobile for adsorption in soil Ibaraki Ushiku and as immobile in soil Hokkaido Kamikawa.

I. MATERIALS AND METHODS

A. MATERIALS

1. Test Item

[phenyl-UL-^{14}C]flufenacet	
CAS No	142459-58-3
Specific activity	6.11 MBq/mg
Radiochemical purity	> 99% HPLC with radioactivity detector and TLC, scan

2. Test Soils

The soils (Table 7.1.3.1.1- 4) were sampled from the field (upper horizon of 0 to 30 cm), sieved to a particle size of ≤ 2 mm and stored at ambient temperature for approx. 19 month before study start. The soils were air-dried before application. The soils were taken from agricultural areas representing different geographical origins and different soil properties as required by the guidelines.

[17] Briggs, G. G.: A Simple Relationship Between Soil Adsorption of Organic Chemicals and their Octanol/Water Partition Coefficients; Proc. 7th British Insecticide and Fungicide Conference, Nottingham/UK, 1973.

Table 7.1.3.1.1- 1: Physico-chemical properties of test soils

Parameter	Results / Units	
Soil Designation	Ibaraki Ushiku	Hokkaido Kamikawa
Geographic Location		
City	Ushiku city	Kamikawa-gun
State	Ibaraki pref.	Hokkaido island
Country	Japan	Japan
Soil Taxonomic Classification (USDA)	no information available	
Soil Series	volcanic ash OECD type 2	alluvial soil OECD type 4
Textural Class (USDA)	sandy loam	loam
Sand [%] [50 µm – 2 mm]	63	49
Silt [%] [2 µm – 50 µm]	26	32
Clay [%] [< 2 µm]	11	19
pH		
- in $CaCl_2$ (soil/$CaCl_2$ 1/2)	5.6	4.9
- in water (soil/water 1/1)	5.9	5.3
- in KCl	5.2	4.4
Organic Carbon [%]	4.3	2.1
Organic Matter [%] [1]	7.4	3.6
Cation Exchange Capacity [meq/100 g]	15.9	12.2
Water Holding Capacity at 0.33 bar (pF 2.5) [%]	41.9	36.5
Bulk Density (disturbed) [g/cm³]	0.78	0.97

[1] calculated as: OM [%] = OC [%] * 1.724 USDA: United States Department of Agriculture

B. STUDY DESIGN

1. Experimental Conditions

The test system for adsorption and desorption in batch equilibrium experiments consisted of Teflon® centrifuge tubes (volume 43 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.

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 1.5:10 (3 g soil $_{dry\ weight}$/20 mL solution). Flufenacet was applied at nominal concentrations of 1.0, 0.3, 0.1, 0.03 and 0.01 mg/L in aqueous 0.01 M $CaCl_2$ solution. The adsorption step was carried out for 24 hours in the dark at 25 ± 1 °C under continuous agitation.

2. Analytical Procedures

After each adsorption and desorption step the aqueous supernatant was separated from the soil by centrifugation and the amount of flufenacet in the supernatants was analyzed by liquid scintillation counting (LSC).

In the preliminary parental mass balance test, the soil was additionally extracted three times using acetonitrile/water (8:2, *v/v*). The aqueous supernatant and the combined soil extracts were analyzed by LSC and reversed phase HPLC/radiodetection to determine the stability of the test item and to establish the parental mass balance. The limit of detection (LOD) and limit of quantitation (LOQ) for HPLC/radiodetection analysis were 0.2 and 0.6% 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. After the adsorption steps, the soil was air-dried and the radioactivity content was determined by combustion/LSC to establish the material balance.

Adsorption and desorption isotherms were calculated by linear regression analysis of the adsorption or desorption data according to the Freundlich equation.

II. RESULTS AND DISCUSSION

A. MATERIAL BALANCE

Mean material balances ranged from 96.5 to 99.3% of applied radioactivity [% AR] (overall mean 98.0% AR) for soil Ibaraki Ushiku and from 94.1 to 98.9% AR (overall mean 96.9% AR) for soil Hokkaido Kamikawa. 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.

B. DEGRADATION OF TEST ITEM

Flufenacet was sufficient stable throughout the study. The parental mass balances were 103.8 and 104.8% of applied radioactivity [% AR] for soil Ibaraki Ushiku and Hokkaido Kamikawa, respectively.

C. FINDINGS

At the end of the adsorption phase, 53.4 – 71.8% AR was adsorbed to soil Ibaraki Ushiku and 57.4 – 63.8% AR to soil Hokkaido Kamikawa. The adsorption constants $K_{F(ads)}$ of flufenacet calculated based on the Freundlich isotherms of the tested soils Ibaraki Ushiku and Hokkaido Kamikawa were 6.916 and 8.956 mL/g, respectively. The normalized adsorption constants $K_{OC(ads)}$ (normalized to organic carbon content) of the tested soils Ibaraki Ushiku and Hokkaido Kamikawa were 160.8 and 426.5 mL/g, respectively. The Freundlich exponents 1/n were 0.8479 and 0.9583 for soils Ibaraki Ushiku and Hokkaido Kamikawa, respectively, indicating that the concentration of the test item affects its adsorption behavior in the examined concentration range (see Table 7.1.3.1.1- 5).

Table 7.1.3.1.1- 2: Percentage of adsorbed flufenacet in soils (mean values)

	Test Concentration [mg/L]				
Soil	**1.0**	**0.3**	**0.1**	**0.03**	**0.01**
Ibaraki Ushiku	53.4	59.1	64.2	67.8	71.8
Hokkaido Kamikawa	57.4	59.5	61.4	63.8	61.1

Table 7.1.3.1.1- 3: Adsorption constants and correlation coefficients of flufenacet in soil at 25 °C

Soil ID	Adsorption			
	K_F [mL/g]	1/n	R^2	K_{OC} [mL/g]
Ibaraki Ushiku	6.916	0.8479	0.9996	**160.8**
Hokkaido Kamikawa	8.956	0.9583	0.9972	**426.5**
Mean	7.936	0.9031	0.9984	**293.6**

III. CONCLUSIONS

The adsorption constants $K_{F(ads)}$ of flufenacet ranged from 6.916 to 8.956 mL/g (arithmetic mean: 7.936 mL/g); the respective normalized adsorption constants $K_{OC(ads)}$ ranged from 160.8 to 426.5 mL/g (arithmetic mean: 293.6 mL/g). The Freundlich exponents 1/n were in the range of 0.8479 to 0.9583 (arithmetic mean: 0.9031), indicating that the concentration of the test item affects its adsorption behavior in the examined concentration range.

*****

Report:	**KCA 7.1.3.1.1/03; [redacted], E. M., 2012**
Title:	[thiadiazole-5-^{14}C]FOE 5043 (flufenacet): Adsorption/Desorption on Five Soils
Report No:	EnSa-12-0517
Document No:	M-439282-01-1
Guidelines:	• OECD Test Guideline No. 106 • US-EPA OCSPP Test Guideline No. 835.1230 • Canadian PMRA Guideline DACO 8.2.4.2
GLP:	yes

Executive Summary

The adsorption/desorption behavior of [thiadiazole-5-^{14}C]flufenacet was studied in five different soils in the dark in the laboratory at 20 ± 2 °C using the batch equilibrium method:

Soil	Source	Texture (USDA)	pH	OC [%]
Laacherhof AXXa	Monheim, Germany	loamy sand	5.8	2.2
Hoefchen am Hobenseh	Burscheid, Germany	silt loam	6.5	1.6
Hauscheider Hof	Burscheid, Germany	silt loam	5.3	2.7
Dollendorf II	Blankenheim, Germany	loam	7.3	4.4
Laacherhof Wurmwiese	Monheim, Germany	sandy loam	5.1	1.7

The adsorption phase of the study was carried out using air-dried soils pre-equilibrated in aqueous 0.01 M $CaCl_2$ solution containing $HgCl_2$ (approx. 50 mg/L) with a soil-to-solution ratio of 1:4 (5 g soil DW/20 mL solution). Flufenacet was applied at nominal concentrations of 1.0, 0.3, 0.1, 0.03 and 0.01 mg/L in aqueous 0.01 M $CaCl_2$. The desorption phase was performed by supplying pre-adsorbed soil samples with fresh aqueous 0.01 M $CaCl_2$ solution containing $HgCl_2$ (approx. 50 mg/L) for all test concentrations. For the highest test concentration (1 mg/L) two additional desorption cycles were performed likewise. The adsorption and desorption steps were carried out each for 24 hours under continuous agitation.

Flufenacet was sufficient stable throughout the study. The parental mass balances were 101.4, 99.3, 100.2, 100.0 and 101.2% AR for soil Laacherhof AXXa, Hoefchen am Hohenseh, Hanscheider Hof, Dollendorf II and Laacherhof Wurmwiese, respectively.

Mean material balances were 101.8, 97.3, 95.9, 97.4 and 97.3% of applied radioactivity [% AR] for soil Laacherhof AXXa, Hoefchen am Hohenseh, Hanscheider Hof, Dollendorf II and Laacherhof Wurmwiese, respectively.

The adsorption constants $K_{F(ads)}$ of flufenacet calculated based on the Freundlich isotherms of the five test soils ranged from 3.280 to 7.495 mL/g (mean: 4.550 mL/g). The Freundlich exponents 1/n were in the range of 0.9033 to 0.9797 (mean: 0.9328), indicating that the concentration of the test item affects its adsorption behavior in the examined concentration range. The corresponding, calculated $K_{OC(ads)}$ values varied between 161.6 and 205.0 mL/g (mean: 185.8 mL/g).

After the first desorption phase between 15.8 – 41.1% of the initially adsorbed radioactivity was desorbed from the respective soils The desorption constants $K_{OC(des)}$ were 1.6 to 1.7 times higher than the $K_{OC(ads)}$ values, indicating a strengthened binding of the test item once adsorbed to the soil.

No correlation between the pH of the soils and the adsorption behavior of the test item was observed.

According to Briggs [17], flufenacet can be classified as low mobile for adsorption and for desorption in all tested soils.

I. MATERIALS AND METHODS

A. MATERIALS

1. Test Item

[thiadiazole-5-^{14}C]flufenacet
CAS No 142459-58-3
Specific activity 1.54 MBq/mg
Radiochemical purity >99% HPLC with radioactivity-detector and TLC, scan

2. Test Soils

The soils (Table 7.1.3.1.1- 4) were sampled freshly from the field (upper horizon of 0 to 20 cm), sieved to a particle size of ≤ 2 mm and stored refrigerated at ≤ 8 °C for a maximum period of 6 months before study start. The soils were air-dried before application. The soils were taken from agricultural areas representing different geographical origins and different soil properties as required by the guidelines.

Table 7.1.3.1.1- 4: Physico-chemical properties of test soils

Parameter	Results / Units				
Soil Designation	Laacherhof AXXa	Hoefchen am Hohenseh	Hanscheider Hof	Dollendorf II	Laacherhof Wurmwiese
Geographic Location					
City	Monheim	Burscheid	Burscheid	Blankenheim	Monheim
State	North-Rhine Westphalia	North-Rhine Westphalia	North-Rhine Westphalia	North-Rhine Westphalia	North-Rhine Westphalia
Country	Germany	Germany	Germany	Germany	Germany
GPS Coordinates	N 51° 04.6 E 006° 53.5'	N 51° 04.0' E 007° 06.3'	N 51° 04.5' E 007° 08.4'	N 50° 22. 9' E 006° 43.0'	N 51° 04.9' E 006° 55.3'
Soil Taxonomic Classification (USDA)	sandy, mixed, mesic Typic Cambudoll	loamy, mixed, mesic, Typic Argudalf	loamy-skeletal, mixed, semi-active, mesic Dystric Eutrudept	fine-loamy, mixed, active, frigid Typic Eutrudept	loamy, mixed, mesic, Typic Argudalf
Soil Series	no information available				
Textural Class (USDA)	loamy sand	silt loam	silt loam	loam	sandy loam
Sand [%] [50 µm – 2 mm]	79	15	31	37	53
Silt [%] [2 µm – 50 µm]	16	70	54	40	30
Clay [%] [< 2 µm]	5	15	15	23	17
pH					
- in $CaCl_2$ (soil/$CaCl_2$ 1/2)	5.8	6.5	5.3	7.3	5.1
- in water (soil/water 1/1)	6.2	6.7	5.7	7.5	5.4
- in water (saturated paste)	6.0	6.8	5.8	7.4	5.5
- in KCl	5.7	6.1	4.9	7.0	4.7
Organic Carbon [%]	3.8	2.8	4.7	7.6	2.9
Organic Matter [%] [1]	2.2	1.6	2.7	4.4	1.7
Cation Exchange Capacity [meq/100 g]	10.0	11.6	9.6	19.2	9.9
Water Holding Capacity					
maximum [g H_2O *ad* 100 g soil DW]	49.9	55.9	61.3	78.5	61.9
at 0.1 bar (pF 2.0) [%]	17.2	31.7	36.7	41.1	20.1
Bulk Density (disturbed) [g/cm³]	1.20	1.11	1.04	0.98	1.08

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

DAT: days after treatment
DW: dry weight
GPS: global positioning system
USDA: United States Department of Agriculture

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.

The adsorption phase was carried out using air-dried soils equilibrated in aqueous 0.01 M $CaCl_2$ solution containing $HgCl_2$ (approx. 50 mg/L) with a soil-to-solution ratio of 1.4 (5 g soil $_{dry\ weight}$/ 20 mL solution). Flufenacet was applied at nominal concentrations of 1.0, 0.3, 0.1, 0.03 and 0.01 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 containing $HgCl_2$ (approx. 50 mg/L) for all test concentrations. For the highest test concentration (1.0 mg/L) two additional desorption cycles were performed likewise. The adsorption and desorption steps were carried out each for 24 hours in the dark at 20 ± 2 °C under continuous agitation.

2. Analytical Procedures

After each adsorption and desorption step the aqueous supernatant was separated from the soil by centrifugation and the amount of flufenacet in the supernatants was analyzed by liquid scintillation counting (LSC).

In the preliminary parental mass balance test, the soil was additionally extracted four times using acetonitrile/water (1:1, *v/v*). The aqueous supernatant and the combined soil extracts were analyzed by LSC and reversed phase HPLC/radiodetection to determine the stability of the test item and to establish the parental mass balance. The limit of detection (LOD) and limit of quantitation (LOQ) for HPLC/radiodetection analysis were 0.3 and 0.9% AR, respectively.

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 steps, the soil was air-dried and the radioactivity content determined by combustion/LSC to establish the material balance.

Adsorption and desorption isotherms were calculated by linear regression analysis of the adsorption or desorption data according to the Freundlich equation.

II. RESULTS AND DISCUSSION

A. MATERIAL BALANCE

Mean material balances were 101.8, 97.3, 95.9, 97.4 and 97.3% of applied radioactivity [% AR] for soil Laacherhof AXXa, Hoefchen am Hohenseh, Hanscheider Hof, Dollendorf II and Laacherhof Wurmwiese, respectively. 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.

B. DEGRADATION OF TEST ITEM

Flufenacet was sufficient stable throughout the study. The parental mass balances were 101.4, 99.3, 100.2, 100.0 and 101.2% AR after the total incubation time of 96 hours (24 h adsorption + 3 x 24 h desorption) for soil Laacherhof AXXa, Hoefchen am Hohenseh, Hanscheider Hof, Dollendorf II and Laacherhof Wurmwiese, respectively.

C. FINDINGS

At the end of the adsorption phase, 47.1-55.8% AR was adsorbed to soil Laacherhof AXXa, 44.3-54.6% AR to soil Hoefchen am Hohenseh, 57.1-65.4% AR to soil Hanscheider Hof, 67.2-76.9% AR to soil Dollendorf II and 44.6-48.9% AR to soil Laacherhof Wurmwiese. The adsorption constants $K_{F(ads)}$

of Flufenacet calculated based on the Freundlich isotherms of the five test soils ranged from 3.280 to 7.495 mL/g (mean: 4.550 mL/g) and the normalized adsorption constants $K_{OC(ads)}$ (normalized to organic carbon content) ranged from 161.6 and 205.0 mL/g (mean: 185.8 mL/g).The Freundlich exponents 1/n were in the range of 0.9033 to 0.9797 (mean: 0.9328), indicating that the concentration of the test item affects its adsorption behavior in the examined concentration range (see Table 7.1.3.1.1- 5).

At the end of the first desorption phase, 33.7-40.7%, 33.5-40.4%, 25.0-30.0%, 15.8-22.7% and 37.6-41.1% of the initially adsorbed amount were desorbed from soil Laacherhof AXXa, Hoefchen am Hohenseh, Hanscheider Hof, Dollendorf II and Wurmwiese, respectively. The desorption constants $K_{F(des)}$ (mean: 7.470 mL/g) and the normalized desorption constants $K_{OC(des)}$ (mean: 309.7 mL/g) were 1.6 to 1.7 times higher than the adsorption coefficients $K_{d(ads)}$ / $K_{OC(ads)}$, indicating a strengthened binding of the test item once adsorbed to the soil.

Table 7.1.3.1.1- 5: Percentage of adsorbed and desorbed flufenacet in soils (mean values)

	Test Concentration [mg/L]									
	Adsorption [1]					Desorption [2]				
Soil	**1.0**	**0.3**	**0.1**	**0.03**	**0.01**	**1.0**	**0.3**	**0.1**	**0.03**	**0.01**
Laacherhof AXXa	47.1	51.6	53.3	55.3	55.8	40.7	37.2	35.5	33.7	35.0
Hoefchen am Hohenseh	44.3	49.0	54.6	52.8	53.1	40.4	37.4	33.5	34.3	34.3
Hanscheider Hof	57.1	60.8	62.0	65.4	64.9	30.0	27.2	26.6	25.0	24.2
Dollendorf II	67.2	71.1	72.8	75.4	76.9	22.7	19.9	18.5	16.7	15.8
Laacherhof Wurmwiese	44.6	47.3	47.2	48.9	46.4	41.1	38.2	38.8	37.6	40.0

[1] end of adsorption phase, mean values expressed as percentage of applied radioactivity
[2] end of first desorption phase, mean values expressed as percentage of the initially adsorbed amount

Table 7.1.3.1.1- 6: Adsorption/desorption constants and correlation coefficients of flufenacet in soil at 20 °C

Soil	Adsorption				Desorption			
	K_F [mL/g]	1/n	R^2	K_{OC} [mL/g]	K_F [mL/g]	1/n	R^2	K_{OC} [mL/g]
Laacherhof AXXa	3.555	0.9285	0.9991	**161.6**	5.580	0.9440	0.9988	**253.6**
Hoefchen am Hohenseh	3.280	0.9262	0.9965	**205.0**	5.637	0.9426	0.9980	**352.3**
Hanscheider Hof	5.101	0.9265	0.9992	**188.9**	8.488	0.9374	0.9996	**314.4**
Dollendorf II	7.495	0.9033	0.9994	**178.5**	11.707	0.9081	0.9996	**278.7**
Laacherhof Wurmwiese	3.319	0.9797	0.9966	**195.2**	5.940	0.9886	0.9967	**349.4**
Mean	4.550	0.9328	0.9982	**185.8**	7.470	0.9441	0.9985	**309.7**

III. CONCLUSIONS

The adsorption constants $K_{F(ads)}$ of flufenacet ranged from 3.280 to 7.495 mL/g (arithmetic mean: 4.550 mL/g); the respective normalized adsorption constants $K_{OC(ads)}$ ranged from 161.6 to 205.0 mL/g (arithmetic mean: 185.8 mL/g). The Freundlich exponents 1/n were in the range of 0.9033 to 0.9797 (arithmetic mean: 0.9328), indicating that the concentration of the test item affects its adsorption behavior in the examined concentration range. No correlation between the pH of the soils and the adsorption behavior of the test item was observed.

CA 7.1.3.1.2 Adsorption and desorption of metabolites, breakdown and reaction products

The adsorption and desorption behavior of the major degradation products FOE oxalate and FOE sulfonic acid in soil in batch equilibrium experiments was evaluated during the Annex I Inclusion and was accepted by the European Commission (7469/VI/98-Final – 3rd July 2003). The following study is included in the Baseline Dossier:

Annex Point / Reference No	Author(s)	Year	Document No
KCA 7.1.3.1.2 /01	[redacted], M. R.; [redacted], P. Y.; [redacted], V. A.	1994	M-002185-01-1

The newly identified major degradation product FOE-thiadone was already characterized within the study M-002185-01-1 (Baseline Dossier, KCA 7.1.3.1.2/01) which was summarized in the Baseline Dossier with regard to the major degradation products FOE oxalate and FOE sulfonic acid.

Furthermore, three additional studies have been performed for the major degradation products FOE methylsulfone, FOE 5043-trifluoroethanesulfonic acid and trifluoroacetic acid and are submitted within this Supplemental Dossier for the flufenacet renewal of approval.

Report:	**KCA 7.1.3.1.2 /01; [redacted], M. R.; [redacted], P. Y.; [redacted], V. A.; 1994**
Title:	Soil Adsorption/Desorption of FOE 5043 Degradates: FOE Sulfonic Acid, FOE Methyl Sulfoxide, FOE Oxalate, FOE Alcohol, and Thiadone
Report No:	MR-106598
Document No:	M-002185-01-1
Guidelines:	• EPA Ref: 163-1, Adsorption/desorption
GLP:	yes

Executive Summary

The adsorption/desorption behaviors of the degradation products FOE methylsulfoxide, FOE sulfonic acid, FOE oxalate, FOE alcohol and FOE-thiadone were studied in four different soils in the dark in the laboratory at 23.5 ± 1.5 °C using the batch equilibrium method:

Soil	Source	Texture (USDA)	pH	OC [%]
Winder	Vero Beach, USA	sand	5.8	0.27
Shipshe	Howe, USA	sandy loam	6.3	0.75
Drummer	Champaign, USA	silty clay loam	6.6	2.13
Oska-Martin	Stilwell, USA	silty clay	6.0	1.21

The adsorption phase of the study was carried out using air-dried soils and aqueous 0.01 M $CaCl_2$ solution with a soil-to-solution ratio of 3:10 (6 g soil $_{dry\ weight}$/20 mL solution). Test item were applied at nominal concentrations of 5.0, 1.0, 0.2 and 0.04 mg/L in aqueous 0.01 M $CaCl_2$ (containing max. 0.5% acetonitrile). The desorption phase was performed by supplying pre-adsorbed soil samples with fresh aqueous 0.01 M $CaCl_2$ solution for all test concentrations. For the highest test concentration (5.0 mg/L) two additional desorption cycles were performed likewise. The adsorption and desorption steps were carried out each for 24 hours under continuous agitation.

In the following those parts of the study are summarized which refer to the newly identified degradation product FOE-thiadone. Data for the adsorption/desorption behavior of the degradation products FOE oxalate and FOE sulfonic acid have been already presented in the Baseline Dossier.

FOE-thiadone was sufficient stable throughout the study. The amount of FOE-thiadone ranged from 95.4 to 100.0% in all adsorption and desorption solutions of the highest test concentration of the definitive test.

Mean material balances were 96.5, 92.1, 84.6 and 84.8% of applied radioactivity (% AR) for soil Winder, Shipshe, Drummer and Oska-Martin, respectively.

The adsorption constants $K_{F(ads)}$ of FOE-thiadone calculated based on the Freundlich isotherms of the four test soils ranged from 0.12 to 0.71 mL/g. The Freundlich exponents 1/n were in the range of 0.673 to 0.807, indicating that the concentration of the test item affects its adsorption behavior in the examined concentration range. The corresponding, calculated $K_{OC(ads)}$ values varied between 29 and 58 mL/g.

After the first desorption phase between 1.3 – 62.2% of the initially adsorbed radioactivity was desorbed from the respective soils The desorption constants $K_{OC(des)}$ were 2 to 4 times higher than the $K_{OC(ads)}$ values.

The results indicate that the adsorption behavior of FOE-thiadone is dependent on the soil organic content.

According to Briggs [17], FOE-thiadone can be classified as very high to high mobile in all tested soils.

I. MATERIALS AND METHODS

A. MATERIALS

1. Test Item

FOE-thiadone	
BAS No	94503
Specific activity	12.40 MBq/mg (≙ 57 mCi/mmol = 335 µCi/mg)
Radiochemical purity	99.7%

2. Test Soils

The soils (Table 7.1.3.1.2-1) were sieved to a particle size of ≤ 2 mm. The soils were taken from agricultural areas representing different geographical origins and different soil properties as required by the guidelines.

Table 7.1.3.1.2- 1: Physico-chemical properties of test soils

Parameter	Results / Units			
Soil Designation	Winder	Shipshe	Drummer	Oska-Martin
Geographic Location				
City	Vero Beach	Howe	Champaign	Stilwell
State	Florida	Indiana	Illinois	Kansas
Country	USA	USA	USA	USA
Soil Series	no information available			
Textural Class (USDA)	sand	sandy loam	silty clay loam	silty clay
Sand [%] [50 µm – 2 mm]	92.5	68.5	11.1	3.1
Silt [%] [2 µm – 50 µm]	1.3	17.6	54.1	47.1
Clay [%] [< 2 µm]	6.3	13.9	34.8	49.8
pH in water (soil/water 1/1)	5.8	6.3	6.6	6.0
Organic Carbon [%]	0.27	0.75	2.13	1.21
Organic Matter [%] [1]	0.5	1.3	3.7	2.1
Cation Exchange Capacity [meq/100 g]	3.3	7.9	22.4	29.3
Water Holding Capacity at 0.33 bar (pF 2.5) [%]	5.0	8.3	24.8	28.1

[1] calculated as: OM [%] = OC [%] · 1.724 USDA: United States Department of Agriculture

B. STUDY DESIGN

1. Experimental Conditions

The test system for adsorption and desorption in batch equilibrium experiments consisted of glass centrifuge tubes closed with Teflon® lined caps. The experiments were performed in triplicate.

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.

The adsorption phase was carried out using air-dried soils and aqueous 0.01 M $CaCl_2$ solution with a soil-to-solution ratio of 3:10 (6 g soil $_{dry\ weight}$ / 20 mL solution). FOE-thiadone was applied at nominal concentrations of 5.0, 1.0, 0.2 and 0.04 mg/L in aqueous 0.01 M $CaCl_2$ solution (containing max. 0.5% acetonitrile). The desorption phase was performed by supplying pre-adsorbed soil samples with fresh aqueous 0.01 M $CaCl_2$ for all test concentrations. For the highest test concentration (5.0 mg/L) two additional desorption cycles were performed likewise. The adsorption and desorption steps were carried out each for 24 hours in the dark at 23.5 ± 1.5 °C under continuous agitation.

2. Analytical Procedures

After each adsorption and desorption step the aqueous supernatant was separated from the soil by centrifugation and the amount of FOE-thiadone in the supernatants was analyzed by liquid scintillation counting (LSC).

The stability of the test item was demonstrated by HPLC/radiodetection analysis of the adsorption and desorption solutions of the highest test concentration of the definitive test. The limit of detection (LOD) for HPLC/radiodetection analysis corresponds to 1.2% of the applied radioactivity.

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 steps, the soil was air-dried and the radioactivity content determined by combustion/LSC to establish the material balance.

Adsorption and desorption isotherms were calculated by linear regression analysis of the adsorption or desorption data according to the Freundlich equation.

II. RESULTS AND DISCUSSION

A. MATERIAL BALANCE

Mean material balances were 96.5, 92.1, 84.6 and 84.8% of applied radioactivity [% AR] for soil Winder, Shipshe, Drummer and Oska-Martin, respectively.

B. DEGRADATION OF TEST ITEM

FOE-thiadone was sufficient stable throughout the study, as demonstrated by HPLC/radiodetection analysis. The amount of FOE-thiadone ranged from 95.4 to 100.0% in all adsorption and desorption solutions of the highest test concentration of the definitive test.

