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Document identifier and Date Data points containing amendments or additions¹ version number and brief description 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 Beport.

Version history



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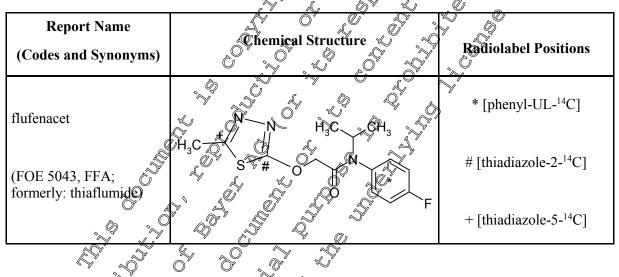
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CA 7 FATE AND BEHAVIOR IN THE ENVIRONMENT

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 no submitted within the Baseline Dossier. However, for a better understanding of the penavior 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, OA 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 fluteracet in the environment were conducted using either [phenyl-UL-¹⁴C]-, [thiadiazole-2-¹⁴C]- or thiadiazole-5-¹⁴C]-labeled flutenacet, as well as unlabeled flutenacet as test item. These radiolabel positions are considered sufficient to define the route of degradation of flutenacet. The structure of flutenacet and the positions of the different radiolabels are depicted below:



The results of the studies are summarized in the sections 7.1 to 7.5. The proposed degradation pathways in soft water and sections 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 oxed ate, FOE sulformed acid FOE methylsulfide, FOE methylsulfone, FOE-thiadone, FOE 5043 trifluoroethapesulfonic acid and trifluoroacetic acid. An overview is given in the table

below to the second sec



Report Name ¹ (Codes and Synonyms)	Chemical Structure	Radiolabel Positions
FOE oxalate (M1)	HO H ₃ C CH ₃ HO HO K CH ₃	* [phenyl-t0L-14C]
FOE sulfonic acid (M2)		* Whenyl-WL-14C]
FOE methylsulfide (M5)		
FOE methylsulfone (M7, BCS-CO62475)	$\begin{array}{c} & & & & \\ & & & & \\ & & & & \\ & & & \\ & & & \\ & & & \\ & & & & \\ & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\$	* [phenyl-UL- ¹⁴ C]
FOE-thiadore (M9, Thiadone)		# [thiadiazole-2- ¹⁴ C]
FOE 5043-trifluoro- ethanesulfénic acid (M4 TFESA	CF3 OH	no radiolabel available
(M45, TFA, BCS-AZ56507)	CF ₃ OH CF ₃ OH CF ₃ OH CF ₃ OH	* [1- ¹⁴ C]
J. N.		

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-trifluoroethanesulfonic 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.



Document MCA: Section 7 Fate and behaviour in the environment Flufenacet

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 ether [phenyl-UL-4C]-, Thiadia [2016-2-10] or [thiadiazole-5-14C]-labeled flufenacet as test item, Flufenacet was stable to photolysis, while degradation was observed in microbial active soil. Q_{a}^{2}

Under aerobic conditions in the dark in the taboratory flugenacet, formed and major degradation products: FOE oxalate (max. occurrence 265% of applied radioactivity (AR)), FOE sulfonic acid (max. occurrence 26.3% AR), FOE methylsalfone (max. occurrence 6.6% (MR), EQE-thiadone (max. occurrence 5.9% AR), FOE 5043-trifluoroethanesulfone acid (max, occurrence 6.0% AR) and trifluoroacetic acid (max. occurrence \$1.5% AR). Additionally, a humber of minor degradation products were formed. Significant mineralization to carbon divide 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 poute of degradation of FOEthiadone under aerobic conditions was additionally studied in a number of soils at 20 °C, using either [phenyl-UL-¹⁴C]- or [thiadiazole-2-4C]-labeled FOE-thiadoxe 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. Ľ

The route and rate & degradation of Hufenass under an aerobic conditions was studied in three soils at 20 °C, using either [pheny) UL-¹⁴ OF or [thadiazole-2-¹⁴CP labeled flufenacet as test item. During the first phase of the study the soils were maintained ander perobic conditions for approx. one half-life of flufenacet in the respective s(i) (30 or 5 days). After wards, the samples were flooded with water and maintained under maerob@ condutions. Under these conditions flufenacet formed five major degradation products. FQE oxalate (max occurrence 11.2% AR aerobic and 14.5% AR anaerobic), FOE sulfonic ford (6.6% AR perobic and anaerobic), FOE-thiadone (max. occurrence 5.9% AR aerobic and 13.6% AR anaerobic), FQF 5043 trifluoroethanesulfonic acid (max. occurrence 6.0% AR aerobic and 3.0% of anacobic) and trifluoroacetic acid (max. occurrence 37.5% AR aerobic and 53.2% AR anaerobic). FOE oxatate, FOE sulfonic acid, FOE-thiadone and FOE 5043-trifluoroethanesa formed under acrobic 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 ($\leq 0.5\%$ AR) during the aerobic or the anaerobic incubation phase. Mineralization to carbon dioxide was observed for both labeling positions during the aetobic incubation phase (1.4 to 1.9% AR) accompanied by the formation of nonextractable 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.



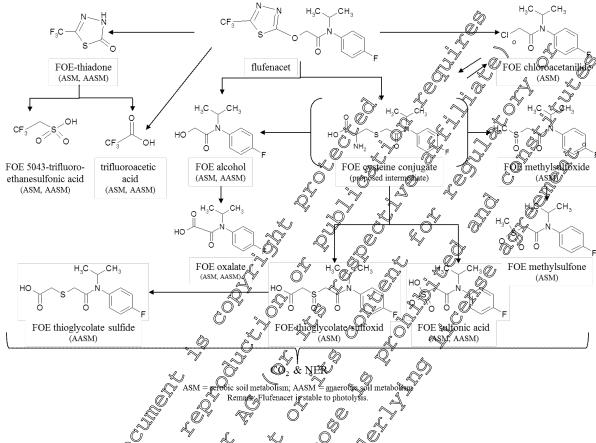


Figure 7.1.1-1: Proposed degradation pathway of flufenacet in soil

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

Degradation Product	Approbic Soil	<u>An</u> aerobic Soil [% AR]
FOE Qualate O O . O	26.5	14.5
FOE sulfonic, acid	26.3	6.6
FOE metholsulfore of O	6.6	-
OE-thisdone	5.9	13.6
FOE 5043-trifuoroethatesulfoncacid	6.0	5.0
trifl@roaceti©acid 0	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:

				~ "O"		/
Annex Point / Reference No	Autho	r(s) 🔊	· ~	Xear	Bocument No	0
KCA 7.1.1.1/01	, N. C.	.; , I). NG (°≈ 4 994	×M-002166-01-	-1
KCA 7.1.1.1/02	, N. C.	;	Q.M. ()	¥1994	M-002165-01-	-1
KCA 7.1.1.1/03	, I. V.;	S.	, MØ	1980	M-002146-01-	-1

Two additional studies have been performed for flufenacet to further elucidate the the date of the thiadiazole heterocylce and are submitted within this Societant Dosser for the flufenacet renewal of approval.

		° .0		
A summary of the route of degradation	of Witopohot	in add to airlan	in addition CA 711 and Fig	niro
A summary of the foule of degradation		. III SOM IS GIVEN	$\Gamma \Pi SCAIOII \subseteq A / .1.1 and \Gamma IS$	zure
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Report: KCA 7.1.1.1/04: E. M.: 2013	
Title: Amendment No I - [thiadiazole 5-14C] Aufenace: Aerobic Degradat	tion /
Metabolism in One Ruropean Soil	
Report No: MEF-11/937 & S	
Document No: M-439105202-1	
Guidelines: • OECO Test Stideline, No. 307	
• OCSPP Test Guiderne No \$35.41.90/4200	
GLP: Yes 4 0 0	

Executive Summary

The degradation of [thiadiazole- 3^{-14} C] the function of the solution of the laboratory for 120 days at 19.7 °C and soil moisture of 55 ± 5% of the maximum water holding capacity:

	× 1				
Soil		Source	Texture (USDA)	рН ¹	OC [%]
Hoefchen am Ho	henseh 📎	Borscheid, Germany	silt loam	6.7	2.5
¹ pH in 0.01 M @Cl ₂					

The study application rate was $162.9 \mu g/100$ 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 $\leq 0.1\%$ AR for all sampling intervals.

Extractable residues decreased from 99.7% AR at DAT-0 to 78.8% AR at DAT 20.

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-000 0.9% AR at DAT

Besides the formation of carbon dioxide (5.6% AR at DAT-1200 three major degradation products were identified: FOE-thiadone (max. 5.8% AR at DAT 10), FOE 5043 trifluors ethane sulfonic acid (max. 6.0% AR at DAT-14) and trifluoroacetic acid (max. 77.7% AR at DAT-20).

I. MATERIALS DMET

A. **MATERIALS**

1. **Test Item**

> [thiadiazole-5-14C]flufenacet CAS No Specific activity Radiochemical purity

with radioactivity-detector and TLC, scan 20% HP

Ò

2. **Test Soils**

The soil (Table 7.1.1.1-) was campled Greshly from the field tupper horizon of 0 to 20 cm) and sieved to a particle size of ≤ 2 nm. The soil was taken from agricultural use area representing one of the common 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 @n Hohenseh
Geographic Location	
City	Burscherd
State	North-Rhin@Westphalia
Country	Gormany O Sormany O
GPS Coordinates	× 51° 04,9 ×
(() ()	È 007 96.3'
Soil Taxonomic Classification (USDA)	loanty, mixed mesic Pypic
Soil Series	no information availables
Textural Class (USDA)	J ^y L silt koam
Sand [%] [50 μm – 2 mm]	
Silt [%] $[2 \ \mu m - 50 \ \mu m]$	
Clay [%] [$< 2 \mu m$]	
pH - in CaCl ₂ (soil/CaCl ₂ 1/2) - in water (soil/water 1/1) - in water (saturated paste)	
- in CaCl ₂ (soil/CaCl ₂ 1/2) O^{4}	Q7 ~ X Q6.7
- in water (soil/water 1/1)	
- in water (saturated paste)	7.0
- in KCl	6.3
Organic Carbon [%]	2.5
Organic Matter [%] ¹	4.3
Cation Exchange Caperity [meg]100 g	<u>لا المراجع الم</u>
Water Holding Capacity	
maximum [g H Q ad 100 g soil Q Q	61.1
at 0.1 bar (pF 2.0) [%]	<i>S</i> ^y 29.8
Bulk Density (disturbed) [g/cms]	1.04
Microbial Biomass mg mistøbial carbon / kg soil DWS	041
	841
DAT-58 (BIO-/BIO+) DAT-121, BIO-/BO+)	693 / 638 563 / 506
	563 / 506
¹ calculated as: $\mathcal{O}^{\mathbf{T}}[\%] = \mathcal{O}^{\mathbf{T}}[\%] \cdot \mathcal{O}^{\mathbf{T}}_{24}$	
² BIO samples were left untreated BIO+ samples were applied	with solvent of application solution
DAT: days after treatment GPS: g	global positioning system
DW: dry Gright St USDA	: United States Department of Agriculture
STUDYOESIGO	

B.

Experimental Conditions 1.

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 $55 \pm 5\%$ 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 Aufenacet of 600 g/ha, resulting in a nominal study application rate 160 μ g/100 g soil (dry weight), equal to 1.6 mg/kg soil (dry weight). The actual SAR was 162.3 μ g/100 g soil (dry weight), equal to 1.6 mg/flufenacet/kg soil (dry weight).

The application solution was prepared in methanol/water $(1:10^{10}/v)$. 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 9.7 °C and soil moisture of $55 \pm 5\%$ of the maximum water holding sapacity in a walk-in climatic chamber %

2. Sampling

Ten sampling intervals were distributed over the entire incubation period of 120 dags. Duplicate test systems were processed and analyzed 0, 2, 4, 7, 10, 44, 35, 60, 87 and 120 days after treatment (DAT). Microbial soil biomass was determined a DAT-0, DAT-6, and DAT-120, 20

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 imperature 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 software separated by centrifugation and decantation.

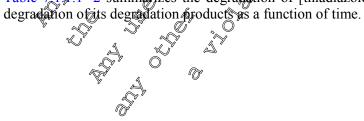
Soil extracts were characterized by liquid scintillation counting and HPLC/radiodetection and TLC/radiodetection the limit of detection (FOD) for the HPPC/radiodetection method was 0.5% AR. The amount of volatiles and non-extractable residues was determined by liquid scintillation counting and combustion/aquid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

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

RESULTS AND DISCUSSION

A. EXORACTIÓN AND QUANTITATION OF RADIOACTIVITY IN SOIL SAMPLES

Table 7.41.1- 2 Summarizes the degradation of [thiadiazole-5-¹⁴C]flufenacet and the formation and degradation of its degradation of the formation of time.



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Document MCA: Section 7 Fate and behaviour in the environment Flufenacet

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)

					D	AT	, C			
Compound	0	2	4	7	10	14	-35	60	8 7 "	, 120
flufenacet	99.7	92.2	87.8	75.6	64.1	54.8	3.8	£.1	1.0	0 0 2
FOE-thiadone	n.d.	3.4	4.5	5.5	5.8	3.4 Ø	1.6	0.6	₹ ‡ OD	₹ ¥OD
FOE 5043-trifluoroethanesulfonic acid	n.d.	0.9	2.3	4.2	3 .4	6.0	4.9	2,60	< LOD	LOD
trifluoroacetic acid	n.d.	1.2	3.7	9.6Ò	16.7	⁾ 25.1 §	61.1	73.0	7	77.6
Unid./Diff. Radioactivity ¹	n.d.	< LOD	0.9	\$0,9	15	1.80	1.8	0.8	LOD	LOD
Total Extractable Residues	99.7	98.2	99.3 J	O95.8	(OR 4	A .1	8302	80.P		78.5
Carbon Dioxide	n.a.	< 0.1	0.4Q	0.3	0.7 🌾	¥ 1.1	3.2	<u>@</u> 5	50	5.6
Volatile Organic Compounds	n.a.	< 0.1	≪0.1	ê.	< (2.1)	< 0.0	× < 0.1	0.1	\$ 0.1	0.1
Non-extractable Residues	0.5	1.4 👌	2.1	~ 3.7	S.3	7.0	125	13.5	D _{13.1}	12.5
Material Balance	100.2	99.9	101.6/	100.2	99.8 99.8	99.5	99.1	98.9	98.6	97.0

¹ Minor degradation products were summed under under the digactivity the maximum amond of a single degradation product was 1.8% AR.

B. MATERIAL BALANCA

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 90 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 sessels 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 (DATQ20) to 12.5%. See also Table 7.1.1.1-2 for details.

D. NOLATILIZATION

The maximum amount of carbon dio de 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 \leq 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-5-¹⁴C]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-5-¹⁴C]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 tester soil. Besides carbon dioxide, three major degradation products were identified: FOE-thiad are (max, 5.8% AR), FOE 5043 trifluoroethanesulfonic acid (max. 6.0% AR) and trifluoroacetic acid (max. 77,7% AR). Formation of nonextractable 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 02. M.; 2013
Title:	Amendment No 1 to: [miadiazole-5-14] flufencet: Aerobic Degradation /
	Metabolisman Three European Soils
Report No:	MEF-11/938 ~ ~ ~ ~ ~ ~
Document No:	M-440348-02-6
Guidelines:	• OEGO Test Guideline No. 307
	• QCSPP Test Guideline No 835.400/4200
GLP:	Yes L

Executive Summary

pHQm 0.01 M CaCl

The degradation of [thiadiaze0-5-¹⁴C] Dufenacet was investigated in three soils under aerobic conditions in the dark in the daboratory for 121 days at 19.8 °C and soil moisture of $55 \pm 5\%$ of the maximum water holding capacity:

Sold 2	Source	Texture (USDA)	рН ¹	OC [%]
Laacherhof AXXa 🔍	Monheim Germany	loamy sand	6.1	2.4
Dot lendor 🕅 🖉	Bankenheim, Germany	clay loam	7.2	5.3
Laacherhof Wurmwiese	Monheim, Germany	loam	5.4	2.2

The study application rate was $152.0 \ \mu g/100 \ g$ 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-12, (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 20.2% AR at all sampling intervals in all soils.

Extractable residues decreased from 98.7% AR at DAT-0 to 79.0% AR at DAT-121 in soil Laacherhof AXXa, from 99.9% AR at DAT-0 to 82.1% AR at DAT-121 in soil Dollerdorf 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 % AR at DAT-63 and slightly decreased to 17.2% AR at DAT-121 in soil Laacherhof AXXa. In soil Dollendor 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 IAT-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 Wurnwises, respectively.

Besides the formation of carbon dioxide one major degradation product was dentified. Trifluoroacetic acid was detected with maximum amounts of 74,1% AR at DAT 221 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.

71. MATERIALS AND METHODS

- A. MATERIALS
- 1. Test Item [thiadiazole -9-14C] flutenaceto CAS No (2000) Specific activity (2000) Radiochemical purity (2000) Page (2000) (1.54-MBq/mg) Radiochemical purity (2000) Page (2000) (

2. Test Soils

The soils (Table 7.1.1- 6 were sampled freshly from the field (upper horizon of 0 to 20 cm) and sieved to a particle size of ≤ 2 mm. The folls were taken from agricultural areas representing different geographical origins and different soil properties as required by the guidelines.

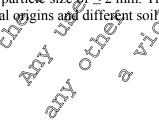




Table 7.1.1.1- 3:	Physico-chemical properties of test soils
-------------------	---

Parameter	Results / Units							
Soil Designation	Laacherhof AXXa	Dollendorf II	Laacherhof					
		. ~ Y	Wurmwiese					
Geographic Location		D ¹						
City	Monheim	Blankenheim	Monheim					
State	North-Rhine	North-Rhine	North-Rhine					
	Westphalia	Westphalia	Westphalia					
Country	Germany	Cormany &	Germany					
GPS Coordinates	N 51° 04.647 🖉	N 50° 22.899'	N 505 04.857					
	E 006° 53.517 🛇	₩ 006° 43.001' Č	E_@6° 55.2\$1'					
Soil Taxonomic Classification	sandy, mixed, mesic	, fune-loamy, mixed,	loamy, mixed, mesic					
(USDA)	typic Cambroolls	active, frigid Typic	Typic Argudalfs					
Quil Quine		Entrudept						
Soil Series		no information availabl						
Textural Class (USDA)	loanty sand	C clay loam	© [°] loam					
Sand [%] [50 μ m – 2 mm]	75 6	²⁹ . 4	<i>Q</i> 49					
Silt [%] $[2 \ \mu m - 50 \ \mu m]$			34					
Clay [%] [< 2 μm]		33 3	17					
pH								
- in CaCl ₂ (soil/CaCl ₂ 1/2)	6.1	√y7.2 √y″	5.4					
- in water (soil/water 1/1)	~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~	² 7.4 _☉	5.7					
- in water (saturated paste)	6.5 ×	Q 7.2	5.8					
- in KCl	5.9	× 2.0	5.2					
Organic Carbon [%]	2.40	£ ⁹ 5.3	2.2					
Organic Matter [%] ¹	L AI O	م© ^v 9.1	3.8					
Cation Exchange Capacity	\$ 9 .9	20.9	10.8					
[meq/100 g]		S ^y						
Water Holding Capacity 2								
maximum	491 5	79.8	59.9					
$[g H_2O ad 100 g so DW]$		16.0	22.2					
at 0.1 bar (pF 2.0) [%]	× 18.7	46.0	23.3					
Bulk Density (distarbed) [5 cm ³]	ي 1.10°	0.95	1.12					
Microbial Biomass								
[mg microbial carbon, kg soft DW] ²		2447	9(2					
		3447	862					
DAT A (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 DW: dry weight OF Calculated (Construction) DW: dry weight OF Calculated



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 $55 \pm 5\%$ maximum water holding capacity by addition of designized 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 2 days prior to application.

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

The application solution was prepared in methanol/water $(1, \mathbb{Q}, v/v)$. 346 µL \mathcal{Q} the application solution were applied drop wise onto the soil sufface of the respective test systems using a pipette. After application the test vessels were closed with the trap attackments (except DAT-Q samples).

The test systems were incubated under aeroble conditions in the dark for 12 days at 19.8 °C and soil moisture of $55 \pm 5\%$ of the maximum water holding capacity in a walk-in 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-101.

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 (21:1), v/2) 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 supernation and soil were separated by centrifugation and decantation

Soil extracts were characterized by liquid scintillation counting and the primary chromatographic method. (HPCC/radiodetection and LCC/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-5-¹⁴C]flufenacet and the formation and degradation of its degradation products as a function of time.

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Document MCA: Section 7 Fate and behaviour in the environment Flufenacet

								-	Po.		
						DAT		, C			
Compound	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	J.6	3.2	14
FOE-thiadone	n.d.	1.8	1.9	2.5	2.8	2.5	2.70	1.6	1.0	LOD	LOD
FOE 5043-trifluoro- ethanesulfonic acid	n.d.	n.d.	< LOD	1.7	3.2	Q4.4	3.2	~2.7 ~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~	1,20	< LOD	0.5
trifluoroacetic acid	n.d.	n.d.	1.6	2.7	7.0	13.9	22.1%	V /	65.9	Ø.5	74.1
Unid./Diff. Radioactivity ¹	n.d.	n.d.	n.d.	n.d.	s≪n, d.	<100D	n.đ.O	1.86	1.0	n.d.	Cn.d.
Total Extractable Residues	98.7	98.8	95.2	96.6		©9 1.7	A\$7.9	80.0	76.9	75.0	76.0
Carbon dioxide	n.a.	< 0.1	< 0.1	0.°R	0.4	0.5 %	1.1	2.9	Ø.0	<u> </u>	5.6
Volatile Organic Compounds	n.a.	< 0.1	< 0.1	∞0.1	₹ 9.1	0.1	0.0	0.1	0.1	§ 0.1	0.1
Non-extractable Residues	0.4	1.0	1.9	¥ 4.1 ·	Q4.0	9.1	9.3	1250	18.6	18.4	17.2
Material Balance	99.1	99.9	97,1	100.9	99.1		8 8	99.0	9 9.3	98.8	98.8
				I A A A A A A A A A A A A A A A A A A A	ſ	a v	/ °@	<i>n</i>	Ô		

Turenacct Table 7.1.1.1- 4: Degradation of flufenacet in Soil Laacherhof AXXa under Aerobic Comparison

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

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

¹ Minor degradation products were summed up to invidentified adioactivity, the maximum amount of a single degradation product was 1.0% AR.

 Table 7.1.1.1- 5:
 Degradation of flurencet in Soil Dollerdorf IL under Acrobic Conditions (expressed as percent of applied radioactivity; upcan value of duplicates)

-	<u>W</u> i	<u> </u>	<u> </u>			<u>^</u>					
Compound		Ũ	T	Or	, O	DAT	, ¥				
Compound	0~	1	2 🦋	4	07	Ň	14	35	63	91	121
flufenacet	29.9	96.8	88.2		~ `	≫65.1	55.9	15.3	2.5	1.2	0.9
FOE-thiadone	n.d.	02.1		ð	4.0	5.6	4.8	3.2	0.7	n.d.	n.d.
FOE 5043-trifluoro-	nçd.	n.d	n.d.a	87	Q.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.	ð.	n.d.	n.d.	< LOD	1.0	n.d.	n.d.	n.d.
Total Extractable Besidues	9959	98.9		_≫ 97.7	92.8	93.1	91.0	88.0	82.4	82.7	81.9
Carbon dioxi	Soy.a.		Q.10 ²	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.	1.8	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
4	J	Å.									

n.d.: not detected, Ta:: 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.</p>

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Document MCA: Section 7 Fate and behaviour in the environment Flufenacet

								,	Ro.		
						DAT					
Compound	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	3.3	3.6	1.3	100
FOE-thiadone	n.d.	1.5	2.0	3.1	4.6	3.3	3.10	1.7	0.7	A.d.	n.d.
FOE 5043-trifluoro- ethanesulfonic acid	n.d.	n.d.	< LOD	0.7	1.6	01.9	0.5	≪LOD	< LOB	< LOD	ر LOD <
trifluoroacetic acid	n.d.	n.d.	1.3	5.2	11.	19:5	31.6%	60.0	70.0	Ø4.8	73.8
Unid./Diff. Radioactivity 1	n.d.	n.d.	n.d.	n.d.	×9.5	j.0	2.40		< LOD	n.d.	On.d.
Total Extractable Residues	98.7	98.3	93.8	95.2 (₽ _{92.5}	Č8 8.8	A\$\$.0	793	75.₽	76,1	74.8
Carbon dioxide	n.a.	< 0.1	< 0.1	0:\$Z	0.4	0.8 %	1.3	2.8	O .7	<u>A</u> A	4.5
Volatile Organic Compounds	n.a.	< 0.1	< 0.1	∞0.1	<u>A</u>	0.1	0.0	0.1	0.1	§ 0.1	0.1
Non-extractable Residues	0.7	1.2	2.3	¥ 4.1 ·	Q 6.7	61 0.1	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 _s	98.9	. 27.7	98.8	96.7
			J.	Ű	d .	<u> </u>	° ~	/	(h)		

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)

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

¹ Minor degradation products were summed up to initentified adioactivity, the maximum amount of a single degradation product was 1.4% AR.

B. MATERIAL BALANCE

The amount of dosed test irom 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 Doblendor H (overall mean 99.7% AR, RSD 1.8%) and from 96.2 to 99.8% AR in soil Laacherhof Wurnwiese foverall mean 98.7% AR, RSD 1.2%), see also Table 7.1.1.0 4 to Table 7.0 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-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 $\leq 0.2\%$ 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-5-¹⁴C]flufenacet in the combined soil extracts decreased from 8.7% 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-124 in soil DD and from 98.7% AR at DAT-0 to 1.0% AR at DAT-121 in soil W.

Besides carbon dioxide, one major degradation product, was identified Frifluoroacetic acid was detected with maximum amounts of 74.1% AR at DAT-121 in soil AX, \$1.5% AR at DAT-91 in soil DD and 74.8% AR at DAT-91 in soil WW. The known degradation products FOF 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.

ji. CONCLUSIONS

[thiadiazole-5-¹⁴C]flufenacet was rapidly degraded in soil onder appoint conditions in the dark in the laboratory.

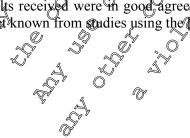
Formation of carbon dioxide was observed up to 5.6% AR in soil Laacherhof AXXa, 6.5% AR in soil Dollendorf II and 4.5% AR as soil Laacherhof Wurmwiese.

Besides carbon dioxides one major degradation product was detected. Trifluoroacetic acid was identified with maximum amounts of 74.1% AR at DAT-121 to soil Laacherhof AXXa, 81.5% AR at DAT-91 in soil Dohendorf 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 186% AR in soil Caacherhof Wurmwiese, declining at study end in all soils was observed.

The formation of carbon dioxid indicates the potential for mineralization of the test item and its transformation products. Therefore, fluctuated 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 gudies using the phenyl-UL-¹⁴C] and the [thiadiazole-2-¹⁴C]label.





CA 7.1.1.2 <u>An</u>aerobic 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 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; , N. C.; , D. M.; 1995
Title:	Anaerobic Soil Metabolism of Ophenyl-U-14C KOE 5043
Report No:	MR106645
Document No:	M-002162-01-1
Guidelines:	• OECD Test Guideline No. 307
	• OCSPP Test Guideline No. \$5.4100 4200 a a a
GLP:	Yes A V V X

Executive Summary

The degradation of [phenyl-UL₅¹⁴O]fluferacet 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 4/3 bar water holding capacity before start of the anaerobic incubation phase (total study period 2) of days)

	Ő	a St		<i>a</i> , <i>¹</i>	V V		
Soi	I N		Source	🖉 Text	vre (USDA)	рН ¹	OC ² [%]
	ve		Indiana, USA	A()) (())	ndy loam	6.2	0.3
1 pH in water	ð ₍ g						

² calculated from organic matter (OM) by $QO^{2} OM/4Q24$

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

During the aerobic incobation phase, est 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, or plicate 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 with 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 C_0 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 $\leq 0.1\%$ 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 DA D210 during the anaerobic incubation phase.

The amount of flufenacet decreased from 99.4% AR at DAP to 69.0% AR at DAP-30 doring 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 evaluate prax. acrobic: 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 N

A. MATERIALS

1. **Test Item**

[phenyl-UL-¹⁴C]flufenacet Batch No Specific activity Radiochemical purity

6.7 MBq/mg ($\triangleq 66.5$ mCi/mmol) 99.2% CLC analyses of application solution before and after application to spil)

2. **Test Soils**

The soil (Table 7.1.1. 21) was sampled freshly from a field and placed inside two 5-gallon (approx. 19 L) buckets which were kept under conditions The soil was initially planted with soybeans to maintain a viable microbial population, but was overrup with weeds just prior to the start of the study. Immediately prior to starking 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 $\leq 2 \text{ mm}$ and air-dried. The soll was taken from agricultural use area representing one of the common agricultural soils of this region.

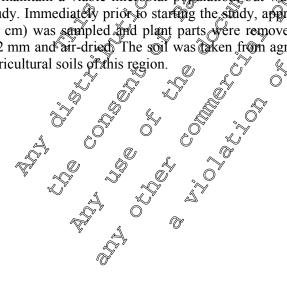




Table 7.1.1.2- 1: Physico-chemical properties of test soil

Parameter	So	
Geographic location		
- city	How	ve X a o o o
- state	India	
- country	UŞ	
GPS Coordinates	n@jnformatie	n available
Site description	The soil was placed into 5-gallo	on buckets (approx. 19/L) and
-	planted with soybeans which we	re overrun with weeds prior to
	start of the study	
Soil taxonomic classification (USDA)	loamy-Skeletal, mixed,	mesic Topic Argodull
Soil series	no informatio	on avallable
Texture class (USDA)	Q sandy	
Sand [%] $[50 \mu\text{m} - 2 \text{mm}]$		54 .Q" (U
Silt [%] $[2 \mu m - 50 \mu m]$		P° O' LA
Clay [%] $[< 2 \mu m]$		5 8 6
pH		K.U
- in water (soil/water 1/1)		
Organic matter [%]	0. V V 0.	
Organic carbon [%] ¹		3
Microbial biomass ²		
[mg microbial carbon/kg soil]		N.
DAT-0		
DAT-30		Í
Microbial mass / activity dupping aerobic	Phospholipid fatty and assay	Plasmalogens ⁴
and anaerobic phases ²		[total detected, pmol]
	flow through/static incubation	flow through/static incubation
- DAT-0	2 2 10^8 2	n.d.
- DAT-30	25×10^{8}	n.d.
- DAT-37 (DASF-7)	. Soff x 10 ⁸ /	189282/ n.a.
- DAT-125 (DASF-95) Q	3° 3°	25810/ n.a.
- DAT-210 (DASF-189)	3.5×10^8 3.2 x 10 ⁸	n.a. / n.a.
DITI 233 (DITIS) ()	$2.6 \times 10^{8} / 1.9 \times 10^{8}$	11756 / 13810
Cation Exchange Capacity [meq/100 g]	6.5 Q 6.5	
Moisture at 1/3 bar (pF 2.5) [%]	13.	
Bulk density Gisturbe (g/cm ³)	1.3	7
ŽŽ Q & Ž		
n.a. = not analyzed, a. = not detected	DAT: days after treatm	ent
GPS: global positioning system	DASE. Days after soil	flooding

DASF. Days after soil flooding

GPS: global positioning system USDA United States Department of Agriculture ¹ calculated ac OC [%] → OM [%0/1.724 ○

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 10⁶ cells/mL water and 2.0 x 10⁷ cc0s/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

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. Abaerobic 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 basks ofth glass stoppers after the barrogen 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 μ g/00 g soil (dry weight), equal to 1.03 mg/kg soil (dry weight).