C. FINDINGS

At the end of the adsorption phase, 1.6 to 7.8% AR was adsorbed to soil Winder, 6.7 to 16.6% AR to soil Shipshe, 8.6 to 36.7% AR to soil Drummer and 11.3 to 28.6% AR to soil Oska-Martin. The adsorption constants $K_{F(ads)}$ of FOE-thiadone calculated based on the Freundlich isotherms of the four test soils ranged from 0.12 to 0.71 mL/g and the normalized adsorption constants $K_{OC(ads)}$ (normalized to organic carbon content) ranged from 29 and 58 mL/g. The Freundlich exponents 1/n were in the range of 0.673 to 0.807, indicating that the concentration of the test item affects its adsorption behavior in the examined concentration range (see Table 7.1.3.1.2- 3).

At the end of the first desorption phase, 13.4 to 62.2% (single sample up to 116.4%), 15.5 to 36.0%, 1.5 to 24.5% and 15.4 to 22.4% (highest test concentration up to - 8.7%) of the initially adsorbed amount were desorbed from soil Winder, Shipshe, Drummer and Oska-Martin, respectively. The desorption constants $K_{F(des)}$ (range from 0.35 to 2.10 mL/g) and the normalized desorption constants $K_{OC(des)}$ (range from 73 to 189 mL/g) were 2 to 4 times higher than the adsorption coefficients $K_{d(ads)}$ / $K_{OC(ads}$.

Table 7.1.3.1.2- 2: Percentage of adsorbed and desorbed FOE-thiadone in soils (ranges of triplicates)

Soil	Test Concentration [mg/L]							
	Adsorption [1]				Desorption [2]			
	5.0	1.0	0.2	0.04	5.0	1.0	0.2	0.04
Winder	2.1 – 3.7	1.6 – 4.4	2.8 – 5.3	6.2 – 7.8	47.6 – 62.2	23.0 – 28.7[3]	24.5 – 50.4	13.4 – 28.8
Shipshe	6.7 – 6.9	8.5 – 10.0	11.0 – 12.7	15.2 – 16.6	15.5 – 26.8	25.3 – 30.0	27.5 – 36.0	27.8 – 29.5
Drummer	8.6 – 10.3	15.9 – 16.2	25.5 – 26.2	35.5 – 36.7	10.4 – 24.5	13.8 – 17.1	1.5 – 4.0	6.0 – 10.1
Oska-Martin	11.3 – 13.3	19.4 – 20.0	24.2 – 25.5	27.2 – 28.6	-5.6 - -8.7	15.6 – 22.4	15.4 – 17.6	14.9 – 19.0

[1] end of adsorption phase, mean values expressed as percentage of applied radioactivity
[2] end of first desorption phase, mean values expressed as percentage of the initially adsorbed amount
[3] single value of 116.4%

Table 7.1.3.1.2- 3: Adsorption/desorption constants and correlation coefficients of FOE-thiadone in soil at 20 °C

Soil	Adsorption				Desorption			
	K_F [mL/g]	1/n	R^2	K_{OC} [mL/g]	K_F [mL/g]	1/n	R^2	K_{OC} [mL/g]
Winder	0.12	0.782	0.975	**43**	0.35	0.705	0.958	**128**
Shipshe	0.33	0.807	0.999	**44**	1.42	0.876	0.998	**189**
Drummer	0.61	0.673	0.999	**29**	1.56	0.654	0.995	**73**
Oska-Martin	0.71	0.798	0.998	**58**	2.10	0.888	0.998	**174**

III. CONCLUSIONS

The adsorption constants $K_{F(ads)}$ of FOE-thiadone ranged from 0.12 to 0.71 mL/g, the respective normalized adsorption constants $K_{OC(ads)}$ ranged from 29 and 58 mL/g. The Freundlich exponents 1/n were in the range of 0.673 to 0.807, indicating that the concentration of the test item affects its adsorption behavior in the examined concentration range. The results indicate that the adsorption behavior of FOE-thiadone is dependent on the soil organic content.

*****

Report:	**KCA 7.1.3.1.2 /03; [redacted], W.; 2011**
Title:	[Phenyl-UL-^{14}C] BCS-CO62475: Adsorption/Desorption in Five Different Soils
Report No:	AS158
Document No:	M-411141-01-1
Guidelines:	• OECD Test Guideline No. 106 • US EPA OCSPP Test Guideline No. 835.1220 • Canadian PMRA Guideline DACO 8.2.4.2 • Commission Directive 95/36/EC amending Council Directive 91/414/EEC
GLP:	yes

Executive Summary

The adsorption/desorption behavior of [phenyl-UL-^{14}C]BCS-CO62475 (≙[phenyl-UL-^{14}C]FOE methylsulfone) was studied in five different soils in the dark in the laboratory at 20 ± 2 °C using the batch equilibrium method:

Soil	Source	Texture (USDA)	pH	OC [%]
Wurmwiese	Monheim, Germany	loam	5.3	1.8
Hoefchen am Hohenseh	Burscheid, Germany	silt loam	6.6	2.4
Dollendorf II	Blankenheim, Germany	clay loam	7.3	4.6
Guadalupe	Guadalupe, USA	sandy loam	6.7	0.7
Springfield	Springfield, USA	silt loam	6.6	1.7

The adsorption phase of the study was carried out using air-dried soils pre-equilibrated in aqueous 0.01 M $CaCl_2$ solution with a soil-to-solution ratio of 1:2 (10 g soil $_{dry\ weight}$/20 mL solution) for soils Wurmwiese, Hoefchen am Hohenseh and Dollendorf II, 1:1 (20 g soil $_{dry\ weight}$/20 mL solution) for soil Guadalupe and 1:10 (2 g soil $_{dry\ weight}$/20 mL solution) for soil Springfield. FOE methylsulfone was applied at nominal concentrations of 1.0, 0.3, 0.1, 0.03 and 0.01 mg/L in aqueous 0.01 M $CaCl_2$. The desorption phase was performed by supplying pre-adsorbed soil samples with fresh aqueous 0.01 M

$CaCl_2$ solution containing $HgCl_2$ (approx. 50 mg/L) for all test concentrations. For the highest test concentration (1 mg/L) two additional desorption cycles were performed likewise. The adsorption and desorption steps were carried out each for 24 hours under continuous agitation.

FOE methylsulfone was sufficient stable throughout the study. The parental mass balances after 96 h were 93.7, 93.8, 90.5, 92.6 and 94.8% AR for soil Wurmwiese, Hoefchen am Hohenseh, Dollendorf II, Guadalupe and Springfield, respectively.

Material balances ranged from 97.9 to 103.4 % of applied radioactivity [% AR] for soil Wurmwiese, from 93.3 to 98.7% AR for soil Hoefchen am Hohenseh, from 96.0 to 99.5% AR for soil Dollendorf II, from 96.9 to 99.7% AR for soil Guadalupe and from 86.1 to 98.6% AR for soil Springfield.

The adsorption constants $K_{F(ads)}$ of FOE methylsulfone calculated based on the Freundlich isotherms of the five test soils ranged from 0.5253 to 2.9201 mL/g (mean: 1.3904 mL/g). The Freundlich exponents 1/n were in the range of 0.8602 to 0.9097 (mean: 0.8898), indicating that the concentration of the test item affects its adsorption behavior in the examined concentration range. The corresponding, calculated $K_{OC(ads)}$ values varied between 33.2 and 171.8 mL/g (mean: 74.1 mL/g).

After the first desorption phase between 24.1 – 60.0% of the initially adsorbed radioactivity was desorbed from the respective soils The desorption constants $K_{OC(des)}$ were 1.1 to 1.2 times higher than the $K_{OC(ads)}$ values.

According to Briggs [17], FOE methylsulfone can be classified as low mobile or mobile in the tested soils.

I. MATERIALS AND METHODS

A. MATERIALS

1. Test Item

[phenyl-UL-^{14}C]BCS-CO62475 (report name: FOE methylsulfone)
Sample ID KML 9082
Specific activity 3.26 MBq/mg
Radiochemical purity > 98% HPLC with radioactivity-detector

2. Test Soils

The soils (Table 7.1.3.1.2-4) were sampled from the field (upper horizon of 0 to 20 cm or 0 to 6 inches), sieved to a particle size of ≤ 2 mm and stored for a maximum period of 25 months before study start. The soils were air-dried before application. The soils were taken from agricultural areas representing different geographical origins and different soil properties as required by the guidelines.

Table 7.1.3.1.2- 4: Physico-chemical properties of test soils

Parameter	Results / Units				
Soil Designation	Laacherhof Wurmwiese	Hoefchen am Hohenseh	Dollendorf II	Guadalupe	Springfield
Geographic Location					
City	Monheim	Burscheid	Blankenheim	Guadalupe.	Springfield
State	North-Rhine Westphalia	North-Rhine Westphalia	North-Rhine Westphalia	California	Nebraska
Country	Germany	Germany	Germany	USA	USA
GPS Coordinates	N 51° 04.9' E 006° 55.2'	N 51° 04.0' E 007° 06.3'	N 50° 22.9' E 006° 43.0'	N 35° 01' W 120° 36'	N 96° 15' W 41° 03'
Textural Class (USDA)	loam	silt loam	clay loam	sandy loam	silt loam
Sand [%] [50 µm – 2 mm]	51	27	31	56.0	12.7
Silt [%] [2 µm – 50 µm]	28	54	38	32.6	60.8
Clay [%] [< 2 µm]	21	19	31	11.4	26.5
pH					
- in $CaCl_2$ (soil/$CaCl_2$ 1/2)	5.3	6.6	7.3	6.7	6.6
- in water (soil/water 1/1)	5.5	6.8	7.4	6.8	7.2
Organic Carbon [%]	1.8	2.4	4.6	0.7	1.7
Organic Matter [%] [1]	3.1	4.1	7.9	1.1	2.9
Cation Exchange Capacity [meq/100 g]	10.8	13.9	21.9	16.1	16.1

[1] calculated as: OM [%] = OC [%] · 1.724 USDA: United States Department of Agriculture

B. STUDY DESIGN

1. Experimental Conditions

The test system for adsorption and desorption in batch equilibrium experiments consisted of borosilicate glass centrifuge tubes (volume 42 mL) closed with Teflon® lined 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.

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 1:2 (10 g soil $_{dry\ weight}$/20 mL solution) for soils Wurmwiese, Hoefchen am Hohenseh and Dollendorf II, 1:1 (20 g soil $_{dry\ weight}$/20 mL solution) for soil Guadalupe and 1:10 (2 g soil $_{dry\ weight}$/20 mL solution) for soil Springfield. FOE methylsulfone was applied at nominal concentrations of 1.0, 0.3, 0.1, 0.03 and 0.01 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 all test concentrations. For the highest test concentration (1.0 mg/L) two additional desorption cycles were performed likewise. The adsorption and desorption steps were carried out each for 24 hours in the dark at 20 ± 2 °C under continuous agitation.

2. Analytical Procedures

After each adsorption and desorption step the aqueous supernatant was separated from the soil by centrifugation and the amount of FOE methylsulfone in the supernatants was analyzed by liquid scintillation counting (LSC).

In the preliminary parental mass balance test, the soil was additionally extracted up to four times using acetonitrile/water (1:1, *v/v*). The aqueous supernatant and the combined soil extracts were analyzed by LSC and reversed phase HPLC/radiodetection to determine the stability of the test item and to establish the parental mass balance.

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 steps, the soil was mixed with approximately 0.4 g cellulose/g soil, air-dried and the radioactivity content determined by combustion/LSC to establish the material balance.

Adsorption and desorption isotherms were calculated by linear regression analysis of the adsorption or desorption data according to the Freundlich equation.

II. RESULTS AND DISCUSSION

A. MATERIAL BALANCE

Material balances ranged from 97.9 to 103.4% of applied radioactivity [% AR] for soil Wurmwiese, from 93.3 to 98.7% AR for soil Hoefchen am Hohenseh, from 96.0 to 99.5% AR for soil Dollendorf II, from 96.9 to 99.7% AR for soil Guadalupe and from 86.1[18] to 98.6% AR for soil Springfield. 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.

B. DEGRADATION OF TEST ITEM

FOE methylsulfone was sufficient stable throughout the study. The parental mass balances after 96 h were 93.7, 93.8, 90.5, 92.6 and 94.8% AR for soil Wurmwiese, Hoefchen am Hohenseh, Dollendorf II, Guadalupe and Springfield, respectively.

C. FINDINGS

At the end of the adsorption phase, 23.8 to 36.4% AR was adsorbed to soil Wurmwiese, 39.4 to 53.3% AR to soil Hoefchen am Hohenseh, 44.1 to 56.2% AR to soil Dollendorf II, 34.4 to 44.9% AR to soil Guadalupe and 22.7 to 36.9% AR to soil Springfield.

The adsorption constants $K_{F(ads)}$ of FOE methylsulfone calculated based on the Freundlich isotherms of the five test soils ranged from 0.5253 to 2.9201 mL/g (mean: 1.3904 mL/g) and the normalized adsorption constants $K_{OC(ads)}$ (normalized to organic carbon content) ranged from 33.2 and 171.8 mL/g (mean: 74.1 mL/g). The Freundlich exponents 1/n were in the range of 0.8602 to 0.9097 (mean: 0.8898), indicating that the concentration of the test item affects its adsorption behavior in the examined concentration range (see Table 7.1.3.1.2- 5).

At the end of the first desorption phase, 39.2 to 49.5%, 27.4 to 36.8%, 24.5 to 31.9%, 24.1 to 33.4% and 51.4 to 60.0% of the initially adsorbed amount were desorbed from soil Wurmwiese, Hoefchen am Hohenseh, Dollendorf II, Guadalupe and Springfield, respectively. The desorption constants $K_{F(des)}$

[18] Recoveries < 90% AR were caused by technical problems during the soil combustion.

(mean: 1.6435 mL/g) and the normalized desorption constants $K_{OC(des)}$ (mean: 87.1 mL/g) were 1.1 to 1.2 times higher than the adsorption coefficients $K_{d(ads)}$ / $K_{OC(ads)}$.

Table 7.1.3.1.2- 5: Percentage of adsorbed and desorbed FOE methylsulfone in soils (mean values)

Soil	Test Concentration [mg/L] Adsorption [1] 1.0	0.3	0.1	0.03	0.01	Desorption [2] 1.0	0.3	0.1	0.03	0.01
Wurmwiese	24.2	28.5	31.7	34.0	34.9	47.5	44.9	42.4	42.2	40.7
Hoefchen am Hohenseh	39.5	44.0	48.0	50.6	53.1	35.7	32.7	30.8	28.7	27.9
Dollendorf II	44.4	48.8	51.7	55.3	56.2	31.6	28.0	27.0	25.2	25.7
Guadalupe	34.4	38.2	40.9	43.2	44.7	33.0	32.7	31.1	29.0	27.1
Springfield	23.0	26.6	29.8	34.0	36.7	59.7	59.7	57.4	53.0	51.7

[1] end of adsorption phase, mean values expressed as percentage of applied radioactivity
[2] end of first desorption phase, mean values expressed as percentage of the initially adsorbed amount

Table 7.1.3.1.2- 6: Adsorption/desorption constants and correlation coefficients of FOE methylsulfone in soil at 20 °C

Soil	Adsorption K_F [mL/g]	1/n	R^2	K_{OC} [mL/g]	Desorption K_F [mL/g]	1/n	R^2	K_{OC} [mL/g]
Wurmwiese	0.6582	0.8915	0.9990	**37.4**	0.7693	0.8980	0.9992	**43.7**
Hoefchen am Hohenseh	1.2797	0.8875	0.9997	**52.9**	1.4666	0.8931	0.9997	**60.6**
Dollendorf II	0.5688	0.9001	0.9996	**33.2**	1.8200	0.9124	0.9993	**38.6**
Guadalupe	0.5253	0.9097	0.9997	**75.0**	0.5671	0.9050	1.0000	**81.0**
Springfield	2.9201	0.8602	0.9999	**171.8**	2.5944	0.8833	0.9994	**211.4**
Mean	1.3904	0.8898	0.9996	**74.1**	1.6435	0.8984	0.9995	**87.1**

III. CONCLUSIONS

The adsorption constants $K_{F(ads)}$ of FOE methylsulfone ranged from 0.5253 to 2.9201 mL/g (arithmetic mean: 1.3904 mL/g); the respective normalized adsorption constants $K_{OC(ads)}$ ranged from 33.2 and 171.8 mL/g (arithmetic mean: 74.1 mL/g). The Freundlich exponents 1/n were in the range of 0.8602 to 0.9097 (arithmetic mean: 0.8898), indicating that the concentration of the test item affects its adsorption behavior in the examined concentration range.

*****

Report:	**KCA 7.1.3.1.2 /04; [redacted], M.; 2013**
Title:	Determination of the Adsorption/Desorption Behavior of FOE 5043-trifluoroethanesulfonic Acid in Five Soils
Report No:	S11-03923
Document No:	M-449893-01-1
Guidelines:	• OECD Test Guideline No. 106 • US EPA OCSPP Test Guideline No. 835.1230
GLP:	yes

Executive Summary

The adsorption/desorption behavior of BCS-CU62474 (2,2,2-trifluoroethanesulfonate; report name: FOE 5043-trifluoroethanesulfonic acid) was studied in five different soils in the dark in the laboratory at 20 ± 2 °C using the batch equilibrium method:

Soil	Source	Texture (USDA)	pH	OC [%]
Laacherhof AXXa	Monheim, Germany	loamy sand	6.4	1.8
Dollendorf II	Blankenheim, Germany	loam	7.4	5.0
Hoefchen am Hohenseh	Burscheid, Germany	silt loam	6.5	1.8
Hanscheider Hof	Burscheid, Germany	silt loam	5.0	2.8
Laacherhof Wurmwiese	Monheim, Germany	sandy loam	5.2	1.9

The adsorption phase of the study was carried out using air-dried soils pre-equilibrated in aqueous 0.01 M $CaCl_2$ solution with a soil-to-solution ratio of 1:1 (50 g soil DW / 50 mL solution). Unlabeled BCS-CU62474 (2,2,2-trifluoroethanesulfonate) was applied at nominal concentrations of 1.0, 0.3, 0.1, 0.03 and 0.01 mg/L in aqueous 0.01 M $CaCl_2$. The adsorption step was carried out each for 96 hours under continuous agitation.

FOE 5043-trifluoroethanesulfonic acid was sufficient stable throughout the study. The parental mass balances after 96 h were 98.3, 102.4, 92.1, 103.0 and 104.6% AR for soil Laacherhof AXXa, Dollendorf II, Hoefchen am Hohenseh, Hanscheider Hof and Laacherhof Wurmwiese, respectively.

Only low to virtually no adsorption and to some extend also negative adsorption were detected at each test item concentration in the definitive test, therefore, no desorption step was conducted. However, using this data 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.

Considering the measured values it can be assumed that FOE 5043-trifluoroethanesulfonic acid has a high mobility in the tested soils.

I. MATERIALS AND METHODS

A. MATERIALS

1. Test Item

unlabeled BCS-CU62474 (sodium 2,2,2-trifluoroethanesulfonate; report name [1]: FOE 5043-trifluoroethanesulfonic acid)

Batch ID	NLL8865-4-1
Certificate No.	MZ 00482
Chemical purity	99.4%, ^{19}F-NMR

2. Test Soils

The soils (Table 7.1.3.1.2- 7) were sampled freshly from the field (upper horizon of 0 to 20 cm), sieved to a particle size of ≤ 2 mm, air-dried and stored at ambient temperature for a maximum period of one year before study start. The soils were taken from agricultural areas representing different geographical origins and different soil properties as required by the guidelines.

Table 7.1.3.1.2- 7: Physico-chemical properties of test soils

Parameter	Results / Units				
Soil Designation	Laacherhof AXXa	Dollendorf II	Hoetchen am Hohenseh	Hanschleider Hof	Laacherhof Wurmwiese
Geographic Location					
City	Monheim	Blankenheim	Burscheid	Burscheid	Monheim
State	North-Rhine Westphalia	North-Rhine Westphalia	North-Rhine Westphalia	North-Rhine Westphalia	North-Rhine Westphalia
Country	Germany	Germany	Germany	Germany	Germany
GPS Coordinates	N 51° 04.6' E 006° 55.5'	N 50° 22. 9' E 006° 43.0'	N 51° 04.0' E 007° 06.3'	N 51° 04.5' E 007° 08.4'	N 51° 04.9' E 006° 55.3'
Soil Taxonomic Classification (USDA)	no information available				
Soil Series	no information available				
Textural Class (USDA)	loamy sand	loam	silt loam	silt loam	sandy loam
Sand [%] [50 µm – 2 mm]	79	35	19	27	55
Silt [%] [2 µm – 50 µm]	16	38	66	56	30
Clay [%] [< 2 µm]	5	27	15	17	15
pH					
- in $CaCl_2$ (soil/$CaCl_2$ 1/2)	6.4	7.4	6.5	5.0	5.2
- in water (soil/water 1/1)	6.6	7.5	6.7	5.3	5.4
- in water (saturated paste)	6.7	7.4	6.8	5.4	5.5
- in KCl	6.1	7.1	6.1	4.7	4.8
Organic Carbon [%]	1.8	5.0	1.7	2.8	1.9
Organic Matter [%]	3.1	8.6	2.9	4.8	3.3
Cation Exchange Capacity [meq/100 g]	9.6	21.5	11.5	10.1	11.0
Water Holding Capacity					
maximum [g H_2O *ad* 100 g soil DW]	43.4	84.6	54.3	63.7	57.4
at 0.1 bar (pF 2.0) [%]	15.2	43.1	27.9	29.1	21.2
at 0.33 bar (pF 2.5) [%]	10.6	33.5	20.6	22.9	17.0
Bulk Density (disturbed) [g/cm^3]	1.27	1.00	1.10	1.04	1.13

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

GPS: global positioning system

DW: dry weight

USDA: United States Department of Agriculture

B. STUDY DESIGN

1. Experimental Conditions

The test system for adsorption and desorption in batch equilibrium experiments consisted of glass flasks (volume 100 mL) closed with PTFE sealed 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.

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 1:1(50 g $soil_{dry\ weight}$ / 50 mL solution). Unlabeled BCS-CU62474 (2,2,2-trifluoroethanesulfonate) was applied at nominal concentrations of 1.0, 0.3, 0.1, 0.03 and 0.01 mg/L in aqueous 0.01 M $CaCl_2$ solution. The adsorption step was carried out for 24 hours in the dark at 20 ± 2 °C under continuous agitation.

2. Analytical Procedures

After the adsorption step the aqueous supernatant was separated from the soil by centrifugation, and an aliquot of the supernatant was diluted with water (1:20, *v/v*) before the amount of FOE 5043-trifluoro-ethanesulfonic acid was analyzed by high performance liquid chromatography hyphenated to tandem mass spectrometry method (HPLC-MS/MS) operated in the multiple reaction monitoring (MRM) mode. The limit of quantification (LOQ) was determined as 0.1 ng/mL and the limit of detection (LOD) was set to 1/5 LOQ, equal to 0.02 ng/mL. At this level the signal to noise ratio was ≥ 3. The LOD of the method was two orders of magnitudes lower than the lowest test concentration of the definitive test (0.01 mg/L = 10 ng/mL).

As only low to virtual no adsorption was observed for the test item, no desorption step was conducted in the definitive test.

For the preliminary parental mass balance test, no additional extraction of the soil became necessary, as the recovered amount of test item in the supernatant of the samples was >90% AA after 96 hours of incubation.

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.

The HPLC-MS/MS method was validated with regard to linearity, accuracy and precision. The mass selective detector was operated in the negative electrospray ionization selected reaction monitoring mode, tuned for the mass transitions of parent and significant product ions. The linearity range of the mass spectrometer was tested in pure extraction solvent and in blank soil matrix solutions (matrix-matched), covering a range from 0.02 ng/mL to 100.0 ng/mL. Based on these results, an external multi-point calibration curve was established for quantitation using standard solutions in 0.01 M $CaCl_2$ solution diluted with water (1:10, *v/v*), as the observed matrix effects were in ≤ 10% in all soils.

The accuracy and precision of the method was assessed on the basis of the recovery rates determined for each soil after fortification with the test item at LOQ level and 1000 x LOQ level. The fortified samples diluted and analyzed as described above. Blank soil matrix solutions were used to determine the background abundance of the test item in the respective soils.

II. RESULTS AND DISCUSSION

A. METHOD VALIDATION

The HPLC-MS/MS method was successfully validated prior to application of the definitive test.

The correlation coefficient (R^2) of the external, multi-point calibration curve was 0.9994. The recovery rates ranged from 85 to 116% of applied amount [% AA] for all soils and both fortification levels. The relative standard deviations for each recovery set ranged from 1 to 9%, showing a good repeatability of this method. Background abundance in blank soil matrix was below 20% of the LOQ in all soils and no interference by other matrix components occurred. The combination of the selective MS/MS detection method used with the preceding HPLC separation leads to a high specificity of the method.

B. DEGRADATION OF TEST ITEM

FOE 5043-trifluoroethanesulfonic acid was sufficient stable throughout the study. The parental mass balances after the total incubation time of 96 hours (24 h adsorption + 3 x 24 h desorption) were 98.3, 102.4, 93.1, 103.0 and 104.6% AR for soil Laacherhof AXXa, Dollendorf II, Hoefchen am Hohenseh, Hanscheider Hof and Laacherhof Wurmwiese, respectively.

C. FINDINGS

At the end of the adsorption phase, the amount of FOE 5043-trifluoroethanesulfonic acid present in the supernatant was in the same range as in the respective soil blank matrix samples, which were used as control, in all soils and for all test concentrations.

Only low to virtually no adsorption and to some extend also negative adsorption were detected at each test item concentration in the definitive test; therefore, no desorption step was conducted. However, using this data 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.

III. CONCLUSIONS

Only low to virtually no adsorption of the test item BCS-CU62474 (2,2,2-trifluoroethanesulfonate) was measured for all soils and all test concentrations. However, using this data 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.

Considering the measured values it can be assumed that FOE 5043-trifluoroethanesulfonic acid has a high mobility in the tested soils.

*****

Report:	**KCA 7.1.3.1.2 /02; [redacted], M.; [redacted], W.; 2011**
Title:	[1-^{14}C] BCS-AZ56567: Adsorption/desorption in five different soils
Report No:	AS155
Document No:	M-406740-01-1
Guidelines:	• OECD Test Guideline No. 106 • US EPA OCSPP Test Guideline No. 835.1230 • Canadian PMRA Guideline DACO 8.2.4.2 • Commission Directive 95/36/EC amending Council Directive 91/414/EEC
GLP:	yes

Executive Summary

The adsorption/desorption behavior of [1-^{14}C]BCS-AZ56567 (≙ [1-^{14}C]trifluoroacetate, report name: trifluoroacetic acid) was studied in five different soils in the dark in the laboratory at 20 ± 2 °C using the batch equilibrium method:

Soil	Source	Texture (USDA)	pH	OC [%]
Wurmwiese	Monheim, Germany	loam	5.3	1.8
Hoefchen am Hohenseh	Burscheid, Germany	silt loam	6.6	2.4
Dollendorf II	Blankenheim, Germany	clay loam	7.3	4.7
Guadalupe	Guadalupe, USA	sandy loam	6.7	0.7
Springfield	Springfield, USA	silt loam	6.6	1.7

The adsorption phase of the study was carried out using air-dried soils pre-equilibrated in aqueous 0.01 M $CaCl_2$ solution with a soil-to-solution ratio of 1:1 (20 g soil $_{dry\ weight}$/20 mL solution). [1-^{14}C]BCS-AZ56567 was applied at nominal concentrations of 1.0, 0.3, 0.1, 0.03 and 0.01 mg/L in aqueous 0.01 M $CaCl_2$. The desorption phase was performed by supplying pre-adsorbed soil samples with fresh aqueous 0.01 M $CaCl_2$ solution for all test concentrations. The adsorption and desorption steps were carried out each for 24 hours under continuous agitation.

Trifluoroacetic acid was sufficient stable throughout the study. The parental mass balances after 48 h were 93.9, 93.4, 92.5, 93.2 and 91.8% AR for soil Wurmwiese, Hoefchen am Hohenseh, Dollendorf II, Guadalupe and Springfield, respectively.

Material balances ranged from 89.9 to 98.7% AR in soil Wurmwiese, from 96.2 to 98.2% AR in soil Hoefchen am Hohenseh, from 97.4 to 103.1 in soil Dollendorf II, from 97.8 to 100.5 in soil Guadalupe and from 96.1 to 98.9% AR in soil Springfield.

Virtually no adsorption and to some extend negative adsorption was measured. However, using this data 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.

Considering the measured values it can be assumed that trifluoroacetic acid has a high mobility in the tested soils.

I. MATERIALS AND METHODS

A. MATERIALS

1. Test Item

[1-^{14}C]BCS-AZ56567 (trifluoroacetate sodium salt; report name [1]: trifluoroacetic acid)

Sample ID	KML9027
Specific activity	3.48 MBq/mg
Radiochemical purity	> 98% HPLC with radioactivity-detector

2. Test Soils

The soils (Table 7.1.3.1.2- 8) were sampled from the field (upper horizon of 0 to 20 cm or 0 to 6 inches), sieved to a particle size of ≤ 2 mm and stored for a maximum period of 20 months before study start. The soils were air-dried before application. The soils were taken from agricultural areas representing different geographical origins and different soil properties as required by the guidelines.

Table 7.1.3.1.2- 8: Physico-chemical properties of test soils

Parameter	Results / Units				
Soil Designation	Wurmwiese	Hoefchen am Hohenseh	Dollendorf II	Guadalupe	Springfield
Geographic Location					
City	Monheim	Burscheid	Blankenheim	Guadalupe.	Springfield
State	North-Rhine Westphalia	North-Rhine Westphalia	North-Rhine Westphalia	California	Nebraska
Country	Germany	Germany	Germany	USA	USA
GPS Coordinates	N 51° 04.9' E 006° 55.2'	N 51° 04.0' E 007° 06.3'	N 50° 22.9' E 006° 43.0'	N 35° 01' W 120° 36'	N 96° 15' W 41° 03'
Textural Class (USDA)	loam	silt loam	clay loam	sandy loam	silt loam
Sand [%] [50 µm – 2 mm]	51	27	31	56.0	12.7
Silt [%] [2 µm – 50 µm]	28	54	38	32.6	60.8
Clay [%] [< 2 µm]	21	19	31	11.4	26.5
pH					
- in $CaCl_2$ (soil/$CaCl_2$ 1/2)	5.3	6.6	7.3	6.7	6.6
- in water (soil/water 1/1)	5.5	6.8	7.4	6.8	7.2
Organic Carbon [%]	1.8	2.4	4.7	0.7	1.7
Organic Matter [%] [1]	3.0	4.2	8.1	1.1	2.9
Cation Exchange Capacity [meq/100 g]	10.8	13.9	21.9	16.1	16.1

[1] calculated as: OM [%] = OC [%] · 1.724 USDA: United States Department of Agriculture

B. STUDY DESIGN

1. Experimental Conditions

The test system for adsorption and desorption in batch equilibrium experiments consisted of borosilicate glass centrifuge tubes (volume 42 mL) closed with Teflon® lined 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.

The adsorption phase of the definitive test was carried out using air-dried soils equilibrated in aqueous 0.01 M $CaCl_2$ solution with a soil-to-solution ratio of 1:1 (20 g soil $_{dry\ weight}$/20 mL solution). [1-^{14}C] BCS-AZ56567 was applied at nominal concentrations of 1.0, 0.3, 0.1, 0.03 and 0.01 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 all test concentrations. The adsorption and desorption steps were carried out each for 24 hours in the dark at 20 ± 2 °C under continuous agitation.

2. Analytical Procedures

After each adsorption and desorption step the aqueous supernatant was separated from the soil by centrifugation and the amount of trifluoroacetic acid in the supernatants was analyzed by liquid scintillation counting (LSC).

In the preliminary parental mass balance test, the soil was additionally extracted up to five times with water. The aqueous supernatant and the combined soil extracts were analyzed by LSC and reversed phase HPLC/radiodetection to determine the stability of the test item and to establish the parental mass balance.

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 steps, the soil was mixed with approximately 0.4 g cellulose/g soil, air-dried and the radioactivity content determined by combustion/LSC to establish the material balance.

II. RESULTS AND DISCUSSION

A. MATERIAL BALANCE

Material balances ranged from 89.9 to 98-7% AR in soil Wurmwiese, from 96.2 to 98.2% AR in soil Hoefchen am Hohenseh, from 97.4 to 103.1 in soil Dollendorf II, from 97.8 to 100.5 in soil Guadalupe and from 96.1 to 98.9% AR in soil Springfield. 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.

B. DEGRADATION OF TEST ITEM

Trifluoroacetic acid was sufficient stable throughout the study. The parental mass balances after 48 h were 93.9, 93.4, 92.5, 93.2 and 91.8% AR for soil Wurmwiese, Hoefchen am Hohenseh, Dollendorf II, Guadalupe and Springfield, respectively.

C. FINDINGS

At the end of the adsorption phase, -1.7 to 0.9% AR was adsorbed to soil Wurmwiese, - 4.3 to - 2.8% AR to soil Hoefchen am Hohenseh, - 9.6 to -8.2% AR to soil Dollendorf II, - 3.2 to - 1.3% AR to soil Guadalupe and -6.3 to - 4.7% AR to soil Springfield.

Virtually no adsorption and to some extend negative adsorption was measured. However, using this data 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. Since no meaningful results were measured they are not reported.

III. CONCLUSIONS

Virtually no adsorption and to some extend negative adsorption for the test item [1-^{14}C]BCS-AZ56567 (≙ [1-^{14}C]trifluoroacetate) was measured. However, using this data 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.

Considering the measured values it can be assumed that trifluoroacetic acid has a high mobility in the tested soils.

*****

CA 7.1.3.2 Aged sorption

Report:	**KCA 7.1.3.2 /01; [redacted], E.; 2003**
Title:	Time-dependent sorption of FOE5043-sulfonic acid in soil
Report No:	MEF-229/03
Document No:	M-111445-01-1
Guidelines:	• None (Supportive study to Annex II, Fate and Behavior in the Environment, 7171/VI/94-EN, Section 7.1.2)
GLP:	yes

Executive Summary

The results as reported in study KCA 7.1.2.1.2 /08 were used to calculate the sorption constants (K_d) based on the amount of test item adsorbed to soil (sum of recovered FOE sulfonic acid in ambient soil extracts) in relation to the amount of FOE sulfonic acid desorbed during the so-called batch equilibrium shaking test by the 0.01 M $CaCl_2$ solution.

The calculated sorption constants (K_d) steadily increased from DAT-0 to DAT-100 from 0.12 to 0.23 mL/g and from 0.12 to 0.18 mL/g in soil Laacherhof AXXa and Laacherhof AIII, respectively. The corresponding normalized sorption constants (Koc values) steadily increased from DAT-0 to DAT-100 from 8 to 16 mL/g and from 13 to 20 mL/g in soil Laacherhof AXXa and Laacherhof AIII, respectively. During the entire ageing period of 100 days the sorption values (K_d) increased by a factor of 2 and 1.5 in soils Laacherhof AXXa and Laacherhof AIII, respectively. Despite that observed increase of sorption with ageing time FOE sulfonic acid is classified as mobile according to the classifications of Briggs [17] and Verdam et al. [19].

However, the overall results of this results clearly indicate that not a time-dependent sorption behavior of FOE sulfonic acid but rather shorter half-lives under aerobic condition in soil are the most plausible reason for measuring much lower peak concentrations of test item in the leachates of the lysimeter studies than that expected by modeling calculations with the earlier input parameters (longer half-lives).

I. MATERIALS AND METHODS

Details on the study conduct and its results are summarized under KCA 7.1.2.1.2 /08.

The results were used to calculate the sorption constants (K_d) based on the amount of test item adsorbed to soil (sum of recovered FOE sulfonic acid in ambient soil extracts) in relation to the amount of FOE sulfonic acid desorbed during the so-called batch equilibrium shaking test by the 0.01 M $CaCl_2$ solution.

II. RESULTS AND DISCUSSION

A. DATA

Table 7.1.3.2- 1 and Table 7.1.3.2- 2 summaries the time-dependent sorption behavior of [phenyl-UL-^{14}C]FOE sulfonic acid as a function of time.

[19] Verdam, B., Loch, J. P. G. and Maaren, H. L. J. (1988): Bestrijdingsmiddelen in Grondwater onder Kwetsbare Bodemtypen; National Institute of Public Health and Environmental Protection, Rapport Nr. 728473001.

Table 7.1.3.2- 1: Time Dependent Sorption of FOE sulfonic acid in Soil Laacherhof AXXa

Parameter	Replicate	DAT 0	3	7	14	28	56	100
c desorbed [µg/mL] [1]	1	0.110	0.104	0.103	0.094	0.077	0.059	0.029
	2	0.108	0.105	0.101	0.095	0.080	0.064	0.028
c extracted [µg/g] [2]	1	0.0120	0.0177	0.0159	0.0166	0.0161	0.0111	0.0061
	2	0.0145	0.0166	0.0160	0.0150	0.0146	0.0110	0.0068
K_d [mL/g]	mean	0.12	0.16	0.16	0.17	0.20	0.18	0.23
K_{OC} [mL/g]	mean	8	11	11	11	13	12	16
Time-dependent sorption factor [3]	mean	2						

[1] Concentration of test item in desorption solution from soil batch equilibrium shaking test

[2] Concentration of test item in soil after 24 h desorption phase (sum of test item in ambient soil extracts)

[3] Time-dependent sorption factor K_d (DAT-100)/ K_d (DAT-0) = 2

Table 7.1.3.2- 2: Time Dependent Sorption of FOE sulfonic acid in Soil Laacherhof AIII

Parameter	Replicate	DAT 0	3	7	14	28	56	100
c desorbed [µg/mL] [1]	1	0.113	0.107	0.104	0.099	0.084	0.062	0.027
	2	0.109	0.105	0.102	0.095	0.081	0.060	0.030
c extracted [µg/g] [2]	1	0.0125	0.0152	0.0145	0.0131	0.0129	0.0096	0.0069
	2	0.0137	0.0149	0.0145	0.0151	0.0125	0.0093	0.0028
K_d [mL/g]	mean	0.12	0.14	0.14	0.15	0.15	0.15	0.18
K_{OC} [mL/g]	mean	13	16	16	17	17	18	20
Time-dependent sorption factor [3]	mean	1.5						

[1] Concentration of test item in desorption solution from soil batch equilibrium shaking test

[2] Concentration of test item in soil after 24 h desorption phase (sum of test item in ambient soil extracts)

[3] Time-dependent sorption factor K_d (DAT-100)/ K_d (DAT-0) = 2

III. CONCLUSIONS

During the entire ageing period of 100 days the sorption values (K_d) increased by a factor of 2 (0.12 to 0.23 mL/g) and 1.5 (0.12 to 0.18 mL/g) in soils Laacherhof AXXa and Laacherhof AIII, respectively.

However, the overall results of this results clearly indicate that not a time-dependent sorption behavior of FOE sulfonic acid, but rather shorter half-lives under aerobic condition in soil are the most plausible reason for measuring much lower peak concentrations of test item in the leachates of the lysimeter studies than that expected by modeling calculations with the earlier input parameters (longer half-lives).

CA 7.1.4 Mobility in soil

Studies for determination of the plant uptake factor have been performed for the major degradation products FOE sulfonic acid, FOE methylsulfone, FOE 5043-trifluoroethanesulfonic acid and trifluoroacetic acid. See Table 7.1.4- 1 for an overall summary of the results.

Table 7.1.4- 1: Summary of plant uptake factors (PUFs) in wheat of major flufenacet degradation products derived from laboratory studies

Degradation Product	PUF
FOE sulfonic acid	0.46
FOE methylsulfone	1.31
FOE 5043-trifluoroethanesulfonic acid	1.36
trifluoroacetic acid	0.59

The statement KCA 7.1.4 /04 summarizes the results of the plant uptake factor studies of trifluoroacetic acid and demonstrates evidence for the trifluoroacetic acid-specific passive uptake in wheat. All these studies and the statement are submitted within this Supplemental Dossier for the flufenacet renewal of approval.

Report:	**KCA 7.1.4 /01; [redacted], S.; [redacted], R.; 2012**
Title:	Amendment No. 1 to Final Report - Determination of the Plant Uptake Factor of FOE methylsulfone, FOE sulfonic acid and trifluoroethanesulfonic acid in Wheat
Report No:	EnSa-12-0260
Document No:	M-434257-02-1
Guidelines:	none
GLP:	yes

Executive Summary

The plant uptake factors (PUFs) of the degradation products FOE sulfonic acid, FOE methylsulfone and FOE 5043-trifluoroethanesulfonic acid in wheat were determined in a greenhouse climatic chamber over a study duration of 8 days under controlled temperature, humidity and light conditions (temperature: 18 - 21 °C, approx. 60% humidity and a day/night cycle of 14 h/10 h)

The initial test item concentrations in the respective test solutions were 34.44 µg/L for FOE sulfonic acid, 7.86 µg/L for FOE methylsulfone and 15.89 µg/L for FOE 5043-trifluoroethanesulfonic acid.

Pre-grown wheat plants (BBCH code approx. 15) were exposed to the test solution (nutrient solution plus test item) for the whole study duration.

For each test item the test was performed in triplicates with one additional control experiment. Sample aliquots were analyzed 0 h, 4 h, 1 d, 4 d and 8 d after treatment.

The transpiration volume of the treated plants ranged from 80 to 140 mL at study end.

The PUFs were calculated from the amount of the respective test item in the test solution and the volume of test solution each at study start and study end. The plant uptake factor of FOE sulfonic acid in wheat was determined as 0.46, indicating a slight inhibition of the plant uptake of FOE sulfonic acid, due impermeability of the cell walls for polar compounds. The plant uptake factors of FOE methylsulfone and FOE 5043-trifluoroethanesulfonic acid were determined as 1.31 and 1.36, respectively, demonstrating a good plant uptake behavior of these test items.

I. MATERIALS AND METHODS

A. MATERIALS

1. Test Items

unlabeled AE 0841914 (FOE5043-sulfonic acid sodium salt; report name: FOE sulfonic acid)

CAS No.	947601-87-8
Certificate of Analysis:	AZ17542
Batch Code:	AE 0841914-01-02
Chemical Purity:	87.6% (^{19}F-NMR)

unlabeled BCS-CO62475 (report name: FOE methylsulfone)

Certificate of Analysis:	AZ15999
Batch Code:	BCS_CO62475-01-01
Chemical Purity:	97.2%

unlabeled BCS-CU62474 (sodium 2,2,2-trifluoroethanesulfonate; report name: FOE 5043-trifluoroethanesulfonic acid)

Certificate of Analysis:	MZ00482
Batch Code:	BCS-CU62474-01-01
Chemical Purity:	99.4% (^{19}F-NMR)

2. Test Plants

Wheat plants (variety: Thasos) were pre-grown up to BBCH growth stage 15 on an artificial substrate (vermiculite) and a commercial nutrition solution in a greenhouse under controlled temperature, humidity and light conditions. These conditions were kept similar to the natural conditions of Central Europe. When the plants have reached BBCH growth stage 15, they were transferred to the test vessels.

B. STUDY DESIGN

1. Experimental Conditions

The hydroponic test systems for the plant uptake factor (PUF) experiments consisted of brown glass bottles (volume 1000 mL), filled with 800 mL test solution and ten wheat plants/test vessel. The plants were fixed with elastomer foam and the test vessels were covered with aluminum foil to prevent evaporation of the test solution. The experiments were performed in triplicate with one additional control experiment (test systems without plants for determination of test item stability). For each test item separate test systems were used.

The initial test item concentrations in the respective test solutions were 34.44 µg/L for FOE sulfonic acid, 7.86 µg/L for FOE methylsulfone and 15.89 µg/L for FOE 5043-trifluoroethanesulfonic acid.

For each test item separate application solutions were prepared. 1 mL of each application solution was mixed with 3500 mL commercial available nutrient solution to yield the respective test solutions.

During the study, the test systems were incubated in a greenhouse climatic chamber under controlled temperature (day: 20 – 21 °C; night: 18 – 19 °C), humidity (approx. 60%) and light conditions (at least 35 klx and a day/night cycle of 14 h/10 h).

2. Sampling

For each test item the test was performed in triplicates with one additional control experiment. Sample aliquots were analyzed 0 h, 4 h, 1 d, 4 d and 8 d after treatment. The initial and final test solution volume was determined at study start (day 0) and study end (8 days after treatment ≙ DAT-8).

3. Analytical Procedures

At each sampling interval aliquots of 1 mL each were taken from each test system. The samples were stored refrigerated until HPLC-MS/MS analysis. The initial and final test solution volume was determined at study start (day 0) and study end (8 days after treatment ≙ DAT-8).

The mass selective detector was operated in the electrospray ionization selected reaction monitoring mode, tuned for the mass transitions of parent and significant product ions. For quantitation external multi-point calibration curves were used. The linear range of the HPLC-MS/MS method was tested over a concentration range from 0.3 to 45.0 µg/L for FOE sulfonic acid, from 0.07 to 10.50 µg/L for FOE methylsulfone and from 0.15 to 22.50 µg/L for FOE 5043-trifluoroethanesulfonic acid. The correlation coefficient (R^2) of the external multi-point calibration curve was 0.9999 for FOE sulfonic acid, > 0.9999 for FOE methylsulfone and 0.9995 for FOE 5043-trifluoroethanesulfonic acid. The relative standard deviations for each concentration of the calibration curve ranged from 0.4 to 2.3% for FOE sulfonic acid, from 1.1 to 7.3% for FOE methylsulfone and from 1.3 to 6.2% for FOE 5043-trifluoroethanesulfonic acid, showing a good repeatability of this method.

The plant uptake factors were calculated according to the following formula:

$$PUF = \frac{ln\left(\frac{m_{DAT-8}}{m_{DAT-0}}\right)}{ln\left(\frac{V_{DAT-8}}{V_{DAT-0}}\right)}$$

with:

m_{DAT-0}	= initial amount of test item in test solution	[µg]
m_{DAT-8}	= amount of test item in test solution at study end (DAT-8)	[µg]
V_{DAT-0}	= initial volume of test solution	[L]
V_{DAT-8}	= volume of test solution at study end (DAT-8)	[L]

II. RESULTS AND DISCUSSION

A. FINDINGS

The transpiration volume of the treated plants ranged from 80 to 140 mL at study end.

All test items were stable during the entire test period of 8 days, as demonstrated by the control experiments.

The concentrations of FOE sulfonic acid in the test solutions increased slightly over the entire incubation period of 8 days, while the concentrations of FOE methylsulfone and FOE 5043-trifluoro-ethanesulfonic acid stayed nearly constant over the entire incubation period (see Table 7.1.4- 2).

The mean PUF in wheat for FOE sulfonic acid amounted to 0.46, indicating that the plant uptake of FOE sulfonic acid was slightly inhibited, likely due to the impermeability of the cell walls for polar compounds. The mean PUFs in wheat for FOE methylsulfone and FOE 5043-trifluoroethanesulfonic acid amounted to 1.31 and 1.36, respectively, demonstrating a good plant uptake behavior of these test items.

Table 7.1.4- 2: Plant Uptake Factors of FOE sulfonic acid, FOE methylsulfone and FOE 5043-trifluoro-ethanesulfonic acid in Wheat

Test Item	Replicate	DAT-0			DAT-8			PUF
		V [L]	c [µg/L]	m [µg]	V [L]	c [µg/L]	m [µg]	
FOE sulfonic acid	1	0.80	34.27	27.42	0.66	39.28	25.92	0.29
	2	0.80	34.58	27.66	0.67	37.90	25.45	0.47
	3	0.80	34.47	27.58	0.70	36.24	25.37	0.63
	Mean	**0.80**	**34.44**					**0.46**
FOE methylsulfone	1	0.80	7.86	6.29	0.69	7.66	5.29	1.17
	2	0.80	7.91	6.33	0.69	7.47	5.15	1.39
	3	0.80	7.82	6.26	0.72	7.52	5.41	1.37
	Mean	**0.80**	**7.86**					**1.31**
FOE 5043-trifluoro-ethanesulfonic acid	1	0.80	15.78	12.62	0.69	15.53	10.72	1.11
	2	0.80	15.94	12.75	0.72	15.21	10.95	1.44
	3	0.80	15.96	12.77	0.71	15.00	10.65	1.52
	Mean	**0.80**	**15.89**					**1.36**

DAT: days after treatment
V: volume of test solution
m: mass of test item in test solution
PUF: plant uptake factor
c: concentration of test item in test solution

III. CONCLUSIONS

The plant uptake factors in wheat were determined as 0.46 for FOE sulfonic acid, 1.31 for FOE methylsulfone and 1.36 for FOE 5043-trifluoroethanesulfonic acid.

The plant uptake factor of FOE sulfonic acid indicates a slight inhibition of the plant uptake, due impermeability of the cell walls for polar compounds. The plant uptake factors of FOE methylsulfone and FOE 5043-trifluoroethanesulfonic acid demonstrates a good plant uptake behavior of these test items.

*****

Report:	**KCA 7.1.4 /02; [redacted], R.; 2013**
Title:	Amendment No 2 to Determination of the Plant Uptake Factor of trifluoroacetic acid (TFA) in Wheat
Report No:	EnSa-13-0357
Document No:	M-456754-03-1
Guidelines:	none
GLP:	yes

Executive Summary

The plant uptake factor (PUFs) of [1-^{14}C]trifluoroacetate (report name: trifluoroacetic acid) in wheat was determined in a greenhouse climatic chamber over a study duration of 8 days under controlled temperature, humidity and light conditions (temperature: 20 °C, approx. 60 - 75% humidity and a day/night cycle of 14 h/10 h)

The initial test item concentration in the test solution was 75.6 µg/L.

Pre-grown wheat plants (BBCH code approx. 15) were exposed to the test solution (nutrient solution plus test item) for a maximum period of 8 days.

The test was performed in quintuplicates (5 replicates) with two additional control experiments (test systems without test item). Sample aliquots were analyzed 0, 2, 5 and 8 days after treatment (DAT).

The transpiration volume of the treated plants ranged from 380 to 540 mL at study end.

An additional recovery experiment demonstrated that the reduced test item amount in test solution at study end could be recovered in the plants with a recovery of 92.6%, confirming the reliability of the plant uptake experiment.

PUFs were calculated from the amount of the respective test item in the test solution and the volume of test solution each at study start and study end. The plant uptake factor of trifluoroacetic acid in wheat was determined as 0.59, indicating a restricted permeability of trifluoroacetic acid through the root cell walls.

I. MATERIALS AND METHODS

A. MATERIALS

1. Test Items

[1-^{14}C]trifluoroacetate (sodium salt; report name [1]: trifluoroacetic acid)
Batch Code: KML 9494
Specific Activity: 4.08 MBq/mg
Radiochemical Purity: ≥ 98% (HPLC/radiodetection)

2. Test Plants

Wheat plants (variety: Thasos) were pre-grown up to BBCH growth stage 15 on soil in a greenhouse under controlled temperature, humidity and light conditions. These conditions were kept similar to the natural conditions of Central Europe. On the day of study start, the soil was removed from the root system by watering and washing with a gentle water shower. Afterwards the plants were transferred to the test vessels.

B. STUDY DESIGN

1. Experimental Conditions

The hydroponic test systems for the plant uptake factor (PUF) experiments consisted of brown glass bottles (volume 1000 mL), filled with 800 mL test solution and ten wheat plants/test vessel. The plants were fixed with elastomer foam and the test vessels were covered with aluminum foil to prevent evaporation of the test solution. The experiments were performed in triplicate with two additional control experiments (test systems without test item for determination of the water uptake (transpiration volume)).

The initial test item concentration in the test solution was 75.6 µg/L.

The application solution was prepared in water. 24 mL of the application solution were mixed with 4.5 L nutrient solution (0.01 M 2-morpholino-ethanesulfonic acid and 0.01 M $CaCl_2$ adjusted with sodium hydroxide solution to pH 6.5) to yield the test solution.

During the study, the test systems were incubated in a greenhouse climatic chamber under controlled temperature (20 °C), humidity (approx. 60 - 75%) and light conditions (at least 35 klx and a day/night cycle of 14 h/10 h).

2. Sampling

The test was performed in quintuplicates (5 replicates) with two additional control experiments (test systems without test item). Sample aliquots were analyzed 0, 2, 5 and 8 days after treatment (DAT). The initial and final test solution volume was determined at study start (DAT-0) and study end (DAT-8), respectively.

3. Analytical Procedures

At each sampling interval aliquots of 1 mL each were taken from each test system. The initial and final test solution volume was determined at DAT-0 and DAT-8, respectively. Additionally, at study end (DAT-8) the roots of each bunch test plants and the respective test vessel were washed with 200 mL acetonitrile/water (1/1, *v/v*). Afterwards, the wheat plants of each test systems were combined, weighed and homogenized.

Test and washing solutions were characterized by liquid scintillation counting (LSC) and HPLC/radiodetection. The amount of residues in the wheat plants was determined by combustion/ liquid scintillation counting.

The recovery rate of the test item was calculated from the amount of test item taken up theoretically by the plants and actually recovered in the plants. The theoretical amount of test item taken up by the plants was calculated from the initial test item amount in test solution minus the test item amount recovered at DAT-8 in test and washing solutions.

The identity of the test item was confirmed by HPLC/radiodetection.

The plant uptake factors were calculated according to the following formula:

$$PUF = \frac{ln\left(\frac{m_{DAT-8} + m_{wash}}{m_{DAT-0}}\right)}{ln\left(\frac{V_{DAT-8}}{V_{DAT-0}}\right)}$$

with:

m_{DAT-0}	= initial amount of test item in test solution	[µg]
m_{DAT-8}	= amount of test item in test solution at study end (DAT-8)	[µg]
m_{wash}	= amount of test item in washing solution	[µg]
V_{DAT-0}	= initial volume of test solution	[L]
V_{DAT-8}	= volume of test solution at study end (DAT-8)	[L]

II. RESULTS AND DISCUSSION

A. FINDINGS

The transpiration volume of the treated plants ranged from 380 to 540 mL at study end. The transpiration volumes of the controls (untreated test systems) ranged from 350 to 360 mL.

The test items were stable during the entire test period of 8 days. The reliability of this plant uptake experiment was confirmed as the reduced test item amount in test solution at DAT-8 could be recovered in the plants with a recovery of 92.6%.

The concentrations of trifluoroacetic acid in the test solution increased towards end of the study (see Table 7.1.4- 3), indicating that its plant uptake lower compared to the water up take of the plants. Most probably this is caused by a restricted permeability of the test compound through the root cell walls.

The mean PUF in wheat for trifluoroacetic acid was determined as 0.59.

Table 7.1.4- 3: Plant Uptake Factors of trifluoroacetic acid in Wheat

Replicate	DAT-0			DAT-8				PUF
	V [L]	c [µg/L]	m [µg]	V [L]	c [µg/L]	m [µg]	m_{wash} [µg]	
1	0.80	75.5	60.4	0.26	100.9	26.2	6.5	0.54
2	0.80	75.3	60.2	0.27	103.4	27.9	6.5	0.51
3	0.80	75.4	60.3	0.42	82.2	34.5	4.1	0.69
4	0.80	75.5	60.4	0.28	105.1	29.4	5.7	0.52
5	0.80	76.5	61.2	0.37	86.9	32.1	4.5	0.66
Mean	**0.80**	**75.6**						**0.59**

DAT: days after treatment — PUF: plant uptake factor
V: volume of test solution — c: concentration of test item in test solution
m: mass of test item in test solution — m_{wash}: mass of test item in washing solution

III. CONCLUSIONS

The plant uptake factors of [1-^{14}C]trifluoroacetate (report name: trifluoroacetic acid) in wheat was determined as 0.59.