The application solution was prepared in acetonitrile/water (13, v/v) f mL of the application solution was applied drop wise onto the solf surface of the respective test systems using a pipette. The flasks were shaken after each application, at 500 μ L increments, to and in the dispersal of the treatment solution. After application the solf moisture was adjusted to 75% of 1/3 bar water holding capacity and the test vessels were closed with the gap attachments Q

The test systems over incubated inder aerobic conditions in the dark for 30 days at 21 ± 1 °C in a walkin climatic chamber. During the anaerobic incubation plase 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 acrobic invubation phase, est 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 WAT -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 chloric $(1:2, \mathbb{Q}/v)$ using approx. twice the volume of the soil extract.

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

The soil extracts and, if applicable, the water were characterized by liquid scipulation counting as well as by HPLC/radiodetection and/or TLC/radiodetection. The water was additionally partitioned into organic solvents to allow for TLC/radiod tection analysis. All sample extracts were analyzed at sufficient concentrations to detect amount 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.

RESULTS AND DISCUSSION

EXTRACTION AND QUANTIFATION OF RADIOACUIVITY IN SOIL SAMPLES A.

Table 7.1.1.2- 2 summarizes the degradation of [ptenyl-UL-⁴C]flufenacet and the formation and degradation of its degradation products as a function of time.

ADD ATION OF RA agradation products as a function of the degradation of [pteny agradation products as a function of the degradation of [pteny agradation products as a function of the degradation of [pteny agradation products as a function of the degradation of [pteny agradation products as a function of the degradation of [pteny agradation products as a function of the degradation of [pteny agradation products as a function of the degradation of [pteny agradation products as a function of the degradation of [pteny agradation products as a function of the degradation of [pteny agradation products as a function of the degradation of [pteny agradation products as a function of the degradation of [pteny agradation products as a function of the degradation of [pteny agradation products as a function of agradation products agradation of agradation products agradation of



ble 7.1.1.2- 2: Degradation of flufenacet in Soil Howe under Aerobic and <u>Anaerobic Conditions</u> (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 🔬	ۍ 67	@123	0180
flufenacet		99.4	82.2	78.7	69.0	60.3	55. C	52.00	44,2	39.0
FOE oxalate		n.d.	4.9	9.8	11.2	Ø ² .2	^{14.5}	°∼ <u>1</u> 0.9	<u>1</u> .4	\$ 9.9
FOE sulfonic acid	ł	n.d.	2.1	4.7	6.6 [©]	6. 1	5.3	4.7	5.0	4 .5
FOE thioglycolate	e sulfoxide	n.d.	0.9	2.7	Å.6	Č ^{0:5}	p.d.	p.d.	pe.q.	ngd.
FOE alcohol		0.4	0.3	n.d.Q	n.d.	0.3	n.d.	0.6) 1.4	0.9
FOE thioglycolate FOE methylsulfor		n.d.	n.d.	n,d.		L.	Q.	1.5		1.4
Unidentified Rad	ioactivity 5	0.0	0.2	0.1	, 0.2 (0.2	لي 0.0 پر	©0.2	0.7	1.1
Total Extractable	Residues	99.9	90.6	96.1	89.7	80.9	7.7.0	70.0	64.0	56.8
Carbon dioxide		n.a. 🕻) 0.3 🎭	0°0.9	J ^{1.4}	Õ ¹ .3	QI.3	Q.4	1.5	1.8
Volatile Organic Compounds		n.a	n.C	n.d.	n.d.	n.a	n.a	n.a	<0.1	<0.1
Non-extractable I	Residues	پ 0.1 و	5.0	8.0	≈~~8.4	Øp0.2	AB .8	22.9	27.2	32.6
Material Balanc	e 🖉	1000	95.9	105.0	99.5	92.2	94.1	94.3	92.7	91.3

Flufenacet

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

¹ The results from DAT-30 samples (end of acrobic incuration phase), were also taken for DASF-0.

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

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

- ⁴ The mass spectral analysis of the is dated FOE thiogly state fraction revealed, that this fraction contained also FOE methylsulfore and also FOE methyls
- ⁵ Minor degradation products were summer up to unidentified radioactivity, the maximum amount of a single degradation product was < 1.9% AR atomy sampling interval.

B. MATERIAL BALANCE

The amount of dosed set iter 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 95.3 to 961% 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 84% AR at DAT 30 during the aerobic incubation phase and further to 32.6% AR at DXT-210 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 includation 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 ampling intervals. See also Table 7.1.1.2-2 for details.

DEGRADATION OF TEST ITEM E.

The amount of [phenyl-UL-14C]flufenace(in the entire system decreased from 994% AR at DAT-0 to 69.0% AR at DAT-30 during the aeropic incubation phase and further to 300% AR at DAT-210 during the anaerobic incubation phase See al Table 7.1.1.2 for details.

Two major degradation products overe identified: FOE oxafate (max. aerobic: 11.2% AR at DAT-30; anaerobic: 14.5% AR at DAT-60) and DOE sulfonic and (max aerobic and anaerobic: 6.6% AR at DAT-30). Additionally, the known degradation products FOE this glycolate, FOE this glycolate, FOE this glycolate sulfoxide, FOE alcohol and COE 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 aDDAT-210.

CONCLUSIONS Ŵ

[phenyl-UL-¹⁴C] JufenaceOwas degraded in soil under aerobic and anaerobic conditions in the dark in the laboratory.

Formation of carboo dioxid was observed up to 4.4% AR in the tested soil during the aerobic incubation phase. Two major degradation products were identified: FOE oxalate (max. aerobic: 11.2%; anaerokue: 14.5% AR3 and FDE sulforic 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 Ppheny PUL-14 Full function and the soil, thus, no additional degradation products were formed during the anaerobic phase of the study.

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



Report:	KCA 7.1.1.2 /02; , 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 Or You

Executive Summary

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

				N N N N N N N N N N N N N N N N N N N
Soil	Source 🖓	Jexture (ÛSDA)∥	γ pH ¹ ↔	⁷ OC [%]
Hoefchen am Hohenseh	Burscheid, Germany	🖉 siltAøam 🖉	61	2.0
Dollendorf II	Blankenheim, Germany	þóam 📎	60	4.6

¹ pH in 0.01 M CaCl₂

The study application rate (SAR) was $1502 \mu g/100 \text{ g soil}$ (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, 29, 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 maerobic conditions. Parts concerning evaluation of rate of degradation are reported in section CA 7 Ω .2.1.3 (Study KCA 7.1.2.1.3 /02) of this document.

Overall mean material balance was 96.2 and 965 of applied radioactivity (% AR) for soil Hoefchen am Hohensen 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 Höefchen am Hohenseh and 1.9% AR in soil Dollendorf II. Formation of volatile organic compounds was not significant, values being $\leq 0.1\%$ 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 Hoefen 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 Hoefen 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. actobic: 5.9% AR at DAT-15; anaerobic: 13.6% AR at DAT-77), FOE 5043-triduoroethanesulfonic acid/max. aerobic: 6.0% AR at DAT-15; anaerobic 5.1% AR at DAT-15) and trifluoroacetic actid (max, aerobic: 37.5% AR at DAT-15; anaerobic: 53.2% AR at DAT-105

MATERIALS AND I.

MATERIALS A.

1. **Test Item**

ctor and TLC, scan with radioactivity-det

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	Soi	1	Soil				
r ar ameter	Hoefchen am	Hohenseh	🖉 Dollendorf II				
Geographic location		9/	Å √°	al a			
- city	Bursch	& 1	Blanke				
- state	North-Rhine	Westphalia 🔗	North-Rhine	e Westphalia			
- country	Germa		🔊 🖉 Gen	pany 🔊			
GPS Coordinates	N 51° (No 00	22.9			
	E 007	06.3' 🖓 🧳	∳″ € ∕006	° 43>0'			
Soil taxonomic classification (USDA)	loamy, mixed,	mesiOf ypic 🕅		s .			
	Ørgud	Brgudalts 7 A C 2					
Soil series		by information	avanable 0				
Texture class (USDA)	silt lo	am 🔬 🖉		am			
Sand [%] $[50 \ \mu m - 2 \ mm]$	$Q' \sim 2^2$	N C	1 (b) 4	80			
Silt [%] $[2 \mu m - 50 \mu m]$	<u>ک</u> کړ کړ که ک			&			
Clay [%] $[< 2 \ \mu m]$	2 N 16		<u> </u>	4			
pH			jo o				
- in CaCl ₂ (soil/CaCl ₂ 1/2)	9 .1		<i>Q</i> , 7	.0			
- in water (soil/water 1/1)	6.3	Û X	0 V	.1			
- in KCl	5.8	<u>v , 9 </u>	/// 6	.7			
Organic matter ¹ [%]	$\sqrt{0}$ $\sqrt{2}$ $3/2$		C 7	.9			
Organic carbon [%]		<u> </u>	/	y 4.6			
Cation Exchange Capacity [meq400 g]			19	0.5			
Water Holding Capacity		<u>× 6</u>					
maximum [g H2O ad 100 g sốt/DW]	<u>\$4</u>	v v, v	79.1				
at 0.33 bar (pF 2.5) [%]	20.2		35.1				
Bulk density (disturbed) [Scm ³]	0.10 V	00	1.03				
Microbial biomass ²	[mg	microbial carbo					
	BIG- 2	BIO +	BIO -	BIO +			
DAT-0 Or or A	Q ^v , 4989 , S ^v	1075	3789	3788			
DAT-15	<u>چ م</u> 972 م	998	3612	3519			
Anaerobic Plate Count Assay ²	[C	FU / g soil in 10					
	Brog	BIO +	BIO -	BIO +			
DAT-135 2 40° 0° 0°	<u>7.33</u> x 10 ⁴	$1.30 \ge 10^5$	$3.30 \ge 10^3$	$1.33 \ge 10^4$			
	, <u> </u>						
¹ calculated as M [%] C [%] C 724	\bigcirc						

² BIO- samples were left untreated, BIO+ samples were applied with solvent of application solution DAT: day after treatment GPS: global positioning system

DW: drw weight

USDA: United States Department of Agriculture

B.

Experimental Conditions 1.

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 $55 \pm 5\%$ 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 flass 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 flutenacet 0000 g ka, 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 flutenacet/kg soil (dry weight).

The application solution was prepared in methanol/water (1, v/v) 369 μ t 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 ρ samples).

The test systems were incubated in the dark for the total study period of 135 days at 19.7 °Cor a walkin 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 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, 16, 20, 35, 62, 99 and 120 days after soil flooding (DASF).

Determinations of microbial biomass were performed at DAG-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 of 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 decontation.

At each sampling interval of the anacrobic phase, the test systems were connected to a combustion oven unit to determine the voratiles 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 RADIOACTIVITS IN SOUL SANDELES

Table 7.1.1.2- 4 and Table 7.1.1.2- 5 summarizes the degradation of [thudiazol@5-14C] flufenacet and the formation and degradation of its degradation products as a marction of time.

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

	duplicat	es)		、 1		K N	No.	<i></i>	, ,	, Ĉ)	Ş
	DAT	0	15 ¹	15 ²	17	21 %	ر 29 ا	3 35	48	77	105 Ø0	135
Compound	DASF	N	/A	0	2	Ś	14	20 🔍	, 33 ,	62	Ø0	120
flufenacet		96.4	30.8	42.8	\$38.8 <i>"</i>	3 3.3	25 .5	12.A	18.2	13.00	9.7	6.4
FOE-thiadone		n.d.	5.9	4.8	8.5	10.5	11.6	¢12.7 ٍ	¥3.1	d 3.6	12.2	10.6
FOE 5043-triflu ethanesulfonic a		n.d.	2.5		\$5.0	4.0		2:8 2:8	4.2	2.1	2.2	2.3
trifluoroacetic a	cid	n.d.	37.5	31.4	32,8	36.5	P43.5	42.3	A.1	47.3	46.0	47.9
Unid./Diff. Radio	activity	n.d.°	1.3	3 2.5	<u></u> 1.2	ntigd.	n	n.d.	n.d.	n.d.	n.d.	0.8
Total Extractabl	e Residues	96.4	780	86.6	- 86.4 [°] ∕	≫ ¥84.4 _∿ ≽	8 2.3	80.3	77.6	76.0	70.1	68.3
Carbon dioxide		n.a.	€¶.6	S.	ίζο D	16	1.6	1.6	1.6	1.6	1.7	1.6
Volatile Organio Compounds	~0~	n.a.	< 0.4	< 0.1%	× 0.1	Q 0.1	0 .1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1
Non-extractable	Residues	\$0.8	J.0.9	102	9.5	10.9	12.5	13.9	16.0	19.1	21.4	24.5
Material Balan		97.2	96.5	98.3 _~	97.5	96.9	96.4	95.9	95.2	96.6	93.3	94.4
	~0	0	- N	. 0	, K	Ĵ	•	-	-	•	•	

DAT: days after treatment

ASF: days after soil flooding

n.d.: not detected

Bayer CropScience

Document MCA: Section 7 Fate and behaviour in the environment Flufenacet

FOE 5043-trifluoro- ethanesulfonic acid n.d. 6.0 3.2 1.7 1.1 0.7 6.0 trifluoroacetic acid n.d. 28.0 40.4 46.5 48.7 5332 51. Unid./Diff. Radioactivity n.d. 2.4 2.4 1.1 1.0 n.d. 40.4) •,33	77 ³ 62 ³	105	135
flufenacet 93.1 44.2 35.4 27.0 23.3 18.2 15. FOE-thiadone n.d. 4.3 7.1 11.3 12.4 14.5 114 FOE 5043-trifluoro- ethanesulfonic acid n.d. 6.0 3.2 1.7 1.1 0.7 10.7 trifluoroacetic acid n.d. 28.0 40.4 46.5 48.7 53.3 51. Unid./Diff. Radioactivity n.d. 2.4 2.4 1.1 1.0 n.d. 4.0		62 ³	00	
FOE-thiadone n.d. 4.3 7.1 11.3 12.4 FOE 5043-trifluoro- ethanesulfonic acid n.d. 6.0 3.2 1.7 1.1 0.7 FOE trifluoroacetic acid n.d. 28.0 40.4 46.5 48.7 53 ³ / ₂ 51. Unid./Diff. Radioactivity n.d. 2.4 2.4 1.1 1.0 n.d. 40.4	0 006		90	120
FOE 5043-trifluoro- ethanesulfonic acid n.d. 6.0 3.2 1.7 1.1 0.7 EC trifluoroacetic acid n.d. 28.0 40.4 46.5 48.7 53.32 51. Unid./Diff. Radioactivity n.d. 2.4 2.4 1.1 1.0 n.d. 40.4	.9 Q 10.0 %	(J12.1	4.5	ØĨ
trifluoroacetic acidn.d. 28.0 40.4 46.5 48.7 53.2 $51.$ Unid./Diff. Radioactivityn.d. 2.4 2.4 1.1 1.0 $n.d.$ 40.4	\$ \$	75	5.3	2.7
Unid./Diff. Radioactivity n.d. 2.4 2.4 1.1 1.0 n.d. 1.0	DD 0.8	0 0.7	≪L∕OD	1.2 °
	.30° 52.5°	47.2	53.2	\$1.5
	1. <, OD	< LOD	RGT.	0.7
Total Extractable Residues 93.1 85.0 88.5 87.7° 860° 83.6° $79.^{\circ}$.8 73.8	68.9	Ø63.7	59.4
Carbon dioxide n.a. 1.9 1.8 1.9 9.9 1.9	y 19	h	1.9	1.9
Volatile Organic Compoundsn.a. $< 0.1 < 0.1 < 0.1 < 0.1 < 0.1 < 0.1 < 0.1 < 0.1 < 0.1 < 0.1 < 0.1 < 0.1 < 0.1 < 0.1 < 0.1 < 0.1 < 0.1 < 0.1 < 0.1 < 0.1 < 0.1 < 0.1 < 0.1 < 0.1 < 0.1 < 0.1 < 0.1 < 0.1 < 0.1 < 0.1 < 0.1 < 0.1 < 0.1 < 0.1 < 0.1 < 0.1 < 0.1 < 0.1 < 0.1 < 0.1 < 0.1 < 0.1 < 0.1 < 0.1 < 0.1 < 0.1 < 0.1 < 0.1 < 0.1 < 0.1 < 0.1 < 0.1 < 0.1 < 0.1 < 0.1 < 0.1 < 0.1 < 0.1 < 0.1 < 0.1 < 0.1 < 0.1 < 0.1 < 0.1 < 0.1 < 0.1 < 0.1 < 0.1 < 0.1 < 0.1 < 0.1 < 0.1 < 0.1 < 0.1 < 0.1 < 0.1 < 0.1 < 0.1 < 0.1 < 0.1 < 0.1 < 0.1 < 0.1 < 0.1 < 0.1 < 0.1 < 0.1 < 0.1 < 0.1 < 0.1 < 0.1 < 0.1 < 0.1 < 0.1 < 0.1 < 0.1 < 0.1 < 0.1 < 0.1 < 0.1 < 0.1 < 0.1 < 0.1 < 0.1 < 0.1 < 0.1 < 0.1 < 0.1 < 0.1 < 0.1 < 0.1 < 0.1 < 0.1 < 0.1 < 0.1 < 0.1 < 0.1 < 0.1 < 0.1 < 0.1 < 0.1 < 0.1 < 0.1 < 0.1 < 0.1 < 0.1 < 0.1 < 0.1 < 0.1 < 0.1 < 0.1 < 0.1 < 0.1 < 0.1 < 0.1 < 0.1 < 0.1 < 0.1 < 0.1 < 0.1 < 0.1 < 0.1 < 0.1 < 0.1 < 0.1 < 0.1 < 0.1 < 0.1 < 0.1 < 0.1 < 0.1 < 0.1 < 0.1 < 0.1 < 0.1 < 0.1 < 0.1 < 0.1 < 0.1 < 0.1 < 0.1 < 0.1 < 0.1 < 0.1 < 0.1 < 0.1 < 0.1 < 0.1 < 0.1 < 0.1 < 0.1 < 0.1 < 0.1 < 0.1 < 0.1 < 0.1 < 0.1 < 0.1 < 0.1 < 0.1 < 0.1 < 0.1 < 0.1 < 0.1 < 0.1 < 0.1 < 0.1 < 0.1 < 0.1 < 0.1 < 0.1 < 0.1 < 0.1 < 0.1 < 0.1 < 0.1 < 0.1 < 0.1 < 0.1 < 0.1 < 0.1 < 0.1 < 0.1 < 0.1 < 0.1 < 0.1 < 0.1 < 0.1 < 0.1 < 0.1 < 0.1 < 0.1 < 0.1 < 0.1 < 0.1 < 0.1 < 0.1 < 0.1 < 0.1 < 0.1 < 0.1 < 0.1 < 0.1 < 0.1 < 0.1 < 0.1 < 0.1 < 0.1 < 0.1 < 0.1 < 0.1 < 0.1 < 0.1 < 0.1 < 0.1 < 0.1 < 0.1 < 0.1 < 0.1 < 0.1 < 0.1 < 0.1 < 0.1 < 0.1 < 0.1 < 0.1 < 0.1 < 0.1 < 0.1 < 0.1 < 0.1 < 0.1 < 0.1 < 0.1 < 0.1 < 0.1 < 0.1 < 0.1 < 0.1 < 0.1 < 0.1 < 0.1 < 0.1 < 0.1 < 0.1 < 0.1 < 0.1 < 0.1 < 0.1 < 0.1 < 0.1 < 0.1 < 0.1 < 0.1 < 0.1 < 0.1 < 0.1 < 0.1 < 0.1 < 0.1 < 0.1 < 0.1 < 0.1 < 0.1 < 0.1 < 0.1 < 0.1 < 0.1 < 0.1 < 0.1 < 0.1 < 0.1 < 0.1 < 0.1 < 0.1 < 0.1 < 0.1 < 0.1 < 0.1 < 0.1 < 0.1 < 0.1 < 0.1 < 0.1 < 0.1 < 0.1 < 0.1 < 0.1 < 0.1 < 0.1 < 0.1 < 0.1 < 0.1 < 0.1 < 0.1 < 0.1 < 0.1 < 0.1 < 0.1 < 0.1 < 0.1 < 0.1 < 0.1 < 0.1 < 0.1 < 0.1 < 0.1 < 0.1 < 0.1 < $.1, 4 0.1	Ø 0.1	< 0.1	< 0.1
Non-extractable Residues $3.7 10.1 8.6 8.8 0.1 12.6 15.6 $	5 ⁹ 190 ⁹	24.5	27.9	31.6
Material Balance 96.9 97.0 98.4 98.4 98.8 98.0 97.	.2 \$95.1	95.4	93.6	92.9

Degradation of flufenacet in Soil Dollendorf II (Entire System) under Anaerobic

DAT: days after treatment

n.a.: not analyzed

Table 7.1.1.2- 5:

ASF: days after n.d.: not detected

¹ before soil flooding (aerobic picubation 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.

MATERIAL BALANCE B.

The amount of dosed test item was determined a 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 (4%) and from 2.9 to 8.9% 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 a all sampling intervals demonstrated that no significant portion of radioactive dissipated from the xessels or was lost during processing of theses samples. A

♥ĨABL AND NON-EXTRACTABLE RESIDUES C. EXTRA

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 ap DAT 45 (end of aerobic incubation phase): 1.6% AR in soil Hoefchen am Hohensch and 1.9% AR in soil Dollendorf II. Formation of volatile organic compounds was not significant values being $\leq 0.1\%$ AR at all sampling intervals in both soils. See also Table 7.1.1.2-4 and Table 2.1.2-5

E. DEGRADATION OF TEST ITEM

The amount of flufenacet in the entire test system decreased from DAT to DAT-15 ming the aerobic incubation phase from 96.4 to 30.8% AR a DAT 13 in soil Hoefchen am Orohenser 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 and of the study (DAT 55) 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-totadone, FOE 5043trifluoroethanesulfonic 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 IK 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 5 (aerobic) and 5.1% AR at DAT-15 (anaerobic) as well as in soft 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 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 amaximum of 2.5% AR at DAT-15 (aerobic) in both soils.

CONCLUSIONS

[thiadiazole 52¹⁴C] Notenace Ovas degraded in soil under aerobic and anaerobic conditions in the dark in the laboratory.

Formation of carbon croxide was observed up to 1.6% AR in soil Hoefchen am Hohenseh and 1.9% AR in soil Dollendorf II during the aeropic 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-16) anaerobic 5.1% AR at DAT-) and trifluoroacetic acid (max. aerobic: 37.5% AR at DAT-15; anaerobic: 5.2% AR at DAT-105). Formation of non-extractable residues was observed in paratter 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-5-¹⁴C]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/WI/98-Final – 3rd July 2003). The following studies are included in the Baseline Dossier:

Annex Point / Reference No	Auth	or(s)	Ű		Document No
KCA 7.1.1.3/01	, A. M.;	β. A.	**	1995	Ø -00214\$401-1
		. V	¥ .	N '	\otimes \checkmark

An additional study has been performed for FOE-thandone on request of the US Snivironmental Protection Agency (EPA) and is submitted within this Supplemental Possier for the flutenace denewal of approval. A summary of the route of degradation of flutenacet in soil is given in section CA 7.1.1 and Figure 7.1.1-1.

Report:	KCA 7.1.1.3 /02; , R.; , A. M.; 2001
Title:	Soil photolysis of thiadone on loamy sand (a metabolite of FOE 5043)
Report No:	108721 \checkmark \bigcirc \bigcirc \bigcirc \bigcirc \checkmark \bigcirc
Document No:	M-106297-01-1
Guidelines:	• EPA Ref: Subdiversion no 161-30 Soil Photolysis Study
GLP:	Yes in the second secon

Executive Summary

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

 C	· Y S S			
Soil	Source S	Texture (USDA)	pН	OC [%]
Janes Will	Howa, USA	🔊 loamy sand	7.2	1.11
		Q Q		

A study approximately 3.2 mg perky 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 freatment (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 patteral 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 97.2% AR for irradiated and dark control samples, respectively.

The maximum mount 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-16 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 22.0% AR dark control). However, this degradation product would occur only in minor amounts 1% and in agradation studies of the parent flufenacet, as FOE-thiadone itself was detected with max. appounts of 5.9% AR in aerobic soil degradation studies.

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

It is concluded that the route and rate of degradation of FOE hiadone, 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.

A.

1.

see Table 7.128-1) which was sampled freshly from the field and sieved to a the second secon [thiadiazole-2-14C]FOE-thiadon@ **Registry No:** Specific Activity: Radiochemical Purity: Chemical Purity:

I.

2.

One soil was used (see particle size of



Table 7.1.1.3- 1:	Physico-chemical	properties of test soil
1 abic / 11 11 0 11	i nysico chemicai	properties of test son

Parameter	Results / Units
Soil Designation	Iowa loamy sand (EFS11@)
Geographic Location	
City	Janesville
State	Janesville Iowa
Country	USA O V V OV
Soil Taxonomic Classification (USDA)	Two soils in close proximity:
	Lesparta Leamy fine Sand
Soil Series	2. Dickinson fine Sandy Loam
	no information available C Q
Textural Class (USDA)	loamy sand
Sand $[50 \ \mu\text{m} - 2 \ \text{mm}]$	
Silt $[2 \mu m - 50 \mu m]$	
Clay [< 2 μm]	
pH OY	
Organic Carbon ¹	1/11% ~ ~ ~ ~ ~ ~ ~ ~ ~ ~ ~ ~ ~ ~ ~ ~ ~ ~
Organic Matter	
Cation Exchange Capacity [meq/100/g]	5.6
Water Holding Capacity at 1/3 bar (pF 2,5)	9.9%
Bulk Density (disturbed) [g/ ()	ÚI.34 D
Microbial Viability [CFU 2106/g soft DW]	
DAT-0 Q ^V Q ^V C A	9.7 (bacteria) 0.12 (fungi)
DAT-14	35 (bacteria) / 0.13 (fungi)
CFU: coloury forming units DAT: days after treatment SDA: United	At 1 States Department of Agriculture
$1 \text{ Caladenta I as } OO(1) \rightarrow OO(1)/1000 \text{ (I)}$	
² Test systems for determination of the microbial via	b \mathcal{B} ty were applied with 250 µL application
Solution S & S &	

B. STUDY PESIGN

1. Experimental Conditions

Static test systems were used, consisting of flint glass sample jars filled with soil and equipped with opaque sorew caps fitted with Tetlon 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 Q-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 owo 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 μ g [thiadiazole-2-¹⁴C]FOE-thiadone per test system.

The application solution was prepared in acetonitrile/water (1:10, v/v). 260 μ L of the application solution were applied drop wise onto the soil surface of the respective test systems using a gas light 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 $3 \times 250 \mu$ application solution and connected to the flow-through system.

The irradiated test systems were incubated using a 12-hour light (32-hour dark cycle for 4 days at $20 \pm 1^{\circ}$ 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 wavelogths (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 incobated in the dark for 14 days at 20 ± 1 % 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 (70.5, 1, 2, 3, 5, 7, 10 and 14 days after treatment (DAT) for both irradiated and dark samples.

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

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

3. Analytical Procedures

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

The entire soil of each jar was extracted once with acetonitrile followed by an acidic extraction with acetonitrile/water (1:1v/v) containing 0.1 N HCl. After each extraction step, extracts were separate from soil by illtration. The widic 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 acotonitrile 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 RADIOACTIVE 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)
	(expressed as percent of applied radioactivity; mean value of duplicates)

	-			$ \bigcirc $		an		C C	Ŵ	1
C	Maaa	0		Â D ' 1 A	ĭ∼y ,	DAT	- S		H	14
Compound	Mean	0	0.5	≶ I	y 2 🦼	∕≫ 3	5 ر			14
FOE-thiadone	irradiated	96.7	79£2)	77.3	52. 3	48,2 ₀	[≫] 35.2 @	21.6	€ 12.5	7.2
	dark	96.7	\$3.6	78)Ĭ	650	59:8/	41,1	28.9 ^O	18.3	13.3
FOE-thiadone propionic	irradiated	n.d. 🤉	0.6	0.9	23	¥ ⁷	<i>3</i> .8	5.4	6.1	2.9
acid conjugate	dark	n.d	0.2 🔘	° [≫] 0.4 ຼ(ي 1.3 گ	\$3.6 📡	≪ 1 .7	2 .0	8.6	1.2
Reg #1	irradiated	<u>60</u>	0,2	n.d. 🗸	0.5	n.d.	[♥] n.d. (0.9	n.d.	n.d.
(fortification impurity)	dark	Ø.5	0.0	(()	007	0.7%	1.00	0.5	0.4	n.d.
Reg #2	irradiated	^{1.2}	∕≫0.9 ∾	¥.1	₽.1	Ĩ	°Q,9	0.8	0.8	1.1
(fortification impurity)	dark 🖏	1.2	1.3	⁷ 0.9	1.2	€ <u>1.0</u> '	∕∕0.9	0.9	0.7	0.8
Unidentified	irradiated	33	0.4	n.d.Q	n.d.🖓	1.2	1.6	2.3	3.5	3.3
Radioactivity ¹	dark	9 .2	<u>0.2</u>	°p.d.	0 <i>3</i> 4	0,4	1.0	1.2	1.5	1.1
Total Extractable	irradiated		81.0	, 79.3	°56.2	\$\$%.2	41.5	31.0	22.9	14.5
Residues	dark Q	101.6	86.3	¥ 80.3 _@	, 69.2 _≫	6 5.5	51.7	43.5	29.5	17.3
Carbon dioxide	Firradiated	n.a.	6.0	11.2	23.4	² 27.9	38.8	43.8	53.5	57.8
Q	dark	sha.	S.I	102	18.90	25.0	34.7	43.0	53.2	60.1
Volatile Organic	irradiated 4	©n.a.	n.a.	nsa.	nça.	1.0	1.0	2.8	3.9	4.7
Compounds	ark 🖉		, n.a. 🗳	n.a. 🛛	Ĵn.a.	0.8	0.8	1.7	2.0	2.5
	rradiated	0,5	6.8Q	6.3	14.4	16.4	14.5	20.9	21.2	19.4
Residues	dark	0.5	~2.9	A.6	6.8	8.9	13.9	14.4	17.1	15.7
Material Balances	irradiated	0402.1	B 3.8	\$96.8	94.0	100.5	95.8	98.5	101.5	96.4
Material Balances	dark 🦪	102.]	[⊮] 95.1≬	96.1	94.2	99.4	100.3	100.9	99.8	93.1
		~ U	<u> </u>	/						

DAT: days after reatment of n.d.: Of detected n.a.: not analyzed

¹ All individual areas of regioactivity 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 behance 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. EXTRACT BLE 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% AP at Date 14 in tradiated and dark control samples, respectively.