The reliability of this plant uptake experiment was confirmed by an additional recovery experiment which demonstrated that the reduced test item amount in test solution at study end could be recovered in the plants with a recovery of 92.6%.

The plant uptake of the test item was lower compared to the water up take of the plants. Most probably this is caused by a restricted permeability of the test compound through the root cell walls.

*****

Report:	**KCA 7.1.4.03; [redacted], R.; 2012**
Title:	Determination of the Plant Uptake Factor of TFA (trifluoroacetic acid) in Wheat, Corn and Tomatoes
Report No:	EnSa-12-0581
Document No:	M-440106-01-1
Guidelines:	none
GLP:	no

Executive Summary

The plant uptake factor (PUFs) of [1-^{14}C]trifluoroacetate (report name: trifluoroacetic acid) in wheat, tomatoes and corn was determined in a greenhouse climatic chamber over a study duration of 8 days (wheat and tomatoes) or 11 days (corn) under controlled temperature, humidity and light conditions (temperature: 20 °C, approx. 75% humidity and a day/night cycle of 14 h/10 h).

The initial test item concentration in the test solution was 767.8 µg/L for wheat, 711.8 µg/L for tomatoes and 769.1 µg/L for corn.

Pre-grown wheat and tomato plants were exposed to the test solution (nutrient solution plus test item) for the whole study duration.

For wheat one test system with ten wheat plants was used, whereas for tomatoes and corn two and three test systems with single plants were used, respectively.

Sample aliquots were analyzed 0, 0.1 to 0.2 (equal to 2 to 4 hours), 1, 4, 8 and 11 (only corn) days after treatment (DAT).

PUFs were calculated from the amount of the respective test item in the test solution and the volume of test solution each at study start and study end. The plant uptake factors of trifluoroacetic acid were determined as 0.66 in wheat, 0.74 in tomatoes and 0.98 in corn.

The results indicate that the plant uptake in wheat and tomato was lower than the water uptake, probably to a restricted permeability of the test item through the root cell walls, whereas the plant uptake in corn was not restricted.

I. MATERIALS AND METHODS

A. MATERIALS

1. Test Items

[1-^{14}C]trifluoroacetate (sodium salt; report name [1]: trifluoroacetic acid)
Batch Code: KML 9072 (used for wheat and corn)
KML 9241 (used for tomatoes)

Specific Activity: 3.48 MBq/mg
Radiochemical Purity: ≥ 98% (HPLC/radiodetection)

2. Test Plants

Wheat plants (variety: Thasos), tomatoes and corn were pre-grown on an artificial substrate (Vermiculite) in a greenhouse under controlled temperature, humidity and light conditions. These conditions were kept similar to the natural conditions of Central Europe. On the day of study start, the Vermiculite was removed from the root system by watering and washing with a gentle water shower. Afterwards the plants were transferred to the test vessels.

B. STUDY DESIGN

1. Experimental Conditions

The hydroponic test systems for the plant uptake factor (PUF) experiments consisted of brown glass bottles (volume 1000 mL), filled with 800 mL test solution and either ten wheat plants/test vessel or one corn or tomato plant/test vessel. The plants were fixed with elastomer foam and the test vessels were covered with aluminum foil to prevent evaporation of the test solution. One test system was prepared for wheat, two test systems for tomatoes and three for corn.

The initial test item concentration in the test solution was 767.8 µg/L for wheat, 711.8 µg/L for tomatoes and 769.1 µg/L for corn.

A definite volume of the application solution was applied to 800 mL of nutrient solution (pH 6) to yield the test solution.

During the study, the test systems were incubated in a greenhouse climatic chamber under controlled temperature (20 °C), humidity (approx. 75%) and light conditions (at least 35 klx and a day/night cycle of 14 h/10 h).

2. Sampling

The test was performed with a single replicate for wheat, in duplicates for tomatoes and in triplicates for corn. Sample aliquots were analyzed 0, 0.1 to 0.2 (equal to 2 to 4 hours), 1, 4, 8 and 11 (only corn) days after treatment (DAT). The test solution volume was determined in parallel.

3. Analytical Procedures

At each sampling interval aliquots of 0.1 mL each were taken from each test system and the test solution volume was determined. Additionally, at study end (DAT-8) the roots of the test plants were washed with 50 mL water.

The radioactivity amount in test and washing solutions was determined by liquid scintillation counting (LSC).

The plant uptake factors were calculated according to the following formula:

$$PUF = \frac{ln\left(\frac{m_{DAT-x} + m_{wash}}{m_{DAT-0}}\right)}{ln\left(\frac{V_{DAT-x}}{V_{DAT-0}}\right)}$$

with:

m_{DAT-0}	= initial amount of test item in test solution	[µg]
m_{DAT-x}	= amount of test item in test solution at study end (DAT-8 or DAT-11)	[µg]
m_{wash}	= amount of test item in washing solution	[µg]
V_{DAT-0}	= initial volume of test solution	[L]
V_{DAT-x}	= volume of test solution at study end (DAT-8 or DAT-11)	[L]

II. RESULTS AND DISCUSSION

A. FINDINGS

The transpiration volume of the treated plants at study end was 250 mL for wheat (DAT-8) and ranged from 215 to 265 mL for tomatoes (DAT-8, mean 240 mL) and from 128 to 160 mL for corn (DAT-11, mean 140 mL).

Overall, the concentration of trifluoroacetic acid in the test solutions from wheat and tomato experiments increased towards study end (see Table 7.1.4- 4 and Table 7.1.4- 5, indicating a restricted permeability of the test item through the root cell walls. The concentration of trifluoroacetic acid in the test solutions from corn experiments was nearly stable during the whole study period (see Table 7.1.4- 6).

The mean PUFs for trifluoroacetic acid were determined as 0.66 in wheat, 0.74 in tomatoes and 0.98 in corn.

Table 7.1.4- 4: Plant Uptake Factors of trifluoroacetic acid in Wheat

Replicate	DAT-0			DAT-8				PUF
	V [L]	c [µg/L]	m [µg]	V [L]	c [µg/L]	m [µg]	m_{wash} [µg]	
1	0.800	767.8	614.3	0.550	854.1	469.8	9.1	0.66
Mean	**0.80**	**767.8**						**0.66**

DAT: days after treatment
PUF: plant uptake factor
V: volume of test solution
c: concentration of test item in test solution
m: mass of test item in test solution
m_{wash}: mass of test item in washing solution

Table 7.1.4- 5: Plant Uptake Factors of trifluoroacetic acid in Tomato

Replicate	DAT-0			DAT-8				PUF
	V [L]	c [µg/L]	m [µg]	V [L]	c [µg/L]	m [µg]	m_{wash} [µg]	
1	0.800	700.9	560.7	0.535	806.5	431.5	6.0	0.62
2	0.800	722.7	578.2	0.585	742.2	434.2	7.9	0.86
Mean	**0.80**	**711.8**						**0.74**

DAT: days after treatment
PUF: plant uptake factor
V: volume of test solution
c: concentration of test item in test solution
m: mass of test item in test solution
m_{wash}: mass of test item in washing solution

Table 7.1.4- 6: Plant Uptake Factors of trifluoroacetic acid in Corn

Replicate	DAT-0			DAT-11				PUF
	V [L]	c [µg/L]	m [µg]	V [L]	c [µg/L]	m [µg]	m_{wash} [µg]	
1	0.800	762.0	609.6	0.640	750.2	480.1	3.6	1.04
2	0.800	772.6	618.0	0.672	758.1	509.5	4.4	1.06
3	0.800	772.8	618.2	0.670	785.9	526.5	4.3	0.86
Mean	**0.80**	**769.1**						**0.98**

DAT: days after treatment
PUF: plant uptake factor
V: volume of test solution
c: concentration of test item in test solution
m: mass of test item in test solution
m_{wash}: mass of test item in washing solution

III. CONCLUSIONS

The plant uptake factors of [1-^{14}C]trifluoroacetate (report name: trifluoroacetic acid) were determined as 0.66 in wheat, as 0.74 in tomato and as 0.98 in corn.

The results indicate that the plant uptake in wheat and tomato was lower than the water uptake, probably to a restricted permeability of the test item through the root cell walls, whereas the plant uptake in corn was not restricted.

*****

Report:	**KCA 7.1.4 /04; [redacted], B.; 2013**
Title:	Determination of a Suitable Plant Uptake Factor (PUF) of trifluoroacetic acid (TFA) for use in Environmental Fate Models in the Target Crop Wheat
Report No:	EnSa-13-0545
Document No:	M-468684-01-1
Guidelines:	• EFSA PPR-panel on the use of the Plant Uptake Factor in exposure models (2013)
GLP:	no

Executive Summary

The EFSA PPR-panel (2013) has recognized in an opinion that plant uptake via roots is significant when calculating leaching exposure concentrations and has recommended the use of the Plant Uptake Factor (PUF) in exposure models, if evidence for the actual occurrence of the process is demonstrated.

Evidence for the occurrence of plant uptake of the degradation product trifluoroacetic acid has been demonstrated consistently in crop specific plant uptake studies and supportive confined rotational crop studies, indicating significant trifluoroacetic acid translocation from soil to various plant matrices. Given the evidence on the occurrence of the plant uptake, the EFSA PPR-Panel (2013) found the use of measured PUF values appropriate for parameterization of environmental leaching models. From the study results of the target crop (wheat) specific trifluoroacetic acid plant uptake study, the average trifluoroacetic acid PUF of 0.59 is justified for modeling purposes.

I. MATERIAL AND METHODS

Evidence on the occurrence of trifluoroacetic acid uptake by plants was provided by confined rotational crop studies on wheat, turnip, swiss chard, radish and lettuce using TFA-precursor as well as the two plant uptake studies KCA 7.1.4 /02 and KCA 7.1.4 /03.

1. Confined Rotational Crop Studies

The two confined rotational crop studies indicated that the plant uptake of trifluoroacetic acid occurs. One study examined the metabolism of a trifluoroacetic acid precursor in wheat, turnip and swiss chard, the second study in wheat, radish and lettuce. Transfer from soil into plant matrices was clearly shown as significantly high residues of trifluoroacetic acid were measured in all rotations, while the residues in soil declined simultaneously. Hence, both studies confirmed the occurrence of plant uptake of trifluoroacetic acid.

2. Quantification of Plant Uptake

Quantification of plant uptake is calculated by according to the following definitions and formulae.

The PUF is defined as the ratio of the concentration of a compound in the solution taken up by the plant (c_{uptake}) to the concentration of that compound in the soil solution ($c_{porewater}$).

$$PUF = \frac{c_{uptake}}{c_{porewater}}$$ **equation 1**

and $$c_{uptake} = \frac{m_{uptake}}{V_{Uptake}}$$

with:

PUF	= plant uptake factor	[-]
c_{uptake}	= test item concentration in plants	[µg/L]
$c_{porewater}$	= test item concentration in porewater	[µg/L]
m_{uptake}	= amount of test item taken up by plants	[µg]
V_{uptake}	= volume of test solution taken up by plants	[L]

Leaching models (e.g. PEARL and PELMO) use the PUF to calculate the amount of a compound taken up by a plant with the transpiration stream in each time step according to:

$$m_{uptake} = c_{porewater} \cdot V_{uptake} \cdot PUF$$ **equation 2**

with:

m_{uptake}	= amount of test item taken up by plants	[µg]
$c_{porewater}$	= test item concentration in porewater	[µg/L]
V_{uptake}	= volume of test solution taken up by plants	[L]
PUF	= plant uptake factor	[-]

The EFSA PPR-Panel (2013) has stated in its opinion that plant uptake via roots is of significance when calculating leaching exposure concentrations and has recommended the use of the PUF in exposure models. Due to the possible variability of the PUF between different compounds and crops, evidence on the actual occurrence of the process is to be provided when using a PUF > 0 as a higher tier in exposure modeling.

To demonstrate evidence for plant uptake and set an appropriate PUF factor for exposure modeling, EFSA PPR (2013) outlines a tiered approach:

1 Briggs' formula estimating crop independent uptake factors based on the K_{oc} (FOCUS, 2000)

2 Plant uptake experiments with target crop (or justified substituted) of intended PPP use

A maximum PUF of 1.0 is defined as the upper limit for simulating passive uptake of a compound.

The Briggs approach consists of a relationship between plant uptake and the K_{ow} derived from experimental data showing the uptake and translocation into barley shoots (i.e. the transpiration stream concentration factor (TSCF) for a limited set of non-ionic compounds). As trifluoroacetic acid is strongly ionic, it does not fall in the range of validity of Briggs equation. Furthermore EFSA PPR (2013) sees high levels of uncertainty in the K_{ow} based relationships and suggest to limit the use of K_{ow} based approaches (Briggs' formula) to lower tier estimates and recommends plant uptake experiments for further refinement of the PUF. Consequently plant uptake experiments have been conducted.

3. Plant Uptake Experiments

In study KCA 7.1.4 /02 the actual trifluoroacetic acid-specific passive uptake via the aqueous xylem stream was investigated in a target crop specific plant uptake study designed to determine an experimental evidence based plant uptake factor (PUF) for use in higher tier environmental leaching model calculations following the recommendations EFSA PPR Panel (2013).

The study design mimics the soil pore water containing a test compound and focuses on determination of the gross uptake of this compound from the soil pore water via the root systems into the plant. Other processes influencing the concentration of a compound in soil such as degradation or adsorption to soil particles are on purpose excluded in the test system as these processes are considered separately in leaching models.

In study KCA 7.1.4 /02 the plant uptake of trifluoroacetic acid was studied using five independent replicates of ten wheat plants (target crop) each were maintained in the test solution of ^{14}C-labelled test item at a pH of 6.5. Two additional test systems containing water were prepared as the control. Since the plants take up water from the test solution, an exclusion of the test compound from the water taken up will lead to an increase of the concentration in the remaining solution. The concentration of test item in the solution and the volume of test solution over time are measured during the study. As a result the concentration of the test item over time is known as well as the amount of water consumed by the plant. A comparison of the concentrations in the test solution at the start and at the end of the study (reduced volume of the remaining test solution) allows an indirect estimate of the plant uptake factor of the test item through the following calculation:

$$PUF = \frac{ln\left(\frac{m_{final} + m_{wash}}{m_{DAT-0}}\right)}{ln\left(\frac{V_{final}}{V_{DAT-0}}\right)} \qquad \textbf{equation 3}$$

with:

m_{DAT-0}	= initial amount of test item in test solution	[µg]
m_{final}	= amount of test item in test solution at study end	[µg]
m_{wash}	= amount of test item in wash solution at study end	[µg]
V_{DAT-0}	= initial volume of test solution	[L]
V_{final}	= volume of test solution at study end	[L]

To further confirm the reliability of the PUF determined indirectly by calculating the concentration differences in the test solution over time additional recovery experiments were conducted. The actual radioactivity taken up by the plant after combustion of the test samples was measured and compared it to the estimated amount of trifluoroacetic acid taken up by the plant from the test solution in the PUF experiment.

A supportive study KCA 7.1.4 /03 on the plant uptake of trifluoroacetic acid on the target crop wheat and additionally on corn and tomatoes was also conducted.

II. RESULTS AND DISCUSSION

A. Findings

1. Confined Rotational Crop Studies

In the first confined rotational crop study addressing the metabolism in wheat, turnip and swiss chard the radioactive residues were extracted conventionally from all raw agricultural commodities (RACs) amounting to > 97% of the total radioactive residues (TRRs). From the extract, the metabolites – amongst them trifluoroacetic acid - were quantified by HLPC and TLC with a high identification rate of > 92.5% of the TRR.

In the target commodity wheat, the highest plant residues were extracted from the matrices of the 2nd rotation and a decline was noted from the material of the 3rd rotation. This is explained by the formation of the trifluoroacetic acid metabolite in soil over time followed by significant plant uptake in the 2nd rotation resulting in lower availability in soil for further uptake in the third rotation. This is

fully coherent with the steady decline of soil residues with the precursor metabolizing into trifluoroacetic acid which is taken up by the plant leading to a decrease in soil from 0.162 mg/kg (day 30) to 0.034 mg/kg (day 317).

Furthermore, trifluoroacetic acid was shown to be by far the major metabolite in all commodities of all rotations, ranging from 83.6% to 99.9% suggesting that the process of plant uptake explains the declining trifluoroacetic acid soil residues rather than further metabolization.

In the second study addressing the metabolism in wheat, radish and lettuce the transfer of trifluoroacetic acid from soil into the plant matrices was clearly shown; as significantly high total radioactive residues were measured in all rotations, while the residues in the soil declined simultaneously.

The residue in 30 day plantings was found to be highly polar in nature with only small quantities of the trifluoroacetic acid precursor or non-polar metabolites present in any sample. The residue from the later 120 and 365 day plantings comprised almost entirely polar material. The main single component of the polar residue was trifluoroacetic acid, accounting for up to 80% of the TRR in the 30 day grain sample.

The results of this study indicate that the uptake of the trifluoroacetic acid precursor by rotational crops occurs at low levels only. Clearly identified the soil metabolite trifluoroacetic acid as the major component of the resultant crop residue and with it confirmed the occurrence of trifluoroacetic acid plant uptake.

2. Plant Uptake Studies

A summary of the results of the plant uptake factor study of trifluoroacetic acid in wheat is shown in Table 7.1.4- 7.

Table 7.1.4- 7: Plant Uptake Factors of Five Independent Test Systems in Wheat
(test period: 8 days, single values)

Replicate	V_{DAT-0} [L]	c_{DAT-0} [µg/L]	m_{DAT-0} [µg]	V_{DAT-8} [L]	c_{DAT-8} [µg/L]	m_{DAT-8} [µg]	m_{DAT-8} [µg]	PUF
1	0.800	75.5	60.4	0.260	100.9	26.2	6.5	0.54
2	0.800	75.3	60.2	0.270	103.4	27.9	6.5	0.51
3	0.800	75.4	60.3	0.420	82.2	34.5	4.1	0.69
4	0.800	75.5	60.4	0.280	105.1	29.4	5.7	0.52
5	0.800	76.5	61.2	0.370	86.9	32.1	4.5	0.66
mean		**75.6**						**0.59**

DAT: days after treatment
V: volume of test solution
m: mass of test item in test solution
PUF: plant uptake factor
c: concentration of test item in test solution

Additional recovery experiments demonstrate that the reduced test item amount in test solution at study end could be recovered in the plants (recovery of 92.6%) and thus, it was confirmed that the results of the PUF experiments are reliable.

The significant recovery provides further evidence on the occurrence of trifluoroacetic acid plant uptake and indicates the reliability of the test method.

From the supportive studies on wheat, corn and tomatoes, the single test on the target crop wheat provided a PUF value of **0.66**, which is in the same range as the values found in the five independent

test systems. In the other two varieties corn and tomatoes higher plant uptake was determined with average PUF values of **0.98** and **0.74** respectively.

III. CONCLUSIONS

The EFSA PPR-panel (2013) has recognized in an opinion that plant uptake via roots is significant when calculating leaching exposure concentrations and has recommended the use of the Plant Uptake Factor (PUF) in exposure models, if evidence for the actual occurrence of the process is demonstrated.

Investigations into the trifluoroacetic acid-specific passive uptake in wheat determined an experimental evidence-based plant uptake factor (PUF) of 0.59 for trifluoroacetic acid for use in higher tier environmental leaching model calculations. The translocation of TFA from the test solution into the plant was further confirmed by a high recovery rate of trifluoroacetic acid of 92.6% in the combusted plant material.

Supportive experiments showed a trifluoroacetic acid PUF-factor of 0.66 for the target crop wheat, which is in the same range as the values found in the multi-replicate wheat study.

Supplementary evidence for the occurrence of plant uptake of trifluoroacetic acid is demonstrated in confined rotational crop studies of in which increasing concentrations of trifluoroacetic acid in various crop matrices coincided with decreasing soil residues of trifluoroacetic acid and its precursors.

Evidence for the occurrence of plant uptake of trifluoroacetic acid has been demonstrated consistently in a number of studies, which according to EFSA PPR-Panel (2013) is the necessary condition to justify the use of a PUF > 0 in environmental leaching models. For model assessment of plant protection products applied in wheat a trifluoroacetic acid PUF of 0.59 is justified from study evidence.

CA 7.1.4.1 Column leaching studies

CA 7.1.4.1.1 Column leaching of the active substance

The leaching behavior of flufenacet in soil in the laboratory was evaluated during the Annex I Inclusion and was accepted by the European Commission (7469/VI/98-Final – 3rd July 2003). The following study is included in the Baseline Dossier:

Annex Point / Reference No	Author(s)	Year	Document No
KCA 7.1.4.1.1 /01	[redacted], I. V., [redacted] S.	1993	M-002198-01-1

No additional studies are submitted within this Supplemental Dossier for the flufenacet renewal of approval.

CA 7.1.4.1.2 Column leaching of metabolites, breakdown and reaction products

The leaching behavior of flufenacet degradation products in soil in the laboratory was evaluated during the Annex I Inclusion and was accepted by the European Commission (7469/VI/98-Final – 3rd July 2003). The following study is included in the Baseline Dossier:

Annex Point / Reference No	Author(s)	Year	Document No
KCA 7.1.4.1.2 /01	[redacted], I. V., [redacted] S.	1993	M-002198-01-1

An additional study has been performed for trifluoroacetic acid to refine the results from the batch equilibrium experiments summarized in section CA 7.1.3.1 and is submitted within this Supplemental Dossier for the flufenacet renewal of approval.

Report: **KCA 7.1.4.1.2 /02; [redacted], E.-M., 2014**
Title: [1-^{14}C]trifluoroacetate: Soil Column Leaching
Report No: EnSa-14-0050
Document No: M-477737-01-1
Guidelines: • OECD Test Guideline No. 312
• US EPA OCSPP Test Guideline No. 835.1240
GLP: yes

Executive Summary

The adsorption/desorption behavior of [1-^{14}C]trifluoroacetate (report name [1]: trifluoroacetic acid) was studied in four different soils in the dark in the laboratory at 20.1 °C using two different soil column leaching experiments:

Soil	Source	Texture (USDA)	pH	OC [%]
Laacherhof AXXa	Monheim, Germany	loamy sand	6.2	1.8
Dollendorf II	Blankenheim, Germany	loam	7.4	5.2
Hoefchen am Hohenseh	Burscheid, Germany	silt loam	6.5	1.6
Laacherhof Wurmwiese	Monheim, Germany	sandy loam	5.3	1.9

[1-^{14}C]trifluoroacetate was used as test item. 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 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, 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 and reference items were sufficient 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 test item amount 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 tracer amount 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 reference item amount 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 again 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 there.

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[20], Hamaker[21] and McCall[22] 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 in both test designs. Thus, virtually no adsorption was determined for the test item, when calculation was performed according to Ketelle[23] and Swoboda[24]. According to the Briggs [17] classification system, the mobility of trifluoroacetic acid can be classified as "very mobile" in all soils.

Considering the experimental results it can be assumed that trifluoroacetic acid has a high mobility in the tested soils.

I. MATERIALS AND METHODS

A. MATERIALS

1. Test Item

[1-^{14}C]trifluoroacetate (report name: trifluoroacetic acid)	
CAS No	2923-18-4
Specific activity	3.48 MBq/mg
Radiochemical purity	> 98% HPLC with radioactivity detector

2. Test Soils

The soils (see Table 7.1.4.1.2- 1) were sampled freshly from the field (upper horizon of 0 to 20 cm), sieved to a particle size of ≤ 2 mm and stored refrigerated at ≤ 8 °C for 18 days before study start. The soils were air-dried before application. The soils were taken from agricultural areas representing different geographical origins and different soil properties as required by the guidelines.

[20] S. M. Lambert; J. J. Porter and H. L. Pease: Movement and sorption of chemically applied to the soil, Weeds 13, 185, 1965.

[21] J. W. Hamaker: "The interpretation of soil leaching experiments", in: Environmental dynamics of pesticides, (Eds. R. Haque and V. H. Freed), pp 135-172, Plenum Press, N. Y., 1975.

[22] P. J. MCCall; D. A. Laskowski; R. L. Swann and H. J. Dishburger: "Measurment of sorption coefficients of organic chemicals and their use in environmental fate analysis", in: Test Protocols for Environmental Fate and Movement of Toxicants; Proccedings of AOAC Symposium, AOAC, Washington DC, 1981.

[23] B. H. Ketelle and G. E. Boyd: The exchange adsorption of ions from aqueous solutions by organic zeolites. The separation of the Yttrium group rare earths, J. Amer. Chem. Soc. 69, 2800, 1947.

[24] A. R. Swoboda and G. W. Thomas: Movement of parathion in soil columns, J. Agr. Food Chem. 16, 923, 1968.

Table 7.1.4.1.2- 1: Physico-chemical properties of test soils

Parameter	Results / Units			
Soil Designation	Laacherhof AXXa	Dollendorf II	Hoefchen am Hohensch	Laacherhof Wurmwiese
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
GPS Coordinates	N 51° 04.647 E 006° 53.517'	N 50° 22. 899' E 006° 43.001'	N 51° 04.001' E 007° 06.327'	N 51° 04.857' E 006° 55.251'
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	57
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/cm^3]	1.22	1.01	1.12	1.13

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

DAT: days after treatment
DW: dry weight
GPS: global positioning system
USDA: United States Department of Agriculture

B. STUDY DESIGN

1. Experimental Conditions

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 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 test item [1-^{14}C]trifluoroacetate for the treatment of the soil columns was based on the intended single maximum field application rate of the parent, resulting in a nominal application rate of 11.0 µg test item per soil column.

All application solutions were prepared in water. The 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 drop wise onto the soil surface of the respective soil columns

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

The volume and the pH value of each leachate fraction were determined.

The 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 column segment extracts was determined by liquid scintillation counting. Additionally, selected leachate fractions and soil column segment extracts were analyzed 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 including accurate mass determination. The identity of the reference test item was elucidated by HPLC-MS/MS including accurate mass determination.

The adsorption values for leaching compounds (e.g. the test item) were calculated according to Ketelle [23] and Swoboda [24].

The adsorption values for non-leaching compounds (e.g. the reference item) were calculated according to Lambert [20] and according to Hamaker [21] / McCall [22]; the results of both mathematical models 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 sufficient 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 test item amount 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 tracer amount 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 reference item amount 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 again 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 there.

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 test item amount was found in leachate fraction 8 of soil Laacherhof AXXa, in leachate fraction 3 of soil Dollendorf II, in leachate fraction 9 of soil Hoefchen am Hohenseh and in leachate fraction 3 or 10 of soil Laacherhof Wurmwiese. The tracer peak was likewise found in leachate fraction 7 to 9 of soil Laacherhof AXXa, in leachate fraction 3 to 4 of soil Dollendorf II, in leachate fraction 9 of soil Hoefchen am Hohenseh and in leachate fraction 3 or 10 of soil Laacherhof Wurmwiese. 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 atrazine 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). According to the Briggs **Fehler! Textmarke nicht definiert.** classification system, the mobility of atrazine can be classified as "intermediate" to "low", according to this system.

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 in both test designs. Thus, virtually no adsorption was determined for the test item. According to the Briggs [17] classification system, the mobility of trifluoroacetic acid can be classified as "very mobile" in all soils.

Table 7.1.4.1.2- 2: Adsorption coefficients of the test item and reference item in soils
(mean values of duplicate soil columns)

Soil	[1-^{14}C]trifluoroacetate		[triazine-UL-^{14}C]atrazine	
	K_d [mL/g]	K_{OC} [mL/g]	K_d [mL/g]	K_{OC} [mL/g]
Laacherhof AXXa	0.0	0.0	5.1	281.3
Dollendorf II	0.0	0.0	6.3	120.4
Hoefchen am Hohenseh [1]	0.0	0.0	5.4	337.1
Laacherhof Wurmwiese	0.0	0.0	5.6	294.9
Overall Mean	**0.0**	**0.0**	**5.6**	**258.4**

[1] only one soil column was considered

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 in both test designs. Thus, virtually no adsorption was determined for trifluoroacetic acid. According to the Briggs classification system for mobility of organic chemicals in soil, the mobility of trifluoroacetic acid can be classified as "very mobile" in all soils.