E. DEGRADATION OF TEST ITEM

The amount of FOE-thiadone in the soil extracts decreased from DAT to to DAT-14 from 96.7 to 7.2% AR in irradiated samples and from 96.7 to 13 % 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, invadiated and dark control, samples: FOE-thiadone propionic acid conjugate (max. 64% AR irradiated; 12.0% AR dark control).

The experimental half-lives of FOE-thiadone in irradiated and dark samples were ediculated using single first order (SFO) kinetics (see Table 201.3-2).

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

æ.	\sim	. %/	
Test System	Kinetic Model	DT3 [days]	Ry Ry
Irradiated	SFQ	3.7	0.9904
Dark 🔊	`Z⊕Q```	≪ٽ 4 <i>.</i> 7 [®]	D .9858
	CONC	LESIONS	

FOE-thiadone was rapidly degraded in soil both under exposure to simulated sunlight as well as under dark conditions in the laboratory. The exposimental 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 propublic and 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 patent fluxenacet, as FOE thiadone itself was detected with max. amounts of 5.9% AR in aerobic soil degradation studies.

It is concluded that the oute 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 verall fate of FOE-thiadone.



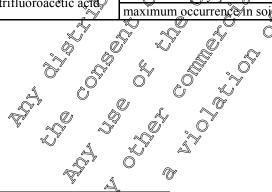
CA 7.1.2 Rate of degradation in soil

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-fi) 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_{sil}), groundwater (PEC_s) and surface water (PEC_{sw}) were derived from studies and kinetic evaluations according to POCUS kinetics (2005, 2006, 2011)^{2, 3, 4} summarized in sections CA 7.1.1, CA 70.2 and CA 72, and are submitted within this Supplemental Dossier for the flufenacet renewal of approval. The DT_{s0} 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:	DT50 values and maximum occurrences in soil of furenacet and its major degradation products used as modeling input values for calculation of PECsoil
	products used as modeling input values for calculation of PECsoil

Compound	Modeling Input Pa@meter 🖉	Encopint	Comment
flufenacet	DT ₅₀ in soil [days] 🔬 🔪	¢\$2.2 0	worst esse, lab., non-normalized
FOE oxalate	DT50 in sol [days]	20.7	worst case, lab., non-normalized
TOE Oxalate	maximum occurrence in soil [%]	≩ 26.5 ≶	lata aerobic soil
FOE sulfonic acid	DT 50 m soil [@ys] 🕓 📎		worst case, lab., non-normalized
FOE sufforme actu	maximum cocurrence in soil [%]	26.3	lab. aerobic soil
FOE methylsulfone	$\mathfrak{G}^{\mathfrak{s}_{50}}$ in $\mathfrak{G}^{\mathfrak{s}}$ days $\mathfrak{G}^{\mathfrak{s}}$	@ 163.0♥	worst case, lab., non-normalized
	maximum occurrence in soil [%]	Q 6.67	lab. aerobic soil
EOE_thiadone	DT_{50} in soil [ϕ_{3} ys] \mathcal{A}	0	worst case, lab., non-normalized
FOE-thiadone 🏷	maximum eccurrence in soil [%]	5.9	lab. aerobic soil
FOE 5043-trifl@ro-	DT 50 in son [days] Q	22.5	worst case, lab., non-normalized
ethanesulfonic/acid ⊀	maximum occurence in soil [%]	6.0	lab. aerobic soil
trifluoroacetic acto	DT ₅₆ m 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:DT50 values and formation fraction / maximum occurrences in soil of flufenacet and its
major degradation products used as modeling input values for calculation of PECgw

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	geoman, lab nomalized
FOE Oxalate	FF flufenacet \rightarrow FOE oxalate	0.41409	mean lab.
FOE sulfonic acid	DT ₅₀ in soil [days]	20.5	mechan, field, normalized
FOE suitoille actu	FF flufenacet \rightarrow FOE sulfonic acid	0.192	nyean, lalO 🔍 💭
FOE methylsulfone	DT ₅₀ in soil [days]		geomean, lab. normalized
POE methylsunone	FF flufenacet \rightarrow FOE methylsulfon	0.066	meanylab. 🖉 🛒 °
FOE-thiadone	DT ₅₀ in soil [days]	1.6	geomean, ab., normalized
FOE-tilladolle	FF flufenacet \rightarrow FOE-thiadone \bigcirc	@ 570	Brean, lab
FOE 5043-trifluoro-	DT_{50} in soil [days]	9.1	geomean, lab., armalized
ethanesulfonic acid	FF FOE-thiadone \rightarrow FOE 5043-triffeoro-	0.469	mean, lab.
	ethanesulforit acid O	60	
	DT ₅₀ in soil [days]	1000	default, morst case
trifluoroacetic acid	FF flufenacettrifluor cacetic acad	∞0.430 🖉	mean_lab.
	FF FOE-thiadone 🖓 trifluoroacetic acid	\$ 0.531 [°]	mean lab.

FF: formation fraction

Table 7.1.2- 3:DT50 values and maximum occurrences in soil and aquatic systems of flufenacet and its
major degradation products used as modeling input values for calculation of PECsw

Compound	Mødeling input Parameter	Endpoint	Comment
	DTe in soil@ays]	18.3	geomean, lab., normalized
	Dr ₅₀ in water [days]	49:6	degradation total system
flufenacet	DT ₅₀ in sediment [days]	2000	worst case default
ð	max occurrence in secondent [%]	32.4	lab., water/sediment study
Ĉ	DIQ 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
** ~0	DT ₅₀ in sediment [days]	1000	worst case
FOE oxalate	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
A O	max. occurrence in water [%]	0	no major degradation product in water
	DT ₅₀ in soil [days]	20.5	median, field, normalized
	max occurrence in soil [%]	26.3	lab. aerobic soil
A	DT in water [days]	1000	worst case
	DT ₅₀ in seriment [days]	1000	worst case
FOE sulfonic acid	max. occurrence in total system [%]	0	no major degradation product in water/sediment studies
-0	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
	DT ₅₀ in soil [days]	1000	worst case de fault
	max. occurrence in soil [%]	0	no major soil degradation product
	DT ₅₀ in water [days]	1000	worst case 🖉 🔿
FOE methylsulfide	DT ₅₀ in sediment [days]	1000	worst wase
-	max. occurrence in total system [%]	11.4	total system,
	max. occurrence in sediment [%]	9 .5	water/sediment study
	max. occurrence in water [%]	\$ 8.0	water/sedimentotudy &
	DT ₅₀ in soil [days]	0 67.7	geomean, lab. normalized 1, °
	max. occurrence in soil [%]	66	lab. aerobio soil
	DT ₅₀ in water [days]		Georst case O
	DT ₅₀ in sediment [days]	××1000~~~	worst case 🐎 🖉
FOE methylsulfone	max. occurrence in total system [%]		no major degradation product in grater/sediment studies
	max. occurrence in sediment [%]		no majo degradation product in
	max. occurrence in water [%]		no major degradation product in water
	DT ₅₀ in soil [days]	<u></u> *.6	geomean, lab., normalized
	max. occurrence in soil [%]	ن 5.9	lab. aensbic soil
	DT ₅₀ in water [days]	1000	worst case
FOE-thiadone	DT ₅₀ in sediment days]	1000	worst case
	max. occurrence in total system [%]	<u>∘ 8</u> 4.3 ∘,	total system
	max doccurrence in sectiment [26]	3.8	water/sediment study
	max. occultence in Water [%	81.8	water/sediment study
	D^{T}_{50} in soll [days] \swarrow O^{\checkmark}	_@v	geomean, lab., normalized
<u> </u>	max. occurrence in soil [%]	. 0	lab. aerobic soil
, ,	DT in water days]	ي%1000	worst case
FOE 5043-trifteoro-	DT Sin water days DT so in second to the second se	1000	worst case
ethanesulforty acid (TFESA)	max. occurrence in total system f	0	no major degradation product in water/sediment studies
	mater occurtence in sediment [%]	0	no major degradation product in sediment
	max. occurrence in water [%]	0	no major degradation product in water
	DT min soil @ays]	1000	default, worst case
A C	max. occurrence in soil [%]	81.5	lab. aerobic soil
	pT ₅₀ in water [days]	1000	worst case
	DT ₅₀ in sediment [days]	1000	worst case
trifluoroacetic acid (TFA)	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
Ŏ,	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-¹⁴C], [thiadiazole-2-¹⁴C] and [thiadiazole-2-¹⁴C] as wellas 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. 2.1- 1 to Table 7.1.2.1-14.

Furthermore, a supportive study concerning the evolution of the microbial biomass in cometer flask systems during degradation studies in soil under aerobic conditions in the date in the Paboratory 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(Year	Document No
KCA 7.1.2.1/01		0 995	M-002164-01-1

Table 7.1.2.1- 1:	Summary of DT50 and	T ₉₀ values	for de	gradation	of flafe	nacet 🕅	aerobic soils 20 °	С
	for trigger evaluation *	Ő.	Č)	- S	° N	, Oʻ		

Soil	Texture	🏹 Annex Doint / C	Kinetic	DT ₅₀	DT90
\$	(USDA)	Reference No	Model ¹	[days]	[days]
Howe Indiana	sandy loam	KC&J.1.2.1.1/01	OS FO	33.8 ²	n.d.
Howe Indiana	sandy loan	KCX 7.1.2. 1/02 >	SFO	63.6 ³	n.d.
BBA 2.2	hoamy sand	& A	1.5 st order	25.5	132
Laacherhof AIII	silt Noam	OKCA 7.4.2.1.1.03	1.5 st order	10.1	52.6
Hoefchen im 🏹 👋	silt loam 🔬	Ő Á	1.5 st order	27.1	90.0
Laacherhof AXa	sandy load	K 🔍 7.1.2 OI /04	SFO	7	34
Hoefchen am Hohensen	silt loan	KCA 7.1.2.1.1 /05	DFOP	14.7	44.7
Laacherkof AXXa	loam@sand &		SFO	18.5	61.6
Dellendorf 🦉 🕐	clayloam	KCA .1.2.1.1 /06	DFOP	15.4	46.4
Murmwiese O	Hoam 🔊	L.	SFO	13.5	44.8
~ ¥					

¹ SFO: single first order, DEOP: double first order in parallel

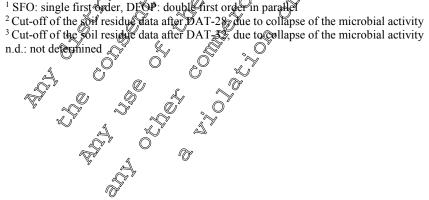




Table 7.1.2.1- 2: Summary of DT₅₀ values for degradation of flufenacet in aerobic soils 20 °C for modeling purpose (non-normalized)

			l?a	
Soil	Texture	Annex Point /	Kinetic	DT50
	(USDA)	Reference No	Model ¹	∘ [days]
Howe Indiana	sandy loam	KCA 7.1.2.1.1 /07	SFO (× 25.2 ¢
Howe Indiana	sandy loam	KCA 7.1.2.1.1 /09	SFO 🔊	55.0 ⁻² ∅
BBA 2.2	loamy sand	. 0	SFQ O	31.9
Laacherhof AIII	silt loam	KCA 7.1.20.1 /07	SFQ (J 15%2
Hoefchen im Tal	silt loam		ی ores	20.4
Laacherhof AXXa	sandy loam	KCA 7.1.2.1.1	ار SFO SFO (SFO)	۵٫۲.4 ،
Hoefchen am Hohenseh	silt loam	KCA9.1.2.140/08	° SFQ℃	\$15.8 ×
Laacherhof AXXa	loamy sand		, SEO	19
Dollendorf	clay loam	KCA 7.% 2.1.1 /08	∕\$FO ∧	103
Wurmwiese	loam	\mathbb{N}	SFO SFO	4.9
	۷.			

¹ SFO: single first order ² Outlier not considered for selection of DT₅₀ for PPO_{soil} calculation.

Table 7.1.2.1- 3:	Summary of DT50 and DA	'90 values for	r degradation	of FOE	oxalate in	aerobic soils 20 °C
	for trigger evaluation	S I	à dà		. Õ	

Soil	Texture (USBA)	Annex Point / C C Reference No	Binetic ~	DT ₅₀ [days]	DT90 [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 loan	KCA 7.1.2.1.2 /11	S∰Ø*-SFO	23.4	44.5
Hoefchen im Tal	silt bam	T O D	ĴŤØMC*-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 chalate degradation were derived based on the pathway fit using the best-fit kinetics selected from the parent only fits.

Sommary of DT50 Calues, for degradation of FOE oxalate in aerobic soils 20 °C for Table 7.1.2.1 modeling purpose (non-pormalized)

Soil J	Texture USDA0	Annex Point / Reference No	Kinetic Model ¹	DT50 [days]
Mowe Indiana 🖉 🖉 s	andy loam	KCA 7.1.2.1.2 /14	SFO - SFO	6.9
	oany sand		SFO - SFO	20.7
Laacherhof ADA	stat loam	KCA 7.1.2.1.2 /14	SFO - SFO	19.4
Hoefchen in Tal	silt loam		SFO - SFO	13.1

¹ SFO-SFO: single first order (degradation product)



Soil	Texture	Annex Point /	Kinetic	DT50	DT90
	(USDA)	Reference No	Model 🌿	[days]	[days]
BBA 2.1	sand		linear	266.9	n.d.
BBA 2.2	loamy sand	KCA 7.1.2.1.2 /01	lin ca r 🕺	1/89.2 🔥	n.d. C
Laacherhof AIII	silt loam	~ 0	linear 🗸	247.3	n d
Laacherhof AXXa	sandy loam	KCA 7.1.202 /08	SFO SFO	61.	≈ \$Ø5
Laacherhof AIII	silt loam	KCA 7.1.20.2 /08	SFQ S	60.2	200
Laacherhof AXXa	loamy sand		SEO ~	73.4	ه 243.8
Dollendorf II	loam	KCA 1.1.2.1 07	SFO 2	6.7 🔊	223
Hoefchen am Hohenseh	silt loam	KCAS .1.2.1/2/0/	,DFOP	24	105.8
Wurmwiese	sandy loam			49.8	65.3
Hanscheider Hof	loam		SFO	Ş7.3 g	90.7
Frankenforst	silt loam 🚿		, SFO 0	21.8	72.4
LUFA 2.3	sandy loap	KCA7.1.2.12/10	[™] ∕SFO _≫	63	212
LUFA 6S	clay	1. ⁶ 8 ×	SFQ	11.9	39.4

 Table 7.1.2.1- 5:
 Summary of DT₅₀ and DT₉₀ values for degradation of FOE sulfonic acid in aerobic soils 20 °C for trigger evaluation

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

 Table 7.1.2.1- 6:
 Summary of DT₂₀ values for degradation of FOE sulfonic acid in aerobic soils at 20 °C for modeling purpose (non-normalized)?

	<u> </u>		<u></u>	
Soil 🔊	OTexture	🔊 🕅 Annex Point / 🖉		DT ₅₀
	(USDA)	Reference No	Model ¹	[days]
Howe Indiana	🖗 samt loam 🔘	KCA@.1.2.1.274	SFO - SFO	> 1000 ³
BBA 2.2	loamy sand		SFO - SFO	> 1000 ³
LaacherhooAIII	silt loam	©CA 7.1.©r.2/14	SFO - SFO	> 1000 ³
Hoefcher m Tal	silt loam		SFO - SFO	> 1000 ³
BBA 2.1	sand Ó		SFO	258.4
BBA 2.3	loarny sand	KC 7.1.2.1.2 /16	SFO	180.8
kacherhot AIII	silt loam		SFO	234.9
Laacherhof AXXa	sandy hoam	" KCA 7.1.2.1.2 /16	SFO	62.3
Laacherhof AII	silt bam	KCA /.1.2.1.2/10	SFO	60.3
Laacherhof AXXa	logyny sand		SFO	73.4
[™] Dollendo∰II	S loam S	VCA 7 1 2 1 2 /07	SFO	6.7
Hoelchen an Mohenseh	silt toam	KCA 7.1.2.1.2 /07	SFO ²	28.6
A Wumwiese	sandyloam		SFO	49.8
Hanscheider Hof	- Joam		SFO	27.3
Frankenförst	∫ ©silt loam	KCA 7.1.2.1.2/10	SFO	21.8
🖉 LUFA 2.3	sandy loam		SFO	63.9
LUEA 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 DT₅₀ > 1000 not considered for further evaluation: non-reliable DT₅₀ estimation due to slow metabolite formation and limited decay observed until end of experimental study.



Table 7.1.2.1- 7:	Summary of DT50 and DT90 values for degradation of FOE methylsulfone in aerobic
	soils at 20 °C for trigger evaluation

Soil	Texture	Annex Point /	Kinetic DT50 DT90
	(USDA)	Reference No	Model 1 [days] [days]
Laacherhof AXXa	loamy sand		SFQ 43.1 0143.3 @
Dollendorf II	loam	KCA 7.1.2.1.2 /06	SO 23.3 77.4
Hoefchen am Hohenseh	silt loam	KCA /.1.2.1.2 /00	DFOP 40.9 149
Laacherhof Wurmwiese	sandy loam	Ď	[™] SFO → 96.0 [™] 549.4
Hanscheider Hof	loam		SFO 82.5 274
Frankenforst	silt loam		SEO 54.0 213 .
LUFA 2.3	sandy loam	KCA 7, .2.1.2, 09	®FO \$147.0 488
LUFA 6S	clay		, SFO 163:0 642

¹ SFO: single first order, DFOP: double first order in paraller

Summary of DT₅₀ values to degradation of COE methylsulfore in aerobic soils 20 °C for modeling purpose (non-normalized) Table 7.1.2.1- 8:

	- 47			
Soil	Texture	Annex Point /	Kinetite	DT 50
	QUSDA	Beference No	Model ¹	[days]
BBA 2.2	foamy sand		SFQ - SFO	> 1000 ²
Laacherhof AIII	silt sam	KCA 7.1.2.1.2 44	Ŝ₽∕Ŏ - SFO	82.7
Hoefchen im Tal 👋	sil 10am		SFO - SFO	> 1000 ²
Laacherhof AXXa 🔬	Joamy sand		SFO	43.1
Dollendorf II 炎	🔏 loam		SFO	23.3
Hoefchen am Hohersch	silt Gam	CA 7.1.2.1.2 /	SFO	43.8
Wurmwiese	sandy loam		SFO	96.1
Hanscheider Hof	//loam		SFO	82.5
Frankenforst		XCA 7 2.1.2 /09	SFO	64.0
LUEA 2.3) sand Soam	JACA 1.52.1.2/09	SFO	147.0
ĽAJFA 65 🏸 🔗	🏹 ay	, D	SFO	163.0
		~~~		

¹ SFO-SFO^{*} single (ist order (arent) - Gingle fir Gorder (arent) arent)

 SFO: single first order
 SFO: single first order
 ² DT₅₀ > 1000 not considered for further evaluation: normeliable DT₅₀ estimation due to slow metabolite formation and limited decay observed until and of experimental study. "nı

## Summary of DC and BT w values for degradation of FOE-thiadone in aerobic soils 20 ° Cor trigger evaluation Table 7.1,2.1-

	• Pexture (USDA)	Annex Point / Reference No	Kinetic Model ¹	DT50 [days]	DT90 [days]
Icova O	loamy sand		SFO	2.5	n.d.
Indiana 🖉	sandy loam	KCA 7.1.2.1.2 /03	SFO	2.0	n.d.
Nebrask	silt loam		SFO	2.8	n.d.

¹SFO: single first order

n.d.: not determined



#### Summary of DT50 values for degradation of FOE-thiadone in aerobic soils 20 °C for Table 7.1.2.1-10: modeling purpose (non-normalized)

Soil	Texture (USDA)	Annex Point / Reference No	Kinetic Model ¹	DT50 ∘ [days]
Iowa	loamy sand		SFO 🕡	Č Č
Indiana	sandy loam	KCA 7.1.2.1.2 /15	SFO 🛠	₹ 1.4 ©
Nebraska	silt loam	~ 0	SFQ 0	2.9
Hoefchen Am Hohenseh	silt loam	Ŏ.	SFO SFO	)″_1.∜√
Laacherhof AXXa	loamy sand	KCA 7 2.1.2 /0	SEO SFO	
Dollendorf II	clay loam	KCA (392.1.2/0	SFO - SFQ	چگوگری ک
Laacherhof Wurmwiese	loam		∕%\$FO - S€DÓ	2.0

¹ SFO: single first order SFO-SFO: single first order (parent) - single first order degradation products

#### Summary of DT50 and DT90 alues for degradation of FOE 5043-trifluor oethanesulfonic Table 7.1.2.1-11: acid in aerobic soils for trigger evaluation X

Soil	Texture (USDA)	Annex Point Reference No	Kinetic Model ¹	DT50 [days]	DT90 [days]
Hoefchen am Hohenseh	solt loam	KGA 7.1.2. 2 /12 ~	SFO*-SFO	9.1	30.2
Laacherhof AXXa	loamy sand	N Ó Á	SFQ*-SFO	4.5	14.9
Dollendorf II	clay loam	KCA 7, 1.2.1.2 /	SFO [⊮] SFO	22.5 ²	74.7 ²
Wurmwiese	hoạm (		Ô - ³	-	-
×.		°~` 0	LY.		

¹ SFO: single first order

² Worst case estimate based on decline first steady degradation product formation is not considered in the evaluation). ³ No valid trigger value could be estimated based on both pathway for and decline fit.

* Kinetic parameters of FQC 5043-trifleoroethinesulfonic acid de Cation Were derived based on the pathway fit using the best-fit kinetics selected from the parent or by fits.

### Table 7.1.2.1- 12: Summary of D2 50 values for degradation of FOE 5043-trifluoroethanesulfonic acid in aerobic soits at 20 °C for modeling purpose (non-normalized)

Soil	Textaye (USDA)	Annex Point / Ø Reference No	Kinetic Model ¹	DT ₅₀ [days]
Hoefchen am Hohenseh	silt loam		SFO - SFO	9.1
Laacherhof &XXa	toamy sand	KCA 7.1.2.1.2 /13	SFO - SFO	4.5
Dollenderf II	Sclay loam	KCA /.1.2.1.2/13	SFO - SFO	22.5 ²
A Wurmwiese	, lotam		SFO - SFO	7.6 ²

A

¹ SNO-SFO: sugle first order (paront) – 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 DT50 and DT90 values for degradation of trifluoroacetic acid in aerobic soils
	at 20 °C for trigger evaluation

Soil	Texture	Annex Point /	Kinetic 🖉 D	T50 DT90
	(USDA)	Reference No	Model 🌾 [d	ays] [days]
Laacherhof AXXa	sandy loam		SFQ >	1000 × 1000
Dollendorf II	clay loam	KCA 7.1.2.1.2 /04	Stop &	1000 ( > 100 C
Laacherhof Wurmwiese	sandy loam		SFO SFO	1000 > 1600
Hoefchen am Hohenseh	silt loam	Ĩ,	SFO > 1	1000 ×1000

¹ SFO: single first order

 Table 7.1.2.1- 14:
 Summary of DT50 values for degradation of trifluoreacetic acid in aerobic soils at 20 °C for modeling purpose (non-normalized)

Soil	Texture (USDA)	Amiex Point / Reference No	O Kinetto ✓ Model ¹	DT50 [days]
Hoefchen am Hohenseh	silt loan	L 64 W	SFØ-SFO	> 1000
Laacherhof AXXa	loamy sand	KCAG.1.2.1.2013	⇒SFO - SFO	> 1000
Dollendorf II	clay loam	KCAQ.1.2.1.2013	∾ <b>∭S</b> FO - <b>S</b> FO	> 1000
Wurmwiese	^O loam O ^V		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 the fenaces in soil under derobic 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	<u></u>	S.	Author(s)		Year	<b>Document</b> No
	Ý (		N. C.	, D. M.	1994	M-002166-01-1
KC \$1.2.1.292	, C	2	N.C.	, D. M.	1994	M-002165-01-1
KCA 7.1.2 1/03		, X.,	, S.;	, M.	1995	M-002146-01-1
	Ő,					

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 sontable 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 7.1.20.

Report:	KCA 7.1.2.1.1 /04; E.; 1999
Title:	Perobic Degradation of Flufenacet in Lysimeter Soil Laacherhof AXXa
<b>Report No:</b>	MR-388/99
<b>Document No:</b>	M-009592-01-1
<b>Guidelines:</b>	• 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-14C]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	Dexture (USDA) pHO OCCP/6]
Laacherhof AXXa	Monheim, Germany	sandy loam / 6,1 / 1.41

¹ in 0.01 M CaCl₂

equal to 0.63 mg flutenacet kg soil (dry The study application rate was 63  $\mu$ g/100 g soil (d weight). 1

Duplicate test systems were processed and analyzed 0.1, 1, 30 14, 28, 42 and 56 days after treatment.

Mean material balances ranged from 94.8 to 99.5 of applied rad activity (% AB).

The maximum amount of carbon diox Qe was 9.5% &R at DAT-56 (study en Q). Formation of volatile organic compounds was not significant, values being  $\leq 0.1$  AR for all sampling intervals.

Extractable residues decreased from 93.6% AR at DAT-001 to 200% AR at DAT-56.

Non-extractable residues increased from 5.9% AR at DAT-09 to 56,9% AR at DAT-42 and slightly decreased to 55.2% AR at @AT-56

The amount of flufenace decreased from 92.3% AR at PAT-0 \$ 4.9% AR at DAT-56.

Only carbon dioxide was identified & major degradation product.

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

, offer , neally evaluated , or shufenace. The salcu. , offer , offer



96% TLC/ractive detection

### Document MCA: Section 7 Fate and behaviour in the environment Flufenacet

#### I. **MATERIALS AND METHODS**

#### A. **MATERIALS**

1. **Test Item** 

> [phenyl-UL-¹⁴C]flufenacet CAS No Batch No Specific activity

142459-58-3 94-38 2.0 MBq/mg

>95% HPLC/radio detection, 96% ALC radio detection **5. Test Soils** The soils (Table 7.1.2.1.1-1) were sampled freshly from the field and sieved for a particle size of s 2 mm resonance of the guideline the soil broperties were taken from an agricultural real and its soil broperties met the guideline **1. Test Soils 1. Tes** 



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

Parameter	Results / Units
Soil Designation	Laacherhof AXXa
Geographic Location	× > 4
City	Monterin 🖉 🔘
State	North-Rhite Westpualia
Country	Germany O ^Y
GPS Coordinates	₩ 51°04.0'
Soil Taxonomic Classification (USDA)	sandy, mixed, mesic typic Cambueoils
Soil Series	O Ono information Brailable
Textural Class (USDA)	sandy loam or 🖉
Sand [%] $[50 \ \mu m - 2 \ mm]$	\$ \$ 7 <b>1</b> 77 \$
Silt [%] [2 μm – 50 μm]	Q 4 6.47 0
Clay [%] [< 2 μm]	
pH 5 0 ³	
- in CaCl ₂	~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~
- in water	
Organic Carbon [%]	
Cation Exchange Capacity [meq/200 g]	<u>کې کې 61</u>
Water Holding Capacity O maximum [g H ₂ O ad 100 g Soil DWD	2 5 34.4 2 5 34.4
Particle Density disturbed [g/m]	0 [°] 2.5
Microbial Biomass	
[mg microbial carbon kg soft DW] DAT-0@eplicate A/B)	م 667 / 702
DAT-56 (replicate A /B) 2	392 / 356
	Ký 5927550 Kj
DAT: days after treatment	DW: dry weight
USDA: United States Department of Agriculture	Drivery worght
¹ calculated as: $\mathcal{A}^{4}$ [%] = $\mathcal{O}C$ [%] $\mathcal{L}^{7}$ 24	
² The biomass samples of DAT-56 were applied with	the application solvent:
475 $\mu$ L AOV/water ():7, $\nu/\nu$ ) ()	
STUDY DESIGN A A	

## 1. Experimental Conditions

B.

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  $\mu$ g/100 g soil (dry weight), equal to 1.6 mg /kg soil



(dry weight). The actual SAR was 62.51  $\mu$ g/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  $\psi$ L 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 perobic 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 chamber.

## 2. Sampling

Eight sampling intervals were distributed over the entire incupation period of 56 days Duplicate test systems were processed and analyzed 0.1, 1, 97, 14, 28, 42, and 56 days after treatment (DAT).

Microbial soil biomass was determined a DAT-0 and DAY-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 opunting 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 HPL Gradiodetection 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 CAT-0. Evere net considered. DP50 and DT90 values were calculated from the resulting kinetic parameters.

## **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-¹⁴C]flufenacet as a function of time.



aftertreatment

### Document MCA: Section 7 Fate and behaviour in the environment Flufenacet

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

	11			5,		1	æ.		
				D	AT		Ŵ		
Compartment	0 1	0.1	3	7	14	28	<mark>∛</mark> 42 -	56	Ly a
flufenacet	92.3	88.0	58.1	46.7	25.6	1404	5,2°	4.9	
Unknown Z2 ²	2.9	1.0	0.7	0.4	0.7	Ø.3	. <b>603</b>	0.4	
Unknown Z3 ²	1.5	1.1	0.9	0,00	2.2	[♥] 2.6 Å	¥2.7	Q.5	
Origin ³	1.9	2.5	7.1	¥¥0.7	<u>10</u> .1	13%6	12.00		
Unid./Diff. Radioactivity	1.4	1.0	4.2	0.9 🔬	3.7	0.6	J.S	1.4	ے پ
Total Extractable Residues	n.d.	93.6	700	59.9	43.2	31.5	21.8	20.0	
Carbon dioxide	n.d.	n.a. 🦼	0 [°] 1.6	\$∕3∕.2	<a>6.0</a>	11.81	17.0	19.5	Ê.
Volatile Organic Compounds	n.d.	n:sa)	× 0.4	< 0.1		<b>6</b> 0.1	<b>A9</b> .1	< 0,1	
Non-extractable Residues	n.d.	<b>\$</b> .9	24:5	303	46.2	52.10	\$56.7	\$5.2	
Material Balance	n.el./	99.5°	^{97.1}	<b>98.1</b>	<b>Q5</b> .5	<b>95</b> A	95.5	94.8	
			~	1 .	Ø	N N			_

n.d.: not detected

notanalyzed ¹ Results of purity and homogeneity control of application

² Fortification impurities

³ Degradation pro in earlier studies. origní zone ed in the

#### B. MATERIAL

Mean material balances ranged from 4.8 to 99.5% oppplie adioactivity [% 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. EXTRACTOBLE AND NON-EXTRACTABLE RESIDUES

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

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

### **SYÖLATILIZA**@ION D.

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  $\leq 0.1\%$  AR for all sampling intervals.

### DEGRADATION OF TEST ITEM E.

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 aerolue conditions for trigger avaluation

evaluation			N.	. Á' b
Soil	DT ₅₀ ¹	DT90	Modeling	
	[d]	<b>∫</b> [d]₀	Likelihood 🦾	
Laacherhof AXXa	7	<u>3</u> 4	× _ 2.9908 √	
				ā.

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

#### III. CON

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

Only carbon dioxide was identified as major degradation produce fup to 19.5% AR at study end.

Report:	KCA 7.1.2.1.1 /05; , EAM.; 2013
Title:	Amendment No 1 [thiadiazole-5, C]flutenacet: A erobic Degradation /
	Metabolism in Que European Soil
<b>Report No:</b>	MEF M/937
<b>Document No:</b>	M-439105-92-1 9 4
<b>Guidelines:</b>	• OECD Test Guideline No. 307 OCSPP Test Guideline No. 835,4100/4200
	OOCSPP Test Quideling No. 835 4100/4200
GLP:	

## Executive Sammary

The degradation data as reported in study KCA7 1.1.1/04 were kinetically evaluated according to FOCUS (2005), 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 helf-life of flufenacet under aerobic conditions was 14.7 days.

C It is concluded that flufenacet has do potential for accumulation in the environment.

C

## 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 document² on degradation kinetics as ing the software KinGUI 2 to derive the DT₅₀ and DT₉₀ 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% HPL CLOD. 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. (GPO), 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] flufenacet as a function of time.

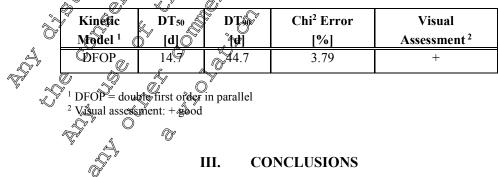
 Table 7.1.2.1.1- 4:
 Degradation of flufenacet in Soil Hoetchen and Hohenseh under Aerobic Conditions (expressed as percent of applied radioactivity; Sogle values)
 Output flufenacet in Soil Hoetchen and Hohenseh under Aerobic Conditions

Replicate	0 ¹	2		C A	) <b>P</b> 10	АТ 14	35_ 35_	) 2 60 (	87	120
А	99.1	93.3 [©]	87.4°	74.8	<b>%6</b> 1.8	Q.8	1394	4_1 ^O	1.7	0.9
В	100.4	<u>\$</u>	883	76.3	⁷ 66.3	56.8	<b>∮</b> ¥4.2	3%4	1.6	0.9

¹ Material balances at DXI-0 were 9.5% AR for replicate A and 100.9% AR for replicate B

The chi² error values of the fits of all investigated functic models were below 9 and the visual assessment of the regression curves give good results. The togradation of flufenacet followed DFOP kinetics in soil Hoefen and Hohensch (sill foam), 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 aeroble conditions in the dark in the laboratory.



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; , E. M.; 2013	
Title:	Amendment No 1 to: [thiadiazole-5-14C]flufe	nacet: Aerobic Degradation /
	Metabolism in Three European Soils	
<b>Report No:</b>	MEF-11/938	
<b>Document No:</b>	M-440348-02-1	
<b>Guidelines:</b>	<ul> <li>OECD Test Guideline No. 307</li> </ul>	
	• OCSPP Test Guideline No. 835.4100/4200	
GLP:	Yes	

### **Executive Summary**

The degradation data as reported in study KCA 7.1.4 /05 were kinefically valuated according to FOCUS (2005)² as part of the study to derive best fits for triggor endpoint determination. The experimental data could be well described by a single first order kinetic model for soils paacherhof AXXa (loamy sand) and Laacherhof Wurmwiese (loam) as welk as by a double first order in parallel kinetic model for soil Dollendorf II (clay loam). The eaculated half-lives of flutenace under aerobic conditions were between 18.5, 15.4 and 105 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. MATERIALSAND METHODS

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

The data for the test item were valuated according to the FQCUS 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 flux-nacet found in each replicate test system at each sampling interval (see Table 71.2.1.166 to Table 70.2.1.1-8). The initial total recovery (material balance) a 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.

ТЮ[®]

• 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  $\Delta_{2}$ , time diagrams of residuals vs. time).



## **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)

						DAT			, O	<del>)</del>	
Replicate	0 1	1	2	4	7	10	14	35	° 63	-91°	121
Α	98.9	97.9	92.3	89.7	80.6	70.7	60.2	29.0	⁰ 5.1 *	3.0	9.6
В	98.5	96.2	91.3	90.0	82.2	70.5	<u>59</u> .6	22.4	10.00	3.3	1.3

¹ Material balances at DAT-0 were 99.3% AR for replicate A and 8.9% 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 radio@ivity; single values)
 Image: Condition of the second sec

	<b>`</b> 1	1		11	L.			1°	d.		<u>s</u>
		_			, Q	DAT			¥	ð,	Ű
Replicate	0 ¹	1	2	4	&7	, JO	<u>t</u>	35	63		121
А	101.2	97.7	88.0	86.0	75.1 4	¢62.7	\$7.6	15.9	24	000	1.0
В	98.6	96.0	88.4	\$8.5	78.9	67	54.3	^J 14.8☆	2.6	@1.5	0.9
				2		A a	01	°~/	C	Ø	

¹ Material balances at DAT-0 were 102 BAR for veplicate A and 99 K AR for veplicate B

 Table 7.1.2.1.1- 8:
 Degradation of Bufenacet in Soil Laacherhof Wurthwiese under Aerobic Conditions (expressed as percent of applied tadioactivity; single values)

			_0°	C		Ø DAT	Q.	Ś			
Replicate	0.1	ີ ປ້ຳ	<b>2</b> 2	Č4	I,	10	14		63	91	121
А	97.3	96.8	<i>n°</i>	87.5	74.6	64.3	46,5	13.8	3.4	1.3	1.2
В	09.9	96.8	91	85,0	74.2 _C	02.0	48.3	12.8	3.8	1.4	0.8
(	Öř,	(N)	1	Qjî		, C	ý				

¹ Material balances at DAP-0 were 8.1% Ap for replicate A and 100.6% AR for replicate B

The chi² 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 (SFQ) kinetics in sets Laacherhof @XXa and Laacherhof Wurmwiese and double first order in parallel (DFQP) kinetics in set Dollendorf II, according to the lowest chi² error value.

The amount of flucture was declining rapidly during the test period of 121 days. The half-lives for flucture were 13.5 days in soil Laacherhof AXXa, 15.4 days in soil Dollendorf II and 13.5 days in soil Laacherhof Wurmprise 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

SoilKineticDT50DT90chi² errorVisual(Soil Type)Model 1[d][d][d][%]AssessmentLaacherhof AXXa (loamy sand)SFO18.561.62.58%4.4.4Dollendorf II (clay loam)DFOP15.446.43.944.4.4Laacherhof Wurmwiese (loam)SFO13.544.83.444.4.4					
Laacherhof AXXa (loamy sand)     SFO     18.5     61.6     2.58       Dollendorf II (clay loam)     DFOP     15.4     46.4     3.94     4       Laacherhof Wurmwiese     SFO     18.5     61.6     3.94     4	Soil	Kinetic	<b>DT</b> 50	DT90	chi ² error
Image: Constraint of the state of the st	(Soil Type)	Model ¹	[d]	[d]	[%] Assessment
(clay loam)     DFOP     15.4     46.4     3.94     +     +       Laacherhof Wurmwiese     CEO     12.5     CEO     12.5     CEO     12.5		SFO	18.5	61.6	2.30
		DFOP	15.4	46.4	
		SFO	13.5		

¹ SFO = single first order; DFOP = double first order in paral

² Visual assessment: + good

III. CONCEUSIO

Flufenacet was rapidly degraded in soil under aetobic conditions in the Cark in the laboratory. Its calculated half-lives were 18.5 days in soil LaaCherhof XXXa 5.4 days in soil Dollendorf II and 13.5 days in soil Laacherhof Wurmwies

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

<b>Report:</b>	KCA 7, 5,2.1.1/07; , , G.; , , S,; 2014
Title:	Kineti@ $\ell$ valuation of the Degradation of [nhere] $I$ -UL - ¹⁴ C] flutenacet and its
	Degradation Products under Aerobic Soil Conditions in Laboratory According
	to GOCUS Kinetigs Using the King UI 2 1661
<b>Report No:</b>	$\Re$ nSa-12-0575 $\Re$ $\Re$ $\Re$
Document No:	M-477878-01 A S S
Guidelines: 🔬	• FQCUS kapetics (2006, 20Q) ^{3,4}
GLP:	$\begin{array}{c} \text{SnSa-12-0575} \\ \text{M-477878-01} \\ \text{M-477878-01} \\ \text{\bullet} \\ \text{FOCUS kapetics (2006, 20Q)}^{3,4} \\ \text{no} \\ \end{array}$

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-002046-01-1 (Baseline Dossier, KCA 7.1.2.1.1/03) and M-009592-01-D (Supplemental Dossier, KCA 7.1.2.1.1/04) was performed with the software KinGUI 2 according to FOCUS kinetics (2006, 2041)^{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 ( $1 \times \text{loamy sand}$ ,  $2 \times \text{silt loam}$ ,  $2 \times \text{sandy loam}$ ) under aerobic conditions in the dark in the laboratory at  $20 \pm 2$  °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  $20 \pm 1$  °C, 40% MWHC), 32.2 days ( $21 \pm 1$  °C, 75% FC at 1/3 bar) and 7.4 days ( $20 \pm 1$  °C, 50% MWHC).



#### I. **METHODS**

Soil residue data from the aerobic soil degradation studies M-002166-01-2 (Baseline Dossier, KCA 7.1.2.1.1/01)⁵, M-002146-01-1 (Baseline Dossier, KCA 7.1.2.1.1/03)⁶ and M-009592-01-1 Supplemental Dossier, KCA 7.1.2.1.1 /04) were used. In these studies, the degradation of Aufenacet was studied in a total of 5 soils (1  $\times$  loamy sand, 2  $\times$  silt loam, 2  $\times$  sandy loam) under aerosic conditions in the dark in the laboratory at  $20 \pm 2$  °C and soil moistures ranging from 40% MWHC to 

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 apounts of flufence tough in each repleate test system at each sampling interval. The initial regivery at DAT 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  $0.5 \times LOD$ . They became  $\mathcal{LOD}$  / 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 statistical 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.

The single first order (SFO) was the most appropriate kinetic model 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 t	he degradation	of flufenacet in so	il under aerobic conditions for
	0.	. 89		
	modeling purpose accor	ding to FOCAS	~	

Soil		DTs [@ys]	chi ³ error [%]	t-test	Visual Assessment ²
Howe, Indiana ³	SFO SFO	32.2 C	2.4	<< 0.001	+
BBA 2.2	SFO 1	p″31.9‰°	8.5	<< 0.001	0
Laacherhof AII	SFO N	1ø.2	8.9	<< 0.001	+
Hoefchen im Tay ⁶	sfo r	20.4	5.5	<< 0.001	+
Laacherhof &XXa 7 0	≪ [™] SFO_©	₹7.4 ^{a)}	11.2	< 0.001	0
¹ SFO: single first mer ² visual assessment: + = go	SFO O ood, o = acceptable	Sr.			

³ sandy from  $21 \pm 1 \degree C 0.5\%$  FC 1/3 bar (KCA 7.1.2.1.1/01) ⁶ off of the soil restaue data after DAT 28, due to collapse of the microbial activity ⁴ loamy sand,  $20 \pm 1 \degree C$ , 40% AGWHC (K CA 7.1.2.1.1/03) ⁵ silt loam,  $20 \pm 1 \degree C$ , 40% AGWHC (K CA 7.1.2.1.1/03) ⁶ silt loam,  $20 \pm 1 \degree C$ , 40% AGWHC (K CA 7.1.2.1.1/03)

⁷ sandy loam, 20 C, 50% MWHC (CA 7.1.2.1.1 /04)

a) taken from parent on the fit

⁶ silt loam, 20 ± (20, 40%) WHC (KCA 7.1.2.1.1/03)

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 aeropic 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 flufencet and its major degradation products in soil in the laboratory given in section CA 7.1.2.1  $\beta$ 

Report:	KCA 7.1.2.1.1 /09; , G.; , S.; 2014
Title:	Kinetic Evaluation of the Degradation of [thiadiazofe-2-14Cfulufenacet and its
	Degradation Products under Aerobic Soil Conditions in Laboratory According
	to FOCUS Kinetics Using the KinGUI&Tool 🖉 🕺 🥳
<b>Report No:</b>	EnSa-12-0576
<b>Document No:</b>	M-477885-01-1
Guidelines:	• FOCUS kinetics $(2006 2011)^{3}$
GLP:	no X & X O

### **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)³⁴ to derive half-lives for flufencet 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, why the results for flufencet 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 erobic conditions in the dark in the laboratory at  $21 \pm 1$  °C and soil moisture of 75% of the field capacity ( $\mathcal{C}$ ) at 15 bar.

The calculated half-life of flufenacet was \$5.0 days.

**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  $21 \pm 1$  °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 KinGM 2 with four different kinetic models: single first order (SFO), first order multi-compartment (FOMC), kockey-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 sommarizes the results of the kinetic analysis.

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

Soil	Kinetic Model ¹	DT ₅₀ Chi ² erfor [days] [%]	or-test	Visual Assessment ²
Howe, Indiana ³	SFO	55 6 2 3 70	§ 0.0 <b>03</b>	8

¹ SFO: single first order

² visual assessment: o = acceptable

³ sandy loam,  $21 \pm 1$  °C, 75% FC 1/3 bar (KCA 7.10)1.1/02)

Cut-off of the soil residue data after DAT-32, due to collapse of the incrobial activity

ÖİII. ÖNCLÖSIONS

The calculated half-life of flufenacet for modeling purpose in soil under acrobic conditions in the dark in the laboratory was 55.0 days in the tested soil 2 2 2

The results are included in the summary of the degradation rates of Alufenacet in soil in the laboratory given in section CA 7.1.2

Report: 0KCA 71.2.1.1408; 0.1.1408; 0.1.1408; 0.1.1408; 0.1.1408; 0.1.1408; 0.1.1408; 0.1.1408; 0.1.1408; 0.1.1408; 0.1.1408; 0.1.1408; 0.1.1408; 0.1.1408; 0.1.1408; 0.1.1408; 0.1.1408; 0.1.1408; 0.1.1408; 0.1.1408; 0.1.1408; 0.1.1408; 0.1.1408; 0.1.1408; 0.1.1408; 0.1.1408; 0.1.1408; 0.1.1408; 0.1.1408; 0.1.1408; 0.1.1408; 0.1.1408; 0.1.1408; 0.1.1408; 0.1.1408; 0.1.1408; 0.1.1408; 0.1.1408; 0.1.1408; 0.1.1408; 0.1.1408; 0.1.1408; 0.1.1408; 0.1.1408; 0.1.1408; 0.1.1408; 0.1.1408; 0.1.1408; 0.1.1408; 0.1.1408; 0.1.1408; 0.1.1408; 0.1.1408; 0.1.1408; 0.1.1408; 0.1.1408; 0.1.1408; 0.1.1408; 0.1.1408; 0.1.1408; 0.1.1408; 0.1.1408; 0.1.1408; 0.1.1408; 0.1.1408; 0.1.1408; 0.1.1408; 0.1.1408; 0.1.1408; 0.1.1408; 0.1.1408; 0.1.1408; 0.1.1408; 0.1.1408; 0.1.1408; 0.1.1408; 0.1.1408; 0.1.1408; 0.1.1408; 0.1.1408; 0.1.1408; 0.1.1408; 0.1.1408; 0.1.1408; 0.1.1408; 0.1.1408; 0.1.1408; 0.1.1408; 0.1.1408; 0.1.1408; 0.1.1408; 0.1.1408; 0.1.1408; 0.1.1408; 0.1.1408; 0.1.1408; 0.1.1408; 0.1.1408; 0.1.1408; 0.1.1408; 0.1.1408; 0.1.1408; 0.1.1408; 0.1.1408; 0.1.1408; 0.1.1408; 0.1.1408; 0.1.1408; 0.1.1408; 0.1.1408; 0.1.1408; 0.1.1408; 0.1.1408; 0.1.1408; 0.1.1408; 0.1.1408; 0.1.1408; 0.1.1408; 0.1.1408; 0.1.1408; 0.1.1408; 0.1.1408; 0.1.1408; 0.1.1408; 0.1.1408; 0.1.1408; 0.1.1408; 0.1.1408; 0.1.1408; 0.1.1408; 0.1.1408; 0.1.1408; 0.1.1408; 0.1.1408; 0.1.1408; 0.1.1408; 0.1.1408; 0.1.1408; 0.1.1408; 0.1.1408; 0.1.1408; 0.1.1408; 0.1.1408; 0.1.1408; 0.1.1408; 0.1.1408; 0.1.1408; 0.1.1408; 0.1.1408; 0.1.1408; 0.1.1408; 0.1.1408; 0.1.1408; 0.1.1408; 0.1.1408; 0.1.1408; 0.1.1408; 0.1.1408; 0.1.1408; 0.1.1408; 0.1.1408; 0.1.1408; 0.1.1408; 0.1.1408; 0.1.1408; 0.1.1408; 0.1.1408; 0.1.1408; 0.1.1408; 0.1.1408; 0.1.1408; 0.1.1408; 0.1.1408; 0.1.1408; 0.1.1408; 0.1.1408; 0.1.1408; 0.1.1408; 0.1.1408; 0.1.1408; 0.1.1408; 0.1.1408; 0.1.1408; 0.1.1408; 0.1.1408; 0.1.1408; 0.1.1408; 0.1.1408; 0.1.1408; 0.1.1408; 0.1.1408; 0.1.1408; 0.1.1408; 0.1.1408; 0.1.1408; 0.1.1408; 0.1.1408; 0.1.1408; 0.1.1408; 0.1.1408; 0.11408; 0.11408; 0.11408; 0.1
Title: Kinetic Evaluation of the Degradation of [thiadiazole-5-14C] flufenacet and its
Degradation Products under Aeroble Soil Conditions in Laboratory According
to FOCUS Kinetics Using the KinGUI 2 Tool
Report No: EnSa-12-0577
Document No ² M-4 ² 7835-0 ² A
Guidelines: • FoCUS kinetics (2006, 11) ^{3,4}
GLP: NO 6 ST ST

## 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 valiable 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  $20 \pm 2$  °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  $\pm$  0.1 °C, 55% MWHC), 19.9 days, 16.3 days and 14.9 days (all  $19.8 \pm 0.2$  °C, 55% MWHC).

#### I. **METHODS**

Soil residue data from the aerobic soil degradation studies M-439105-02-D'(Supplemental Dossier, KCA 7.1.2.1.1 /05) and M-440348-02-1 (Supplemental Dossier, KCA (2.1.1/06) were used In these studies, the degradation of flufenacet was studied in a total of 4 softs (silt loam, loany sand, clay loam and loam) under aerobic conditions in the dark in the laboratory at 20 ± 2, C and soil mousture 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) and using the software KinGUI 2 with four different kinetic models: single first order (SFQ), 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 mounts of flutenacet found inceach replicate test system at each sampling interval. The initial recover at DAT-0 was included in the parameter optimization procedure, but for optimal goodress of fin, the value was allowed to be spimated by the model. Values between LOD and LOQ were set to the measured values. Apsingle 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, chi²-scaled error criterion, t-test significance, correlation analysis and standard deviation. The  $DT_{50}$  values were calculated from the resulting kinetic parameters.

## RESULTS

The single first order (SFQ) was the most appropriate kinetic model to describe the degradation of flufenacet for modeling purpose in the 4 tested soils. Table 7.1.2 12 summarizes the results of the kinetic analysis.

Table 7.1.2.1.1-12:	Kinetic parameters for the begradation of furtheracet in soil under aerobic conditions for modeling purpose according to FOCUS
8	modeling purpose according to reactor as

Sõl	Kinetic Motel ¹	DT₅₀⊘ [days]	chi ² error [%]	t-test	Visual Assessment ²
Hoefchen Am Hohenseh ³	SFO 🗞	15.8	4.8	< 2e-16	+
Laacherhof AXX $a_{4}^{4}$ $\swarrow$	SFO Ö	₹19.9	3.0	< 2e-16	+
Dollendorf II 5	SFQ SFQ	^{16.3}	4.7	< 2e-16	+
Laacherhof Wurmwiese		14.9	4.3	< 2e-16	+

Ô ¹SFO: single first order

² visual assessment: + = good

³ silt loam, 19.7 ± 0.1 °C 55% MWHC (KC 7.1.2.1.1 /05) ⁴ loamy sand 99.8 ± 0.2 °C, 55% MWHC (KCA 7.1.2.1.1 /06)

⁵ clay loam 19.8 ± 0.2 °C, 55% MWHC 2KCA 7.1.2.1.1 /06)

⁶ loam, 19.8 ± 0.2 , 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:

		07		1 %
Annex Point / Reference No	Author(s) 🔊	° 4	Year	DocumentNo
KCA 7.1.2.1.2 /01	, E		1996	× N-004028-01-2
KCA 7.1.2.1.2 /02	, <b>j</b> \$		1995	≫M-004447/9-02-1
	Ű.			