Considering the experimental results it can be assumed that trifluoroacetic acid has a high mobility in the tested soils.

CA 7.1.4.2 Lysimeter studies

The leaching behavior of flufenacet in soil in lysimeter studies was evaluated during the Annex I Inclusion and was accepted by the European Commission (7469/VI/98-Final – 3rd July 2003). The following study is included in the Baseline Dossier:

Annex Point / Reference No	Author(s)	Year	Document No
KCA 7.1.4.2 /01	[redacted]	1996	M-002190-01-2
KCA 7.1.4.2 /02	[redacted]	1995	M-002192-01-2
KCA 7.1.4.2 /03	[redacted]	1995	M-002195-01-1
KCA 7.1.4.2 /04	[redacted]	1995	M-002194-01-1
KCA 7.1.4.2 /05	[redacted]	1997	M-002187-01-1

No additional studies are submitted within this Supplemental Dossier for the flufenacet renewal of approval.

CA 7.1.4.3 Field leaching studies

Field leaching studies have not been conducted for flufenacet or its major degradation products as sufficient information can be derived from the existing studies.

CA 7.2 Fate and behavior in water and sediment

The route and rate of degradation of flufenacet under aerobic conditions was studied in a number of aquatic test systems at different temperatures, using either [phenyl-UL-^{14}C]- or [thiadiazole-2-^{14}C]-labeled flufenacet as test item. Flufenacet was stable to hydrolysis and photolysis in sterile aquatic systems, while degradation was observed in microbial active aquatic systems, like water/sediment systems and surface water. Under aerobic conditions flufenacet was degraded in water, sediment and the entire system to two major degradation products: FOE-thiadone (max. occurrence 84.3% of applied radioactivity [% AR], entire system) and FOE methylsulfide (max. occurrence 11.4% AR, entire system). Additionally, a number of minor degradation products were formed. Significant mineralization to carbon dioxide was observed for both labeling positions (2 to 15% AR) accompanied by the formation of non-extractable residues (2 to 46% AR).

On request of the US environmental protection agency (EPA) the route of degradation of FOE-thiadone under aerobic conditions was additionally studied in a number of aquatic test systems at different temperatures, using either [phenyl-UL-^{14}C]- or [thiadiazole-2-^{14}C]-labeled FOE-thiadone as test item. FOE-thiadone was stable to hydrolysis and sterile aqueous photolysis, while indirect photochemical degradation was observed in microbial active natural water, forming carbon dioxide and carbon monoxide as final major degradation product.

In addition to the aerobic water/sediment studies in the laboratory a microcosm study with 11 microcosm systems was performed in the Netherlands. Measurement of the disappearance of flufenacet from the water phases showed that under more realistic conditions, in systems containing not only biologically active sediment but also different aquatic organisms, the disappearance rate is much faster than determined in simple water/sediment systems.

A summary of maximum occurrences in water of major degradation products derived from laboratory studies is shown in Table 7.2- 1. The degradation pathway in aerobic aquatic systems (see Figure 7.2-1) was similar to that observed in aerobic soil (see Figure 7.1.1- 1).

The kinetic models and DT_{50} values in aquatic systems of flufenacet used for modeling purpose and trigger evaluation (best-fit) are summarized in Table 7.2- 2 to Table 7.2- 3. For the major degradation products FOE methylsulfide and FOE-thiadone no half-lives for modeling purposes and trigger evaluation could be calculated from aerobic water/sediment studies. However, for FOE-thiadone half-lives for trigger evaluation were derived for indirect photochemical degradation and are summarized in Table 7.2- 4.

The DT_{50} values and maximum occurrences / formation fractions in aquatic systems of flufenacet and its major degradation products used as modeling input values for the calculation of PECs are summarized in Table 7.1.2- 3.

.

Table 7.2- 1: Summary of maximum occurrences in aquatic systems of major flufenacet degradation products derived from laboratory studies (in percentage of applied radioactivity [% AR])

Degradation Product	Entire System [% AR]	Water [% AR]	Sediment [% AR]
FOE methylsulfide	11.4	8.0	3.5
FOE-thiadone	84.3	81.8	3.8

Figure 7.2- 1: Proposed degradation pathway of flufenacet in aquatic systems

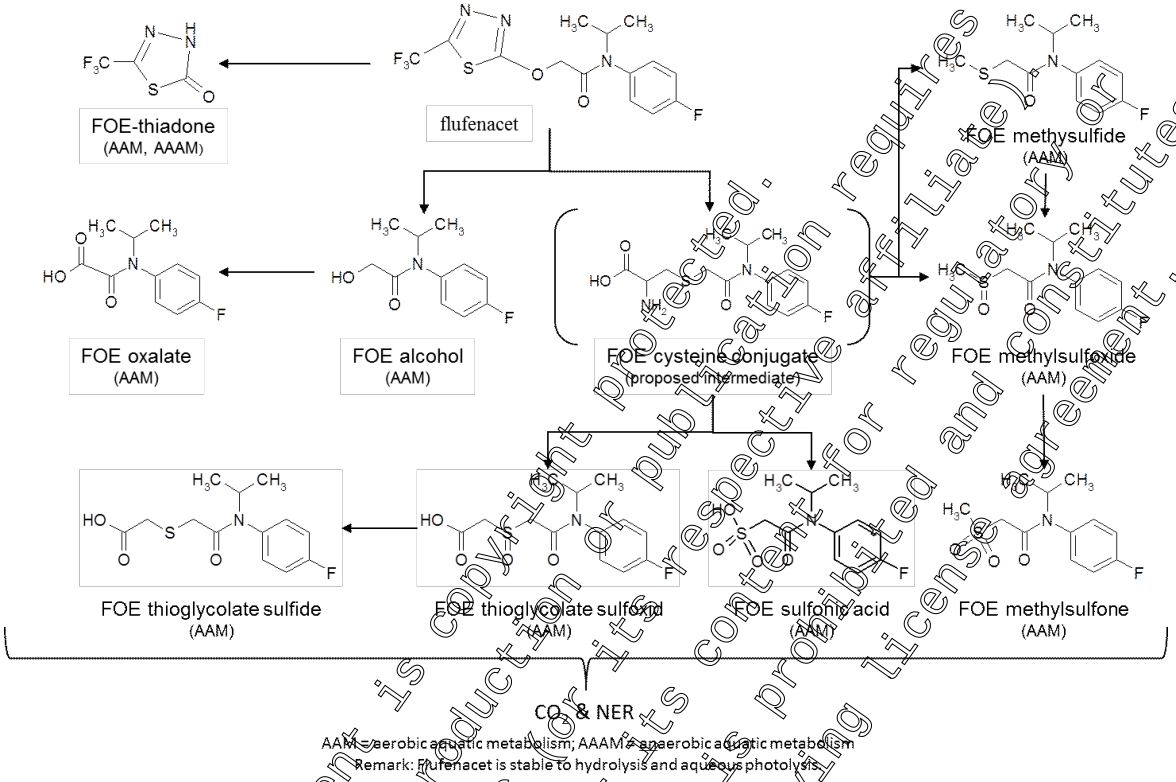


Table 7.2- 2: Summary of DT_{50} and DT_{90} values for degradation of flufenacet in aerobic surface water at 25 °C for trigger evaluation

Surface Water	Annex Point / Reference No	Kinetic Model [1]	DT_{50} [days]	DT_{90} [days]
Branchton	KCA 7.2.2.2 /01	SFO	618.3	> 1000

[1] SFO: single first order

Table 7.2- 3: **Summary of DT_{50} and DT_{90} values for degradation of flufenacet in aerobic water/sediment systems at 20 °C for modeling purpose (non-normalized) and trigger evaluation**

Water/Sediment System	Annex Point / Reference No	Modeling Purpose		Trigger Evaluation		
		Kinetic Model [1]	DT_{50} [days]	Kinetic Model [1]	DT_{50} [days]	DT_{90} [days]
Entire System						
Nelson Environmental Study Area (NESA)	KCA 7.2.2.3 /04	SFO	90.3	SFO	90.3	300.1
Bayer Research Park (BRP)	KCA 7.2.2.3 /04	SFO	89.0	SFO	89.0	295.7
Nelson Environmental Study Area (NESA)	KCA 7.2.2.3 /04	SFO	19.7	SFO	19.7	65.3
Bayer Research Park (BRP)	KCA 7.2.2.3 /04	SFO	38.1	SFO	38.1	126.6
Water						
Nelson Environmental Study Area (NESA)	KCA 7.2.2.3 /04	SFO	58.7	SFO	58.7	195.1
Bayer Research Park (BRP)	KCA 7.2.2.3 /04	SFO	40.9	DFOP	31.5	171.6
Nelson Environmental Study Area (NESA)	KCA 7.2.2.3 /04	SFO	17.0	SFO	17.0	56.4
Bayer Research Park (BRP)	KCA 7.2.2.3 /04	SFO	23.8	DFOP	18.6	94.3
Sediment						
Nelson Environmental Study Area (NESA)	KCA 7.2.2.3 /04	SFO	140.5	SFO	140.5	466.8
Bayer Research Park (BRP)	KCA 7.2.2.3 /04	SFO	120.5	SFO	120.5	400.2
Nelson Environmental Study Area (NESA)	KCA 7.2.2.3 /04	SFO	17.6	SFO	17.6	58.6
Bayer Research Park (BRP)	KCA 7.2.2.3 /04	SFO	47.9	SFO	47.9	159.1

[1] SFO: single first order, DFOP: double first order in parallel

Table 7.2- 4: **Summary of DT_{50} and DT_{90} values for indirect photochemical degradation of FOE-thiadone in aerobic surface water at 25 °C for trigger evaluation**

Surface Water	Annex Point / Reference No	Kinetic Model [1]	DT_{50} (experimental) [days]	DT_{50} (natural conditions) [days]
Rhine	KCA 7.2.1.3 /01	SFO	5.8	15.5 (Phoenix, USA) 24.0 (Athens, Greece)

[1] SFO: single first order

CA 7.2.1 Route and rate of degradation in aquatic systems (chemical and photochemical degradation)

CA 7.2.1.1 Hydrolytic degradation

The hydrolytic route and rate of degradation of flufenacet in buffers under sterile conditions in the dark in the laboratory were evaluated during the Annex I inclusion using [phenyl-UL-14C] labeled flufenacet, and were accepted by the European Commission (7469/VI/98-Final – 3rd July 2003). The following studies are included in the Baseline Dossier:

Annex Point / Reference No	Author(s)	Year	Document No
KCA 7.2.1.1 /01	[redacted] C.; [redacted] S.	1992	M-002203-01-1

Two additional studies have been performed for FOE-thiadone on request of the US Environmental Protection Agency (EPA) and are submitted within this Supplemental Dossier for the flufenacet renewal of approval. A summary of the route and rate of degradation of flufenacet in water and sediment is given in section CA 7.2 and Figure 7.2- 1.

Report:	**KCA 7.2.1.1 /03; [redacted], J. F.; [redacted], A. M.; 1999**
Title:	Hydrolysis Study of Thiadone (A Metabolite of FOE 5043)
Report No:	108719
Document No:	M-009620-01-1
Guidelines:	• EPA Ref. Subdivision N, Guideline Section 161-1
GLP:	yes

Executive Summary

The hydrolytic route and rate of degradation of [thiadiazole-2-^{14}C]FOE-thiadone were studied in sterile buffer solutions at pH 5, 7 and 9 in the dark in the laboratory for 30 days at 25 ± 1 °C.

A test item concentration of 0.5 mg/L (≙ 0.5 ppm) was applied.

Duplicate samples were processed and analyzed 0, 3, 7, 14, 21 and 30 days after treatment (DAT).

Mean material balances ranged from 99.3 to 99.5% of applied radioactivity [% AR] for all samples and tested pH values.

FOE-thiadone did not degrade during the study period of 30 days. Therefore, it is concluded that FOE-thiadone is stable to hydrolysis at pH 5, 7 and 9 and 25° C.

I. MATERIALS AND METHODS

A. MATERIALS

1. Test Item

[thiadiazole-2-^{14}C]FOE-thiadone

Lot No:	97B064-130
Specific Activity:	10.88 MBq/mg (50 mCi/mmol; 652,680 dpm/µg)
Radiochemical Purity:	97.7% (stated) and 95.5% measured at DAT-0

2. Test Buffers

Three 0.05 M buffers were used. The pH 5 buffer was prepared from glacial acid with sodium acetate, the pH 7 buffer was prepared from potassium dihydrogen phosphate with sodium hydroxide and the pH 9 buffer was prepared from potassium chloride/boric acid with sodium hydroxide. All buffer solutions were filter-sterilized before use.

B. STUDY DESIGN

1. Experimental Conditions

Sterile auto sampler vials filled with 4.7 mL test solution and closed with caps were used as test systems. As in preliminary experiments all applied radioactivity was recovered from the test solution, no provisions were made to collect volatiles.

The study application rate (SAR) of FOE-thiadone was approximately 0.5 mg/L (≙ 0.5 ppm)

The application solution was prepared in acetonitrile. 680 µL of the application solution were applied to 80 mL of the respective buffers using a gas-tight syringe to prepare the test solutions. The acetonitrile concentration in the final test solution was ≤ 1%. Afterwards, the test solutions were distributed to the auto sampler vials, which were then capped.

The test systems were incubated in the dark for 30 days at 25 ± 1°C in an environmental chamber.

2. Sampling

Six sampling intervals were distributed over the entire incubation period of 30 days. Duplicate samples were processed and analyzed 0, 3, 7, 14, 21 and 30 days after treatment (DAT).

Sterility of the test solutions was checked at DAT-0 and DAT-30 for each of the three buffers.

3. Analytical Procedures

At each sampling interval, duplicate test systems were removed from the environmental chamber and the pH value of the test solution was determined.

Test solutions were then characterized by liquid scintillation counting (LSC) and HPLC/radiodetection (aliquots for chromatographic analysis were acidified before measurement). The limit of detection (LOD) for the HPLC/radiodetection method was 0.6% AR.

The identity of the test item was elucidated by HPLC-MS.

Since FOE-thiadone did not undergo hydrolysis under study conditions, neither the rate of degradation nor the half-life was calculated.

II. RESULTS AND DISCUSSION

A. EXTRACTION AND QUANTITATION OF RADIOACTIVITY IN SOIL SAMPLES

Table 7.2.1.1- 1 to Table 7.2.1.1- 3 summarizes the degradation of [thiadiazole-2-^{14}C]FOE-thiadone as a function of time.

Table 7.2.1.1- 1: Degradation of FOE-thiadone in Buffer at pH 5
(expressed as percent of applied radioactivity; single values)

Compound	Mean	DAT 0	3	7	14	21	30
FOE-thiadone	A	96.2	95.6	95.9	95.8	96.1	96.0
	B	95.7	95.7	96.0	95.7	96.2	96.4
Unidentified Radioactivity [1]	A	3.9	4.4	4.1	4.2	3.9	4.0
	B	4.3	4.3	4.0	4.3	3.9	3.6
Material Balance [2]	**mean**	**100.0**	**99.7**	**100.6**	**100.7**	**98.4**	**97.9**

DAT: days after treatment
[1] More than one component - due to the impurities in the fortification solution.
[2] Mean values of duplicates.

Table 7.2.1.1- 2: Degradation of FOE-thiadone in Buffer at pH 7
(expressed as percent of applied radioactivity; single values)

Compound	Replicate	DAT 0	3	7	14	21	30
FOE-thiadone	A	95.6	97.0	96.2	96.7	96.9	97.8
	B	95.2	97.3	97.3	96.4	97.2	97.1
Unidentified Radioactivity [1]	A	4.4	3.0	3.8	3.3	3.1	2.3
	B	4.8	2.7	2.7	3.6	2.8	2.9
Material Balance [2]	**mean**	**100.0**	**99.1**	**99.3**	**101.1**	**98.7**	**97.8**

DAT: days after treatment
[1] More than one component - due to the impurities in the fortification solution.
[2] Mean values of duplicates.

Table 7.2.1.1- 3: Degradation of FOE-thiadone in Buffer at pH 9
(expressed as percent of applied radioactivity; single values)

Compound	Mean	DAT 0	3	7	14	21	30
FOE-thiadone	A	95.3	96.5	97.2	97.1	96.8	97.2
	B	96.0	97.1	96.6	97.4	96.6	97.4
Unidentified Radioactivity [1]	A	4.7	3.5	2.8	2.9	3.2	2.9
	B	4.0	2.9	3.4	2.6	3.4	2.6
Material Balance [2]	**mean**	**100.0**	**99.6**	**98.4**	**98.9**	**98.9**	**99.7**

DAT: days after treatment
[1] More than one component - due to the impurities in the fortification solution.
[2] Mean values of duplicates.

B. MATERIAL BALANCE

Mean material balances ranged from 97.9 to 100.7% of applied radioactivity [% AR] for all samples at pH 5, from 97.8 to 101.1% AR for all samples at pH 7 and from 98.4 to 100.0% AR for all samples at pH 9.

The complete material balance found at all sampling intervals demonstrated that no significant portion of radioactivity dissipated from the vessels or was lost during processing of these samples.

C. STERILITY

The sterility of the samples was maintained throughout the study.

D. DEGRADATION OF TEST ITEM

FOE-thiadone was stable to hydrolysis under the tested conditions.

III. CONCLUSIONS

FOE-thiadone did not degrade during the study period of 30 days. Therefore, it is concluded that FOE-thiadone is stable to hydrolysis at pH 5, 7 and 9 and 25° C.

*****

Report:	**KCA 7.2.1.1./02; [redacted], P.; 2009**
Title:	[thiadiazole-2-^{14}C]FOE5043-thiadone (BCS-AA41715): Hydrolytic Degradation
Report No:	M-358419-01-1
Document No:	MEF-09/308
Guidelines:	• OECD Test Guideline No. 111 • Commission Directives 94/37/EC and 95/36/EC amending Council Directive 91/414/EEC
GLP:	yes

Executive Summary

The hydrolytic route and rate of degradation of [thiadiazole-2-^{14}C]FOE-thiadone were studied in sterile buffer solutions at pH 4, 7 and 9 in the dark in the laboratory for 7 days at 50 ± 1 °C.

A test item concentration of 1.0 mg/L was applied.

Duplicate test systems were processed and analyzed 0, 0.1 (2.4 h), 0.25 (6 h), 1, 2, 5 and 7 days after treatment.

Mean material balances ranged from 91.4 to 102.1% of applied radioactivity [% AR] for all samples and tested pH values.

FOE-thiadone was hydrolytically stable during the entire study period of 7 days at 50 °C. From study M-009620-01-1 (Supplemental Dossier, KCA 7.2.1.1 /03) it is known that FOE-thiadone is also stable at 25 °C over the study period of 30 days, therefore, the optional test at 20 °C was omitted.

The half live of FOE-thiadone at 50 °C was estimated as > 1 year at pH 4, pH 7, and pH 9, and therefore at 25 °C as well.

Considering the hydrolytic stability determined under environmental pH conditions it is expected that hydrolytic processes will not contribute to the degradation of FOE-thiadone in the environment.

I. MATERIALS AND METHODS

A. MATERIALS

1. Test Item

[thiadiazole-2-^{14}C]FOE-thiadone

Batch No:	KATH 6249
Specific Activity:	4.28 MBq/mg
Radiochemical Purity:	> 99 (HPLC/radiodetection and TLC/radiodetection)

2. Test Buffers

The following three 0.01 M buffers were used: an acetate buffer for pH 5, a TRIS buffer for pH 7 and a borate buffer for pH 9. All buffer solutions were sterilized before use.

B. STUDY DESIGN

1. Experimental Conditions

Sterile crimp-top vials (volume 10 mL) filled with 5 mL test solution and closed with crimp caps were used as test systems. Traps for volatiles were not used.

The study application rate (SAR) of FOE-thiadone was approximately 1.0 mg/L.

The application solution was prepared in acetonitrile. 123 µL of the application solution were applied to 100 mL of the respective buffers using a pipette to prepare the test solutions. Afterwards, the test solutions were distributed to the vials, which were then capped.

The test systems were incubated in the dark for 7 days at 50 ± 1°C in a temperature controlled water bath.

2. Sampling

Seven sampling intervals were distributed over the entire incubation period of 7 days. Duplicate samples were processed and analyzed 0, 0.1 (2.4 h), 0.25 (6 h), 1, 2, 5 and 7 days after treatment.

Sterility of the test solutions was checked at DAT-0 and DAT-7 for each of the three buffers.

3. Analytical Procedures

At each sampling interval, duplicate test systems were removed from the water bath and the pH value of the test solution was determined.

Test solutions were then characterized by liquid scintillation counting (LSC) and HPLC/radiodetection without any processing. The limit of detection (LOD) for the HPLC/radiodetection method was < 1% AR.

The identity of the test item was elucidated by HPLC-MS(/MS).

No kinetic evaluation was performed due to the stability of the test item.

II. RESULTS AND DISCUSSION

A. EXTRACTION AND QUANTITATION OF RADIOACTIVITY IN SOIL SAMPLES

Table 7.2.1.1- 4 to Table 7.2.1.1- 6 summarizes the degradation of [thiadiazole-2-^{14}C]FOE-thiadone as a function of time.

Table 7.2.1.1- 4: Degradation of FOE-thiadone in Buffer at pH 4
(expressed as percent of applied radioactivity; mean values of duplicates)

Compound	DAT 0	0.1	0.25	1	2	5	7
FOE-thiadone	98.6	100.7	99.5	100.3	98.7	93.5	92.6
Unidentified Radioactivity	0.4	0.7	1.2	0.1	0.1	0.4	0.3
Material Balance	**99.0**	**101.4**	**100.7**	**100.4**	**98.8**	**93.9**	**92.9**

DAT: days after treatment

Table 7.2.1.1- 5: Degradation of FOE-thiadone in Buffer at pH 7
(expressed as percent of applied radioactivity; mean values of duplicates)

Compound	DAT 0	0.1	0.25	1	2	5	7
FOE-thiadone	99.2	100.2	100.1	100.0	100.4	98.5	99.7
Unidentified Radioactivity	0.6	0.4	0.7	0.4	0.3	0.8	0.1
Material Balance	**99.8**	**100.6**	**100.8**	**100.4**	**100.6**	**99.2**	**99.8**

DAT: days after treatment

Table 7.2.1.1- 6: Degradation of FOE-thiadone in Buffer at pH 9
(expressed as percent of applied radioactivity; mean values of duplicates)

Compound	DAT 0	0.1	0.25	1	2	5	7
FOE-thiadone	99.5	100.5	100.1	101.5	99.7	100.1	99.8
Unidentified Radioactivity	0.5	0.3	0.6	0.2	0.9	0.4	0.2
Material Balance	**100.0**	**100.9**	**100.6**	**101.6**	**100.6**	**100.5**	**100.0**

DAT: days after treatment

B. MATERIAL BALANCE

Mean material balances ranged from 92.9 to 101.4% of applied radioactivity [% AR] for all samples at pH 4, from 99.2 to 100.8% AR for all samples at pH 7 and from 100.0 to 101.6% AR for all samples at pH 9.

The complete material balance found at all sampling intervals demonstrated that no significant portion of radioactivity dissipated from the vessels or was lost during processing of theses samples.

C. STERILITY

The sterility of the samples was maintained throughout the study.

D. DEGRADATION OF TEST ITEM

FOE-thiadone is considered to be hydrolytically stable under environmental conditions at pH values of 4 to 9.

III. CONCLUSIONS

FOE-thiadone did not degrade during the study period of 7 days.

The half live of FOE-thiadone at 50 °C was estimated as > 1 year at pH 4, pH 7 and pH 9, and therefore at 25 °C as well.

Considering the hydrolytic stability determined under environmental pH conditions it is expected that hydrolytic processes will not contribute to the degradation of FOE-thiadone in the environment.

CA 7.2.1.2 Direct photochemical degradation

The photolytic route and rate of degradation of flufenacet in sterile buffers in the laboratory was evaluated during the Annex I inclusion using [phenyl-UL-^{14}C]-labeled flufenacet and was accepted by the European Commission (7469/VI/98-Final – 3rd July 2003). The following studies are included in the Baseline Dossier:

Annex Point / Reference No	Author(s)	Year	Document No
KCA 7.2.1.2 /01	[redacted], A. M.; [redacted], B. A.	1995	M-002206-01-1
KCA 7.2.1.2 /02	[redacted], E.	1993	M-002208-01-1

An additional study has been performed for FOE-thiadone on request of the US Environmental Protection Agency (EPA) and is submitted within this Supplemental Dossier for the flufenacet renewal of approval.

Report:	**KCA 7.2.1.2 /03; [redacted], N. R.; [redacted], A. M.; 1999**
Title:	Aqueous photolysis of thiadone (a metabolite of FOE 5043)
Report No:	108720
Document No:	M-017985-01-1
Guidelines:	• EPA Ref: Subdivision N, Guideline Section 161-2
GLP:	yes

Executive Summary

The photolytic route and rate of degradation of [thiadiazole-2-^{14}C]FOE-thiadone were studied in sterile aqueous buffer at pH 7 under exposure to simulated sunlight (12 h light/12 h dark cycle) in the laboratory for 30 days at 25 ± 2 °C.

A study application rate of 0.49 mg/L (≙ 0.49 ppm) was applied.

The radiation intensity, spectral distribution and exposure time under experimental conditions would match natural sunlight exposure during the month of June in Painesville, Ohio. Additionally, dark control samples were incubated in parallel.

Duplicate samples were processed and analyzed 0, 3, 7, 14, 21 and 30 days after treatment (DAT) for both irradiated and dark samples.

Mean material balances ranged from 96.4 to 104.7% of applied radioactivity [% AR] for all samples and averaged 100.2% AR for both irradiated and dark control samples.

FOE-thiadone did not photodegrade under the test conditions.

I. MATERIALS AND METHODS

A. MATERIALS

1. Test Item

[thiadiazole-2-^{14}C]FOE-thiadone	
Batch No:	C-784
Specific Activity:	10.88 MBq/mg (50 mCi/mmol; 652,680 dpm/µg)
Radiochemical Purity:	95.3% (HPLC/radiodetection)

2. Test Buffer

A 50 mM phosphate buffer with a pH of 7 was used for the study. FOE-thiadone was found to be hydrolytically stable at this pH value. The buffer solution was sterilized before use.

B. STUDY DESIGN

1. Experimental Conditions

Static test systems were used, consisting of flint glass sample jars (volume 59 mL) filled with 10 mL buffer and equipped with opaque screw caps fitted with Teflon liners (dark control samples were additionally wrapped with foil). For the irradiated samples the tops of the sample jar caps were previously cut out and a quartz disk was attached with glue. The Teflon liners were also cut out to leave an O-ring gasket. Since a preliminary study indicated no loss of radioactivity from the pH 7 test systems, no trapping system was employed for volatiles in the definitive study.

The study application rate (SAR) of FOE-thiadone was 0.49 mg/L (≙ 0.49 ppm), based on one-half the application rate used for the aqueous photolysis study of flufenacet (KCA 7.2.1.2 /01).

The application solution was prepared in acetonitrile. 50 µL of the application solution were applied drop wise onto the buffer of the respective test systems using a gas-tight syringe to yield the test solution (finale acetonitrile concentration < 1%). After application, the DAT-0 samples were immediately processed. The remaining test systems were sealed and incubated either under dark or irradiated conditions.

The irradiated test systems were incubated with a 12-hour light/12-hour dark artificial sunlight cycle for 30 days at 25 ± 2°C in a water bath placed in a solar simulator 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 continuously determined using a radiometer. The radiation intensity, spectral distribution and exposure time under experimental conditions would match natural sunlight exposure during the month of June in Painesville, Ohio.

The dark control test systems were incubated in the dark for 30 days at 25 ± 2°C.

2. Sampling

Six sampling intervals were distributed over the entire incubation period of 30 days.

Duplicate samples were processed and analyzed 0, 3, 7, 14, 21 and 30 days after treatment (DAT) for both irradiated and dark samples.