Within the additional route studies of flufenacet (Supplemental Dossier, KCA7.1.1.1.04 and KCA 7.1.1.1.05) three new major degradation products were identified, FOE-thiadone, FOE 5043trifluoroethanesulfonic 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. 1407/2009 and SONCO/16802/2010. 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 7.1.1.103). Thus, sight additional studies have been performed for major degradation products in total and are submitted within this Supplemental Dossier for the flufenacet renewar of approval using [phenyl-UL-14C]-labeled and unlabeled FOE sulfonic acid, unlabeled FOE methylsulfone, [thiadfazole-2⁻¹⁴C]-labeled FOE-thiadone and [1-14C]-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 latoratory have been performed according to FOCUS kinetics (2006, 2011) ³⁴ 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 latoratory is given in section CA 7.1.2.1.

Report: K KCA 7.0.2.1.2 08; E.; 2003
Title: Time-dependent sorption of PQE5043-sulfonic acid in soil
Report No: WEE-229/09 O
Document No: M 111445-01-1
<b>Document No:</b> M111445-01-1 <b>Guideline:</b> None (Supportive study to Annex II, Fate and Behavior in the Environment,
3 717 HVI/94-EN, Section 7.1.2)
GLP yes
Executive Symmary

The objective of the soldy was to clarify why simulation runs overestimate the groundwater concentrations  $(PEC_{GV})$  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-¹⁴C]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)	рН ¹	OC [%]
Laacherhof AXXa	Monheim, Germany	sandy loam	6.3	1.47
Laacherhof AIII	Monheim, Germany	silt loam	<b>@</b> .7	0.88

¹ in 0.01 M CaCl₂

The study application rate was 12.3  $\mu$ g/100 g soil (dry weight), equal to 0.123 mg FOF sulformer acid /kg soil (dry weight).

Duplicate test systems were processed and analyzed 0, 3, \$14, 28, 56 and 100 days after freatment.

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 otal material halances, e.g. novolatiles were determined, the recovery of radioactivity decreased to approx. 60% of the applied adioactivity [% AR] in soil Laacherhof AXXa and to approx. 56% AR in soil Laacherhof AMI.

Extractable residues decreased from 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 pAT-0 to DAT-100 from 2.1 to 39.7% AR in soil Laacherhof AXXa and from 2.2 to 28.4% AR in soil Laacherhof AIIP.

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 10 3.34 µg in soil Laacherhof AUL

The experimental data were kinetically evaluated according to the Single First Order kinetic model in order to derive half lives for FOE suffonic 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 (LCA 7) 2.1.2 [1], where only weak degradation of FOE sulfonic acid was found in three soils after 100 days (DT₅₀ 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 carly 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 est item in the leachates of the lysimeter studies than that expected by modeling calculations with the earlier input parameters (longer half-lives).

## MATERIALS AND METHODS

A. MATERIALS

1. Test Item

[phenyl-UL-14@FOE5043-sulfonic acid ammonium salt (report name 1: FOE sulfonic acid)Batch No#C-606BSpecific activity2.66 MBq/mgRadiochemical 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  $\leq 2$  mm. The soils were taken from agricultural areas representing different geographical origins and different soil properties as required by the guidelines Ò

Parameter	Results	Winits 📎 🖉
Soil Designation	Laacherhof AXXa	, Laacherkof AIII
Geographic Location		
City	Monheim 🔨	Monheim
State	North-Rhine Westphalia	North-Rhine Westphal
Country	Germany	Geppany 🖉
Soil Taxonomic Classification	sandy, mixed wesic typic	loamy, mixed, meste typic
(USDA)	Cambodolls	Agrudalfs
Soil Series		ion available
Textural Class (USDA)	Sandy loann	silploam
Sand [%] $[50 \ \mu m - 2 \ mm]$		36.9
Silt [%] $[2 \ \mu m - 50 \ \mu m]$		51.1
Clay [%] [< 2 μm]		× 12.0
pH		
- in CaCl ₂ (soil/CaCl ₂ 1/2) - in water (soil/water 1/1)		6.8 7.6
- in KCl		7.2
Organic Carbon [%] S Organic Matter [%]		0.88 1.51
Cation Exchange Capacity		9.8
[meq/100 g]		2.0
Water Holding Capacity		
maximum	34.42	36.40
[g H2@ad 100@Soil DW]		2.55
Bulk Density (disturbed) [g/cm ³ ]	2.5	2.55
Microbial Biomass () [mg microbal carbon / kg sou DW]		
DAT-Q	242	275
	209	195
	<del>v</del>	
$\mathbb{C}$ alculate $\mathbb{C}$ as: $OM[\mathcal{D}_{0}] = OC[\mathcal{D}_{0}] \cdot 1.724$	Ĩ	
DAT: days after treatment	DW: dry weight	
USDA: United States Department of Agric	ulture	
~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~		

T

Experimental Conditions 1.

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, $\sqrt{2}$). 73 µL of the application solution were applied drop wise onto the soil surface of the respective test systems asing a pipette. After application the soil moisture was re-adjusted to the initial value of 40% MWHQ using deionized 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 106 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, 2, 7, 14, 28, 56 and 100 days after treatment (DAT).

Microbial soil biomass was determine Pat DAD-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 sulform acid. Therefore, the soils were supplemented with 100 mL 0.01 M CaCk solution (soil solution ratio = 1:1) and agitated for 24 h in the dark at 20 °C. Afterwards, supernation and soil were separated by contribution and decantation.

Following, the soils were extracted four times at amoient temperature using 0.01 M CaCl₂ solution (1x), acetonitrile/water (1 x 1:1, v_A) or accentric 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 CaCl₂ 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 pen-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. Kineth 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-¹⁴C]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)

				DAT		,Ŵ	2		
Compartment	0	3	7	14	28	~50	1 0 0 °	S	\$
Carbon dioxide					(Ĉ.	L,		Ŋ
Volatile Organic Compounds			no	t analyz	zed 🖉				
Total Extractable Residues	97.9	96.9	93,4	87.2	C 74.6	\$58.6	29,4		
Non-extractable Residues	2.1	3.0	5Ŵ	7:2	13.5%	20.2	30.7		c
Material Balance	100.0	99.9	98.4	24.4	88.1	78	60.1C		
		Ś		\mathcal{O}	S C	L.	<u> </u>		

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

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

	e 1					, <i>©</i>	<i>a</i> .
Compound (replicate)	0 <	0°	~7	DAST SH4	·28	56	100
(A)	12,2	1,2:2	11.9	11.1	\$9.3	\mathcal{Y}_{1}	3.5
FOE sulfonic acid (A2)	¢12.3	12.2	11.7	11.0	9.5 [™]	≱ 7.5	3.5
mean	12.2°	[≫] 12.2 s	Ú1.8	11.0	9Ô)	7.3	3.5
DAT: days aft@treatment	N N N	d'a			N N		

 Table 7.1.2.1.2-4:
 Distribution of Radioactivity in Soil Loacherhoft AIII under Aerobic Conditions

 expressed in as percent of applied radioactivity mean value of duplicates)

				~ ¥	X				
				Ã.	Ň	DAT			
R	🖉 🖉	ound) 0	³ 3	©7	14	28	56	100
K.	Carboodioxide	o ò		Ł	1	4 a.u.a.1			
	Organic Volati	les 🖉	ĴĊ ^Ÿ	×	по	t analyz	ed		
	Jotal Expractal	~ (N)	97.8	94.4	90.6	86.1	74.1	55.9	27.8
ŝ	Non-extractabl	e Residues	<u>2</u>	3.4	5.2	6.5	11.9	18.4	28.4
	Material Bala	nce &	×100.0	97.9	95.8	92.6	86.1	74.3	56.2
			1 and a start of the start of t						

W.d.: not detected a.d.: 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)

					DAT		Ű	2	
Compound (rep	licate)	0	3	7	14	28	~56	1 0 0 °	à V A-
	(A1)	12.6	12.2	11.9	11.2	9.7	7.2	S .4	
FOE sulfonic acid	(A2)	12.2	11.9	11.6	<u>11</u> ,0	9 Ø	6.9	کر 3.3	
	mean	12.4	12.1	11.7	91.1	9.6		3,30	
				4		S o	67		

DAT: days after treatment

B. MATERIAL BALANCE

As the study design was not intended to determine total material balances, e.e. 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 AXIII; see also Table 7.1.2.1.2- 2 and Table 7.1.2.1.2- 4.

C. EXTRACTABLE AND NON EXTRACTABLE RESPOLES

Extractable residues decreased from DAT-0 @ 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. VOLATILIZA DON &

No volatiles were determined within this study.

E. DEGRADATION OF PST INCM

The amount of [phenor-UL-¹⁴C]FOF Olfonic acid decreased from DAT-0 to DAT-100 from 12.23 to 3.46 μ g in soil Laacherhof AXXa and from 2.4 to 3.34 μ g in soil Laacherhof AIII.

The experimental data were kinetically evaluate Daccording to the Single First Order kinetic model in order to derive half-lives for FOE sulfonc acid.

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

Ÿ	Soil S	DT T	DT90 [d]	k [d ⁻¹]	Correlation Coefficient (R ²)
	Laacherhof A&Xa		205	0.0112	0.985
	Laacherhof AIII	60.2	200	0.0115	0.986
		•		•	•

III. CONCLUSIONS

[phenyl-UL-¹⁴C]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} 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.

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

Report:	KCA 7.1.2.1.2 /07; EM. 2013
Title:	Amendment No 1 - FOE sulformer acid: Aerobic Degradation in Four European
	Soils Soils
Report No:	EnSa-13-0442
Document No:	M-461413-02-1
Guidelines:	• OECD Test Guideline No. 307
GLP:	yes dy o' o' a dy o

Executive Summary

The degradation rate of FOE sulfonic acide a soil degradation product of fluttenacet 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 Source	⁹ Texture (USDA)	рН *	OC [%]
	Monheim, Germany	Joamy sand	6.2	1.7
Dollendorf II	Blankenheim, Germany	loam	7.0	4.6
Hoefchen am Hohens	Borscheid, GermanyQ	🖉 silt loam	6.1	2.0
Wurmwiese	Monheim Germany	≫ sandy loam	5.0	1.8

* pH value was derived from aqueous 0.01 M CaCl₂ suspension

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

The amount of FOP sulforic acident the soil extracts decreased from study start (DAT-0) to study end from 105.2 to 33.9% of applied amount (% AA] (DAT-120) in soil Laacherhof AXXa, from 94.8 to 2.6% XA (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% XA (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 and 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**

nic aci unlabeled AE 0841914 (FOE5043-sulfonic acid sodium salt; report name) Certificate of Analysis: AZ 17486 Batch Code: AE 0841914 00 1 C86 001 86% (w/w) with 19 F-NMR Chemical Purity:

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 solf properties as required by the guidelines. No plant protection products were used for the previous 9 years. The solfs were sampled freshly from the fields (upper horizon of 0 to 20 cm) and speved to a particle size of ≤ 2 mf. Solf collection and handling were in accordance to ISO 10381-60 representing different geographical origin and different soil properties as required by the guidelines. No plant protection products were used for the previous years. The softs were sampled freshly from



Table 7.1.2.1.2- 7:	Physico-chemical	properties of test soils
	i nysico chemicai	properties of test sons

Parameter	Results / Units 🔗					
Soil Designation	Laacherhof	Dollendorf II	Hoefcher am	Laacherhof		
	AXXa		Hohenseh –	° Wurmwiese		
Geographic Location				O' <i>Ş</i>		
City	Monheim	Blankenheim	Burscheid	Monheim		
State	North-Rhine	NorthRhine	North-Rhine	North		
	Westphalia	Wegyphalia	Westphalia	Westphalia		
Country	Germany	Germany	Germany	Germany		
Soil Taxonomic Classification (USDA)	sandy, mixed,	@ine-loamy,	Joamy, mixed,	loamy, mixed,		
	mesic, Typic Cambudoll	mixed active, frigid Typic	mesic, Oypic AFgudalf	Omesic Cypic Argudalf		
		Eutrudept				
Soil Series			on available	Ĵ		
Textural Class (USDA)	loamy	loan 🤅	silt loam	Sandy loam		
Sand [%] [50 µm – 2 mm]	\$\$A _ ^	× 298	i joz (° 60		
Silt [%] $[2 \mu m - 50 \mu m]$	10 ×	28	_ ≪_ 62 _ ©	26		
Clay [%] [< 2 μm]	<i>6</i> , €	₹ 2 <u>4</u> 0°		14		
pH	P [×] , O [×] , 4		Y p			
- in CaCl ₂ (soil/CaCl ₂ 1/2)	6.2	9 .0	\$~,6.1	5.0		
- in water (soil/water 1/1)	Č 6.3	7.1	6.3	5.2		
- in water (saturated paste)	6 (V 7,1 V	Ô) 6.3	6.3		
- in KCl	6.0	\$\$.7 \$~	5.8	4.7		
Organic Carbon	© 1.7 [©] 2.9 [©]	4.6	2.0	1.8		
Organic Matter 1		6 7.9 C	3.4	3.1		
Cation Exchange Capacity [meq/100 g]	\$ \$ \$	0 19	11.1	10.4		
Water Holding Capacity	Î Î S	, Ş				
maximum [g H ₂ Q ad 100Q soil D \mathfrak{D}] ^y	48.5	≈79.1	54.8	56.3		
at 0.1 bar (pF2,0) [%]	2 12.9 V	@ 45.4	33.1	19.8		
Bulk Densit (disturbed) [g/cm]		× 1.03	1.09	1.17		
Microbial Biomass ing microbial						
carbon per kg soil DW] ² DAT-0 (BIO)	924 [°]	3883	1100	770		
DAT-60 $(BiO-/BIO-)$	510 3 17	2116/2057	657/623	770 476/498		
DAT-120(BIO-/BIO+)	°41/2/399	n.d./n.d. ³	472/510	367/362		
		n.u./ n.u.	7/2/310	3077302		

1 P DAT days after treatment EW: dry weight USDA: United States Department of Agriculture

¹ Calculated as OM [%] OC [%] x 1.724
 ² BIO- samples were left untreated, BIQ samples were applied with solvent of application solution (400 μL methanol/water (γ (ν/ν)).

³ Due to strong or radation of the test tem in soil "Dollendorf II" until DAT-37, the study was terminated for this soil after this time point. Mitopolial biomass measurements at DAT-120 of this soil were discarded.

STUDY DESIGN B.

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 $55 \pm 5\%$ 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 furtenace of 600 g per hectare and a maximum formation of 26.3% of FOE sulfonic acid in actobic soil metabolism study M-002146-01-1 (Baseline Dossier, KCA 7.1.1.1/03), resulting in a nominal SAR of 344 rg FOE sulfonic acid per kg soil dry weight.

The test item was applied drop wise onto the soil surface of the respective est systems in $A00 \,\mu\text{L}$ methanol/water 1/1 (ν/ν) using a pipette. After application, the test results except DAT-0 camples) were closed with PU foam plugs.

2. Sampling

Ten sampling intervals were distributed over the entire incubation period of 120 days. Duplicate samples were processed and analyzed 0, 1^7 , 9^7 , 7, 1^4 , 21, 2^5 , 58^8 , 86^8 and 120^8 days after treatment (DAT). Microbial soil biomass was determined at start, middle and of the study (DAT-0, DAT-60 and DAT-120⁸).

At each sampling interval, concurrent recovery samples were prepared freshly by fortification of a representative soil (Laacherrof 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 Proceedures

The entire solv of each test system was extracted three times at ambient temperature using a mechanical shaker and aceton trile/water $1/10^{\nu/\nu}$). For thermore, two accelerated extraction steps using a microwave with a magnetic stirrer were performed, first with acetonitrile/water 1/1 (ν/ν) at 70 °C and second with methanol/water 1/1 (ν/ν) at 50 °C. After each extraction step, extract and soil were separated by contribution approx. We minutes at 4200 x g) and decantation. All soil extracts were combined, made up to a tinal volume of 400 mL with acetonitrile/water (1/1, ν/ν) and mixed thoroughly.

Aliquets 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 (2005) 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 mput 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 celected on the basis of the chi² scaled error criterion and on the basis of a visual assessment of the goodness of the fits. DT₅₀ and DT₉₀ values were calculated from the resulting kinetic parameter.

I. 🔊 RESULTS AND DECUSSION 🔍

A. DATA

			0	¥.	<u> </u>		al				
	Ŭ_	r.	, . L	. 📣	C) Da	уŤ				
Soil	Replicate	0		307	72	D2 140	21	37	58	86	120
Laacherhof	Ă	303.2	na.	a.a.	93.0	202	85.7	70.9	58.1	44.4	33.9
AXXa	ͺŶΩB °≈	,103.2) n.a. 💉) n.a.	Q94.1	88.9	84.5	70.6	58.0	46.0	34.0
Ŕ	Mean	103.2	n.a C	n.a	93.5	89.5	85.1	70.7	58.1	45.2	33.9
Dollendorf 🕼	AO AO	93,7	90,5	67 %	39£2)*	31.2	6.9	3.7	n.a.	n.a.	n.a.
	°} ₽×	95.9	92.6	68.5	¢47.6	22.6	16.0	1.5	n.a.	n.a.	n.a.
	Mean 🖉	[≫] 94.8 _√		65.4	Å 3.4	26.9	11.5	2.6	n.a.	n.a.	n.a.
Hoefchen am	õ A O	104	100 🗶	° 94.4	69.9	56.4	60.7	46.3	28.2	12.9	3.6
Hohenseh	R 3	104.9	100.8	950	75.7	66.4	60.4	46.9	25.5	15.2	3.1
4	Mean	4.6	P01.3	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
²	Mean	AQ2.1	n.	n.a.	92.3	85.9	78.4	57.2	42.9	29.5	25.3
	A (A)								

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

n.a.: not analyzed

B. METHOD ALIDATION

DAT: days after treatment

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% o 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 LageherhoDAXXa from 94.8 to 2.6% AA in soil Dollendorf II, from 104.6 to 3.3% AA in soil Doefchen am Hohensek 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 chi² error values and visual assessments. Table 7 (2.1.2) summarizes the best-fit results of the DT₅₀ and DT₉₀ calculations.

Table 7.1.2.1.2- 9:	Best-fit degradation kipetics of FOE s	ulfonic acid i	n soïls under	aerobic conditions for
	trigger evaluation according to FOC	s S		

Soil	Best Fit Kinetie Model	> DT ₅₀ [da \$ 5]	DToo [d@ys]	chi ² error [%]	Visual Assessment ²
Laacherhof AXXa	SFO O	\$79.4	243.8	1.3	+
Dollendorf II	SFO SFO	6.7 °≈	22.3°	5.6	+
Hoefchen am Hohenseh		24.0	105.8	5.7	+
Wurmwiese	SFO U	496	165.3	3.7	+

¹ SFO: single first order \bigcirc FOP: double first \bigcirc do

HI. CONCLUSIONS

FOE sulfonic acid, a soil degradation product of flufenacet was well degraded in soil under aerobic conditions in the dark on 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 suffonic and has in potential for accumulation in the environment.

	, Ø	" "O"	****	
	Q A	1 M		
	J U	. 0		
Report:	KCA(7.1.2	2.1,2/10;	, K.;	, T.; 2013
Title:	, FOE sulfo	nic acid: Deg	gradation in Fou	r Aerobic Soils
Report No:	EnSa-13-Q	2		
Document No:	467862	-01-1		
Guidelines:	🔊 • OECD T	est Guideline	e 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)	рН 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 CaCl₂

A study application rate of 419 μ g 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 POE subtonic acid of 26.3% in a flufenacet aerobic soil degradation study.

The amount of FOE sulfonic acid in the soil extrator decreased from study start (PAT-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 (DAP-120) in soil UFA 2.3 and from 98.5 to 3.0% AA (DAT-120) in soil LUOA 6S.

The experimental data could be well described boa single first order kinetic model for all soils. The half-life of FOE sulfonic acid under arobic conditions was 27.3, 24.8, 63.9 and 11.9 days in soil Hanscheider Hof, Frankenforst, LUFA 2.3 and LUFA 0S, respectively.

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

MATERIALS AND METHODS

A. MATERIALS

1. Test Item

unlabeled AE 084 14 (FOE 5043 Sulfonic acid solution saft, report name ¹: FOE sulfonic acid) Certificate of Analysis: AZ 17542 Batch Code: AE 0841914-01-02 Chemical Party: AF 0841914-01-02 87.6% (Ww) with ¹⁹F-NMR

2. Test Soils

Four soils were used used the Table 7.1 (21.2-10). 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	Frankenforst	LUFA 🖉 3	LUFA 6S			
	Hof		~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~	° L			
Geographic Location			S' O	°O' (?			
City	Burscheid	Vinxel	Offenbach	Siebeldingen			
State	North-Rhine	North Rhine	Hesse Hesse	Ý Řhinefand-			
	Westphalia	Westonalia		Palatinate			
Country	Germany	Germany	Germany 🔗	Gormany			
Soil Taxonomic Classification (USDA)	loamy-	n@information	no information	no Information			
	skeletal,	available	availate	© ^v avaikable			
	mixed,						
	semiactive						
	Eutrudept	J O		L.			
Soil Series		9 no informat	ion available	7 7			
Textural Class (USDA)	Joan 🔨	si Oloam 👋	sandy loam	clay			
Sand [%] [50 μ m – 2 mm]	42 0	L, 30 0	مَنْ 63 مَنْ	35			
Silt [%] $[2 \mu m - 50 \mu m]$	<i>6</i> ⁹ ′ 45€ ⁷	51	27 ⁵ 27 ⁵	23			
Clay [%] [< 2 μm]	AS X	° Ô S	, û	42			
pH 🔅		<u> </u>	\sim				
- in CaCl ₂ (soil/CaCl ₂ 1/2)	میں 5.6 <i>م</i> ر	6.8 Q	6.8	7.0			
- in water (soil/water 1/1)	0° 58° %	700	Ç 7.1	7.2			
- in water (saturated paste)	Č~5.8 "	6.9	7.1	7.1			
- in KCl	₹ ⁷ 5.3 O	© 6.3	6.7	6.6			
Organic Carbon	£ 2. &	O LO	1.1	1.9			
Organic Matter ¹			1.9	3.3			
Cation Exchange Capacity meq/100 g	10.8 J	₹ 5.4	8.9	21.5			
Water Holding Capacity		Ø					
maximum [g 0 20 ad 100 g soft DW]	o 64.∳	Ş 56.7	39.3	48.3			
at 0.1 bar (pF 2.0) (9)	s <u>3</u> 9.1	30.5	17.8	32.8			
Bulk Density (disturbed) [gcom ³]	Ci.04	1.15	1.28	1.22			
Microbial Biomass [mg microbial	Û a						
carbon per ke soil DW		10/7	200	0.55			
	\$70	1065	398	957			
DAT-58 (BIO- (BIO-)	×8/13/787	999/1024	736/671	1305/1019			
DAT 20 (BIO- / BIO-	601/566	800/757	227/242	984/875			

DAT: days after treatment DW: dw weight USDA: United States Department of Agriculture ¹ Calculated as OM[%] = OO[%] 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/m))



B. STUDY DESIGN

1. Experimental Conditions

The static test system for degradation in soil under aerobic conditions consisted of Erlenmover glass flasks (volume e.g. 300 mL). Each flask was closed with a polyurethane (PG) foamolug 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 $55 \pm 5\%$ of the maximum water holding equacity (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 FOQ sulfonic acid in aerobic soil netabolism study M-002146-01-1 (Baseline Dossier, KCA 7.1.1.1/03), resulting in a nominal SAR of 344 μ g FOE sulfonic acid per kg soil dry weight. The actual SAR was 419 μ g 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 μ L methanol/water 1/1 (ν/ν) using a pipette. After application, the respective test systems in 400 μ L were closed with PU foam plugs.

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

2. Sampling

Nine sampling intervals were distributed over the entire incubation period of 120 days. Duplicate samples were processed and analyzed 0, 7, 4, 7, 94, 30, 58, 91 and 120^{9} days after treatment (DAT). Microbial soil biomass was determined at start, middle and 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 (LUCA 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 1/4 (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 (ν/ν) 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 ion.

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 LOO 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 FOCOS 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 procedue, 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 chi² 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.

S II. A RESULTS AND DISCUSSION

A. DATA

		_ •	0,01			,,,				
× ×		J.		0		DAT			_	
Soil 🔊	Replicate	~0		A	7	14	30	58	91	120
Hanscheide	A A	101.3	§ 98.3	92.2	88.6	76.5	53.3	22.4	4.7	n.a.
A (B B	104.4	1020	98.3	85.9	76.2	51.8	23.1	4.5	n.a.
	Meen	1,02.9	160.1	95.3	87.2	76.3	52.5	23.3	4.7	
Frankenforst	Â	j 03.1	9 7.8	84.2	73.9	66.3	45.1	14.2	< LOD	n.a.
d v		× 106.9	y 98.3	85.4	71.4	69.5	45.6	13.6	< LOD	n.a.
C	Mean	105.0	98.1	84.8	72.6	67.9	45.3	13.9	< LOD	
LUFA 2.3	A	103.5	99.6	94.8	91.5	87.7	72.8	53.3	36.4	27.4
v v	, 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	А	98.9	91.4	86.6	80.1	76.8	64.2	37.7	13.8	2.5
	В	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

Table 7.1.2.1.2 11: Degradation of FOF sulform acid in soils under aerobic conditions (expressed as percentage of applied amount [% AA})

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 0.9992 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 the 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 way 101.3% AA prange 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 star (FDAT-0) to study end from 102.9 to 4.7% (DAT-91) of applied amount [23 AA] for soil (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) an 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 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 offonic and in soils under aerobic condition trypger evaluation according to FOE S	ions ior

Salt N	Best Fit Kinetic Model	D150 *	DT90 [days]	chi ² error [%]	Visual Assessment ²
Hanscheider Not 🔊	SFO N	\$7.3	90.7	3.2	+
Frankenforst S S	Or SFO	21.8	72.4	6.4	+
LUFA 2.3	SFO SFO	63.9	212	1.5	+
LUFA 6S	S STO	11.9	39.4	6.5	+

¹ SFO: single First orde DFOP: Souble first order in Parallel

² visual assessment: \bigoplus good O

CONCLUSIONS

FOE sulfonic acide 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; 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 flufence twas studied in four soils under aerobic conditions in the dark in the laboratory for up to 20 days at 19 \pm 20 days at 19 \pm 5% of the maximum water holding capacity:

Soil	Source So
Laacherhof AXXa	Monheim, Germany loamy sand 62 01.7
Dollendorf II	Blankenheim, Germany Dioam O 7.0 4 4.6
Hoefchen am Hohenseh	Burscheid, Gernany Q silt loan A 6.1 \sim 2.0
Laacherhof Wurmwiese	Monheim, Germany & sand& oam & 5,0 1.8

¹ pH in 0.01 M CaCl₂

A study application rate of 81. Taig per kg soil dry weight was applied based on a single field application rate of flufenacet of 600 g per hectary and a maximum formation of FOE methylsulfone of 6.6% in a flufenacet aerobic soil degrapation study.

The amount of FOE methodsulfore in the soil extracts decreased from study start (DAT-0) to study end from 94.0 to 11.4 % DAT 20) of applied amount % AAltin soil Laacherhof AXXa, from 102.5 to 5.8% AA (DAT-92) in soil Dollendorf II, from 106 to 14 2% AA (DAT-120) in soil Hoefchen am Hohenseh and from 92.7 to 39.4% A (DAF-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 Faacherhof Wurnwiese and by a double first order in parallel kinetic model for soil Hoefenen am Hohensen. The half-life of FOE methylsulfone under aerobic conditions was 434, 23.3, 40.9 and 96.1 days in soil Laacherhof AXXa, Dollendorf II, Hoefchen am Hohenseh and Laacherhof Wurnwiese, respectively.

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

\mathcal{G}^{O} MATERIALS AND METHODS

A. MATERIAL

 1.
 Test Item

 unlabeled FOR 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.



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Document MCA: Section 7 Fate and behaviour in the environment Flufenacet

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
1 4010 / 11/20102 100	i nysieo enemieur	properties of test sons

Parameter	Results / Units							
Soil Designation	Laacherhof	Dollendorf II	Hortchen and	Laacherho				
	AXXa	× °	Hohensen	Wurmwiese				
Geographic Location		Ŭ,		p' 💭				
City	Monheim	Blaxkenheim	Burscheid	Monheim				
State	North-Rhine	North-Rhine	North-Rhine	North-Rhine				
	Westphalia	Westphalia	Westphalia	Westphalia				
Country	Germany	O Germany	Germany	Ger ® any				
GPS Coordinates	N 51° 04.64	N 50 22.899	N 51×04.00	N 50 04.857				
	E 006° 53,517	E.006° 43.001'	E \$ 007° 06.227'	E@06° 55.251				
Soil Taxonomic Classification (USDA)	sandy, mixed,	Tine-loandy, mixed active,	wamy, mixed,	mesic Typic				
	mesictypic Cambudolls(frigid Typic	mesic Typic /	Argudalfs				
				Aigudalis				
Soil Series			tiomavailable					
Textural Class (USDA)	loam and		silt Joam	sandy loam				
Sand [%] [50 µm – 2 mm]	× 84 ×		°~22	60				
Silt [%] $[2 \mu m - 50 \mu m]$.0 10	a 28	~ 62	26				
Clay [%] [< 2 μm]	6		ث 16	14				
pH		¥ • 4 •						
- in CaCl ₂ (soil/CaCl ₂ 1/2)	گ6.3 🖧	7.1	6.3	5.2				
- in water (soil/water 1/1)	₹ 6.4 °	© 7.1 Å	6.3	6.3				
- in water (saturated poste)	60		5.8	4.7				
- in KCl	\$.0	6.1	5.0				
Organic Carbon 🕼 👾 🔊	5 1.7 Q	4.6	2.0	1.8				
Organic Matter 🖓 🔬	^ر کړي ک	7.9	3.4	3.1				
Cation Exchange Capacity [meg/100 g]	}` % % ≪	1 9.5	11.1	10.4				
Water Holding Capacity								
maximum [g H ₂ O ad 100 g soil DW]	48.5 O [♥]	79.1	54.8	56.3				
at 0.33 bar (pf2.5) [% 🖓 👘	10.8	35.1	20.9	15.6				
Bulk Densit disturked [g/cm3]	<u>کې (</u>	1.03	1.09	1.17				
Microbiak Biomase mg microbial carbon	n per 100 g soil D'	W] ²						
DAT (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 the atment		USDA: United S	tates Department of	Agriculture				
		GDG 111 1						

DW: dry weight

USDA: United States Department of Agriculture GPS: global positioning system

A. 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 Erlenmover 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 $55 \pm 5\%$ 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 notabolism study M-002146-01-1 (Baseline Dossier, KCA 7.1.1.1.03), resulting in a nominal SAR of 79.4μ g FOE methylsulfone per kg soil dry weight. The actual SAR was 817 μ g FOE methylsulfone per kg soil dry weight

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