For each of the samples, duplicate sterility checks were performed during preparation of the test systems. The agar plates were allowed to incubate at 25° C for 7 days, before they were checked for colony growth.

3. Analytical Procedures

At each sampling interval, duplicate non-irradiated and irradiated test systems were removed from the environmental chamber or photolysis apparatus.

The entire content of each jar was transferred to graduated cylinders and the volume was recorded. For irradiated samples the probe and the sample jars were rinsed with a small amount of methanol. The rinses were added to the aqueous sample in the graduated cylinder and the total volume was recorded.

The test solutions were characterized by liquid scintillation counting (LSC) and HPLC/radiodetection. The limit of detection (LOD) for the HPLC/radiodetection method was 1.5% AR.

The identity of the test item was elucidated by HPLC-MS.

As only minimal degradation of the test item was observed in sterile aqueous buffer (pH 7), no photolytic half-life was calculated.

II. RESULTS AND DISCUSSION

A. EXTRACTION AND QUANTITATION OF RADIOACTIVITY IN SOIL SAMPLES

Table 7.2.1.2- 1 summarizes the degradation of [thiadiazole-2-^{14}C]FOE-thiadone and the formation and degradation of its degradation products as a function of time.

Table 7.2.1.2- 1: Degradation of FOE-thiadone in Aqueous Buffer (pH 7) under Photolytic Conditions
(analysis obtained from the Integrated HPLC Chromatogram [1]; mean value of duplicates)

Compound	Mean	DAT 0	3	7	14	21	30
FOE-thiadone	irradiated	n.a.	98.6	99.3	99.8	100.0	100.0
	dark	97.1	98.9	99.3	99.0	98.9	100.0
Reg #1 (fortification impurity)	irradiated	n.a.	0.9	0.4	n.d.	n.d.	n.d.
	dark	1.2	1.1	1.0	1.1	1.1	n.d.
Reg #2 (fortification impurity)	irradiated	n.a.	0.3	n.d.	n.d.	n.d.	n.d.
	dark	1.8	n.d.	n.d.	n.d.	n.d.	n.d.
Unidentified Radioactivity	irradiated	n.a.	0.3	0.3	0.2	0.0	0.0
	dark	0.0	0.0	0.0	0.0	0.0	0.0
Material Balances	irradiated	**n.a.**	**104.3**	**101.3**	**100.5**	**96.4**	**95.0**
	dark	**104.7**	**101.5**	**98.2**	**101.9**	**100.7**	**97.2**

DAT: days after treatment n.d.: not detected n.a.: not analyzed
[1] Since virtually all of the applied radioactivity was recovered in each photolysis solution, the percent degradation product was obtained directly from the integrated HPLC chromatogram

B. MATERIAL BALANCE

Mean material balances ranged from 96.4 to 104.7% of applied radioactivity [% AR] for all samples and averaged 100.2% AR for both irradiated and dark control samples.

The complete material balance found at all sampling intervals demonstrated that no significant portion of radioactivity dissipated from the vessels or was lost during processing of theses samples.

C. STERILITY

The sterility of the samples was maintained throughout the study.

D. DEGRADATION OF TEST ITEM

The amount of FOE-thiadone in both irradiated and dark control samples stayed nearly constant over the whole study period, ranging from 97.1 to 100.0% AR. Thus, virtually no degradation of FOE-thiadone was observed for the irradiated and dark control samples at any of sampling intervals throughout the whole study period.

Two minor degradation products were present in both the irradiated and dark samples. Each of them accounted for less than 2% AR at DAT-0. Since these degradation products were detected in the DAT-0 samples and were not present anymore in the DAT-30 irradiated or dark control samples, neither was considered products of photolysis.

III. CONCLUSIONS

FOE-thiadone was stable to photodegradation under the test conditions.

CA 7.2.1.3 Indirect photochemical degradation

On request of the US Environmental Protection Agency a study for the determination of the photolytic route and rate of degradation of FOE-thiadone in natural water has been performed and is submitted within this Supplemental Dossier for the flufenacet renewal of approval.

Report:	**KCA 7.2.1.3 /01; [redacted], H. P.; [redacted], M.; 2011**
Title:	[thiadiazole-2-^{14}C]BCS-AA41715 (FOE-5043-thiadone) - Phototransformation in natural water
Report No:	MEF-09/506
Document No:	M-404931-01-1
Guidelines:	• EPA Ref: Subdivision N, Guideline Section 161-2 • Japanese MAFF New Test Guidelines 12 Nousan 8147, Annex No. 2-6-2 • Canadian PMRA Guideline DACO 8.2.3.3.2 • Commission Directives 94/37/EC and 95/36/EC amending Council Directive 91/414/EEC
GLP:	yes

Executive Summary

The photolytic route and rate of degradation of [thiadiazole-2-^{14}C]FOE-thiadone were studied in sterile, natural water from river Rhine under exposure to simulated sunlight in the laboratory for 14 days at 25 ± 1 °C.

A study application rate of 0.8 mg/L was applied.

Duplicate test systems of irradiated samples were processed and analyzed 0, 1, 2, 6, 8, 9 and 14 days after treatment (DAT). Duplicate test systems of dark control samples were processed and analyzed 0, 1, 2, 5, 6, 8 and 14 days after treatment.

The exposure time and radiation intensity under experimental conditions would match high intensive natural solar radiation found in Phoenix, AZ, USA for 30 days in summer.

Mean material balances ranged from 92.6 to 98.5% of applied radioactivity [% AR] for irradiated samples and from 99.6 to 100.2% AR for dark control samples.

The maximum amount of volatiles was 57.8% AR in irradiated samples at DAT-9. They were identified as carbon dioxide and carbon monoxide. Formation of other volatile organic compounds was not significant, as demonstrated by values being ≤ 0.5% AR at all sampling intervals. No formation of volatiles was observed in dark control samples.

The amount of FOE-thiadone in irradiated samples decreased from 98.5% AR at DAT-0 to 20.4% AR at DAT-14. Under dark conditions FOE-thiadone was stable during the test period.

Beside the formation of carbon dioxide and carbon monoxide, one minor degradation product was observed in irradiated samples with a maximum amount of 7.5% AR at DAT-8, rapidly declining to 4.2% at DAT-14. No degradation products were detected in dark control samples.

The experimental half-lives of FOE-thiadone in irradiated samples were calculated as 5.8 days, equal to 15.5 solar summer days at Phoenix, AZ, USA or 24.0 summer days at Athens, Greece. In dark control samples FOE-thiadone was stable over the whole study period.

It is considered, that photo-degradation of FOE-thiadone in natural water systems contributes significantly to the elimination of this compound from the aqueous environment.

I. MATERIALS AND METHODS

A. MATERIALS

1. Test Item

[thiadiazole-2-14C]FOE-thiadone
CAS No: 84352-75-0
Batch No: KATH 6249
Specific Activity: 4.28 MBq/mg
Radiochemical Purity: > 99% (HPLC/radiodetection)

2. Test Water

Water from the Rhine River (see Table 7.2.1.3- 1) was sampled at a distance of about 1 m from the river bank in a water depth of about 10-30 cm. The Rhine River is well known and represents typical natural water in agricultural areas. 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 filtered and sterilized before use.

Table 7.2.1.3- 1: Physico-chemical properties of test soils

Parameter	Results / Units
Water Designation	Rhine River
Geographic Location	
km	717 - 718
City	Monheim
State	North-Rhine Westphalia
Country	Germany
pH [1]	8.0
Suspended Solids [mg/L] [1]	130
Total Evaporation Residues [mg/L] [1]	370
Oxygen Saturation at 22.5 °C [%] [1]	95.3
Conductivity [µS/cm] [1]	529
Total Organic Carbon [mg/L]	2
Water Hardness [° dH]	10.5
Total Phosphorous [mg/L]	0.0815
Total Nitrite and Nitrate [mg/L]	3.1

[1] measured after sampling

B. STUDY DESIGN

1. Experimental Conditions

Static test systems were used, consisting of quartz glass vessels (50 mm x 26 mm x 16 mm), each containing 20 mL (main test 1) or 19 mL test solution (main test 2). A glass neck was attached to the test vessels. Results of preliminary tests indicated the formation of volatiles which did not adsorb to soda lime or polyurethane. Therefore, the test systems for irradiated samples were either equipped with a solid trap attachment for collection of carbon dioxide and volatile organic compounds (replicate A) or sealed with crimp caps to allow for analysis of the headspace e.g. by combustion (replicate B).

Test systems for dark control samples were closed with glass stoppers as no formation of volatiles was expected.

The study application rate (SAR) of FOE-thiadone was 0.8 mg/L, chosen with respect to the water solubility of FOE-thiadone and the limit of detection of the analytical methods.

The application solution was prepared in acetonitrile. 540 µL of the application solution were added to 540 mL of sterile, filtered natural water to yield the test solution (finale acetonitrile concentration 0.1%). After distribution of the test solution into the test vessels (main test 1), the DAT-0 samples were immediately processed. The remaining test systems were either equipped with trap attachments or sealed with crimp caps and incubated either under irradiated or dark conditions.

Due to the non-sufficient material balances found for the irradiated samples of main test 1, the irradiation experiment was repeated by exposing the dark control samples of main test 1 to light (main test 2). For main test 2 all test systems were sealed with crimp caps to allow for investigation of the headspace by combustion.

The irradiated test systems were incubated under continuous irradiation for 14 days at 25 ± 1 °C in the Suntest 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 study start and end using an irradiance sensor. The exposure time and radiation intensity under experimental conditions would match high intensive natural solar radiation found in Phoenix, AZ, USA for 30 days in summer.

The dark control samples were incubated for 14 days in a climatic cabinet protected from light at 25 ± 1 °C.

2. Sampling

Seven sampling intervals were distributed over the entire incubation period of 14 days.

Duplicate test systems of irradiated samples were processed and analyzed 0, 1, 2, 6, 8, 9 and 14 days after treatment (main test 2). Duplicate test systems of dark control samples were processed and analyzed 0, 1, 2, 5, 6, 8 and 14 days after treatment (main test 1).

Sterility checks of the test systems as well as measurements of the oxygen saturation were performed at DAT-0 and DAT-14 of main test 1 and at DAT-14 of main test 2.

3. Analytical Procedures

At each sampling interval, duplicate test systems of irradiated and dark control samples were removed from the Suntest unit or the climatic chamber.

Prior to opening an irradiated test system equipped with a trap attachment, volatiles possibly still present in the headspace were transferred into the trap attachment by a gentle nitrogen stream. Prior to opening an irradiated test system sealed with a crimp cap, the headspace of the test system was carefully sucked through an oxidizer oven for about 1 hour.

After sampling of the volatiles, the test solutions were directly characterized by liquid scintillation counting (LSC) and HPLC/radiodetection. The limit of detection (LOD) for the HPLC/radiodetection method was 0.4% AR. The amount of volatiles was determined either by LSC (test systems equipped with trap attachments) or by combustion/ LSC (sealed test systems; volatiles were detected as carbon dioxide).

The identity of the test item was elucidated by HPLC-MS(MS). Carbon dioxide was identified due to its adsorption to soda lime and carbon monoxide was identified due to the positive results of an indicator test tube (color change).

4. Kinetic Evaluation

The degradation kinetics of the test item was determined for irradiated samples using single first order kinetics. Input datasets were the mean residual amounts found at each sampling interval (main test 2). DT_{50} values were calculated from the resulting parameters. No kinetic evaluation was performed for dark control samples, as virtually no degradation of FOE-thiadone was observed over the whole study period.

II. RESULTS AND DISCUSSION

A. EXTRACTION AND QUANTITATION OF RADIOACTIVITY IN SOIL SAMPLES

Table 7.2.1.3- 2 and Table 7.2.1.3- 3 summarize the degradation of [thiadiazole-2-^{14}C]FOE-thiadone and the formation and degradation of its degradation products in irradiated and dark control samples as a function of time.

Table 7.2.1.3- 2: Degradation of FOE-thiadone in Natural Water under Photolytic Conditions
(main test 2; mean values of duplicates)

Compound	DAT 0	1	2	6	8	9	14 [1]
Volatiles [2]	n.a.	6.5	12.3	40.5	49.7	53.2	18.7
FOE-thiadone	98.5	88.9	79.1	45.8	37.4	34.9	20.4
Unknown #1	n.d.	1.1	2.3	5.9	7.5	6.3	4.2
Unidentified/Diffuse Radioactivity	0.0	0.0	0.0	0.4	0.5	0.7	1.1
Total Residues in Test Solution	98.5	90.0	81.4	52.1	45.4	42.0	25.7
Material Balances	**98.5**	**96.5**	**93.7**	**92.6**	**95.2**	**95.2**	**44.4**

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

[1] The drop of the material balance at DAT-14 was caused by a leak in the oxidizer. However, this loss did not influence the distribution of radioactivity in solution and thus, the results of DAT-14 were also used for the final evaluation.

[2] Sum of carbon dioxide & carbon monoxide. Other volatile organic compounds were not detected in significant amounts in the PU plugs of trap attachments from irradiated samples of main test 1.

Table 7.2.1.3- 3: Degradation of FOE-thiadone in Natural Water under Dark Conditions
(main test 1; mean values of duplicates)

Compound	DAT 0	1	2	5	6	8	14
Volatiles	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
FOE-thiadone	100.0	100.1	99.6	99.6	100.2	100.2	99.7
Unknown #1	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Unidentified/Diffuse Radioactivity	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Total Residues in Test Solution	100.0	100.1	99.6	99.6	100.2	100.2	99.7
Material Balances	**100.0**	**100.1**	**99.6**	**99.6**	**100.2**	**100.2**	**99.7**

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

B. MATERIAL BALANCE

Main Test 1

For irradiated samples equipped with the solid trap attachments, the material balances were not sufficient due to formation of volatiles which were neither adsorbed by the polyurethane plug nor the soda lime. For irradiated samples sealed with crimp caps the material balances scattered from 21.1 to 99.9% of applied radioactivity [% AR].

Due to the non-sufficient material balances found for the irradiated samples of main test 1, the irradiation experiment was repeated and the results from main test 1 were not used for final evaluation of the irradiated samples.

Mean material balances for dark control samples ranged from 99.6 to 100.2% AR. Thus, results from main test 1 were used for final evaluation of the dark control samples.

Main Test 2

Mean material balances for irradiated samples ranged from 92.6 to 98.5% AR (DAT-0 to DAT-9). At DAT-14 a drop of the material balance to 44.4% AR was observed, caused by a leak in the oxidizer oven. However, this loss did not influence the distribution of radioactivity in solution and thus, the results of DAT-14 were also used for the final evaluation of irradiated samples.

The complete material balance found at all sampling intervals for irradiated samples (main test 2) and dark control samples (main test 1) demonstrated that finally no significant portion of radioactivity dissipated from the vessels or was lost during processing of theses samples (except irradiated samples at DAT-14).

C. STERILITY AND OXYGEN SATURATION

Sterility and oxygen saturation of the samples were maintained throughout the study (main test 1 and main test 2).

D. VOLATILIZATION

The maximum amount of volatiles was 57.8% AR in irradiated samples at DAT-9 (main test 2). They were identified as carbon dioxide and carbon monoxide. Formation of other volatile organic compounds was not significant, as amounts ≤ 0.5% AR were recovered in the polyurethane plugs of the solid trap attachments at all sampling intervals (main test 1).

The complete material balances found at each sampling interval in dark control samples and the observed stability of the test item demonstrate that no volatiles were formed in dark control samples.

E. DEGRADATION OF TEST ITEM

The amount of FOE-thiadone in irradiated samples decreased from 98.5% AR at DAT-0 to 20.4% AR at DAT-14.

Beside the formation of carbon dioxide and carbon monoxide, one minor degradation product was observed in irradiated samples with a maximum amount of 7.5% AR at DAT-8, rapidly declining to 4.2% at DAT-14.

The amount of FOE-thiadone in dark control samples stayed nearly constant over the whole study period, ranging from 99.6 to 100.0% AR. Thus, no degradation of FOE-thiadone was observed for dark control samples over the whole study period.

The DT_{50} values of FOE-thiadone in irradiated samples under experimental and natural conditions were calculated using single first order (SFO) kinetics (see Table 7.2.1.3- 4). No kinetic evaluation was performed for dark control samples, as no degradation of FOE-thiadone was observed.

Table 7.2.1.3- 4: Photodegradation Kinetics (single first order) of FOE-thiadone in Natural Water

DT_{50} (experimental) [d]	DT_{50} (natural conditions) [d]
5.8	15.5 (Phoenix, USA) 24.0 (Athens, Greece)

III. CONCLUSIONS

FOE-thiadone was rapidly degraded in sterile, natural water under exposure to simulated sunlight in the laboratory. No degradation of FOE-thiadone was observed in dark control samples.

The experimental half-lives in irradiated samples were calculated as 5.8 days, equal to 15.5 solar summer days at Phoenix, AZ, USA or 24.0 summer days at Athens, Greece.

Beside the formation of carbon dioxide and carbon monoxide, one minor degradation product was observed in irradiated samples with a maximum amount of 7.5% AR at DAT-8, rapidly declining to 4.2% at DAT-14.

It is concluded that photolytic degradation will contribute to the overall fate of FOE-thiadone under natural aqueous conditions.

CA 7.2.2 Route and rate of biological degradation in aquatic systems

CA 7.2.2.1 "Ready biodegradability"

Flufenacet was stated to be not ready biodegradable. This was accepted by the European Commission (7469/VI/98-Final – 3rd July 2003). Therefore no additional study was performed for the flufenacet renewal of approval.

CA 7.2.2.2 Aerobic mineralisation in surface water

According to regulation (EC) no. 1107/2009 the fate of an active substance in open water needs to be addressed. In case of flufenacet this data requirement will be met by the study KCA 7.2.2.2 /01, conducted according to the Canadian guideline T-1-255.

The statement KCA 7.2.2.2 /02 evaluates the essential experimental facts of the study KCA 7.2.2.2 /01 in comparison to the requirements set by OECD Test guideline No. 309 and demonstrates that the study KCA 7.2.2.2 /01 is suitable to address the fate of flufenacet in open water as required according to regulation (EC) No. 1107/2009. Additionally, a re-evaluation KCA 7.2.2.2 /03 of the residue data of study KCA 7.2.2.2 /01 was performed to meet the current guideline requirements.

Report:	**KCA 7.2.2.2/01; [redacted], M. J.; [redacted], P. Y.; [redacted], S. L.; 1995**
Title:	[phenyl-U-^{14}C]FOE 5043 - Determination of Aerobic Aquatic Biotransformation at 25 °C
Report No:	BR106961
Document No:	M-002210-01-1
Guidelines:	• Canadian Guidelines T-1-255
GLP:	yes

Executive Summary

The degradation of [phenyl-UL-^{14}C]flufenacet under aerobic conditions was investigated in one natural pond water under a standard daily lighting regime (16 h light, 8 h dark) in the laboratory for 368 days at 25 ± 1 °C:

Freshwater Pond	Source	Dissolved Oxygen [mg/L]	pH
Branchton	Branchton, Ontario, Canada	9.6	7.5

The test concentration of flufenacet was 1.3 mg/L.

Duplicate test systems were processed and analyzed 0, 4, 7, 15, 29, 60, 95, 188, 278 and 368 days after treatment (DAT). Sterile test systems (one replicate per sampling interval) were processed and analyzed in parallel.

Mean material balances ranged from 96.8 to 109.6% of applied radioactivity (% AR) for non-sterile samples (mean of duplicates) and from 98.9 to 108.2% AR for sterile samples (single replicates).

The maximum amount of carbon dioxide formed in the test systems was 3.0% AR for non-sterile test systems and 0.8% AR for sterile test systems at study end. Formation of volatile organic compounds was insignificant in non-sterile and sterile test systems as demonstrated by values of ≤ 0.3% AR at all sampling intervals.

Residues in water stayed nearly constant over the entire incubation period, ranging from 96.9 to 108.4% AR for non-sterile samples and from 98.9 to 108.2% AR for sterile samples.

The amount of flufenacet in non-sterile test systems decreased from 99.8% AR at DAT-0 to 92.6% AR at DAT-95 and further to 57.4% AR at DAT-368. The amount of flufenacet in sterile test systems stayed constant from 98.9% AR at DAT-0 to 101.9% AR at DAT-95 and decreased to 93.1% AR at DAT-368.

Three degradation products were identified in non-sterile test systems during the study: FOE oxalate (max.4.9% AR at DAT-95 and 24.0% AR at DAT-368), FOE sulfonic acid (not detected up to DAT-188, max. 8.6% AR at DAT-368) and FOE alcohol (max. 3.6% AR at DAT-95 and 4.4% AR at DAT-368). In sterile samples the degradation product FOE alcohol was identified with max. amounts of 6.8% AR at DAT-368.

The calculated half-life of flufenacet under aerobic was 458 days conditions in non-sterile test systems and 2212 days in sterile test systems, assuming first order kinetics.

I. MATERIALS AND METHODS

A. MATERIALS

1. Test Item

[phenyl-UL-^{14}C]flufenacet	
Batch No	C-584
Specific activity	6.77 MBq/mg (≙ 66.5 mCi/mmol)
Radiochemical purity	> 99.0%

2. Test Water

Natural unfiltered water from a freshwater pond near Brancliton/St. George Ontario, Canada (Table 7.2.2.2- 1) was sampled from a depth of 30 to 60 cm below the surface. After sampling and shipping (3 days) the water was stored in an incubator at 5 °C.

For control samples, an aliquot of the water were sterilized. Water characterization, including the determination of suspended solids, was performed prior to sterilization.

Table 7.2.2.2- 1: Physico-chemical properties of test water

Parameter	Water	
Geographic location - city - state - country	Branchton /St. George Ontario Canada	
Total alkalinity as $CaCO_3$ [mg/L]	230	
Total Hardness as $CaCO_3$ [mg/L]	329	
Suspended solids [mg/L]	8.5	
Dissolved oxygen [mg/L]	9.6	
pH	7.5	
Specific conductivity	500	
Microbial biomass [cfu/mL]	non-sterile water	sterile water
7 days prior study start	5.9×10^3	0
DAT-35	3.0×10^5	n.a.
DAT-278	3.0×10^3 / 3.0×10^3	3.3×10^2
DAT-368	1.7×10^3 / 3.8×10^2	2.0×10^2

n.a. = not analyzed, n.d. = not detected DAT: days after treatment
cfu: colony forming units

B. STUDY DESIGN

1. Experimental Conditions

Flow-through test systems which permit the collection of volatile products were used, consisting of sterilized Erlenmeyer flasks (volume 250 mL) fitted with a glass Dreschel cap having inlet and outlet ports for air exchange. The flasks were connected to volatile trapping trains and to a vacuum pump, which provided a flow of air through the system for approximately 30 minutes daily at a rate of approximately 1 to 2 bubbles per second. The test vessels were connected in parallel to a trapping train and trapping vials for collection of volatile organic compounds and carbon dioxide.

Each flask was filled with 150 mL of either sterile or non-sterile pond water.

The study application rate (SAR) was based on a single field application rate of flufenacet of 1 kg/ha, resulting in a SAR of 1.3 mg/L.

The application solution was prepared in acetonitrile 1.5 mL of the application solution was applied drop wise to the respective test systems using a gas tight syringe. After application the test vessels were connected to the flow-through system.

The test systems were incubated under aerobic conditions under a daily lighting regime of 16 hours light and 8 hours dark (light intensity ranged from 7.3 to 7.5 W/m^2) for 368 days at 25±1 °C in a walk-in climatic chamber. Aeration was provided to the aerobic test system by daily purge. Water levels of all test systems were monitored throughout the whole incubation period of 368 days and maintained if necessary.

2. Sampling

Ten sampling intervals were distributed over the entire incubation period of 368 days. Duplicate non-sterile test systems were processed and analyzed 0, 4, 7, 15, 29, 60, 95, 188, 278 and 368 days after treatment (DAT). One sterile test system was processed in parallel at each sampling interval.

The traps for volatiles were replaced at each sampling interval and additionally at DAT-153, -215, -243, -312 and -337.

Aerobic plate counts were performed to estimate the size of the microbial population 7 days prior to study start, at DAT-35, -278 and -368.

3. Analytical Procedures

At each sampling interval the test system were aerated for approximately 30 minutes prior to disconnecting them from the flow-through system. Afterwards, the test vessels were swirled gently and an aliquot was submitted for microbial enumeration, when applicable.

The residual water was characterized by liquid scintillation counting as well as by HPLC/radiodetection. The amount of volatiles was determined by liquid scintillation counting at each sampling interval.

The identity of the test item and its degradation products was elucidated by GC-EI/MS, either directly or after derivatization or by thermospray HPLC-MS.

The residue data for the test item were evaluated assuming first order kinetics. Model input datasets were the residual amounts of flufenacet found at each sampling interval. See Table 7.2.2.2- 2 and Table 7.2.2.2- 3 for input values.

II. RESULTS AND DISCUSSION

A. EXTRACTION AND QUANTITATION OF RADIOACTIVITY IN SOIL SAMPLES

Table 7.2.2.2- 2 and Table 7.2.2.2- 3 summarizes the degradation of [phenyl-UL-^{14}C]flufenacet and the formation and degradation of its degradation products in non-sterile and sterile test systems as a function of time.

Table 7.2.2.2- 2: Degradation of flufenacet in Non-sterile Pond Water under Aerobic Conditions
(expressed as percent of applied radioactivity, mean value of duplicates)

Compound (replicate)		DAT 0	4	7	15	29	60	95	188 [1]	278	368
flufenacet	A	100.0	106.6	107.5	103.5	105.0	104.0	88.0	~~60.2~~ [1]	77.0	57.2
	B	99.7	108.5	107.3	106.9	102.4	100.4	97.3	87.0	71.4	57.5
	mean	**99.8**	**107.5**	**107.4**	**105.2**	**103.7**	**102.2**	**92.6**	**73.6**	**74.2**	**57.4**
FOE oxalate		n.d.	n.d.	n.d.	n.d.	n.d.	2.1	4.9	5.9	13.8	24.0
FOE sulfonic acid		n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	6.5	8.6
FOE alcohol		n.d.	n.d.	n.d.	n.d.	n.d.	2.8	3.6	2.7	3.5	4.4
Unidentified Radioactivity [2]		n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	1.2	n.d.
Residues in Water		**99.8**	**108.4**	**107.8**	**105.4**	**103.7**	**107.6**	**101.1**	**96.9**	**100.1**	**97.8**
Carbon dioxide		n.a.	0.0	0.0	0.0	0.0	0.2	0.3	1.0	1.6	3.0
Volatile Organic Compounds		n.a.	0.0	0.0	0.0	0.0	0.0	0.1	0.1	0.1	0.3
Material Balance		**99.8**	**108.4**	**107.8**	**105.4**	**103.7**	**107.8**	**101.4**	**98.0**	**101.7**	**101.0**

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

[1] only one replicate was considered, as the other one was not representative due to inadvertent sample loss during aeration

[2] Minor degradation products were quantified if they amounted > 1% AR and were summed up to unidentified radioactivity (unknown #1 + #2). The maximum amount of a single degradation product was ≤ 1.2% AR at any sampling interval.

Table 7.2.2.2- 3: Degradation of flufenacet in Sterile Pond Water under Aerobic Conditions
(expressed as percent of applied radioactivity; single values)

Compound	DAT									
	0	**4**	**7**	**15**	**29**	**60**	**95**	**188**	**278**	**368**
flufenacet	98.9	105.3	107.3	103.2	105.2	107.2	101.9	9.8	95.5	93.1
FOE oxalate	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
FOE sulfonic acid	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
FOE alcohol	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	4.5	4.8	6.8
Unidentified Radioactivity [1]	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	1.3
Residues in Water	**98.9**	**106.0**	**108.2**	**103.2**	**105.2**	**107.2**	**101.9**	**104.3**	**101.6**	**102.0**
Carbon dioxide	n.a.	0.0	0.0	0.0	0.0	0.1	0.2	0.6	0.8	0.8
Volatile Organic Compounds	n.a.	0.0	0.0	0.0	0.0	0.0	0.6	0.0	0.1	0.0
Material Balance	**98.9**	**106.0**	**108.2**	**103.2**	**105.2**	**107.3**	**102.2**	**105.0**	**102.5**	**102.8**

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

[1] Minor degradation products were quantified if they amounted > 1% AR and were summed up to unidentified radioactivity (unknown #1 + #2). The maximum amount of a single degradation product was ≤ 1.3% AR at any sampling interval.