The test systems were incubated in the dark for 120 days at 49.7 °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 0, 1, 2, 6, 13, 07, 61, 00¹⁰, 92 and 120 days after treatment (DAT). Microbial solutions 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-5) and DAT-120).

At each sampling interval, concurrent recovery samples were prepared freshly by fortification of a representative soil (Fracherhof 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 for fiftcation level.

3. Analytical Proceedures

The entire soil of each test system was extracted three times at ambient temperature using a mechanical shaker and aceton trile/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 4/4 (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 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 solve.

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 folutions 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 fighthe value was allowed to be estimated by the 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. DT₅₀ and DT₉₀ 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

 Image: Contract of the second state of

		-	<u>~</u>								
l l	l L	_Ø	Ŭ,			DA	ΑT				
Soil 🔬	Replicate		A ≯	2 0″	6	13	27	61	70	92	120
Laacherhởf		92.7	\$ 5.8	Q 4.7	90.3	83.6	69.5	35.6	n.a.	21.3	12.5
AXXa	S B ≤	/ 95.3	§99.0	Q103.7	88.5	82.3	67.1	38.4	n.a.	20.7	10.3
- 1	» ^O Mean ^O	94,0	97. A _'	99.2	89.4	82.9	68.3	37.0		21.0	11.4
	A A B A B A	107.6	10021	105.8	88.6	73.7	48.1	12.2	n.a.	4.5	n.a.
Dottendorf I	S ^B	69 7.4	8.5	99.0	87.8	73.1	49.9	13.7	n.a.	7.0	n.a.
	🔪 Mean 🕂	(A)	∛ 99.3	102.4	88.2	73.4	49.0	13.8		5.8	
Hoefchen am 🔍		101.3	103.3	96.1	93.9	77.7	66.0	40.9	n.a.	29.5	13.0
Hohenseh	B	1407.5	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	[™] A	102.6	100.4	95.8	102.6	89.4	79.7	72.2	68.2	55.9	37.5
Wurmwiese	В	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



B. METHOD VALIDATION

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

The correlation coefficient (R²) 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 and unt [% AA] for all soils and both fortification levels. The relative standard deviations for each recovery set ranged from 18 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 \$16.4% AA.

C. DEGRADATION OF TEST ITEM

The amount of FOE methylsulfone in the soft extracts decreased from study start (pAT-0) to study end from 94.0 to 11.4% of applied amount [% AA] (DAT-020) in soil Laadaerhof AXXa, from 102.5 to 5.8% AA (DAT-92) in soil Dollendor [17, from 06.4 to 14.2% AA (DAT-120) in soil Hoefchen am Hohenseh and from 102.7 to 39.4% AAQDAT-120) in soil Laadberhof Wurmwicse.

The degradation of FOE methylsulfone followed single first order to netices in soils Laacherhof AXXa, Dollendorf II and Laacherhof Wummwiese and double first order in parallel kinetics in soil Hoefchen am Hohenseh according to the lowest chi² error value and visual assessments. Table 7.1.2.1.2-15 summarizes the best-fit results of the 197_{50} and 97_{90} calculations.

Table 7.1.2.1.2- 15:	Best-fit degradation kinetics of FQE methylsulfone in soils under aerobic conditions for trigger evaluation according to FOCUS
	triage Suplus Ret and Ring to BOCUS
	trigge evaluation according to POCUS

Soil 8	Best-Fit Kinetic Model ¹	DT 50 [[days]]	DT90 [days]	chi ² error [%]	Visual Assessment ²
Laacherhof AXXa 🔘	SEO A	° 43.1∾°	143.3	3.4	+
Dollendorf II	¥ \$\$F0 [™]	23	77.4	3.0	+
Hoefchen Sm Hobenseh	<u>∧</u> @FOP ∕∕	A Ø.9	149.1	2.9	+
Laacherhof Wurnwiese 🔍	Or SFQ	96.1	319.4	3.3	+

¹ SFO: single firstorder, DEOP: double first order in paral

² visual assessment: $+ = g \otimes d$

J CONCLUSIONS

FOE methyls flore, 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:	КСА 7.1.2.1.2 /09; , К.; , Т.; 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 flufenceet was studied in four soils under aerobic conditions in the dark in the laboratory for up to 120 days at 99.9 °C and 54.4% of the maximum water holding capacity:

Soil	Source Texture (USDA) apH ¹ OC [%]
Hanscheider Hof	Burscheid, Germany, Joam Jacob 2.8
Frankenforst	Vinxel, Germany V Visilt Land V 6.8 1.8
LUFA 2.3	Offenbach Germany sandy bam 🐎 6.8 1.1
LUFA 6S	Siebeldingen, Germany & Kalay Ø 7.0 1.9

¹ pH in 0.01 M CaCl₂

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

The amount of FOE methods allow in the soil expacts 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 LUFO 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 FOP methylsulfone under aerobic conditions was 82.5, 64.0, 147 and 163 days in soil Hanscheider Hof, Erankenforst, LUFA 2.3 and LUFA 6S, respectively.

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

ATERIALS AND METHODS

A. MATERIAL

1. Test Item unlabeled FOE methylsultone 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.

Parameter		Results /	Units	
Soil Designation	Hanscheider Hof	Frankenforst	ONUFA 2.3	LUFA 65
Geographic Location		s° 4		
City	Burscheid	Øinxel 💦	Offenbach	Siebeldingen
State	North-Rhine	North-Rlune	Hesse	Rhineland-
	Westphalia	Westphalia	Nº N	Palatingte
Country	Germany 🐇	Germany	Germany	Germany
Soil Taxonomic Classification (USDA)	loamy-skeleta	no information	, no	no information
	mixed, Q	available	information Vavailable	available
	semiactive, mesic Dystric	F Ö U	D ^{yavana} one	S
	Eucodept		~~~ (
Soil Series		no information	n available 🧷	•
Textural Class (USDA)	loam	🕻 silt loom	sandy loam	clay
Sand [%] [50 µm – 2 mm]		, 30 ×	Ê, Ê	35
Silt [%] $[2 \ \mu m - 50 \ \mu m]$	\$^A5K)	0 ⁹ 51 ~ 7	<u>`</u> 27	23
Clay [%] [< 2 μm]	13	19	∼y ^y 10	42
pH			2	
- in CaCl ₂ (soil/CaCl ₂ 1/2)	5.6 °~	\$\$6.8	6.8	7.0
- in water (soil/water 1/1)	5.8 L	7.0	7.1	7.2
- in water (saturated paster)	₹ 5.8 O″	6.9	7.1	7.1
- in KCl	K \$3 C	¢ ¢3	6.7	6.6
Organic Carbon	2.8 L V	1.8	1.1	1.9
Organic Matter 1	4.8 5	گ 3.1	1.9	3.3
Cation Exchange Capacity [meq/100 g]		15.4	8.9	21.5
Water Holding Capacity			20.2	10.2
maximum [gH ₂ Q, aq100 g sol DW]		56.7	39.3	48.3
at 0.1 bar (pF 2.00 [%]	<u> </u>	30.5	17.8	32.8
Bulk Density (disturbed) [g/cm ³]	^{1.04}	1.15	1.28	1.22
Microbial Bioprass [mg/microbial carbo		1055	2(0	071
DAT-0 (BHO-)	* * 764 \$ 659/679 ³	1055	269 270/276	871
$DAT = 39$ (BIO- \land BIO+) DAT = 20 (BHO- \land BIO+) \land	621/575	827/627 790/761	270/276 268/245	976/871 943/878
	Ø 021/3/3	/90//01	200/243	743/0/0

Table 7.1.2.1.2-16: Physico	-chemical pro	operties of test soils
-----------------------------	---------------	------------------------

DAT: days after treatment DW: weight USDA: United States Department of Agriculture ¹ Calculated as QAP⁶/₀] = OC⁶(³) x 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 (vO).

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 Erlenmover glass flasks (volume e.g. 300 mL). Each flask was closed with a polyurethane (PG) foamolug 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 $55 \pm 5\%$ 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 nethylsulfone in aerobic soil notabolism study M-002146-01-1 (Baseline Dossier, KCA 7.1.1.1/03), resulting in a nominal SAR of 79 μ g FOE methylsulfone per kg soil dry weight.

The test item was applied drop wise onto the soft surface of the respective test systems in 400 μ L methanol/water 1/1 (v/v) using a pipette. After application, the test sessels (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, 2, 14, 30, 59, 90 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 (LEFA 2.3) with the test item at 0.00 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 Proceedingres

The entry soil of each test system was extracted three times at ambient temperature using a mechanical shaker and aceton brile/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 contributing (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 ($\sqrt{2}$, 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 (ν/ν) 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 soil.

4. Kinetic Evaluation

The degradation kinetics of the test item was determined according to COCUS 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 fighthe value was allowed to be estimated by the model. The best-fightinetic 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. DT₅₀ and DT₉₀ values were calculated from the resulting kingure parameters.

II. RESULTS AND DISCUSSION

A. DATA ô

 Table 7.1.2.1.2
 T
 Degradation of FOF methylsulfone in soils under aerobic conditions

 (copressed)
 percent of applied amount [% AA])

	Č ^y K		Č.	Ŵ	DA	۸T			
Soil 🔬	Replicate	~9	3	\bigcirc_7	14	30	59	93	120
	ČÅ ,	95.4	101.9 ×	> 91.9	88.9	80.7	59.3	43.3	34.4
Hanscheide	S [™] B ≪	1 98.2	° 95₅Q ^O	90.6	87.6	81.2	59.4	45.5	37.1
A (Mean O	96.8	98.3	91.3	88.3	81.0	59.4	44.6	37.0
		98.8	10 0.0	95.7	84.2	75.2	52.7	33.4	26.3
Frankenforst	, B	6 92.9	³ 99.1	93.6	84.6	76.4	55.9	34.7	26.8
d v	🔪 Mean 🔨		99.5	94.6	84.4	75.8	54.3	34.1	26.6
		95.6	99.1	94.2	85.6	84.9	72.6	62.0	56.8
LUFA 2.3 🔗	₿	Ø.9	99.0	93.1	87.8	80.6	70.4	61.9	56.9
, v	Mean	96.7	99.0	93.7	86.7	82.7	71.5	62.0	56.9
	́О ^У А	100.7	95.8	92.5	87.8	86.5	74.9	66.4	58.9
LUFA 6S	В	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 (B) 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 congrittent 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 starf (DAT-0) to DAT-120 from 96.8 to 37.0 of applied amount [% AA] in soil Hanscheider 40 f, from 95.8 to 26.6% AA in soil Frankenforst, from 96.7 to 56.9% AA in soil LUFA 2.3 and from 400.2 for 58.9% AA (DAT-120) in soil LUFA 6S.

The degradation of FOE methyls alfone. Followed single first order kinetics in all soils according to the lowest chi² error values and visual assessments. Table 7.1.2. 2- 18 sommarizes the best-fit results of the DT₅₀ and DT₉₀ calculations.

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

Soji	Best-Fit Binetic Model 1	√ĎT50 √ ∑[days]	DT90 [days]	chi ² error [%]	Visual Assessment ²
Hanscheider Hof	[≪] §F0 [~] ≪	8205	274	2.1	+
Frankenforst	_OŠFO ∕∕	64 .0	213	2.9	+
LUFA 2.3 O	Of SFO	¥47.0	488	2.1	+
LUFA65 K	SFO SFO	/ 163.0	542	1.7	+

¹ SFO: single first order, DUOP: double first order in parallel ² visual assessment: + = 2000

CONCLUSIONS

FOE methy sulfone, 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 \mathcal{D}

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



Report:	KCA 7.1.2.1.2 /03; , N. R.; , 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 Q Q X

Executive Summary

The degradation of [thiadiazole-2-¹⁴C]FOE-thiadon was investigated in three soils under aerobic conditions in the dark in the laboratory for 14 days at 20 ± 4 , C and a soil moisture of approx. 75% of the water holding capacity at 1/3 bar:

				6
Soil	Source 🖓	Texture (USDA)	₽H	OC ¹ [%]
Iowa (EFS115)	Jowa, KSA	Agamy sand	" <i>@</i> .2	1.1
Indiana (EFS117)	Andiana, USA 😽	Sandy Joam	6.4	0.8
Nebraska (EFS118)	Nebraska, USA	siht loam 🖉	² 7.7	1.0
		×		

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

The study application rate was 25 μ 50 g soil (div weight) (\triangleq 05 ppm), equal to 0.5 mg FOEthiadone/kg soil (dry weight).

Duplicate test systems were processed and analyzed 0, (a).25, 1, (2), 3, 5, 7 and 10 days after treatment (loamy sand); 0, 0.5, (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 bram).

Overall mean material belance was 95.7% of applied radioactivity (% AR) for soil Iowa, 96.4% AR for soil Indiane and 94.9% AR for soil vebraska.

The following maximum amounts of carbox 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 40% AR at all sampling intervals in all soils.

Extractable desidues 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 at soil Nebraska.

Non-extractable residues (NFR) 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 FOP-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

MATERIALS AND M I.

MATERIALS A.

1. **Test Item**

≙ 0.**29**4

The soils (Table 7.1.1.1-3) were sampled from the field and signed to a particle size of ≤ 2 mm. The soils were taken from agricultural areas representing dufferent geographical origins and different soil

PTB06 130(10.8 MBq0rg, 97.7% Wete sampled from the field and s, cultural areas representing different ge the guidelines.



Table 7.1.2.1.2- 19	Physico-chemical	l properties of test soils
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Parameter		Results / Units	Ô
Soil Designation	Iowa (EFS115)	Indiana (EFS117)	Nebraska (EFS118)
Geographic Location		25	
City	Janesville	Howe	Minden
State	Iowa	Indiana	0 Nebraska
Country	USA	USA S	O ^V USA
Soil Taxonomic Classification	Two soils in close	🖉 loam skeletst.	Coly silt loam:
(USDA)	proximity:	mixed mesic Kypic	fine-sifty, mixed ^o
	1. sandy, mixed	Waplustolls	(calcareous), mesic
	mesic Entic ⊘ Hapludoll\$		Typic Ustor hents
			2. Kenesaw silt
	2. coarse-Joamy, 🍣		loam: coarse-silty,
	mixed, mesic Typic	V V N	mixed mesic Typic
	Hapludolls		Haplustolls
Soil Series		no information available	12- 12-
Textural Class (USDA)	Noamy sand	sandy loan	silt loam
Sand [%] $[50 \ \mu m - 2 \ mm]$			25.6
Silt [%] $[2 \mu m - 50 \mu m]$	× 12.0 ×		55.6
Clay [%] [< 2 μm]	8.8		18.8
pH	ð Ö v	× 6.50	7.7
Organic Carbon [%] Organic Matter [%] ¹			1.0 1.66
Cation Exchange Capacity	5.64	215.12	6.44
[meq/100 g]			0.11
Water Holding Capacity	V Q Q	<u> </u>	
at 15 bar	4.06	3.87	9.16
at 0.3 bar (pF 2.9) [%]	5 9.9Q	13.27	24.19
Bulk Density (disturbed) [g/cm2]	0 1 34 ~~	1.62	1.37
Microbial Biomass 🖓 🛛 🔍			
[cfu/g] ² DAT-0 (fungi / Bacteria)	$3\sqrt[3]{8} \times 10^4 / 02 \times 10^7$	4.8 x 10 ⁴ / 9.1 x 10 ⁶	$1.0 \ge 10^5 / 1.0 \ge 10^7$
			$1.0 \times 10^{5} / 1.0 \times 10^{7}$ $1.1 \times 10^{5} / 6.0 \times 10^{7}$
		2.8 X 10 / 1.2 X 10	1.1 X 10 / 0.0 X 10
¹ calculated as: $OM[\%] = OC[\%] \cdot 1.724$	Ť, ĴŢ		
2 cfu = celony forming unikater g of soil	, W		
DAT: days after treatment?	UNITED States Dep	artment of Agriculture	
 ² cfu = Colony forming uni@per g of soil DAT. Mays after the atment DW: dry weight B. STUDY DESIGN Or 	USDA: United States Dep		
B. STUDA 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 μ g/50 g soil (dry weight) ($\triangleq 0.5$ 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/acres = 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 $\frac{1}{2}$ /v). 100 µL of the application solution were applied drop wise onto the soil surface of the respective test system using a gas-tight syringe. After application the test vessels were connected to the flow through system (except DA CO samples).

The test systems were incubated under aerobic conditions in the dark for 14 days at $20^{4} \pm 1^{\circ}$ C and a soil moisture of approx. 75% of the water holding capacity at 73 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 et soil samples the each of the three soils:

Iowa (EFS115): 0, 0.25, 1, 2, 3, 5, 7 and 0 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, 4, 5, 0 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 doxide were changed and analyzed at DAT-0.25, 0.5, 1, 2, 3, 4, 5, 7 and 10. The traps for carbon doxide were changed and analyzed at DAT-0.25, 4 and 10. Microbal soil bromass was determined at DAT-0 and DAT-10.

Nebraska (EFS118): DAT-0, 4, 2, 3, 0, 7, 10 and 14, Duplicates were analyzed for the following time points: DAT-0, 1, 3, 3 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. Metrobial soil biomass was determined at DAT-0 and DAT-14.

3. Analytical Procedures

At each sampling interval, the softs were extracted at ambient temperature using acetonitrile (1 x) and acetonitrile/water with 0.1 N HCl (1 x \cdot :1, v/v). After each extraction step, supernatant and soil were separated by diltration. The cridic 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 HPPC/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. and BT₉₀ values were calculated from the resulting kinetic parameters.

П. **RESULTS AND DISCUSSIO**

EXTRACTION AND QUANTITATION OF RADIOACTIVISTY A.

Table 7.1.2.1.2- 20 to Table 7.1.2.1.2- 22 summarizes the degradation of thiadiazole CIFOEthiadone 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 Lowa under Aerobic Conditions (expressed as percent of applied radioactivity; single values)

	\sim	¥)°	"O"	
		Å.		D A		, 	1	
Compound		0.25	۶1 ¹		ر می	5	7	10
FOE-thiadone	× 983	812	57 5	36.6	¥26.6	\$ 46 .1	8.9	6.6
FOE-thiadone propionic acid conjugate	n.d.	°≪}¥.3	Ċs	100	7, 3	3.1	1.2	0.1
Reg #1 ²	ک ۵.6	0.7 @	0.3	Q.d.	n.d.	0.2	n.d.	n.d.
Reg #4 ²	Q.P	1.3	0.9	1.0 🔊	≫1.8	1.4	1.5	0.9
Unid./Diff. Radioactivit	3.0	2.3	2.3	2.6	1.5	2.0	3.2	2.0
	% 102.6	86.8	6 8.7	50.4	37.4	22.8	14.8	9.6
Carbon dioxide	n:a	2,0	13.2	27.2	36.6	48.9	57.0	63.2
Volatile Organi@ompomads	Qn.a.	na.	pr.s.	n.a.	1.9	1.9	1.9	2.3
Non-extractable Residues	Š 1.1 (7.3	12.9	14.9	19.7	19.7	20.1	19.5
Material Balance & &	163,7	96.Q	95.5	92.5	95.6	93.3	93.8	94.6
	<u> </u>	Ś				-	-	-

n.d.: not detected

n.a.: not analyz

DAT: days after treatment

¹ Mean values of duplicates

- rorutication impublies 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)

0.1				AT .	"O		
0 ¹	0.5 ¹	11	2	3 ^L	[∀] 5 ¹ ≈	°7	L10
94.8	69.1	54.3	29.0	167		4.6	3.0
n.d.	0.8	4.1	。7.0	4 .9	°6	ŋ.đ	0,4
0.5	n.d.	n	n.d.		¥ 0.6 م	Q0.3	n.d.
1.6	1.3	₹¥.4	, Ô	1.8	1.80	1.5	1.8
2.1	2.1	2.5 🔬	3.1	©ł.4	L.	3.4	1,300
99.0	7 ® 3	62:30	40.4	25.1	16.8	¢9.8	<u>B</u> Ž
n.a. 🏿	Q13.9	27.5	\$03	59.1	69.	76.9	82.1
n.a.	n.a.	n.a. /	h.a.	Å¥.0	ź.	3.0	4.0
26	5Q	6.9U	7.4	/ 8.2 🎓	8.4	9Ì3	7.6
¥99.6	§93.1	90.7	984	95.P	97.3	97.0	99.9
	n.d. 0.5 1.6 2.1 99.0 n.a. n.a.	n.d. 0.8 0.5 n.d. 1.6 1.3 2.1 2.1 99.0 703 n.a. 13.9 n.a. 13.9 0.6 50 99.6 93.1	n.d. 0.8 4.1 0.5 n.d. n.g. 1.6 1.3 1.4 2.1 2.1 2.5 × 99.0 7 3 62.3 n.a. 13.9 21.5 n.a. 13.9 21.5 n.a. 13.9 21.5 9.6 5 4 9.0	n.d. 0.8 4.1 7.0 0.5 n.d. n.g. n.d. 1.6 1.3 4 03 2.1 2.1 2.5 3.1 99.0 703 62:3 40.4 n.a. 13.9 21.5 50.3 n.a. 13.9 21.5 50.3 n.a. 1.3 1.4 9.4 99.0 703 62:3 40.4 n.a. 13.9 21.5 50.3 n.a. 13.9 21.5 50.3 n.a. 1.3 1.4 9.4	n.d. 0.8 4.1 7.0 4.9 0.5 n.d. n.d. n.d. 0.3 1.6 1.3 1.4 03 1.8 2.1 2.1 2.5 3.1 1.4 99.0 703 623 40.4 25.1 n.a. 13.9 27.5 503 59.1 n.a. 13.9 27.5 503 59.1 n.a. 1.3 1.4 34.0 35.0 0.6 50 6.9 7.4 8.2 99.6 93.1 90.7 98.4 95.4	n.d. 0.8 4.1 7.0 4.9 2.6 0.5 n.d. $n.d.$ $n.d.$ 0.3 0.6 1.6 1.3 4.4 0.3 1.80 2.1 2.1 2.5 3.1 0.4 29 99.0 7.03 62.3 40.4 25.1 16.8 $n.a.$ 13.9 21.5 50.3 59.1° 69.7 $n.a.$ $n.a.$ $n.a.$ $n.a.$ 9.6 59.1° 69.7 9.6 59.1 69.7 98.4 95.4° 97.3°	n.d. 0.8 4.1 7.0 4.9 2.6 \mathbf{n} d 0.5 n.d. \mathbf{n} d \mathbf{n} d 0.3 0.6 0.3 1.6 1.3 1.4 0.3 1.8 1.8 1.5 2.1 2.1 2.1 2.5 3.1 0.4 2.9 3.4 99.0 703 623 40.4 25.1 16.8 9.8 $\mathbf{n.a.}$ $1.3.9$ 21.5 50.3 59.1 69.5 76.9 $\mathbf{n.a.}$ $\mathbf{n.a.}$ $\mathbf{n.a.}$ $\mathbf{n.a.}$ $\mathbf{n.a.}$ 3.0 3.0 0.6 50 6.9 7.4 8.2 8.4 23 99.6 93.1 99.7 98.4 95.4 97.3 97.0

n.a.: not analyzed

¹ Mean values of duplicates

² Fortification impurities

³ All individual areas of radioactivity - were tess than 2% of the applied radioactivity

 Table 7.1.2.1.2-22:
 Degratation of OE-thindone in Soil Nebraska under Aerobic Conditions (expressed as percent of applied radioactivity; single values)

	Ň							
Compound		R	Å,	DA	٩T			
Compound	0 ¹	² 1 ¹	≫ ₂	3 ¹	5 ¹	7 ¹	10	14
FOE-thiadouc 🖉 🖉	23.5	79	62.7	52.2	28.9	16.2	7.7	3.3
FOE-thiadone proponic aco conjugate	@0.2	×¥.3	1.1	1.0	0.7	0.2	n.d.	n.d.
$\operatorname{Reg} \#1^2$ if is a constant of the second secon	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./Ditt Radioa Givity &	Ô0.7	1.6	1.4	1.1	1.4	1.8	1.7	1.9
Total Extractable Residue	97.0	84.0	66.4	54.9	31.5	18.9	10.1	5.5
Carlon dioxide	n.a.	8.1	18.9	27.7	43.9	56.1	66.0	71.8
Volatile organic Compound	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 0

n.d.: not detected

DAT: days after treatment

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 Nebrasa (overall mean 94.9% AR), see also Table 7.1.2.1.2-20 to Table 7.1.2.1.2-20.

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 of was lost during processing of theses samples.

C. EXTRACTABLE AND NON-EXTRACTABLE RESIDUES

Extractable residues decreased steadily from 102.6% AR at DAT to 9.6% AR at DAT 10 in soil Iowa, from 99.0% AR at DAT-0 to 6.2% AR at DAT-10 soil Indiana and from 7.0% R at DAT-0 to 5.5% AR at DAT-14 in soil Nebraska.

The formation of non-extractable residues (NER) increased from KJ% AR@t DAT-0 to 20.1% AR at DAT-7 and slightly decreased to 19.5% AR at DAT-10 fr soil from 0.6% AR at DAT-0 to 8.4% AR at DAT-5 and slightly decreased 7.6% AR at DAT-10. In soil Nebraska NER increased from 1.4% AR at DOT-0 to 4.7% AR from DAT-7 shwards. 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 dexide 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 33% AR in soil Nebrasta. See also Table 7.1.2.1.2- 20 to Table 7.1.2.1.2- 22 for details.

E. DEGRADATION OF TEST OF M

The amount of FOFOhiadoke 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-0 163.3% 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 radioa@ivity.abounted to a maximum of 2% AR at each sampling interval and for each soft.

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



conditions for trigger evaluation

Soil [d] Coefficient (R ²) Iowa 2.5 0.9512 Indiana 2.0 0.9490 Nebraska 2.8 0.9671		DT50	Correlation	
Indiana 2.0 0.9490 7	Soil	[d]	Coefficient (R ²)	á é
	Iowa	2.5	0.9512	A. V
Nebraska 2.8 0.9971	Indiana	2.0	0.9490 × ×	
	Nebraska	2.8	× 0.9971 ×	L.

Flufenacet

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

III. CONCUSION

[thiadiazole-2-¹⁴C]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% AROIN soil Iowa, 80.1% AR in soil Indiana and 71.8% AR in soil Nebraska.

Besides carbon dioxide, one degradation product was identified. OE-thadone 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 Nebrasta. 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 FOT-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 201% 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 of the environment.

Report: (KCA %).2.1.2 (04; 100 , N.; 2012	
Title: $\sqrt[3]{9}$ [1-14C]triflug@acetate? Aerobic Degradation in Four European Soils	
Report No: 5 EnSa-12-0393	
Document No ² M-43928 ² -01-1	
Guidelines Guideline No. 307	
مَنْ سَعْنَ US CPA QC PP Test Guidelines 835.4100	
GLP: yes y i	

Executive Summary

The degradation of $J^{-14}C$]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	<i>Q</i> 23	5.5
Laacherhof Wurmwiese	Monheim, Germany	sandy loam	5 .1	。 1.9
Hoefchen am Hohenseh	Burscheid, Germany	silt loam 🔊	6.4	24
		é.Y		0

¹ in 0.01 M CaCl₂

The study application rate was 20.0 μ g/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, 4, 28, 43, 59, 52 and 20 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, 1000% AR for soil Laacherhof Wormwiese and 101.2% AR for soil Hoefchen am Hohenseh.

Volatiles were detected with amounts $\leq 0.4\%$ AR a every campling 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 $\leq 3\%$ AR at every sampling interval in all four soils.

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

The degradation data were kinetically evaluated according to $OCUS (2005)^2$ 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

A. **ATERIALS AND METHODS**

A. MATERIALS

1.

Test Item [1-14C] trifluoroacetate (sodium salt; report name ¹: trifluoroacetic acid) CAS No Specificactivity Radiochemical purity Solution CAS No Specificactivity Specificac

2. Test Solls

The soils (Table 7 (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: P	hysico-chemical properties of test soils
-----------------------	--

Parameter	Results / Units							
Soil Designation	Laacherhof	Dollendorf II	Laachedrof	Hoefchen am				
	AXXa		Wurmwiese	'Høhenseh				
Geographic Location			D' O	O' (?				
City	Monheim	Blankenheim	Monheim	Burscheid				
State	North-	North-Rhime °	Nørth-Rhine	North-Rhine				
	Rhine	Westphalia	Westphalia	Westphalia				
Country	Westphalia Germany		Germany	Germany				
Country		Germany 📎						
GPS Coordinates	N 51° 04.65'	₩\$0° 22 \$0'	N 51° @586' ∅ E 006 [®] 55.25' ℃	D [®] N 51 [®] 04.01' E 00 ^{9®} 06.33'				
	E 006°	£ 006° 40.00'						
	53.52'		4 4	Ű				
Soil Taxonomic Classification	sandy	fine-loamy,	& Poamy, mixed,	Joamy, mixed,				
(USDA)	mixed	mixed, active,	mesio Typic	mesic Typic				
	mesic Fypic Cambudoll (, frigid⊘fypic ≪	Argudalf	Argudalf				
Soil Series	Canlibudion	Eutwidept	ation available					
				.17.1				
Textural Class (USDA)	sandy loam	clay loam	sand Joam	silt loam				
Sand [%] $[50 \ \mu m - 2 \ mm]$ Silt [%] $[2 \ \mu m - 50 \ \mu m]$	Č,		~~~57	25				
Silt [%] $[2 \ \mu m - 50 \ \mu m]$ Clay [%] $[< 2 \ \mu m]$			26 Ô	60				
		× 31	17	15				
pH - in CaCl ₂ (soil/CaCl ₂ 1/2)	Č		¥ 5.1	C A				
- in CaCl ₂ (soil/CaCl ₂ 1/2)			5.1	6.4				
- in water (saturated paste)	6.5	0 7 1.3	5.4	6.7				
- in KCl		0 7.40°	5.2	6.5				
			4.7	6.1				
Organic Carbon [%]		, 5.5	1.9	2.4				
Cation Exchange Capacity	$0^{-2.8}$	مربع 9.5 هر	3.3	4.1				
[meq/100 g]	8.7 (21.2	10.0	13.6				
Water Holding Capacity	L Ö	7						
maximum [g H ₂ O <i>ad</i> 100 g son DW] & at 0.33 bar (pF 2.0[%] O	4.69 [°]	84.9	57.6	62.0				
at 0.33 bar (pF 2.)[%]	,12 <u>2</u> 2	34.9	18.2	26.3				
	<u></u> ⊘¶.26	0.97	1.13	1.08				
Microbial Biomass [mg microbial carbon / kg sair DW] ² DAT-0	OY							
[mg microbiat carbon 7 kg soit DW] 2		2020	400	022				
		2930	423	833				
DAT-59	589	3344	459	844				
DAT-120	248	1412	424	387				
le la								

¹ calculated as: OM [%] = OC [%] \cdot 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 $55 \pm 5\%$ 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 μ g/100 g soil (dry weight), equal to 0.2 mg/kg soil (dry weight). The actual SAR was 20.9 μ g/100 g soil dry weight), equal to 0.2 mg trifluoroacetate/kg soil (dry weight).

The application solution was prepared in water. 1000 μ L 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 (secept 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 $55 \pm 5\%$ 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 acetonitrite/water (1:1, v/v) at 70 °C. After each extraction step, supernatant and soft were separated by centrifugation and decantation.

Soil extracts were characterized by fiquid sontillation 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 fiquid scintillation counting and combustion/liquid scintillation counting and combustion/liquid scintillation counting.

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% PLC 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 (SFØ), 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 co² scaled error criterion and on the basis of a visual assessment of the goodness of the fits (dragrams of measured and calculated values vs. time, diagrams of residuals vsQtime).

II. RESULTS AND DISCUSSION

A. EXTRACTION AND QUANTITATION OF RADIOACTIVIT VIN SOIL SAMPLES

Table 7.1.2.1.2- 25 to Table 7.1.2.1.2-58 summarizes the degradation of [1-14] trifluoroacetate and the formation and degradation of its degradation products as a function of time?

	A- 8	\bigcirc " \checkmark		
Table 7 1 2 1 2- 25	Degradation of Gifluor a	acetic acid in soil	Laacherhof A'	XXX under aerobic conditions
	(expressed as percent of an	nlied	v: meansvalue ø	sf dunlicates)
	(expressed as percent of ap	price radioucu vi	y, means and p	(auplicates)

			~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~	- 					
			~~		DAT				
Compound	Q°0	O3	ã.	_@ 14	~28	43	59	92	120
replicate A		^{\$} 99.8	100.9	999.9	97.7	100.2	101.3	101.7	98.0
trifluoroacetic acid ¹ Oreplicate B		996	100Q	100	97.3	99.6	101.3	101.0	99.2
mem	<b>97</b> .7	<b>99</b> .7	100.5	1400.2	97.5	99.9	101.3	101.4	98.6
Unid./Diff. Radioactivity	م n.d.	n.d.	n.d.	Øn.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Total Extractable Residues	979	997	100(5)	100.2	97.5	99.9	101.3	101.4	98.6
Carbon dioxide	n.a.	60.1	¢ 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1
Volatile Organic Compounds		≫<0.1	$\mathbb{Q}_{0.1}$	< 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 20 0	<b>98</b> .2	<b>Ì100.4</b>	101.3	101.0	98.2	100.9	102.1	102.1	99.4

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

¹ single values of replicates and mean values of duplicates

 2  Material balances AT-0 Free 98.4% AR for replicate A and 98.1% AR for replicate B

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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)

						DAT		<u></u>		
Compound	d	0	3	7	14	28	43	🎽 59 🦳	° 92 🦼	<b>120</b>
trifluoroacetic acid ¹	replicate A	98.5	98.6	100.5	99.4	96.0	98	100,5	100.3	96.
	replicate B	98.3	101.0	99.9	99.5	°96.7	<b>6</b> 99.6	<b>9</b> 9.5	100.2	96.8
	mean	98.4	99.8	100.2	99.4 ^C	96.4	⁷ 99.4	¥100.0	0100.2×	96.4
Unid./Diff. Radioactivi	ty	n.d.	n.d.	n.d.	n.el.	n d.	n.d/	n.đØ	n.d.	n.d.
Total Extractable Resid	lues	98.4	99.8	100.2	@99.4	96.4	<i>1</i> <b>99</b> .4	100.0	100.2	26.4
Carbon dioxide		n.a.	< 0.1	< 0,0	< 0.	°<0.1⊘	< 0.1	₹0.1 (	×0.1	Ø.1
Volatile Organic Compounds		n.a.	< 0.1	<u>O</u> I	×01	≪ØÌ	< 0.1	< 6	< 0	°<0.1
Non-extractable Residues		1.3	1.2 🦋	1.3	Q1.3	,×¶.4	<b>€</b> ¥.7	<b>1</b> 8	J.7	2.0
Material Balance ²		99.7	101.00	101.Q	100.8	97.8 🖗	√101. <b>Þ</b>	, 101.8	901.9	98.5

² Material balances at DAT-0 were 99.8% AR for replicates Table 7.1.2.1.2- 27: Degradation of the case of the ca 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)

	A			* *	n 1/				
Compound Compound		[©] з		© 14	DAT 28	43	59	92	120
Compound 🖉		•		Q	$\mathcal{D}_{\mu}^{\mu}$	10	07	/-	120
		990	99,Q	99.@	96.3	99.9	100.6	100.0	97.0
trifluoroacetic acid ¹ replicate B		.5	<b>99</b> .8	<b>28</b> 8	95.5	99.4	98.9	99.3	98.2
	م 98.7°	99.7	99.7	₂ ,99.2	95.9	99.6	99.7	99.7	97.6
Unid./Diff. Radroactivity	n	n.d	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Total Extractable Residues	98.7	<b>99</b> .7	Ø9.7	99.2	95.9	99.6	99.7	99.7	97.6
Carbon dioxide	y n.a. /		©¥0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1
Volatile Organic Compounds	n.e	< 0.00	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1
Non-extractable Residues	ð.0	N.	1.0	1.0	1.1	1.2	1.2	1.1	1.3
Material Balance	0 <b>99.7</b> (	100.9	100.8	100.3	97.0	100.9	100.9	100.8	99.0
		2							

n.d.: not detected, n.a.: not analyzed, DAT, brys after treatment ¹ single values of repricates and mean values of duplicates

² Material balance at DAT were 99.5% AR for replicate A and 99.9% AR for replicate B

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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)

			_	_		DAT	(	Ű	_	-
Compound	l	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	¥00.6 _%	Ø01.0	<b>T0</b> 1.7	<b>398</b> .7
	mean	99.1	100.7	100.7	100-0	97_0	100.5	101 TC	102,1	98.3
Unid./Diff. Radioactivit	ty.	n.d.	n.d.	n.d.	n.d.	, Q.	ritsd.	n.0.	n d.	n.d.
Total Extractable Resid	ues	99.2	100.7	100.7	Z100.0×	97.0	¥00.5	Ĵ01.7	Q02.1	×98.3
Carbon dioxide		n.a.	< 0.1	< 00	< 0 1	<0,0	< 0.0	) < 0.1	< 0.1	× < 0.1
Volatile Organic Compounds		n.a.	0.1	.O.1	Â.Ă	<b>≤0</b> .1	< 0.1	<@1	<	< 0.1
Non-extractable Residues		0.9	1.0 🦋	¢ 1.0 €		×1.1		<b>1</b> .3	¥.3	1.2
Material Balance ²		100.1	101.8	101:8	101.00	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 puplicates?

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 irom was determined at DAT-0 before, during and after the application and was set to 100% AR for all samples. The totaOradioaCrivity 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 101.0% AR in soil Dollendorf II (overall mean 100.5% AR, RSD 1.4%), from 97.0 to 100.9% AR in soil Gaacherbor Wurphwiese (overall mean 100.0% AR, RSD 1.2%) and from 98.2 to 103.4% AR in soil Hoefonen am Hohenseh (overall mean 101.2% AR, RSD 1.6%), see also Vable 7.1.2.1.2-2%.

The complete material balance found at all sampling intervals (mean of duplicates) in all soils demonstrated that no significant fortion obradioactivity dissipated from the vessels or was lost during processing of these 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  $\leq 2\%$  AR at every sampling interval in all four soils. Seconds Table 7.1.2.1.2-25 to Table 7.1.2.1.2-28 for details.

# D. VOLATILIZATION

Volatiles were detected with amounts  $\leq 0.1\%$  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- 29 for details.

The chi² error values of the fits of all investigated kinetic models were  $\leq 1.2$  and the visual essence to the second 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 chi² error value.

The half-lives for trifluoroacetic acid were > 1000 days in all soils under agrobic conditions in the dark in the laboratory. ×1

Table 7.1.2.1.2- 29:	Best-fit degradation kinetics of	triflugrøa	cetic acid	in soils	underae	robicconditions	for
	trigger evaluation according to	FOEUS	, Ô	, C	Ű.		

88			n , v		
Soil (Soil Type)	Kinetic Model ¹	DT ₅₀	BT ₉₀	chi ² error	Visual Assessment ²
(Soil Type)	Model		~"[d]	{ (t 76]	⁴⁰ Assessment ²
Laacherhof AXXa (sandy loam)	SFO	م مجمع 1000 رو محمد المحمد ال	> 1000		~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~
Dollendorf II (clay loam)	SFO	>40900	>1000		\$ +
Laacherhof Wurmwiese (sandy loam)	SFO	پ پ ۱۵۵۵۶	, > 1 <b>90</b> 0		+
Hoefchen am Hohenseh (silt loam)	SFO		× → > 10060	× 07.0	+
		9 4			

¹ SFO = single first order; DF $\Phi P$  = double first order in parallel

² Visual assessme

C [1-14C]trifluoroacetere (report name: trifluoroacetic acid) was virtually not degraded in soil under aerobic conditions in the dark in the laboratory doning the incubation time of 120 days.

No significant amounts of volatiles of non-expactable residues were formed during the study course.

The calculated half lives of trifluor acetic acid were > 1000 days in all soils. 

****



Report:	KCA 7.1.2.1.2 /05; , N.; 2012	
Title:	[1- ¹⁴ C]trifluoroacetate: Concentration Dependen	t Mineralization Under Aerobic
	Conditions	
<b>Report No:</b>	EnSa-12-0445	
<b>Document No:</b>	M-441101-01-1	
<b>Guidelines:</b>	<ul> <li>OECD Test Guideline No. 307</li> </ul>	
	• US EPA OCSPP Test Guidelines 835.4100	Ø, Ø A X
GLP:	yes ô	

# **Executive Summary**

The concentration dependent mineralization of [1-14C] trifluor acetate (report name trifluor acetic acid) was investigated in four soils under aerobic conditions in the dark in the aboratory for  $\mathbb{C}20$  days at 20.0 °C and a soil moisture of  $55 \pm 5\%$  of the maximum water holding capacity:

	·	A north		
Soil	Source N	Texture (USDA)	ph 1	<b>9</b> C [%]
Laacherhof AXXa	Monhein Germany	sandy loam	≽ 6.2 (	1.6
Dollendorf II	Blankenheim, Germany	🔊 clastyloam 🖉	7.3	5.5
Laacherhof Wurmwiese	Monferim, Geomany	sandy loam	5	1.9
Hoefchen am Hohenseh	Burcheid, Germany	🔬 silt loam	<u>6</u> 24	2.4
			$\mathcal{O}_{\mathcal{O}}$	

¹ in 0.01 M CaCl₂

Three study application rates were tested

- 20.0 μg/100 g soil (dry weight), equal to 0.2 mg trifhuoroacetate/kg soil (dry weight)
- $1.0 \ \mu g/100 \ g \ soit dry \ weight)$ , equal to  $0.91 \ mg \ ffluor ga cetate/kg \ soil (dry \ weight)$
- 0.1 μg/100 g Soil (dry weight) equal φ 0.00 long trif@oroacetate/kg soil (dry weight)

For each study application rate duplicate with systems were analyzed for the amount of carbon dioxide 30, 59 and 120 days after treatment.

No significant mineralization ( $\geq 1\%$  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 solls.

**PRIALS AND METHODS** 

A. MATERIALS

1.

Text Item[1-14C]trifluoroaceta@ (sodium salt; report name 1: trifluoroacetic acid)CAS No2923-18-4Specific activity3.48 MBq/mgRadiochemical 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  $\leq 2$  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: P	Physico-chemical properties of test soils
-----------------------	-------------------------------------------

AXXaWurnwieseHøhensehGeographic LocationMonheimBlankenheimMonheimCityMonheimBlankenheimMørth-RhineBursohoidStateNorth- RhineNorth-RhineMørth-RhineMørth-RhineCountryGermanyGermanyGermanyGermanyGPS CoordinatesN 51° (04.65')N 51° (04.65')N 51° (06° 42.00')N 51° (06° 42.00')N 51° (06° 42.00')	Parameter		Results / Units				
$ \begin{array}{c c c c c c c c c c c c c c c c c c c $	Soil Designation		Dollendorf II		Hoefchen am Høhenseh		
State     North-Rhine Westphalia Germany     North-Rhine Westphalia Mester Germany     North-Rhine Wester Ger	Geographic Location			ð, O	O" Q		
$\begin{tabular}{ c c c c c c c c c c c c c c c c c c c$	City	Monheim	Blankenheim	Monheim	A Burschoid		
Country         Westphalia Germany         Germany         Germany <td>State</td> <td>North-</td> <td></td> <td></td> <td>North-Rhine</td>	State	North-			North-Rhine		
$\begin{array}{ c c c c c c c c c c c c c c c c c c c$			Westphali	Westphalia	Westphalia		
GPS Coordinates         N 51° 04.65' E 006° 53.52'         N 51° 04.65' E 006° 53.52'         N 51° 006° 63.00' E 006° 53.52'         N 51° 04.6' E 006° 63.00' E 006° 53.52'         N 51° 04.6' E 006° 63.00' E 006° 53.52'           Soil Taxonomic Classification (USDA)         sandy mixed, mesic Typic Caribudoll E 006° 53.52'         file-loams firigid 3ypic Caribudoll E 006° 53.52'         file-loams mesic Typic Caribudoll E 006° 53.57'         file-loams mesic Typic Caribudoll E 006° 57.5'         file 6.0           Soil Series         0         no informatico available'         file 6.5'         file 6	Country	-			ÖC anna an fa		
$ \begin{array}{c c c c c c c c c c c c c c c c c c c $	•	-					
$\begin{array}{ c c c c c c c c c c c c c c c c c c c$	GPS Coordinates		$22,80^{\circ}$	N 51° (24)86' (27) Ø E 006 (255 25' )	E 069 06 33'		
$\begin{array}{ c c c c c c c c c c c c c c c c c c c$							
$ \begin{array}{c c c c c c c c c c c c c c c c c c c $		53.52'			Ũ		
mesic Pypic Cambudoll         frigid Pypic Euffidept         Argudalf         Argudalf           Soil Series         no information available         no information available         sandy loam         silt loam           Textural Class (USDA)         sandy loam         clay loam         sandy loam         sandy loam         sandy loam         silt loam           Sand [%]         [50 µm - 2 µm]         47         29         57         25           Silt [%]         [2 µm - 50 µm]         44         40         26         60           Clay [%]         [<2 µm]		sandy			Moamy, mixed,		
Cambudoll         Eufendept         Sold           Soil Series         no information available           Textural Class (USDA)         sandy, form         clay login         sandy form         silt loam           Sand [%] $[50  \mu\text{m} - 2  \text{mm}]$ $47$ $29$ $577$ $25$ Silt [%] $[2  \mu\text{m} - 50  \mu\text{m}]$ $44$ $400$ $26$ $60$ Clay [%] $[< 2  \mu\text{m}]$ $9$ $31$ $177$ $15$ pH         -         in CaCl ₂ (soil/CaCl ₂ 1/2) $62$ $7.3$ $5.1$ $6.4$ - in water (soil/water 1/4) $6.5$ $7.5$ $5.4$ $6.7$ - in water (sourated paste) $6.3$ $7.4$ $5.2$ $6.5$ - in kCl $47$ $4.7$ $6.1$ $07$ $2.4$ Organic Carbon [%] $2.8$ $9.5$ $3.3$ $4.1$ Cation Exchange Cenacity $84$ $9.5$ $3.3$ $4.1$ Cation Exchange Cenacity $84$ $9.5$ $3.3$ $4.1$ Gato .33 par (pF 2.5) [%] <td>(USDA)</td> <td>mixed</td> <td></td> <td></td> <td></td>	(USDA)	mixed					
Soil Series         no information available           Textural Class (USDA)         sandy loam         sandy loam         sandy loam         silt loam           Sand [%]         [50 $\mu$ m - 2 mm]         29         57         25           Silt [%]         [2 $\mu$ m - 50 $\mu$ m]         14         40         26         60           Clay [%]         [<2 $\mu$ m]         9         31         17         15           pH         - in CaCl ₂ (soil/CaCl ₂ 1/2)         6.5         7.5         5.4         6.7           - in water (soil/water 1/h)         6.3         7.4         5.2         6.5         6.5           - in KCl         6.3         7.4         5.2         6.5         6.5         6.5           - in KCl         6.4         7.4         5.2         6.5         6.5         6.5         6.5         7.5         5.4         6.7           - in kCl         6.3         7.4         5.2         6.5         6.5         7.6         6.1           Organic Carbon [%]         1.6         5.5         1.9         2.4         0.33         4.1           Cation Exchange Canacity         2.8         9.5         3.3         4.1         0.0         13.6		Cambudoll	Eugendent	Avgudalf	Argudali		
Textural Class (USDA)       sandy Joan       clay learn       sandy Joan       sandy Joan       sandy Joan       silt loam         Sand [%] $[50 \ \mu\text{m} - 2 \ \text{mm}]$ $29$ $57$ $25$ Silt [%] $[2 \ \mu\text{m} - 50 \ \mu\text{m}]$ $9$ $31$ $17$ $15$ pH $14$ $40$ $26$ $60$ r in CaCl ₂ (soil/CaCl ₂ 1/2) $9$ $31$ $17$ $15$ pH $6.5$ $7.5$ $5.4$ $6.7$ r in water (saturated paste) $6.3$ $7.4$ $5.2$ $6.5$ r in KCl $6.3$ $7.4$ $5.2$ $6.5$ organic Carbon [%] $2.8$ $9.5$ $3.3$ $4.1$ Organic Matter [%] $2.8$ $9.5$ $3.3$ $4.1$ Cation Exchange Canacity $2.8$ $9.5$ $3.3$ $4.1$ Matter Holding Canacity $4.6$ $84.9$ $57.6$ $62.0$ at 0.33 bar (pF 2.0 [%] $1.26$ $0.97$ $1.13$ $1.08$ Microbrial Biomass       [ma microbria Carbon / kg sait DW] $642$ $3145$ $5$	Soil Series						
Sand [%]       [50 µm - 2 mm]       29       57       25         Silt [%] $[2 µm - 50 µm]$ 9 $31$ 17       15         pH       - in CaCl ₂ (soil/CaCl ₂ 1/2)       9 $31$ 17       15         in water (soil/water 1/h)       6.5       7.5       5.4       6.7         - in water (soil/water 1/h)       6.5       7.5       5.4       6.7         - in water (soil/water 1/h)       6.3       7.4       5.2       6.5         - in water (soil/water 1/h)       6.3       7.4       5.2       6.5         - in water (soil/water 1/h)       6.5       7.5       1.9       2.4         Organic Carbon [%]       1.6       5.5       1.9       2.4         Organic Matter [%]       2.8       9.5       3.3       4.1         Cation Exchange Caracity       9       2.8       9.5       3.3       4.1         Cation Exchange Caracity       9       2.8       9.5       3.3       4.1         Water Holding Caracity       2       2.8       9.5       3.3       4.1         Image: Caracity       2       2.8       9.5       3.3       4.1         Water Holding Caracity       2		Candy logm			silt loam		
Silt [%] $[2 \ \mu m - 50 \ \mu m]$ $44$ $40$ $26$ $60$ Clay [%] $[< 2 \ \mu m]$ $9$ $31$ $17$ $15$ pH       -       in CaCl ₂ (soil/CaCl ₂ 1/2) $6.5$ $7.5$ $5.1$ $6.4$ - in water (soil/water 1/h) $6.5$ $7.5$ $5.4$ $6.7$ - in water (soil/water 1/h) $6.3$ $7.4$ $5.2$ $6.5$ - in water (soil/water 1/h) $6.3$ $7.4$ $5.2$ $6.5$ - in water (soil/water 1/h) $6.3$ $7.4$ $5.2$ $6.5$ - in KCl $6.9$ $7.4$ $5.2$ $6.5$ - in KCl $6.9$ $7.4$ $5.2$ $6.5$ - or Korl $2.8$ $9.5$ $3.3$ $4.1$ Organic Carbon [%] $1.6$ $5.5$ $1.9$ $2.4$ Organic Matter [%] $2.8$ $9.5$ $3.3$ $4.1$ Cation Exchange Caracity $7.4$ $84.9$ $57.6$ $62.0$ at 0.33 bar (pF 2.0 [%] $122$ $34.9$ $18.2$ $26.3$ <tr< td=""><td>Sand [%] $[50  \mu m - 2  mm]$</td><td></td><td></td><td></td><td></td></tr<>	Sand [%] $[50  \mu m - 2  mm]$						
Clay [%]       [< 2 $\mu$ m]       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 1/4)       6.5       7.5       5.4       6.7         - in water (soil/water 1/4)       6.5       7.4       5.2       6.5         - in water (soil/water 1/4)       6.3       7.4       5.2       6.5         - in water (soil/cacl ₂ 1/2)       6.3       7.4       5.2       6.5         - in water (soil/water 1/4)       6.3       7.4       5.2       6.5         - in water (soil/water 1/4)       6.3       7.4       5.2       6.5         - in KCl       6.9       7.4       5.2       6.5         Organic Carbon [%]       16       5.5       1.9       2.4         Organic Matter [%] ¹ 2.8       9.5       3.3       4.1         Cation Exchange Canacity       8       9.5       3.3       4.1         Water Holding Qapacity       4.66       84.9       57.6       62.0         at 0.33 bar (pF 2.0 [%]       12.2       34.9       18.2       26.3         Bulk Definity (disturbed) (g/cm³]       4.26       0.97       1.13 <td></td> <td>\$14 C</td> <td></td> <td></td> <td></td>		\$14 C					
pH       - in CaCl ₂ (soil/CaCl ₂ 1/2)       62       3       5.1       6.4         - in water (soil/water 1/h)       6.5       7.5       5.4       6.7         - in water (soil/water 1/h)       6.3       7.4       5.2       6.5         - in water (soil/water 1/h)       6.3       7.4       5.2       6.5         - in water (soil/water 1/h)       6.3       7.4       5.2       6.5         - in KCl       6.4       7.4       5.2       6.5         Organic Carbon [%]       7.4       5.5       1.9       2.4         Organic Matter [%] ¹ 2.8       9.5       3.3       4.1         Cation Exchange Caracity       8       21.2       10.0       13.6         Water Holding Qapacity       4.65       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/cm ³ ]       4.26       0.97       1.13       1.08         Microbial Biomass       642       3145       598       1016							
- in CaCl ₂ (soil/CaCl ₂ 1/2)       62 $3.3$ $5.1$ $6.4$ - in water (soil/water 1/b) $6.5$ $7.5$ $5.4$ $6.7$ - in water (saturated paste) $6.3$ $7.4$ $5.2$ $6.5$ - in KCl $6.3$ $7.4$ $5.2$ $6.5$ - in KCl $6.3$ $7.4$ $5.2$ $6.5$ - organic Carbon [%] $1.6$ $5.5$ $1.9$ $2.4$ Organic Matter $4^{1/6}$ $2.8$ $9.5$ $3.3$ $4.1$ Cation Exchange Capacity $7.4$ $8.4.9$ $57.6$ $62.0$ Imaximum $9.5$ $3.3$ $4.1$ $1.6$ $5.5$ $1.9$ $2.4$ Water Holding Capacity $8.4.9$ $57.6$ $62.0$ $1.22$ $34.9$ $18.2$ $26.3$ Bulk Datisity (disturbed) $4.6$ (cm ³ ] $0.26$ $0.97$ $1.13$ $1.08$ $1016$ Microbial Biomass $642$ $3145$ $598$ $1016$					15		
- in water (saturated paste)       6.3       7.4       5.2       6.5         - in KCl       6.9       7.4       4.7       6.1         Organic Carbon [%]       7.6       5.5       1.9       2.4         Organic Matter [%]       7.4       9.5       3.3       4.1         Cation Exchange Capacity       8.7       21.2       10.0       13.6         Water Holding Capacity       8.7       21.2       10.0       13.6         Water Holding Capacity       4.65       84.9       57.6       62.0         at 0.33 bar (pF 2.0 [%]       12.2       34.9       18.2       26.3         Bulk Density (disturbed) (g/cm ³ ]       01.26       0.97       1.13       1.08         Microbial Biomass       642       3145       598       1016	- in CaCl ₂ (soil/CaCl ₂ 1/2)	Î Â		۶ 51	64		
- in water (saturated paste)       6.3       7.4       5.2       6.5         - in KCl       6.9       7.4       4.7       6.1         Organic Carbon [%]       7.6       5.5       1.9       2.4         Organic Matter [%]       7.4       9.5       3.3       4.1         Cation Exchange Capacity       8.7       21.2       10.0       13.6         Water Holding Capacity       8.7       21.2       10.0       13.6         Water Holding Capacity       4.65       84.9       57.6       62.0         at 0.33 bar (pF 2.0 [%]       12.2       34.9       18.2       26.3         Bulk Density (disturbed) (g/cm ³ ]       01.26       0.97       1.13       1.08         Microbial Biomass       642       3145       598       1016	- in water (soil/water 1/1)	65	Ø75 Å				
- in KCl       4.7       6.1         Organic Carbon [%]       1.6       5.5       1.9       2.4         Organic Matter [%]       2.8       9.5       3.3       4.1         Cation Exchange Capacity       8       21.2       10.0       13.6         Water Holding Capacity       8       21.2       10.0       13.6         Water Holding Capacity       4.65       84.9       57.6       62.0         at 0.33 bar (pF 2.5) [%]       1.26       0.97       1.13       1.08         Microbial Biomass       642       3145       598       1016	- in water (saturated paste)		740				
Organic Carbon [%]       0.6       5.5       1.9       2.4         Organic Matter [%]       2.8       9.5       3.3       4.1         Cation Exchange Caracity       8.7       21.2       10.0       13.6         Water Holding Caracity       8.7       21.2       10.0       13.6         Water Holding Caracity       9.5       3.3       4.1         [g H ₂ O active Caracity       9.5       64.0       84.9       57.6       62.0         at 0.33 bar (pF 2.6) [%]       12/2       34.9       18.2       26.3         Bulk Density (disturbed) [g/cm³]       01.26       0.97       1.13       1.08         Microbial Biomass       642       3145       598       1016		69	S B				
Organic Matter $[\%]^1$ 2.8       9.5       3.3       4.1         Cation Exchange Capacity       21.2       10.0       13.6         Water Holding Capacity       4.6       84.9       57.6       62.0         maximum       4.6       84.9       57.6       62.0         at 0.33 bar (pF 2.0) $[\%]$ 4.60       84.9       18.2       26.3         Bulk Density (disturbed) $[g/cm^3]$ 41.26       0.97       1.13       1.08         Microbial Biomass       642       3145       598       1016	Organic Carbon [%]	<u> </u>	- 55				
[meq/100 g]       21.2       10.0       13.6         Water Holding Capacity       4.69       84.9       57.6       62.0         maximum       4.69       84.9       57.6       62.0         at 0.33 bar (pF 2.5)[%]       4.69       84.9       18.2       26.3         Bulk Density (disturbed) [g/cm³]       4.26       0.97       1.13       1.08         Microbial Biomass       642       3145       598       1016		2.8~					
Imed/100 g]       Imed/100 g]       Imed/100 g]       Imed/100 g]         Water Holding Capacity       Imed/100 g]       Imed/100 g]       Imed/100 g]         maximum       Imed/100 g soil DW]       Imed/100 g]       Imed/100 g]       Imed/100 g]         [g H ₂ O ad 100 g soil DW]       Imed/100 g]       Imed/100 g]       Imed/100 g]       Imed/100 g]         [g H ₂ O ad 100 g soil DW]       Imed/100 g]       Imed/100 g]       Imed/100 g]       Imed/100 g]         Bulk Density (disturbed) g/cm ³ ]       Imed/1.26       Imed/100 g]       Imed/1.26       Imed/100 g]         Microbial Biomass       Imed/100 g soil DW]       Imed/1.26       Imed/1.26       Imed/1.26       Imed/1.26         DAT-0       Imed/100 g soil DW]       Imed/1.26		8.7	21.2	10.0	13.6		
maximum			4				
Bulk Density (disturbed) [g/cm³]01.260.971.131.08Microbial Biomass [mg microbial carbon / kg soil DW]64231455981016		Ű,					
Bulk Density (disturbed) [g/cm³]01.260.971.131.08Microbial Biomass [mg microbial carbon kg soil DW]64231455981016	$[g H_2O ad 00 g soil DW] \& $	4.69	84.9	57.6	62.0		
Bulk Density (disturbed) [g/cm³]01.260.971.131.08Microbial Biomass [mg microbial carbon / kg soil DW]64231455981016	at 0.33 bar (pF 2.0 [%]	12×2	34.9	18.2	26.3		
Microbial Biomass [mg microbial carbon / kg seit DW] DAT-0 642 3145 598 1016	Bulk Density (disturbed) fg/cm ³ ]		0.97	1.13	1.08		
DAT-0 4 642 3145 598 1016		0 [×]					
DA1-0 042 5145 570 1010	[mg microbiał carbon 7 kg soit DW]	¥ .					
DAT-59 A 484 2798 316 696							
DAT-120 323 1931 173 499	DAT-120	323	1931	173	499		

¹ calculated as: OM [%] = OC [%]  $\cdot$  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 most ure was adjusted to  $55 \pm 5\%$  maximum water holding capacity by addition of de-ionized water. The untreated test systems were equilibrated to study conditions for approx. Adays (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  $\mu$ g/100 g soil (dry weight), equal to 0.2 mg trifluoroacetate/kg soil (dry weight). For the avestigation of a concentration dependency of mineralization two lower doses were tested in addition? 1.0 mg/100 g soil (dry weight), equal to 0.01 mg trifluoroacetate/kg soil (dry weight) and 0.1 mg/100 g soil (dry weight), equal to 0.001 mg trifluoroacetate/kg soil (dry weight).

The application solutions were prepared in water. P000 µC of the espective application solutions were applied drop wise onto the soil surface of the respective test systems using a proette. After application the test vessels were closed with the trap attachments.

The test systems were incubated under actionic conditions in the dark for 1/20 days at 20.0 °C and soil moisture of  $55 \pm 5\%$  of the maximum water holding capacity in awalk 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 reatment. At DACO the priount 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.

### **FIL AT RESULTS AND DISCUSSION**

### A. EXTRACTION AND QUANTITATION OF RADIOACTIVITY IN SOIL SAMPLES

Table 7.1.2.1.2- 31 for 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	<u>"</u> W
			20.0 µg			1.0 µg	° 0.1 4g
Compound (Rep	licate)	DAT-30	DAT-59	DAT-120	DAT-30	DAT-59	DAT 20 DAT 30 DAP-59 DAT-120
Carbon dioxide	А	0.0061	0.0073	0.0074	0.0093	0.0085	0.123
	В	0.0062	0.0074	0.0072	0.0060		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
 Conditions

				- X	- N	SÂR	60	- OF	Ś	
			20.0 µg		, Ŷ	.Q.0 µg	× ĉ	r '0'	0.1 μg	
Compound (Rep	olicate)	DAT-30	DAT-59	Ø <b>∳</b> T-120	DAT-30	DAT-59	DAT%120	DAC-30	DAT-59	DAT-120
Carbon diavida	А	0.0067	0.0075Q	0.0072	0.0139	0:101	<b>©</b> 425	Q9.042	0.227	0.230
Carbon dioxide	В	0.0068	0.0079	0.0076	0.0196	@?0153 ~	0.0158	0.006	0.048	0.129
				st i		Ĉi O	) 🔊			

DAT: days after treatment

# Table 7.1.2.1.2- 33: Mineralization of trifluoreacetic acid in Soil Laacherhof Wurmwiese under Aerobic Conditions (expressed as percent@i applie@radioactivity; mean value of duplicates)

2		20,0 µg	Red E		∕у́А́R √_1.0 µg			0.1 μg	
Compound (Replicat	e) DAT-30	<b>DAT-59</b>	<b>D</b> ĂT-120	DAT-30	DAT-59	DAT-120	DAT-30	DAT-59	DAT-120
Carbon diavid	. 0.0064	0.0072	0.0083	0.0076	0.0134	0.0155	0.039	0.017	0.348
Carbon dioxid	Q 0.00Q	0.0076	0.0080	0.0065	0.0123	0.0194	0	0.045	0.095
L		Ø	Ů.	4					

DAT: days after togatment

# Table 7.1.2.1.2- 34: Mineralization of trifluoroacetic acid in Soil Hoefchen am Hohenseh under Aerobic Conditions (expressed & percent of applied radioactivity; mean value of duplicates)

						SAR				
₩°	A	D'	2000 μg			1.0 µg			0.1 μg	
Compound (Rep	licate)	DAT-30	DAT-59	DAT-120	DAT-30	DAT-59	DAT-120	DAT-30	DAT-59	DAT-120
Carbon dioxide	A A	, 0.0068	0.0074	0.0070	0.0769	0.0115	0.0202	0.115	0.087	0.154
Carbon dioxide	BO	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  $\leq 1\%$  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. CONCLUSTONS

No significant mineralization ( $\geq$  1% of applied radioactivity [%AR]) of the set item [1-¹⁴C]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; , G.; , K.; 2014
Title:	Trigger evaluation for the Degradation of Flutenacet Degradation Product
	FOE oxalate under Acrobic Soil Conditions In Laboratory According to FOCUS
	Kinetics Using the KinG 2 Tool is in the second s
<b>Report No:</b>	EnSa-13-1009
<b>Document No:</b>	M-478440-0161
Guidelines:	• FOCUS kinetics (2006, 201) ^{3,4} $@$
GLP:	no 🔬 🖉 🖉 🗞 🌾

#### **Executive Summary**

A kinetic analysis of residue data from two aerobic sor degradation studies M-002166-01-1(Baseline Dossier, KCA 7.1.2, Q/01) and M-002146-00-1 (Baseline Dossier, KCA 7.1.2.1.1/03) was performed with the software KinGUL according to FOCUS kinetics (2006, 2011)^{3,4} to derive half-lives for FOE oxalate, a degradation product of fufenacet, which are suitable for trigger evaluation.

Single first order (SFO) was the mast appropriate kinetic model to describe the degradation of FOE oxalate for trigger evaluation in the four tested soils ( $1 \times \text{loamy sand}$ ,  $2 \times \text{silt loam}$ ,  $1 \times \text{sandy loam}$ ) under aerobic conditions in the tark in the laboratory at  $20 \pm 2$  °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 fives of FOE evaluate for trigger evaluation were 11.9, 13.4, and 23.4 days (all  $20 \pm 1$  °C, 40% MWHC), and 19.6 days (2)  $\pm 1$  °C, 75% FC at 1/3 bar).

### **METHODS**

Soil residue data from the two activities 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 exalate was studied in a total of four soils ( $1 \times$  loamy sand,  $2 \times$  silt loam,  $1 \times$  sandy loam) under aerobic conditions in the dark in the laboratory at  $20 \pm 2$  °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 decovery 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  $\times$  LOD. If they became < kOD / 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 D. Thereafter (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 produce if this data point was  $\neq$ DAT-0, it was included in the fit by setting values  $\int LOD \delta n$  non-detected (n/d.) to  $0.5 \times LOD$ . Values between LOD and LOQ were set to the measured values of the decline phase of a degradation product all single values < LOD or non-detected (n.d.) were set to 0.5  $\times$  LOD JOThey became  $\Rightarrow$  LOD / n.d. for a second time the curve was cut off until a subsequent value  $\Rightarrow$  LOQ occurred  $\Rightarrow$ 