B. MATERIAL BALANCE

Mean material balances ranged from 96.8 to 109.6% of applied radioactivity (% AR) for non-sterile samples (mean of duplicates) and from 98.9 to 108.2% AR for sterile samples (single replicates).

The complete material balance found at all sampling intervals demonstrated that no significant portion of radioactivity dissipated from the vessels or was lost during processing of these samples.

C. RESIDUES IN WATER

Residues in water stayed nearly constant over the entire incubation period, ranging from 96.9 to 108.4% AR for non-sterile samples and from 98.9 to 108.2% AR for sterile samples. See Table 7.2.2.2- 2 and Table 7.2.2.2- 3 for details.

D. VOLATILIZATION

The maximum amount of carbon dioxide formed in the test systems was 3.0% AR for non-sterile test systems and 0.8% AR for sterile test systems at study end. Formation of volatile organic compounds was insignificant in non-sterile and sterile test systems as demonstrated by values of ≤ 0.3% AR at all sampling intervals. See also Table 7.2.2.2- 2 and Table 7.2.2.2- 3 for details.

E. DEGRADATION OF TEST ITEM

The amount of flufenacet in non-sterile test systems decreased from 99.8% AR at DAT-0 to 92.6% AR at DAT-95 and further to 57.4% AR at DAT-368. The amount of flufenacet in sterile test systems stayed constant from 98.9% AR at DAT-0 to 101.9% AR at DAT-95 and decreased to 93.1% AR at DAT-368. See also Table 7.2.2.2- 2 and Table 7.2.2.2- 3 for details.

Three degradation products were identified in non-sterile test systems during the study: FOE oxalate (max.4.9% AR at DAT-95 and 24.0% AR at DAT-368), FOE sulfonic acid (not detected up to DAT-188, max. 8.6% AR at DAT-368) and FOE alcohol (max. 3.6% AR at DAT-95 and 4.4% AR at DAT-368). In sterile samples the degradation product FOE alcohol was identified with max. amounts of 6.8% AR at DAT-368.

The calculated half-life of flufenacet under aerobic was 458 days conditions in non-sterile test systems and 2212 days in sterile test systems, assuming first order kinetics.

III. CONCLUSIONS

[phenyl-UL-^{14}C]flufenacet was degraded in water under aerobic conditions under a daily lighting regime in the laboratory.

Three degradation products were identified in non-sterile test systems during the study: FOE oxalate (max.4.9% AR at DAT-95 and 24.0% AR at DAT-368), FOE sulfonic acid (not detected up to DAT-188, max. 8.6% AR at DAT-368) and FOE alcohol (max. 3.6% AR at DAT-95 and 4.4% AR at DAT-368).

The calculated half-life of flufenacet under aerobic was 458 days conditions in non-sterile test systems, assuming first order kinetics.

*****

Report:	**KCA 7.2.2.2 /02; [redacted], E.-M., 2013**
Title:	Evaluation of Study: [phenyl-U-^{14}C]FOE 5043 - Determination of Aerobic Aquatic Biotransformation at 25 °C
Report No:	EnSa-13-0268
Document No:	M-450131-01-1
Guidelines:	• Canadian Guidelines T-1-255 • OECD Test Guideline No. 309 • Regulation (EC) No. 1107/2009
GLP:	no

Executive Summary

The statement evaluates the essential experimental facts of the study "[Phenyl-U-^{14}C]FOE 5043 - Determination of Aerobic Aquatic Biotransformation at 25 °C" (see KCA 7.2.2.2 /01 for summary) in comparison to the requirements set by OECD Test guideline No. 309 "Aerobic Mineralization in Surface Water – Simulation Biodegradation Test".

In study KCA 7.2.2.2 /01 the degradation of [phenyl-UL-^{14}C]flufenacet under aerobic conditions was investigated in one natural pond water under a standard daily lighting regime (16 h light, 8 h dark) in the laboratory for 368 days at 25 ± 1 °C.

One test concentration of 1.3 mg/L of flufenacet was used. Flow-through test systems, which permit the collection of volatiles, were used and the water within the test systems was aerated and agitated by daily purge. The microbial activity of the system was proven by plate count assays.

Duplicate test systems were processed and analyzed 0, 4, 7, 15, 29, 60, 95, 188, 278 and 368 days after treatment (DAT). Sterile test systems (one replicate per sampling interval) were processed and analyzed in parallel.

Material balances were established at each sampling interval and degradation products were identified to the current identification triggers of 2 x >5% of applied radioactivity [% AR], 1x >10% AR or >5% AR increasing at study end.

The residue data for the test item were evaluated assuming first order kinetics. Model input datasets were the residual amounts of flufenacet found at each sampling interval.

Thus, the requirements of OECD Test guideline No. 309 are fully met regarding the used test design, lighting conditions, temperature, number of replicates, test system and traps for volatiles as well as regarding the use of sterile controls. Microbial activity of the test systems was proven by plate count assay and by degradation of the test item, instead by degradation of a reference item.

The use of only one test item concentration is considered acceptable by the notifier as it covers a worst case scenario, using a max. field application rate of 1 kg/ha, a complete run-off scenario and a soil depth 5 cm, bulk density 1.5 g/cm^3 and thus, reflects also a worst case scenario referred to the kinetic behavior of the test item under the tested conditions (DT_{50} values).

The study duration of 368 days significantly exceeded the max. study duration of 90 days recommended by the guideline. However, seven sampling intervals were taken within a period of 95 and hence, the study was re-evaluated up to DAT-95 to meet also this guideline requirement (see KCA 7.2.2.2 /03 for summary).

I. CONCLUSIONS

Considering all results of this comparison, the notifier is of the opinion that the re-evaluated aerobic aquatic biotransformation study of flufenacet (see KCA 7.2.2.2 /03 for summary) is suitable to address the fate of flufenacet in open water as required according to regulation (EC) No. 1107/2009.

*****

Report:	**KCA 7.2.2.2 /03; [redacted], G.; [redacted], K.; 2014**
Title:	Kinetic Evaluation for Calculating Refined Half-life Times of [Phenyl-UL-^{14}C]Flufenacet in Natural Pond-Water According to FOCUS Kinetics Using the KinGUI 2 Tool
Report No:	EnSa-13-0970
Document No:	M-478212-01-1
Guidelines:	• FOCUS kinetics (2006, 2011) [3]
GLP:	no

Executive Summary

According to regulation (EC) no. 1107/2009 the fate of an active substance in open water needs to be addressed. In case of flufenacet this data requirement will be met by the study KCA 7.2.2.2 /01, conducted according to the Canadian guideline 1-1-255. The test duration of this study was 368 days. However, according to OECD test guideline No. 309 the duration of the test should not exceed 60 days. Only if the degradation of the test item has started within the first 60 days of the study, the duration can be extended to a maximum of 90 days. Therefore, the residue data from this existing study were re-evaluated up to DAT-95, to meet the current guideline requirement and to derive half-lives for flufenacet. This approach was already outlined in the statement KCA 7.2.2.2 /02. The kinetic analysis was performed with the software KinGUI 2 according to FOCUS kinetics (2006, 2011) [3, 4].

Single first order (SFO) was the most appropriate kinetic model to describe the degradation of flufenacet in the tested pond water (Ontario lake) in the laboratory under aerobic conditions at standard daily lighting regime (16 hours light and 8 hours dark) at 25 ± 1 °C.

The calculated half-life of flufenacet in the natural pond water test system was 618.3 days.

I. METHODS

Residue data up to DAT-95 from the aerobic aquatic biotransformation study KCA 7.2.2.2 /01 were used for re-evaluation. In this study, the degradation of flufenacet in unfiltered and non-sterile pond water was studied under aerobic conditions at standard daily lighting regime (16 hours light / 8 hours

dark) at 25 ± 1 °C for a total incubation period of 368 days. No soil or sediment was added to the test systems.

The kinetic analysis was performed according to FOCUS kinetics (2006, 2011)[3, 4] using the software KinGUI 2 with four different kinetic models: single first order (SFO), first order multi-compartment (FOMC), hockey-stick (HS, DFOS = double first order sequential) and double first order parallel (DFOP). Model input datasets were the residual amounts of flufenacet 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. 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 x LOD. If they became < LOD / n.d. for a second time the curve was cut off until a subsequent value > LOQ occurred. The data set was truncated at 95 days of incubation according to OECD test guideline No. 309 and based on statement KCA 7.2.2.2 /02.

The most appropriate kinetic model was selected on the basis of a detailed statistical analysis including visual assessment of the goodness of the fits, chi²-scaled error criterion, t-test significance, correlation analysis and standard deviation. The DT_{50} values were calculated from the resulting kinetic parameters.

II. RESULTS

The single first order (SFO) was the most appropriate kinetic models to describe the degradation of flufenacet in the natural water test system under aerobic conditions. Table 7.2.2.2- 4 summarizes the results of the kinetic analysis.

Table 7.2.2.2- 4: Kinetic parameters for the degradation of flufenacet in natural water test system under aerobic conditions according to FOCUS [1]

Test System	Kinetic Model [2]	DT_{50} [days]	DT_{90} [days]	chi² error [%]	t-test	Visual Assessment [3]
Ontario lake pond-water system*	SFO	618.3	> 1000	2.4	k: <0.01	+

[1] The existing study was re-evaluated up to DAT-95, to meet the current guideline requirements
[2] SFO: single first order
[3] Visual assessment: + = good

III. CONCLUSIONS

The calculated half-life of flufenacet in natural water sediment system (Ontario lake) in the laboratory under aerobic conditions at standard daily lighting regime (16 hours light and 8 hours dark) at 25 ± 1 °C was 618.3 days.

The results are included in the summary of the route and rate of degradation of flufenacet in water and sediment given in section CA 7.2.

CA 7.2.2.3 Water/sediment study

The route of degradation of flufenacet in water/sediment systems under aerobic and anaerobic conditions in the dark in the laboratory was evaluated during the Annex I Inclusion and was accepted by the European Commission (7469/VI/98-Final – 3rd July 2003). The following studies are included in the Baseline Dossier:

Annex Point / Reference No	Author(s)	Year	Document No
KCA 7.2.2.3 /01	[redacted], N. C.; [redacted], D. M.	1995	M-002215-01-1
KCA 7.2.2.3 /02	[redacted], I. V.; [redacted], S.; [redacted], M.	1995	M-002213-01-1
KCA 7.2.2.3 /03	[redacted], P. R.; [redacted], D. W.	1997	M-004595-01-1

No additional studies are submitted within this Supplemental Dossier for the flufenacet renewal of approval. However, updated kinetic evaluations of the degradation behavior of flufenacet in water/sediment under aerobic conditions in the dark in the laboratory have been performed according to FOCUS kinetics (2006, 2011) [3, 4] to derive kinetic parameters suitable for trigger evaluation, modeling purpose and environmental risk assessment.

Report:	**KCA 7.2.2.3 /04; [redacted], G.; [redacted], K.; 2014**
Title:	Kinetic Evaluation of Degradation and Dissipation Behavior of Flufenacet and its Degradation Products in Water / Sediment Systems According to FOCUS Kinetics Using the KinGUI 2 Tool
Report No:	EnSa-13-0973
Document No:	M-477845-01-1
Guidelines:	• FOCUS kinetics (2006, 2011) [3, 4]
GLP:	no

Executive Summary

A kinetic analysis of residue data from two aerobic water/sediment degradation studies M-002213-01-1 (Baseline Dossier, KCA 7.2.2.3 /02) and M-004595-01-1 (Baseline Dossier, KCA 7.2.2.3 /03) was performed with the software KinGUI 2 according to FOCUS kinetics (2006, 2011) [3, 4] to derive half-lives for flufenacet and its degradation products FOE methylsulfide and FOE-thiadone, which are suitable for modeling purpose and trigger evaluation.

Single first order (SFO) was the most appropriate kinetic model to describe the degradation of flufenacet for both modeling purpose and trigger evaluation in a total of two tested water/sediment systems under aerobic conditions in the dark in the laboratory at 20°± 1 °C.

The calculated half-lives of flufenacet for modeling purposes were 90.3, 19.7, 89.0 and 38.1 days in the entire system, 58.7, 17.0, 40.9 and 23.8 days in water, and 140.5, 17.6, 120.5 and 47.9 days in sediment.

The calculated half-lives of flufenacet for trigger evaluation were 90.3, 19.7, 89.0 and 38.1 days in the entire system, 58.7, 17.0, 31.5 and 18.6 days in water, and 140.5, 17.6, 120.5 and 47.9 days in sediment.

The half-lives of the degradation products FOE methylsulfide and FOE-thiadone could not be calculated, since the residue values of both degradation products were still increasing until the end of study period and just started to decline at the end of the study.

I. METHODS

Residue data from the aerobic water/sediment degradation studies M-002213-01-1 (Baseline Dossier, KCA 7.2.2.3 /02) and M-004595-01-1 (Baseline Dossier, KCA 7.2.2.3 /03) were used. In these studies, the degradation of flufenacet was studied in a total of two water/sediment systems under aerobic conditions in the dark in the laboratory for up to 157 days at 20 ± 1 °C.

The kinetic analysis was performed according to FOCUS kinetics (2006, 2011)[3-4] using the software KinGUI 2 with four different kinetic models: single first order (SFO), first order multi-compartment (FOMC), hockey-stick (HS, DFOS = double first order sequential) and double first order parallel (DFOP). Model input datasets were the residual amounts of flufenacet and its degradation products found in each replicate test system at each sampling interval.

The residue data for the parent were pre-processed as follows: 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. 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 x LOD. If they became < LOD / n.d. for a second time the curve was cut off until a subsequent value > LOQ occurred. Sampling times for sediment phases were shifted, starting with sampling time t = 0 at the day of the maximum measured concentration of flufenacet. For total system, pre-processed values of the water and sediment layer were summed up and used for the kinetic evaluation.

The residue data for the degradation product were pre-processed as follows: amounts of degradation products detected at DAT-0 were set to 0. Thereafter, in the formation phase of a degradation product, values < LOD or non-detected (n.d.) were also set to 0, except for the last data point before the first detectable amount of the respective degradation product. If this data point was ≠ DAT-0, it was included in the fit by setting values < LOD or non-detected (n.d.) to 0.5 x LOD. Values between LOD and LOQ were set to the measured values. In the decline phase of a degradation product all single values < LOD or non-detected (n.d.) were set to 0.5 x LOD. If they became < LOD/n.d. for a second time the curve was cut off until a subsequent value > LOQ occurred. For decline phases at this level, sampling times for entire system, water and sediment were shifted, starting with sampling time t = 0 at the day of the maximum occurrence of FOE methylsulfide and FOE-thiadone in each compartment. Data sets with insufficient number of data points (n < 4 after peak concentrations) were not further processed.

The most appropriate kinetic model was selected on the basis of a detailed statistical analysis including visual assessment of the goodness of the fits, chi^2-scaled error criterion, t-test significance, correlation analysis and standard deviation. The DT_{50} values were calculated from the resulting kinetic parameters.

II. RESULTS

The single first order (SFO) was the most appropriate kinetic model to describe the degradation of flufenacet for modeling purpose and trigger evaluation in both tested water/sediment systems under aerobic conditions. However, the half-lives of the degradation products FOE methylsulfide and FOE-thiadone could not be calculated, since the residue values of both degradation products were still increasing until the end of study period and just started to decline at the end of the study. The kinetic evaluation result shows that degradation rate of these degradation products are not statistically significant by the t-test for both test systems. Therefore, SFO kinetics is not suitable for deriving modeling endpoints.

Table 7.2.2.3- 1 to Table 7.2.2.3- 6 summarizes the results of the kinetic analysis for modeling purpose and trigger evaluation.

Table 7.2.2.3- 1: Kinetic parameters for the degradation of flufenacet in the entire system under aerobic conditions for modeling purpose according to FOCUS

Water/Sediment System	Kinetic Model [1]	DT_{50} [days]	chi^2 error [%]	t-test	Visual Assessment [2]
NESA [3]	SFO	90.3	2.2	k: <0.001	+
BRP [4]	SFO	89.0	3.8	k: <0.001	+
NESA [3]	SFO	19.7	9.8	k: <0.001	+
BRP [4]	SFO	38.1	4.9	k: <0.001	+

[1] SFO: single first order
[2] visual assessment: + = good
[3] Nelson Environmental Study Area (NESA) in Lawrence, Kansas, USA
[4] Bayer Research Park (BRP) in Stilwell, Kansas, USA

Table 7.2.2.3- 2: Kinetic parameters for the degradation of flufenacet in the entire system under aerobic conditions for trigger evaluation according to FOCUS

Water/Sediment System	Best-Fit Kinetic Model [1]	DT_{50} [days]	DT_{90} [days]	chi^2 error [%]	t-test	Visual Assessment [2]
NESA [3]	SFO	90.3	300.1	2.2	k: <0.001	+
BRP [4]	SFO	89.0	295.7	3.8	k: <0.001	+
NESA [3]	SFO	19.7	65.3	9.8	k: <0.001	+
BRP [4]	SFO	38.1	126.6	4.9	k: <0.001	+

[1] SFO: single first order
[2] visual assessment: + = good
[3] Nelson Environmental Study Area (NESA) in Lawrence, Kansas, USA
[4] Bayer Research Park (BRP) in Stilwell, Kansas, USA

Table 7.2.2.3- 3: Kinetic parameters for the degradation of flufenacet in water under aerobic conditions for modeling purpose according to FOCUS

Water/Sediment System	Kinetic Model [1]	DT_{50} [days]	chi^2 error [%]	t-test	Visual Assessment [2]
NESA [3]	SFO	58.7	4.9	k: <0.001	+
BRP [4]	SFO	40.9	6.8	k: <0.001	+
NESA [3]	SFO	17.0	6.8	k: <0.001	+
BRP [4]	SFO	23.8	12.5	k: 0.002	+

[1] SFO: single first order
[2] visual assessment: + = good
[3] Nelson Environmental Study Area (NESA) in Lawrence, Kansas, USA
[4] Bayer Research Park (BRP) in Stilwell, Kansas, USA

Table 7.2.2.3- 4: Kinetic parameters for the degradation of flufenacet in water under aerobic conditions for trigger evaluation according to FOCUS

Water/Sediment System	Best-Fit Kinetic Model [1]	DT_{50} [days]	DT_{90} [days]	chi^2 error [%]	t-test	Visual Assessment [2]
NESA[3]	SFO	58.7	195.1	4.9	k: <0.001	+
BRP[4]	DFOP	31.5	171.6	3.9	k_1: <0.062 k_2: 0.001	+
NESA[3]	SFO	17.0	56.4	6.8	k: <0.001	+
BRP[4]	DFOP	18.6	94.3	8.7	k_1: 0.185 k_2: 0.010	+

[1] SFO: single first order, DFOP: double first order in parallel
[2] visual assessment: + = good
[3] Nelson Environmental Study Area (NESA) in Lawrence, Kansas, USA
[4] Bayer Research Park (BRP) in Stilwell, Kansas, USA

Table 7.2.2.3- 5: Kinetic parameters for the degradation of flufenacet in sediment under aerobic conditions for modeling purpose according to FOCUS

Water/Sediment System	Kinetic Model [1]	DT_{50} [days]	chi^2 error [%]	t-test	Visual Assessment [2]
NESA [3]	SFO	140.5	2.1	k: <0.001	+
BRP [4]	SFO	120.5	7.5	k: 0.010	+
NESA [3]	SFO	17.6	7.3	k: <0.001	+
BRP [4]	SFO	47.9	7.7	k: <0.003	+

[1] SFO: single first order
[2] visual assessment: + = good
[3] Nelson Environmental Study Area (NESA) in Lawrence, Kansas, USA
[4] Bayer Research Park (BRP) in Stilwell, Kansas, USA

Table 7.2.2.3- 6: Kinetic parameters for the degradation of flufenacet in sediment under aerobic conditions for trigger evaluation according to FOCUS

Water/Sediment System	Best-Fit Kinetic Model[1]	DT_{50} [days]	DT_{90} [days]	chi^2 Error [%]	t-test	Visual Assessment[2]
NESA[3]	SFO	140.5	466.8	2.1	k: <0.001	+
BRP[4]	SFO	120.5	400.2	7.5	k: 0.010	+
NESA[3]	SFO	17.6	58.6	7.3	k: <0.001	+
BRP[4]	SFO	47.9	159.1	7.7	k: 0.003	+

[1] SFO: single first order
[2] visual assessment: + = good
[3] Nelson Environmental Study Area (NESA) in Lawrence, Kansas, USA
[4] Bayer Research Park (BRP) in Stilwell, Kansas, USA

III. CONCLUSIONS

The calculated half-lives of flufenacet for modeling purposes and trigger evaluation in water/sediment under aerobic conditions in the dark in the laboratory ranged from 19.7 to 90.3 days in the entire system, from 17.0 to 58.7 days in water and from 17.6 to 140.5 days in sediment.

The half-lives of FOE methylsulfide and FOE-thiadone for modeling purposes and trigger evaluation could not be calculated, since the residue values of both degradation products were still increasing until the end of study period and just started to decline at the end of the study.

The results are included in the summary of the route and rate of degradation of flufenacet and its major degradation products in water and sediment given in section CA 7.2.

CA 7.2.2.4 Irradiated water/sediment study

The route of degradation of flufenacet in a microcosm study was evaluated during the Annex I Inclusion and was accepted by the European Commission (7469/VI/98-Final – 3rd July 2003). The following studies are included in the Baseline Dossier:

Annex Point / Reference No	Author(s)	Year	Document No
KCP 10.2.3/01	[redacted], E. M.; [redacted], R. G.	1999	M-023412-01-1

A short summary of the results of this microcosm study is provided below:

In addition to the aerobic aquatic degradation studies in the laboratory an indoor microcosm study with 11 microcosm test systems was performed in the Netherlands. Measurement of the disappearance of flufenacet from the water phases showed that under more realistic conditions, in systems containing not only biologically active sediment but also different aquatic organisms, the disappearance rate is much faster than determined in simple water/sediment systems. DT_{50}-values for flufenacet in the water phase of the microcosms ranged from 12.7 to 24.1 days (mean of 18.8 days).

An updated kinetic evaluation of the degradation behavior of flufenacet in water/sediment under aerobic conditions in the dark in indoor microcosms have been performed according to FOCUS kinetics (2006, 2011) [3, 4] to derive kinetic parameters suitable for modeling purpose and environmental risk assessment.

Report:	**KCA 7.2.2.4 /01; [redacted], G.; [redacted], K.; 2014**
Title:	Kinetic Evaluation of the Dissipation Behavior of Flufenacet in Aquatic Indoor Microcosm Systems According to FOCUS Kinetics Using the KinGUI 2 Tool
Report No:	EnSa-14-0127
Document No:	M-478447-01-1
Guidelines:	• FOCUS kinetics (2006, 2011) [3, 4]
GLP:	no

Executive Summary

A kinetic analysis of residue data from the aerobic aquatic indoor microcosm dissipation study M-02341-01-1 (Baseline Dossier, KCP 10.2.3/01) was performed with the software KinGUI 2 according to FOCUS kinetics (2006, 2011) [3, 4] to derive half-lives for flufenacet, which are suitable for modeling purposes and trigger evaluation.

Single first order (SFO) was the most appropriate kinetic model to describe the dissipation of flufenacet for modeling purposes and trigger evaluation in the aquatic indoor microcosms under aerobic conditions in the laboratory under a daily lighting regime (14 h light/10 h dark) and air temperatures ranging from 15 to 20 °C using six different test concentrations of flufenacet of 0.75, 1.5, 3.0, 6.0, 12.0, and 24.0 µg/L.

The calculated half-lives of flufenacet in the tested aquatic microcosm system were 18.3, 19.4, 20.5, 14.5, 17.7 and 21.3 days using 0.75, 1.5, 3.0, 6.0, 12.0, and 24.0 µg flufenacet /L, respectively.

I. METHODS

Residue data from the aerobic aquatic indoor microcosm dissipation study M-02341-01-1 (Baseline Dossier, KCP 10.2.3/01) were used. In this study, the dissipation behavior of flufenacet in the aerobic aquatic microcosm test system was studied in the laboratory for 84 days, at an air temperature ranging from 15 to 20 °C and a lighting regime (14 h light/10 h dark) using six different test concentrations of flufenacet of 0.75, 1.5, 3.0, 6.0, 12.0, and 24.0 µg/L.

The kinetic analysis was performed according to FOCUS kinetics (2006, 2011) [3, 4] using the software KinGUI 2 with four different kinetic models: single first order (SFO), first order multi-compartment (FOMC), hockey-stick (HS, DFOS = double first order sequential) and double first order parallel (DFOP). Model input datasets were the residual amounts of flufenacet 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. 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 x LOD. If they became < LOD / n.d. for a second time the curve was cut off until a subsequent value > LOQ occurred. The most appropriate kinetic model was selected on the basis of a detailed statistical analysis including visual assessment of the goodness of the fits, chi^2-scaled error criterion, t-test significance, correlation analysis and standard deviation. The DT_{50} values were calculated from the resulting kinetic parameters.

II. RESULTS

The single first order (SFO) was the most appropriate kinetic models to describe dissipation of flufenacet for both, modeling purposes and trigger evaluation in the aquatic indoor microcosm under aerobic conditions. Table 7.2.2.4- 1 summarizes the results of the kinetic analysis.

Table 7.2.2.4- 1: Kinetic parameters for the dissipation of flufenacet in aquatic indoor microcosm system under aerobic conditions for refined risk and exposure assessments according to FOCUS

Test Concentration [µg/L]	Kinetic Model [1]	DT_{50} [days]	DT_{90} [days]	chi^2 error [%]	t-test	Visual Assessment [2]
0.75	SFO	18.3	60.6	5.0	k: <0.001	+
1.5	SFO	19.4	64.4	5.5	k: <0.001	+
3.0	SFO	20.5	68.0	3.2	k: <0.001	+
6.0	SFO	14.5	48.0	2.5	k: <0.001	+
12.0	SFO	17.7	58.7	3.9	k: <0.001	+
24.0	SFO	21.3	70.6	7.7	k: <0.001	o
Geometric mean		**18.5**				

[1] SFO: single first order
[2] visual assessment: + = good, o = medium/acceptable

III. CONCLUSIONS

The calculated half-lives of flufenacet for modeling purposes and trigger evaluation in the aquatic indoor microcosms under aerobic conditions in the laboratory under a daily lighting regime ranged from 14.5 to 21.3 days for all tested concentrations.

The dissipation geometric mean of 18.5 days may be used for refined exposure and refined risk assessments of flufenacet in aquatic environments.

The results are included in the summary of the route and rate of dissipation of flufenacet in water and sediment given in section CA 7.2.

CA 7.2.3 Degradation in the saturated zone

The degradation of flufenacet in the saturated zone was not studied since flufenacet is not expected to reach the saturated zone after its use according to good agricultural practices. A summary of the route and rate of degradation of flufenacet in water and sediment is given in section CA 7.2 and Figure 7.2-1.

CA 7.3 Fate and behavior in air

Volatilization of flufenacet from plant and soil is not expected and therefore transport and deposition of flufenacet via air are not relevant processes. Local and global effects of flufenacet were not considered since its half-life in air is ≤ 2 days.

CA 7.3.1 Route and rate of degradation in air

The degradation rate of flufenacet in air was evaluated during the Annex I inclusion using the Atkinson method, and was accepted by the European Commission (7469/VI/98-Final – 3rd July 2003). The following study is included in the Baseline Dossier:

Annex Point / Reference No	Author(s)	Year	Document No
KCA 7.3.1 /01	[redacted], E.	1995	M-002236-01-1

No additional studies are submitted within this Supplemental Dossier for the flufenacet renewal of approval.

CA 7.3.2 Transport via air

The volatilization behavior of flufenacet from soil in a field trial was evaluated during the Annex I Inclusion and was accepted by the European Commission (7469/VI/98-Final – 3rd July 2003). The following studies are included in the Baseline Dossier:

Annex Point / Reference No	Author(s)	Year	Document No
KCA 7.3.2/01	[redacted], E.	1995	M-002237-01-2

CA 7.3.3 Local and global effects

Local and global effects of flufenacet were not considered since its half-life in air is ≤ 2 days (DT_{50} = 4.7 h; see M-002236-01-1, Baseline Dossier, KCA 7.3.1 /01).

CA 7.4 Definition of the residue

CA 7.4.1 Definition of the residue for risk assessment

The proposed residue definitions relevant for risk assessment for each compartment are the following:

Compartment	Residue Definition
Soil	flufenacet, FOE oxalate, FOE sulfonic acid, FOE-methylsulfone, FOE-thiadone, FOE 5043-trifluoroethanesulfonic acid and trifluoroacetic acid
Groundwater	same as soil
Surface water	same as soil plus FOE methylsulfide
Sediment	flufenacet
Air	flufenacet

CA 7.4.2 Definition of the residue for monitoring

The proposed residue definition for monitoring is flufenacet only for all compartments since none of the major degradation products is of toxicological or ecotoxicological relevance.

CA 7.5 Monitoring data

Flufenacet and some of its degradation products are frequently on the list of water monitoring programs performed by water authorities throughout Europe. However, results from these monitoring programs are in general not publicly available in peer reviewed literature. Hence only relevant and reliable monitoring studies found in the required literature searches of the peer reviewed open literature are presented here.

The detected concentrations of flufenacet in surface water were always below the European Union drinking water and groundwater limit of 0.1 µg/L.

The detected concentrations of trifluoroacetic acid in ocean water indicate that beside anthropogenic sources also naturally sources for trifluoroacetate exist.

Literature:	**KCA 7.5 /03; [redacted], G.; [redacted], B.; [redacted], W. ; 2003**
Title:	Entry of pesticides into surface waters: new results of the Lamspringe run-off monitoring project 1999-2001
Source:	Peer-reviewed literature: Symposium Pesticide Chemistry, 12th, Piacenza, Italy, June 4-6, 2003 (2003)
Report No:	not applicable
Document No:	M-460945-01-1
Guidelines:	none
GLP:	no

Executive Summary

The article reported the results of a field-scale project over several years to measure the presence of plant protection products in surface water as caused by regular agricultural practice. The catchment area covers the requirements for carrying out post-registration monitoring studies with regard to size, slope relevant cropping, soil type, run-off triggering precipitation, and immediately neighboring permanently water-carrying brook. Under the conditions encountered during the project from October 1995 to April 1999 (e.g., strong precipitation immediately after plant protection product application) flufenacet was detected in investigation period 2 (May 1999 until December 2001) in a maximum concentration of 0.07 µg/L.

I MATERIAL AND METHODS

A. Material

1. Site description (for water)

Location/country:	Lower Saxony, Germany
Amount of water area:	Effluent side of the 100 ha trail area
Cultivated crops:	Winter wheat, winter barley, winter rape and sugar beet
Plant protection products used on fields:	32 plant protection products
History of site (crop, plant protection products):	n/a
Temperature:	n/a
Precipitation:	n/a

B. Study design and methods

1. Application pattern	
Use pattern (crop, season, region….)	n/a
BBCH stage(s):	n/a
Application method:	n/a
Number of applications:	4
Application interval:	Two application per year
Application date and/or season:	1999 and 2000
Application rate per treatment [kg a.s./ha]:	n/a
2. Sampling	
Sampling technique:	Continuous and event related sampling with an automatic sampling device was used.
Sampling frequency:	Samples were drawn over the whole year. For continuous sampling, samples were taken daily and then mixed weekly samples were prepared. Event related samples were taken whenever the water level exceeded a defined threshold.
Number of samples per site/soil type:	n/a
Sampling depth:	n/a
Transport/storage of samples:	4°C until analysis
3. Chemical analysis	
Guideline/protocol:	None
Method:	Multi-residue method: GC/MS and LC/MS(/MS)
Pre-treatment of samples:	Extraction with SPE
Conduction:	n/a
Reference item:	n/a
Recovery:	70 – 120%
Limit of detection:	0.01 µg/L
Limit of quantification:	n/a

II RESULTS

1. Validity criteria

No criteria were defined.

2. Analytical findings

In investigation period 2 (01.05.1999-31.12.2001) flufenacet was detected in three water samples with a maximum value of 0.07 µg/L.

Table 7.5- 1: Findings of flufenacet in surface water

Sampling Period	No of samples with positive findings	Maximum value [µg/L]
01.10.1999 – 30.04.1999	-	-
01.05.1999 – 31.12.2001	3	0.07

III CONCLUSION

The occurrence of plant protection products in the surface water corresponded temporally with plant protection treatment in cultures. Therefore, flufenacet was detected in the second investigation period in a concentration of 0.07 µg/L.

IV COMMENTS BY THE NOTIFIER

The detected concentrations of flufenacet in surface water in this study were always below the European Union drinking water and groundwater limit of 0.1 µg/L. Thus, this study will not be further considered in the risk assessment.

*****

Literature:	**KCA 7.5 /02; [redacted], H., [redacted], L. H.; [redacted], O., [redacted], J. L.; 2002**
Title:	Trifluoracetate in Ocean Waters
Source:	Peer-reviewed literature, Environmental Science and Technology, 36, 1, p.12-15
Report No:	not applicable
Document No:	M-455778-01-1
Guidelines:	none
GLP:	no

Executive Summary

Trifluoroacetate is an atmospheric pollutant which has been proved to accumulate in several environmental compartments as for instance in ocean waters. Although its environmental presence is known to arise from anthropogenic sources, the question arose whether its occurrence might be natural. trifluoroacetate was analytically determined in ocean water samples of different depth collected from various locations. Results indicate that t in ocean waters is occurring naturally being homogeneously distributed in ocean waters of all ages with a concentration of about 200 ng/L.

I MATERIAL AND METHODS

Sampling details are described below:

Sampling technique:	Niskin sampler	
Sampling frequency:	Southern Ocean Location 1: 19. + 25.01.1998 Location 2: 23.01.1999 Location 3: 26.01.1999	Mid-Atlantic Ocean Location 4: 29. + 30.01.1998
Number of samples per site/ocean type:	Three samples per depth	
GPS coordinates of locations:	Location 1: 60.6° S, 56.5°W Location 2: 60.5° S, 57.5° W Location 3:60.25°S, 54.5° W	-
Sampling depth (m):	10, 50, 100, 200, 500, 750, 1000, 1500, 2000	0, 2, 40, 120, 380, 1000, 4000, 4150
Transport/storage of samples:	Storage on land at 4 °C	

The samples were processed and analyzed as summarized below:

Three aliquots of each 10 mL were spiked with a solution of heptafluorobutyric acid in deionized water leading to an in-sample concentration of 134 ng/L heptafluorobutyrate. Following, 2 g sodium chloride were added and the pH value of the solution was adjusted to pH 1 using 350 µL sulfuric acid (98%). This solution was extracted with 1 mL methyl tert-butyl ether (MTBE) under agitation The organic phases were transferred into silanized 1 mL crimp-cap vials and the acids in the organic extracts were derivatized to their pentafluorophenylethyl esters with 5 µL of 1-pentafluoro phenyl-diazoethane (8 vol % in MTBE), prepared from pentafluoro-acetophenone.

Artificial seawater samples (pure salts in deionised water) were spiked with sodium trifluoroacetate in deionized water to give calibration concentrations of 28 to 339 ng/L trifluoroacetate. The final samples were examined by GC-MS with a limit of quantification of 32 ng/L and a limit of detection of 20 ng/L.

Blanks were analysed each sampling year for control. For the sampling period 1998 about 400-year-old mineral water was used as control forwarded to the sampling site. Additionally, mineral water at the University of Bayreuth, deionized water and artificial seawater were used as controls to ensure that there is no contamination with trifluoroacetate during sample transfer. For the sampling period of 1999, artificial seawater was forwarded to the sampling site for control.

II RESULTS

Measured levels of trifluoroacetate and the calculated age of the corresponding seawater sample on basis of CFC-12 concentration are presented in Table 7.5- 2 for the Mid-Atlantic and in Table 7.5- 3 for the Southern ocean.

Table 7.5- 2: Concentrations of trifluoroacetate and CFC-12 age of Mid-Atlantic seawater samples

Depth [m]	Trifluoroacetate [a)] [ng/L]	± SD [a)] [ng/L]	CFC-12 [b)] [year]
0	190	10	< 5
SFC 2	200	8	-
40	210	12	< 5
120	205	16	< 5
380	210	6	12
1000	205	16	46
4000	195	16	> 60
4150	200	16	> 60

a) n = 6
b) calculated using observed CFC-12 concentration

Table 7.5- 3: Concentrations of trifluoroacetate and CFC-12 age of Southern Ocean water samples

Site (Sampling Date)	Location 1 (19. + 25.01.1998)		Location 2 (23.01.1999) Location 3 (26.01.1999)	
Depth [m]	**trifluoroacetate [a] [ng/L]**	**± SD [a] [ng/L]**	**trifluoroacetate [a] [ng/L]**	**± SD [a] [ng/L]**
10	195	22	210	27
50	185	10	220	26
100	195	8	205	22
200	195	6	170	28
50	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	-	-

SD: standard deviation
[a] n = 6

Independent of depth and location, existing trifluoroacetate levels in all water samples were about 200 ng/L.

In the Mid Atlantic, subsurface waters (0 – 200 m) are rapidly ventilated over a few years and were close to equilibrium with the overlaying atmosphere revealing apparent ages less than 5 years. Waters from intermediate depth (200 – 1700 m) are ventilated primarily by subpolar-origin waters yielding in increasing ages. Water samples below 1700 m are relatively isolated, having ages larger than 60 years indicating minimal contact with the atmosphere.

Previous measurements in the Southern Ocean show a similar increase in the age of seawater with increasing depth. Down to 200 m depth the water ventilated with the atmosphere yielding in time scales of a few years whereas in deeper depth the water is isolated from the atmosphere for at least several decades.

III CONCLUSIONS

Existing trifluoroacetate levels in ocean water samples of different depth were measured during two campaigns in 1998 and 1999 in the Mid Atlantic and Southern Ocean. Additionally, the age of the water samples in the different depth was determined. Since trifluoroacetate levels determined in subsurface samples and in samples of deeper depth were nearly similar with levels of about 200 ng/L, trifluoroacetate is likely to be a natural ionic solute in ocean water. Continuous low-level releases from geological or biological sources may have caused the present-day levels in ocean waters.

IV COMMENTS BY THE NOTIFIER

This study indicates that trifluoroacetate in ocean waters is occurring naturally and is homogeneously distributed in ocean waters of all ages. Thus, this study will not be further considered in the risk assessment.

*****

Literature:	**KCA 7.5 /01; [redacted] B. F., [redacted] R. W., [redacted] K., [redacted] A., [redacted] A., [redacted] N., [redacted] L., [redacted] C., [redacted] D. C. G.; 2005**
Title:	Trifluoroacetate profiles in the Arctic, Atlantic, and Pacific Oceans.
Source:	Peer-reviewed literature: Environmental Science and Technology, 39, p. 6555-6560
Report No:	not applicable
Document No:	M-455832-01-1
Guidelines:	none
GLP:	no

Executive Summary

A series of depth profiles was collected at 22 sites in the Arctic, North and South Atlantic and Pacific Oceans to determine spatial patterns for trifluoroacetate concentrations in the marine environment and to investigate possible natural sources of trifluoroacetate. Profiles were also taken over underwater vents in the North and South Pacific and the Mediterranean Sea. At the profile sites, trifluoroacetate values ranged from < 10 ng/L in the Pacific Ocean to greater than 150 ng/L in the Atlantic Ocean. Samples from the Canada Basin of the Arctic Ocean exhibited variable trifluoroacetate concentrations (60-160 ng/L) down to 700 m. Below this depth, the trifluoroacetate concentrations were constant (150 ng/L). Water from the Canadian Arctic had constant high trifluoroacetate values. Profiles from the Northern Atlantic exhibited high values at all depths but were more consistent in the Western Atlantic. The northwestern Pacific Ocean surface profile sites exhibited low trifluoroacetate concentrations in the top 100 m increasing to a maximum of 60 ng/L with depth. Samples from the South Pacific Ocean site had generally low values with a few depths (> 800 m) having concentrations of 50 ng/L or more. Additionally, trifluoroacetate concentrations from profiles over vents in the Pacific and Mediterranean Oceans were taken. The results suggest that some deep-sea vents may be natural sources of trifluoroacetate.

I MATERIALS AND METHODS

Sampling details are described below:

Sampling technique:	Niskin sampler
Sampling frequency:	sampling once per location
Number of samples per site/ocean type:	Varies from site to site: 6 – 23 samples per site, excluding duplicates (68 % of the samples had duplicates)
Sampling depth (m):	site dependent; various depth down to 5300 m
Transport/storage of samples:	Cool and dark storage during shipping; storage on land at 4 °C in the dark

The samples were processed and analyzed as summarized below:

Sample processing:	• Derivatization of the acid with 2,4-difluoroanaline in the presence of dicyclohexylcarbodiimide • A 0.42 ng spike solution of labeled trichloroacetic acid was added to approx. 75% of the samples just prior to introduction of reagents to ensure complete derivatization.
Conduction:	Liquid extracts
Analytical method:	GC/MSD
Reference item:	trichloroacetic acid (TCA)
Recovery:	80–105 % (SD = 15 %) of comparative TCA
Limit of detection:	0.5 ng/L
Limit of quantification:	not stated

II RESULTS

The collection method was validated by comparing samples collected from Lake Superior using different sample systems, i.e. Niskin bottles, van Dorn bottles and PFTE-free pumps and tubing. Measured trifluoroacetate concentrations did not vary between the collection methods.

During seawater sampling, a laboratory blank was included in each daily sample set for control.

Recovery of reference item (trichloroacetic acid) ranges between 80-105 % with a relative standard deviation of 15%. Therefore, results were not recovery corrected.

Measured levels of trifluoroacetate of the corresponding seawater samples are presented in Table 1.

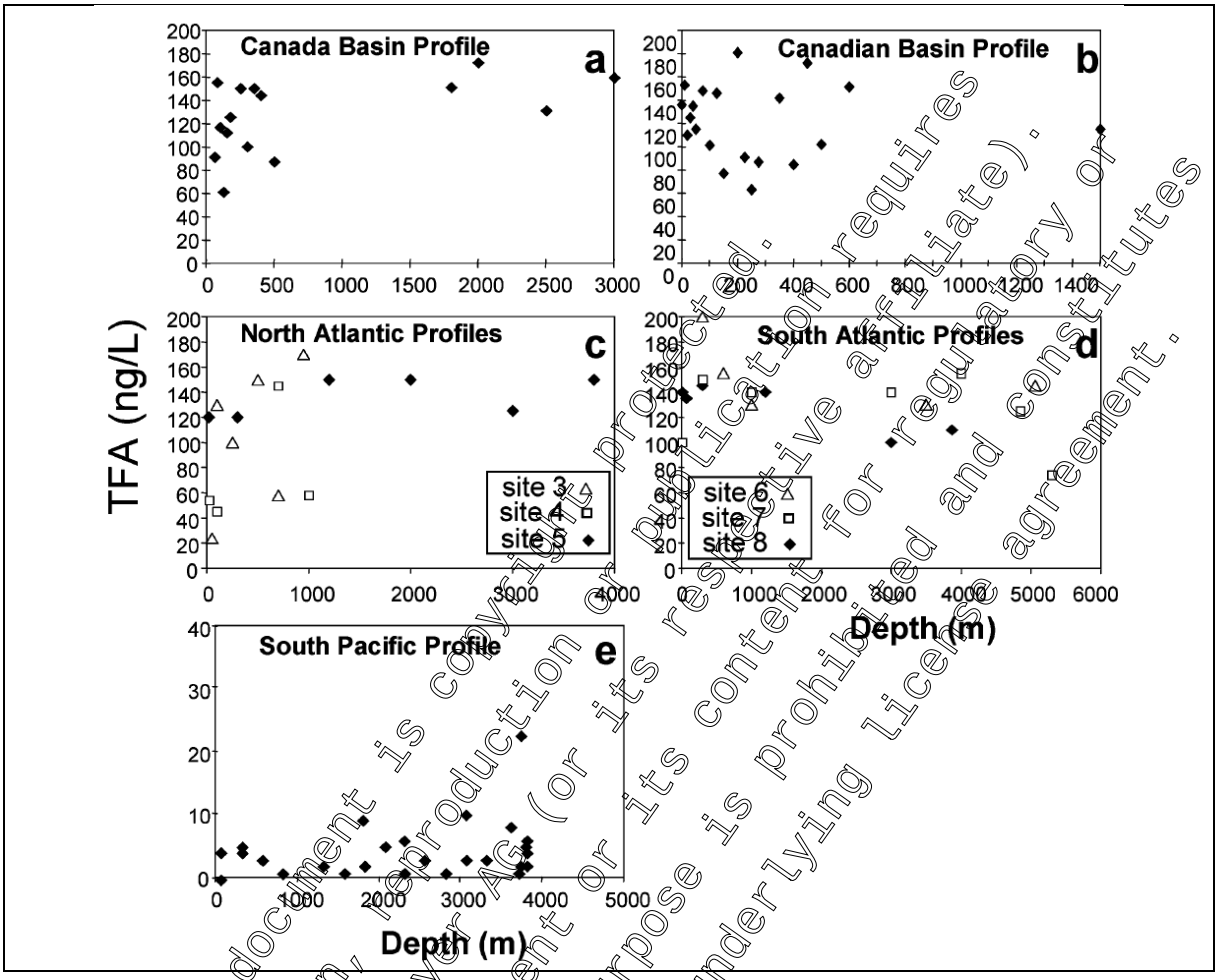
Table 7.5- 4: Measured levels of trifluoroacetate in oceanic waters

Site location	Site no.	max. monitoring depth [m]	trifluoroacetate [ng/L]	Difference between duplicates [%]	No. of samples
Canada Basin (Western Arctic)	1	1500	34–181	5	20[b)]
Canada Basin (Western Arctic)	2	3000	61–172	8	15[b)]
Nares Strait (Eastern Arctic)	3	489	120–170	7	7[b)]
Nares Strait (Eastern Arctic)	4	579	120–170	5	8[b)]
Nares Strait (Eastern Arctic)	5	365	8–125	20	6[b)]
North Atlantic	6	1000	28–190	27	6[b)]
North Atlantic	7	947	97–150	38	7[b)]
North Atlantic	8	3800	120–150	24	5[b)]
South Atlantic	9	3875	145–190	12	6[b)]
South Atlantic	10	5300	64–155	8	8[b)]
South Atlantic	11	5053	200–130	6	6[b)]
South Pacific	12	3830	1–150	-	16
South Pacific[a)]	13	2500	1–90	-	16
North Pacific	14	175	1–25	12	13[b)]
North Pacific	15	200	1–30	8	11[b)]
North Pacific	16	300	1–68	8	10[b)]
North Pacific	17	300	1–80	3	9[b)]
North Pacific	18	300	1–20	8	8[b)]
North Pacific	19	300	2–50	10	11[b)]
North Pacific[a)]	20	1000–2200	3–140	not stated	not stated
North Pacific[a)]	21	3968	2–230	-	23
Mediterranean Sea[a)]	22	200	0.5–50	-	20

[a)] vent
[b)] duplicate samples

Measured trifluoroacetate levels ranged from 0.5 to 230 ng/L at the sampling sites (see Table 7.5- 4). Levels of trifluoroacetate were predominantly higher in the Atlantic Ocean (>100 ng/L) than in the Pacific Ocean (< 100 ng/L) The reproducibility of concentrations between duplicates at most of the sites was < 15%, except for one location in the Eastern Arctic and the three locations in the North Atlantic.

Figure 7.5- 1: Trifluoroacetate depth profiles: trifluoroacetate concentrations (ng/L) as function of depth (m) for (a) Canadian Basin at site 1, (b) Canadian Basin at site 2, (c) North Atlantic at sites 3–5, (d) South Atlantic at sites 6–8 and (e) South Pacific at site 12



Depth profiles of trifluoroacetate for the two Western Arctic sample sites (site nos. 1–2) show much variation in trifluoroacetate levels for the first several hundred meters. Higher concentrations of trifluoroacetate (about 160 ng/L) with less variation were detected for water depth from 800 to 3000 m.

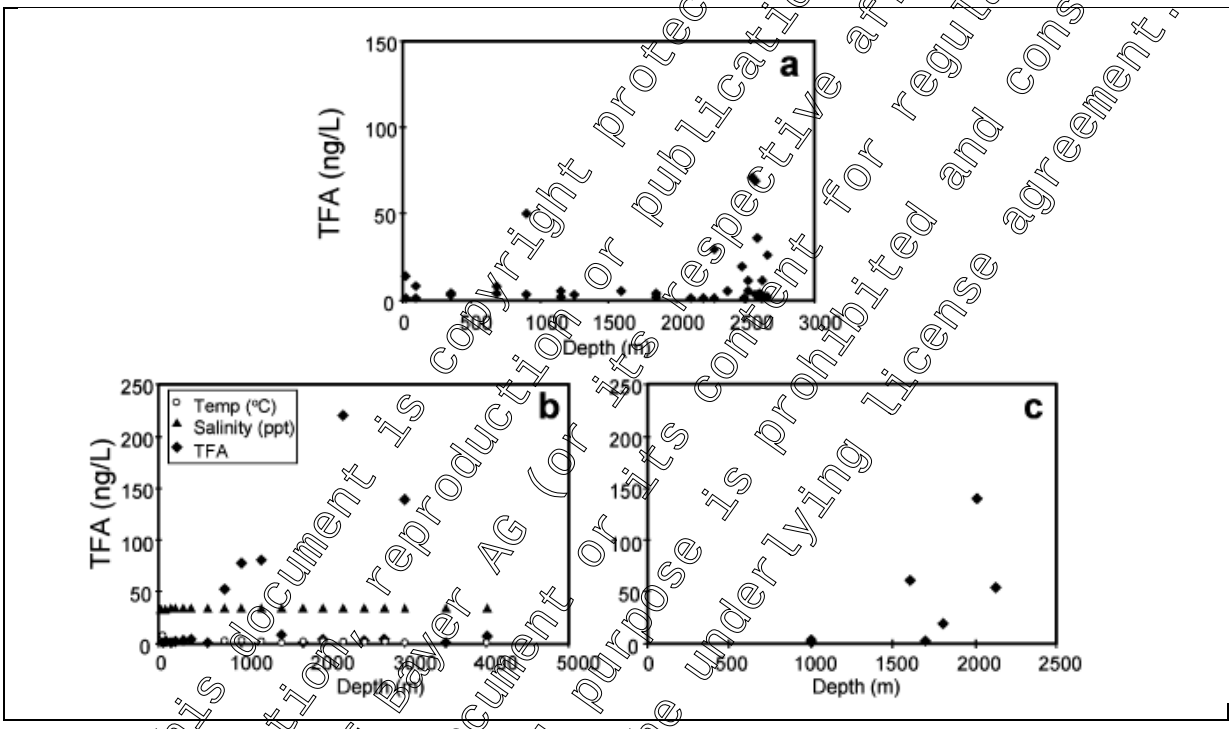
Profile data from the two northern located Eastern Artic sample sites (nos. 3–4) reveal constant concentrations of trifluoroacetate throughout the water column at 150 ng/L with good agreement between duplicate samples (difference between duplicates < 7%). Results for the southern located Eastern Artic sample sites (no. 5) indicate high surface concentrations but significantly lower values down to depth of 250 m with increasing values similar to those observed at the two northern stations. However, differences between the duplicates for the upper 60 m were high (50 %) whereas duplicates below 60 m water depth show smaller differences (< 20%).

Two profiles (nos. 6–7) extending to depths of 1000 m were obtained at the North Atlantic Ocean sample sites with concentrations of trifluoroacetate between 17 to 190 ng/L. Lowest concentrations were measured in the upper 50 m. For deeper water layers the concentration of trifluoroacetate was about 150 ng/L. For the third North Atlantic profile (no. 8) with a depth up to 3800 m concentrations of trifluoroacetate were nearly stable ranging from 120 to 150 ng/L. Overall, the three profiles from the South Atlantic Ocean sample sites exhibited consistent trifluoroacetate concentrations throughout the water column at 150 ng/L.

Trifluoroacetate concentrations from the South Pacific sample site (no. 12) were generally below 20 ng/L throughout the profiles, however duplicate samples were not taken at this location.

Surface water profiles with depths of 0–300 m were obtained at six sites in the North Pacific Ocean (nos. 14–19, data shown in the supportive data to the original study). Measured concentrations of trifluoroacetate were > 10 ng/L in the upper 50 m, 30-60 ng/L at middle depths (150-200 m), and < 10 ng/L below 300 m.

Figure 7.5- 2: Trifluoroacetate vent profiles: trifluoroacetate concentrations (ng/L) as function of depth (m) for sites over active vents: (a) site 13, (b) site 21 and (c) site 20



At one vent sample site (no. 13) near Easter Island in the South Pacific low trifluoroacetate concentration levels throughout the water column were observed. At maximum depths, higher trifluoroacetate values were detected (17 ng/ L). However, measured trifluoroacetate levels at a nearby trifluoroacetate depth profile (no. 9) were significantly higher with concentrations up to 150 ng/L.

At a vent area in the NE Pacific Ocean, two sampling collections (nos. 20–21) were made. One was over a deep-sea vent (4000 m, no. 21) and the other, directly over a volcanic vent (no. 20). For the deep-sea vent (no. 21), measured trifluoroacetate levels showed much variation over the profile. Low concentrations were observed down to a depth of 800 m and for depths around 2500 m and 3500-4000 m. Increased levels of trifluoroacetate were detected from 800 m to 1500 m with concentrations up to 100 ng/L. Peak concentrations of trifluoroacetate were measured at a depth of 2000 m and 3000 m with corresponding trifluoroacetate concentrations of 225 ng/L and 150 ng/L, respectively. At the other site (no. 20), directly over a volcanic vent, samples were collected at the top of the plume (1900 m), the bottom of the plume (2050 m), and within the core of the plume at 1980 to 2010 m. trifluoroacetate levels increased from 3 ng/L at a depth of 1000 m to 140 ng/L at the bottom of the plume (2050 m). No correlation was found between the measured trifluoroacetate values at the vent site with simultaneously measured salinity and temperature data.

For a depth profile taken over a vent in the Mediterranean Sea (no. 22) low concentrations of trifluoroacetate (often < 1 ng/L) were detected. Near the surface, levels of trifluoroacetate were higher (around 15 ng/L).

III CONCLUSIONS

Oceanic trifluoroacetate depth profiles sampled over various sites reveal a high spatial heterogeneity in their horizontal and vertical distribution. Higher trifluoroacetate levels were observed in the Arctic Ocean and the North/South Atlantic (around 150 ng/L) whereas lower trifluoroacetate levels (< 100 ng/L) were measured in the Pacific Ocean. The authors concluded that this variability cannot occur without active sources or sinks. For deeper water layers, having no direct exchange with upper water layers or the atmosphere, existing trifluoroacetate concentrations can be only the result of natural sources. Measurements of trifluoroacetate levels over active vents suggest that some deep-sea vents may be natural sources of trifluoroacetate.

IV COMMENTS BY THE NOTIFIER

This study provides screening data on the occurrence of trifluoroacetate in ocean waters. Measurements of trifluoroacetate levels over active vents suggest that some deep-sea vents may be natural sources of trifluoroacetate. Thus, this study will not be further considered in the risk assessment.