The most appropriate kinetic model was selected on the basks of a detailed statistical analysis including visual assessment of the goomess of the fits, thi2-scaled error criterion, t-test significance, correlation analysis and standard demation Kinetic parameters of FOE or alate degradation were derived based on the pathway fits (flufenacet and POE oxalate) using the best-fit kinetics selected from the parent only fits.

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 kibetic analysis for the trigger evaluation.

Soil	Kinetic Model ¹	DT ₅₀	DT [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	F@MC*-SPØ	¢1.9	39.6	23.3	< 0.001	+
Laacherhof AIII	SOMC*/SFO	23.4	77.7	16.0	< 0.001	+
Hoefchen im Tab ⁶	SFQ*-SFO	13.4	44.5	10.4	< 0.001	+

#### Table 7.1.2.1.2-35: Kinetic parameters for the degradation of KOE oxalate in soil under aerobic conditions , for trigger evaluation according to FOCUS

¹ SFO/FOMC-SFO: single first order / first order multi-compartment (parent - flufenacet)* - single first order (FOE oxalate) ² visual assessment: good

³ sandy form, 21 + 1 °C, 75% FC 1/3 bar (KCA 1.2.1.1/01)

Cut-off of the soil residue data after DAT-20 due to collapse of the microbial activity

⁴ loamy sand  $20 \pm 1$  °C, 40% MWHC (KCA 1.2.1.1/03) ⁵ silt loam, 20 \pm 1 °C 40% MWHC (KCA 1.2.1.1/03) ⁶ silt loam, 20 \pm 1 °C 40% MWHC (KCA 7.1.2.1.1/03 ⁸ kinetic parameters of FOE oxalate degradation were derived based on the pathway fit using the best-fit kinetics selected from the parameters of FOE oxalate degradation were derived based on the pathway fit using the best-fit kinetics selected from the parameters of FOE oxalate degradation were derived based on the pathway fit using the best-fit kinetics selected from the parameters of FOE oxalate degradation were derived based on the pathway fit using the best-fit kinetics selected from the parameters of FOE oxalate degradation were derived based on the pathway fit using the best-fit kinetics selected from the parameters of FOE oxalate degradation were derived based on the pathway fit using the best-fit kinetics selected from the pathway fit using the best-fit kinetics selected from the pathway fit using the best-fit kinetics selected from the pathway fit using the best-fit kinetics selected from the pathway fit using the best-fit kinetics selected from the pathway fit using the best-fit kinetics selected from the pathway fit using the best-fit kinetics selected from the pathway fit using the best-fit kinetics selected from the pathway fit using the best-fit kinetics selected from the pathway fit using the best-fit kinetics selected from the pathway fit using the best-fit kinetics selected from the pathway fit using the best-fit kinetics selected from the pathway fit using the best-fit kinetics selected from the pathway fit using the best-fit kinetics selected from the pathway fit using the best-fit kinetics selected from the pathway fit using the best-fit kinetics selected from the pathway fit using the best-fit kinetics selected from the pathway fit using the best-fit kinetics selected from the pathway fit using the best-fit kinetics selected from the pathway fit using the pathway fit using the pathway fit using the best-fit kinetics selected from from the parent only fite



#### **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 fluf bacet and its major degradation products in soil given in section CA 7.1.2.1.

*****

Report:	KCA 7.1.2.1.2 /12; , G.; , K; 2014 , C.
Title:	Trigger evaluation for the Degradation of flutenaced Degradation Product FOE
	5043-trifluoroethanesulfonic acidoinder Aerobic Soil Conditions in Laboratory
	According to FOCUS Kinetics Using the KinGOI 2 Tool
<b>Report No:</b>	EnSa-13-1010
<b>Document No:</b>	EnSa-13-1010 M-478444-01-1
Guidelines:	• FOCUS kinetics $(2006 \gtrsim 011)^3 \ll \qquad $
GLP:	no X X X V

#### **Executive Summary**

A kinetic analysis of residue data from two aerobic of degradation studies M-439105-02-1 (Supplemental Dossier, KCA 7.1.2.1.1/05) and M440348-02-1 (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 FOF 5043 diffuore than esultonic acid, a degradation product of flufenacet, which are suitable for trigger evaluation.

Single first order (SFQ) was the most appropriate kinetic model to describe the degradation of FOE 5043-trifluoroethanesulforic acid for the trigger evaluation in three of the four tested soils (silt loam, loamy sand, clay loam) under perobic conditions in the dark in the laboratory at  $20 \pm 2$  °C and soil moisture of  $55 \pm 5\%$  of the maximum water fielding capacity (MWHC) - for one soil no valid half-life could be derived for FQE 5043-trifluoroethanesulfonic acid.

The calculated half-lives of FOE 504 Orifluor ethanesal fonic acid for trigger evaluation were 9.1, 4.5 and 22.5 days¹¹.

### METHODS

Soil residue data from the two accobic soil degradation studies M-439105-02-1 (Supplemental Dossier, KCA 7.1,21.1,05) and 07440348-02-1 (Supplemental Dossier, KCA 7.1,2.1,1,06) were used. In these studies, the degradation of POE 5043-trifluoroethanesulfonic acid was studied in a total of four soils (silt loan, loam, sand, clay loam, loam) under aerobic conditions in the dark in the laboratory at  $20 \pm 2$  % and soll moistures of  $55 \pm 5\%$  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 koretic 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 wergeset to the measured values. All single values < LOD or non-detected (n.d.) were set to  $0.5 \times \text{LOD}_{\bullet}$  (1) they became < LOD / n.d. for a second time the curve was cut off until a subsequent value  $> LOQ_{0}curred$ .

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 boint was  $\neq$ DAT-0, it was included in the fit by setting values < LOD or non-detected (n.d.) to 0.5 x OD. 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, tagest significance, correlation analysis and standard deviation? Kinetic parameters of FOE Gxalate degradation were derived based on the pathway fits (flufenacet and FOE 5043-tratuoroethanesultanic acid) using the best-fit kinetics selected from the parent only fits.

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 offour tested soils under aerobic conditions -from one soil no valid Galf-life could be derived. Table 7.1.2.1.2- 36 summarizes the results of the kinetic analysis for the trigger evaluation.

RESULTS

Table 7.1.2.1.2- 36: Kinetic parameters for the degradation of KOE 5043-trifluoroethanesulfonic acid in soil under probic conditions for trigger evaluation according to FOCUS

Soil V L	Kinetic DT ₅₀	DTS [days]	chi ² error [%]	t-test	Visual Assessment ²
Hoefchen Am Hohenseh ³	()SFO* <b>-</b> SEFO (€ 9.1	30.2	5.8	< 0.001	+
Laacherhof AXXa	SFQ*SFO 4.5	14.9	18.3	< 0.001	0
Dollendorf II	SFO*-SFQ 22.5	74.7	24.1	0.004	+
Laacherhof Warmwiege	& - ⁸ & ,_0*	- 8	- 8	_ 8	- 8

¹ SFO-SFO single first order parent - flufenacet single first order (FOE 5043-trifluoroethanesulfonic acid)

² visual assessment; + = good, o = m dium/acceptable ³ silt loam, 19.2  $\times$  0,1 °C, 55% MWOC (KCAO.1.2.1.1/05)

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 BDE 5043-trifluoroethanesulfonic acid degradation were derived based on the pathway fit using the best-fit kinetics selected from the parent only fits.

⁴ loamy sand  $49.8 \pm 0.2$  °C, 55% WHC (FCA 7.1.2.1.1 /06) ⁵ clay loam, 19.8  $\pm 0.2$  °C, 55% WHC (FCA 7.1.2.1.1 /06) ⁶ sandy loam, 19.8  $\pm 0.2$  °C, 55% MWHC (KCA 7.1.2.1.1 /06)



#### 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 flucenacet and its not of degradation products in soil given in section CA 7.1.2.1.

Report:	KCA 7.1.2.1.2 /14; , G.; , S.; 2014
Title:	Kinetic Evaluation of the Degradation of phenyl-UL-14C Optenace and its
	Degradation Products under Aerobic Soil Conditions in Laboratory According
	to FOCUS Kinetics Using the RinGUL Tool
<b>Report No:</b>	EnSa-12-0575
<b>Document No:</b>	M-477878-01-1
<b>Guidelines:</b>	• FOCUS kinetics $(2006, 2011)^{3, 4}$
GLP:	no Á Ó Ó Ó Ó Ó

#### **Executive Summary**

A kinetic analysis of soil residue data from three aerobie 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, 2014) ^{3, 4} to derive Galf-lives for flufenacet and its degradation products FOE exalate 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 909592-01-1 (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 laboratory at  $20 \pm 2$  C and soil moistures ranging from 40% of the maximum water holding capacity (MWHC) (75% of the field capacity (FC) at 1/3 bar.

The calculated half-lives of FOF oxalate were 6.9 days, 20.7 days, 13.1 days (all  $20 \pm 1$  °C, 40% MWHC) and 49.4 days (21  $\pm 1$  °C, 5% FC, at 1/3 bar). The formation fractions of FOE oxalate formed from Hufenacet were calculated as 0.448, 0.375, 0.350 (all  $20 \pm 1$  °C, 40% MWHC) and 0.484 (21  $\pm 1$  °C, 75% FO at 1/3 bar).

For FQE sulfonic acid no reliable half-lives could be derived from the soil residue data. However, the formation fractions for FOE cultonic acid formed from flufenacet could be determined for all of the tested soils and were calculated as 0.257, 0.259, 0.143 (all  $20 \pm 1$  °C, 40% MWHC) and 0.108 ( $21 \pm 1$  °C, 75% FC at 0.3 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  $20 \pm 1$  °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  $\times$  loamy stand, 2  $\times$  silt loam, 1  $\times$ sandy loam) under aerobic conditions in the dark in the laboratory at 20, 2°C and soit moistures 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 mput 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 (n,d) thereafter values < LQP 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  $\neq$  DAT-0, it was included in the fit by setting values < LOD or non-detected (n.d.) to  $0.5 \times LOD$ . Values between LOD and LOQ were set to the measured values. In the decline phase of a degradation produce all single value LOD for non-detected (n.d.) were set to  $0.5 \times \text{LOD}$ . 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 Bactions were calculated from the resulting kinetic parameters.

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 dested soils. Table 7.1.2.1.2-37 to Table 7.1.2.1.2- 39 summarizes the results of the kinetic analysis.

RESULTS

Table 7.1.2.1.2- 37:	Kinetic parameters for	degradation of FØE	oxalate in soils und	er aerobic conditions for
		William to FOCUS	C ¹	
	modeung purpose acco	raing to FUCUS	~~	

Soil	Å,	FF	Kinetic Medel ¹		[°] chi ² error [%]	t-test	Visual
TT T 1' Å	<u></u>			V days		0.017	Assessment ²
Howe, Indiana	2	· · · ·	SFO SFO	19.4	6.2	0.017	+
BBA 2.2.7	5	0.448	SFO - SFO	6.9	25.2	0.006	0
Laacherhot AII		0.375	SFO - SFO	‱20.7	13.1	<< 0.001	0
Hoefchen im Ta	116 V	0.350	SFO-SFO	13.1	10.6	<< 0.001	+
EE formation fraction	y n from	A Stand		/			

FF formation fraction from thufenacet

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

¹ SFO-SFO: single first order (parent) – single first order (degradation product)
² visual assessment: + good file = acceptible fit 0
³ sandy loam, 21 ± 1 0, 75% the field apacity av1/3 bar (KCA 7.1.2.1.1/01)
⁴ loamy sand, 20 ± 0 °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 ± 0 °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

					<u> (78</u>	1
Soil	FF	Kinetic Model ¹	DT50	chi ² error	t-test	Visual
			[days]	[%]	~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~	• Assessment ²
Howe, Indiana ³	0.108	SFO - SFO	> 1000	6.3	$\sim$ n.a. ^{a)}	0 ⁴ Ø
BBA 2.2 ⁴	0.257	SFO - SFO	> 1000	15.4	0.500	+
Laacherhof AIII 5	0.259	SFO - SFO	> 1000	。 9.5 <u> </u>	0,590	+
Hoefchen im Tal ⁶	0.143	SFO - SFO	> 1000	Õ 6.6 ^V	A. a. a)	D″ 、 松
FF formation fraction from ¹ SFO-SFO: single first on ² visual assessment: $+ = g$ ³ sandy loam, $21 \pm 1$ °C, $7$ ⁴ loamy sand, $20 \pm 1$ °C, $40\%$ ⁶ silt loam, $20 \pm 1$ °C, $40\%$ ^{a)} n.a. = not available; not	rder (parent) ood fit 75% of the f 40% MWHC 6 MWHC (1 6 MWHC (1	ield capacity at 1/3 bar (KCA 7.1.2.1.1/03) (KCA 7.1.2.1.1/03) (KCA 7.1.2.1.1/03)	(KCQ7.1.2.10			

Table 7.1.2.1.2- 39: Kinetic parameters for degradation of For methylsulfone in soils under aerobic conditions for modeling purpose according to FOCUS Ż

Soil	FF	KinetieModel	DC50 [days]	Chi ² errory	t-fest	Visual Assessment ²
BBA 2.2 ³	0.061	sFO - SFO	≥ 1000	24,8	<b>≫</b> 0.500	+
Laacherhof AIII ⁴	0.087	SFO SFO	/ 02 ₁ /%	~₩ <b>5</b> .4 ⇔	0.005	+
Hoefchen im Tal ⁵	0.051	SFO-SFO	>1000	٢ 16.1	0.500	+

FF formation fraction from flutenacet

Ungle first order (degradation prod ¹ SFO-SFO: single first order (parent)

² visual assessment: + = good fit³ loamy sand,  $20 \pm 1$  °C, 40% MWHC (KCA) ⁴ silt loam,  $20 \pm 1$  °C, 40% MWHC (KCA)

⁵ silt loam,  $20 \pm 1$  °

### **CONCLUSIONS**

The calculated half-lives of FOE scalate for modeling purpose in soil under aerobic conditions in the dark in the laboratory ranged from 6.9 6 20.7 days in the tested soils. The formation fractions of FOE oxalate formed from Qufenacet ranged from \$350 to 0.484.

For FOE sulfonig acid no reliable half-lives could be derived from the soil residue data. However, the formation fractions for COE sulfonic and formed from flufenacet could be determined for all of the tested soils and ranged from @708 to @2596.

The half-life of FOE methylsulfore for modeling purpose in soil under aerobic conditions in the dark in the laborator 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.



2014-03-19

Report:	KCA 7.1.2.1.2 /16; , G.; , 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
<b>Report No:</b>	EnSa-12-0580
<b>Document No:</b>	EnSa-12-0580 M-477844-01-1
Guidelines:	• FOCUS kinetics (2006, 11) ^{3,4}
GLP:	no Or A Or A

### **Document MCA: Section 7 Fate and behaviour in the environment Flufenacet**

#### **Executive Summary**

A kinetic analysis of soil residue data from two aetobic soil degradation budies  $5^{-004008-01-2}$  (Baseline Dossier, KCA 7.1.2.1.2 /01) and M-011445-01-1 Supplemental Dossier, KCA 7.1.2.1.2 /08) was performed with the software Kin $5^{\circ}$ UI 2 according to FOCUS kinoics (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 to the dark in the laboratory at  $20 \pm 2$  °C and soil moistures ranging from 29% to 44% of the maximum water holding capacity (MWHC).

The calculated half-lives of FOE sulfable acid were 258.4 days ( $20 \pm 2$  °C, 31% MWHC,), 180.8 days ( $20 \pm 2$  °C, 29% MWHC), 234.9 days ( $20 \pm 2$  °C, 44% MWHC), 623 days and 60.3 days (both  $20 \pm 2$  °C, 40% MWHC).

# SI. OMETHODS

Soil residue data from the perobic soil degradation studies M-004098-01-2 (Baseline Dossier, KCA 7.1.2.1.2 /01) and M-11445-015 (Supplemental Dossier, KCA 7.1.2.1.2 /08) were used. In these studies, the degradation of FOR sulfonic acid was studied in a total of five soils ( $1 \times$  sand,  $1 \times$  loamy sand,  $2 \times$  silt loam,  $1 \otimes$  sandy loam) under aerobic conditions in the dark in the laboratory at  $20 \pm 2$  °C and soil moisture ranging from 29% MWHQ 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  $\neq$  double first order sequential) and double first order parallel (DFOP). Model input datasets were the residual abounts 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  $0.5 \times LOD$ . If they became < LOD / n.d. for a second time the curve was cut off until a subsequent value  $\gg LOQ$  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, chic scaled error criterion, thest significance, correlation analysis and standard deviation. The DT₅₀ 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	DT50	chi ² error	t-test	Visual		
5011	Model ¹	[days]	[%]	i-cesi	Assessment ²		
BBA 2.1 ³	SFO	258.4	4.38	<u> </u>	O' + Q		
BBA 2.2 ⁴	SFO	180.8	4.64	0.001			
Laacherhof AIII ⁵	SFO	234.9	11.24	<i>U</i> <≪0,001 ,			
Laacherhof AXXa ⁶	SFO	62.3	<u>©</u> .05	<ul><li>&lt;</li><li>Ø.001</li></ul>			
Laacherhof AIII ⁷	SFO	60.3	3.03	€ 100.0 € ي	×*+		
¹ SFO: single first order ² visual assessment: $+ = gooderightarrow good$	'HC (KCA 7.1.2.1.2 % MWHC (KCA 7. MWHC (KCA 7.1.2 % MWHC (KCA 7.1.2 % MWHC (KCA 7.1.2 MWHC (KCA 7.1.2	1.2.1.2 /01) 1.2.1.2 /01) 1.2.1.2 /02) 1.2.2.2 /02) 1.2.2.2 /02) 1.2.2.2 /02) 1.2.2.2 /02) 1.2.2.2 /02) 1.2.2.2 /01) 1.2.2.2 /01) 1.2.2.2 /01) 1.2.2.2 /01) 1.2.2.2 /02) 1.2.2 /01) 1.2.2.2 /02) 1.2.2 /01) 1.2.2.2 /02) 1.2.2 /02)	S C 4				
The calculated half-live aerobic conditions in th	es for modeling	purpor for the oratory ranged f	degradation of F rom 60.3 to 358.	OE suffonic aci 4 days in the tes	d in soil under ted soils.		
The results are included degradation products in				of flufenacet	and its major		
Report: K							
Title:	netic Evaluation	of the Degradati	ion of Plufenace	Degradation Pr	oduct FOE		
	methy sulfone under Aerobic Spil Conditions in Laboratory According to						
s 🖗 FC	CUS Kinetics U	storg the KanGU	L2 Tool				
	Sa-12,0578		Ø ?				

Executive Summary

Document No:

Guidelines: GLP:

-477839-01-1

DCUS kingtics (2006, 11)&

A kinetic analysis of soil residue data from the aerobic soil degradation study M-443658-01-1 (Supplemental Dossier & CA 7.1.2.1.2.06) was performed with the software KinGUI 2 according to FOCUS kinetics (2006, 2015)^{24, 4} to derive half-lives of FOE methylsulfone, which are suitable for modeling purpose

O

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  $20 \pm 2$  °C and soil moisture of  $55 \pm 5\%$  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  $20 \pm 2$  °C,  $55 \pm 5\%$  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 methyls of the 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  $20 \pm 2$  °C and soil moisture of  $55 \pm 5\%$  MWHC.

The kinetic analysis was performed according to FOCUS kinetics  $(2006/2011)^{0/4}$  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 methylsultone 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 poodness 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  $0.5 \times LOD$ . If they became < LOP/ 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.

### ⁶⁹11. ⁶⁹ RESULTS ⁵

The single first order (SFO) kinetic model was used for modeling prose 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.

	Kinetic parameters for degradation of FOE methyls afone in soil under aerobic
Table 7 1 2 1 2_ 41.	Kinetic meaneters for degradation of FOR methyls fore in soil under aerobic
1 abit /.1.2.1.2- 41.	Kinetic parameters for degradation of FOE freehydratone in son under actobie
	conditions for modeling purpose according to FOCUS
	conductors for innotening part pose according to rec. 05

Soil &		DT 50 Jayo	chizerror	t-test	Visual Assessment ²
Laacherhof AXXa ³	SFO SFO	43,1	3.4	<< 0.001	+
Dollendorf II	SFQ	3.3	3.0	<< 0.001	+
Hoefchen an Hohensch ⁵	SFO	¥3.8	3.6	<< 0.001	+
Laacherhof Wurneviese 6	SFO (	_≫ ^y 96 ₃ 2 y	3.3	<< 0.001	+

¹ SFO: single first order ² visual assessment: + wood ³ loamy sand ⁴ loam ⁵ silt loam ⁶ sandy loam ⁶ sandy loam ⁷ J

The calculated harf-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.



2014-03-19

# **Document MCA: Section 7 Fate and behaviour in the environment Flufenacet**

Report:	KCA 7.1.2.1.2 /15; , G.; , 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
<b>Report No:</b>	EnSa-12-0579
<b>Document No:</b>	M-477840-01-1
<b>Guidelines:</b>	• FOCUS kinetics (2006, 11) 3,4
GLP:	no or of the second sec

#### **Executive Summary**

A kinetic analysis of soil residue data from the actobic soil degradation study  $M^2009828-01-1$  (Supplemental Dossier, KCA 7.1.2.1.2 /03) was performed with the coftware KinGU 2 according to FOCUS kinetics (2006, 2011)^{3,4} to derive half-lives of FOE thiadone, which are solvable 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  $20 \pm 1$  °C and soil moisture of 75% of the field capacity (FC) at 15 bar.

The calculated half-lives of FOE-thiadone were 2.0, 4 and 2.9 days (all 200 1 °C, 75% FC at 1/3 bar).

### [©]I. _ℳ 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 FOF-zhiadone was studied in a total of three soils (loamy sand, sandy load, silt loam) under aerobic conditions in the dark in the laboratory at  $20 \pm 1$  °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 kinetie models: single first order (SFO), first order multi-compartment (FOMC), hockey stick (MS, DROS = 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 in orval. 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 EOD 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 > LOQoccurred. 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 (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	
Indiana ⁵	SFO	1.4	5.7	<001 ×	
Nebraska ⁶	SFO	2.9	3.7	0.001	20 S

¹SFO: single first order

² worst case assumption; sum of residue values of FOE-thiadone and thiadon popionic acid con 

³ visual assessment: o = acceptable

⁴ loamy sand

⁵ sandy loam

⁶ silt loam

Ш.

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 suppriary of the degradation rates of florenacet and its major degradation products in soil in the laboratory given in section CA 7 2

Report:	KCA 7, 2.1.2, 13; , G., G., S.; 2014
Title:	Kinetie Evaluation of the Degradation of [thiathazole-5-14C] flufenacet and its
	Degradation Products under Rerobie Soil Conditions in Laboratory According
	to OCUS Kinetics Using the KinOUI 2 JCol
<b>Report No:</b>	EnSa-12-0577
Document No:	M-477835-017 & 5 5
Guidelines:	• FOCUS kinetics (2006, 11) $3^4$
GLP:	$\begin{array}{cccccccccccccccccccccccccccccccccccc$
E C	

**Executive Summary** 

A kinetic analysis of stil residue data from two aerobic soil degradation studies M-439105-02-1 (Supplemental Dospier, KCA 7 (2.1.1 (5)) and M-440348-01-1 (Supplemental Dossier, KCA 7.1.2.0.1 /06) was performed with the software KinGUI 2 according to FOCUS kinetics (2006, 2011)^{3,} ⁴/₄to derive half-lives for flufenacet and its degradation products FOE-thiadone, FOE 5043trifluoroethanesulfonic 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. Ň

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  $20 \pm 2$  °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  $\pm$  0.1 °C, 55% MWHC), 1.4 days, 2.8 days and 2.0 days (all 19.8  $\pm$  0.2 °C, 55% MWHC). The formation fractions of FOE-thiadone formed from flufenacet were calculated as  $0.913 (19.7 \pm 0.1 \text{ °C}, 55\% \text{ MWHC}), 0.524, 0.438 \text{ and } 0.405$ (all 19.8 ± 0.2 °C, 55% MWHC).



The calculated half-lives of FOE 5043-trifluoroethanesulfonic acid were 9.1 days ( $19.7 \pm 0.1 \text{ °C}$ , 55% MWHC), 4.5 days, 22.5 days¹² and 7.6 days¹² (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 ( $19.7 \pm 0.1 \text{ °C}$ , 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 tall 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 0.8 ± 0.2 °C, 55% MWHC).

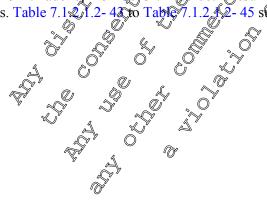
### I. METHODS

Soil residue data from the aerobic soil degradation, studies M-439,05-02, (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 (sur loant, loany sand, clay loam and loam) under aerobic conditions in the dark in the laboratory at 20  $\pm$  °C and soil moisture of 55% MWHC (for details see Table 7.1.2.1.2.43, Table 7.1.2.1.2.45 below).

The kinetic analysis was performed according to FOCUS kinetics (2005, 2011) wing the software KinGUI 2 with four different kinetic models: single first order (SFO). First order multi-compartment (FOMC), hockey-stick (HS, DFOS  $\pm$  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  $\neq$  DAT-0, it was included in the fit by setting values  $\leq$  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 where  $\ll 100 \text{ J}$  n.d. for a second time the curve was cut off antil a subsequent value. LOQ occurred. The DT50 values and formation fractions were calculated from the resulting kinetle parameters.



The single first order (SFO) Dinetic model was used for modeling purpose to describe the degradation of FOE-thiadone. FOE 5043-triftporoethmesulfonic acid and trifluoroacetic acid in the four tested soils. Table 7.1.2, 1.2-42 to Table 7.1.2, 42-45 summarizes the results of the kinetic analysis.



¹² Due to poor chi² error additional decline fits (based on conservative estimates of the true DT₅₀ 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.



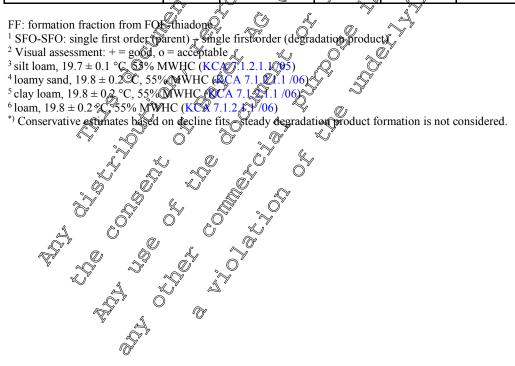
Table 7.1.2.1.2-43: Kinetic parameters for degradation of FOE-thiadone in soils under aerobic conditions for modeling purpose according to FOCUS

					<u>(())</u>	
Soil	FF	Kinetic	DT 50	chi² error	<b>et-test</b>	Visual
		Model ¹	[days]	[%]	~~ ·	Assessment ²
Hoefchen Am Hohenseh ³	0.913	SFO - SFO	1.1	16.4	1.34@09	Õ+Ò
Laacherhof AXXa ⁴	0.524	SFO - SFO	1.4	15.6	8. <b>30e-</b> 08	4 + Ø
Dollendorf II ⁵	0.438	SFO - SFO	2.8	164	∘Z.93e-07	
Laacherhof Wurmwiese ⁶	0.405	SFO - SFO	2.0 0	14.7	√.97e-08 [°]	, X
FF formation fraction from ¹ SFO-SFO: single first order (par ² Visual assessment: $+ =$ good ³ silt loam, 19.7 $\pm$ 0.1 °C, 55% MV ⁴ loamy sand, 19.8 $\pm$ 0.2 °C, 55% M ⁶ loam, 19.8 $\pm$ 0.2 °C, 55% MWH	whC (KCA MWHC (KCA MWHC (KCA	7.1.2.1.1 /05) CA 7.1.2.1.1 /06)				

Table 7.1.2.1.2- 44: Kinetic parameters for degradation of FOE \$43-trifluoroethanesulfonc acid in soils under aerobic conditions for modeling purpose according to FOCUS

Soil	FF	Kinetie Moder	DT 50 3 [@days]_{	Chi ² er Or	ACTrest	Visual Assessment ²
Hoefchen Am Hohenseh ³	0.264	SFQ-SFO 📎	9.1	<u>`</u> 8.**	<2e-16	+
Laacherhof AXXa ⁴	0.534		4.5	×18.3 ×	2.67e-09	+
Dollendorf II ⁵	0.422	≪PO - SEO∕∕	22:5 *)	∞ 24.15	0.0035	+
Laacherhof Wurmwiese ⁶	Ø.Ø55	SFO - SFO	°∼7.6 *) ©	<u>390</u> 8	0.0415	0

FF: formation fraction from FQE thiadone



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#### Document MCA: Section 7 Fate and behaviour in the environment Flufenacet

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

FF ^{a), b)}	Kinetic Model ¹	DT50 [davs]	chi ² error [%]	<b>t</b> -test	Visual Assessment ²
$\begin{array}{c} 0.087^{a)} \\ 0.736^{b)} \end{array}$	SFO - SFO	> 1000	9.2	Q.S	
$\begin{array}{c} 0.476^{a)} \\ 0.466^{b)} \end{array}$	SFO - SFO	> 1000	° 103	°∼y0.5 Å	Č.
$\begin{array}{c} 0.562^{a)} \\ 0.578^{b)} \end{array}$	SFO - SFO	> 1600	6 ^{9.5}	0.5	× +
$\begin{array}{c} 0.596^{a)} \\ 0.345^{b)} \end{array}$	SFO – SFO		9.40	6 ^{0.5}	NO 22
	$\begin{array}{c} 0.087 \text{ a)} \\ 0.736 \text{ b)} \\ 0.476 \text{ a)} \\ 0.466 \text{ b)} \\ 0.562 \text{ a)} \\ 0.578 \text{ b)} \\ 0.596 \text{ a)} \end{array}$	$\begin{array}{ c c c c c c c }\hline & Model \ ^{1} \\\hline 0.087 \ ^{a} \\ 0.736 \ ^{b} \\\hline 0.736 \ ^{b} \\\hline 0.466 \ ^{b} \\\hline 0.562 \ ^{a} \\\hline 0.578 \ ^{b} \\\hline 0.596 \ ^{a} \\\hline \end{array}  SFO - SFO \\\hline \end{array}$	Model 1 [days] $0.087^{a}$ SFO - SFO         > 1000 $0.736^{b}$ SFO - SFO         > 1000 $0.466^{b}$ SFO - SFO         > 1000 $0.562^{a}$ SFO - SFO         > 1000 $0.578^{b}$ SFO - SFO         > 1000 $0.578^{b}$ SFO - SFO         > 1000 $0.596^{a}$ SFO - SFO         > 1000	$\begin{array}{c c c c c c c c c c c c c c c c c c c $	$\begin{array}{ c c c c c c c c c c c c c c c c c c c$

FF: formation fraction; a) from flufenacet; b) from FOE-thiadow

¹ SFO-SFO: single first order (parent) - single first order (degradation)

² Visual assessment: + = good³ silt loam, 19.7  $\pm$  0.1 °C, 55% MWHC (KCA 7.1.2.1.1)

⁴ loamv sand, 19.8 ± 0.2 °C, 55% MWHC (KCA 7.1.2 1/06) f

⁵ clay loam,  $19.8 \pm 0.2$  °C, 55% MWHC (KCA 7.1, 1.06)

⁶ loam, 19.8 ± 0.2 °C, 55% MWHC (KCA 7.1.2.1/±+)06)

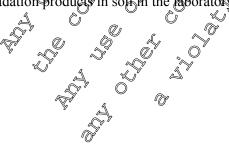
CONCLUSIONS

The calculated half-lives of FOE thiadour for modeling purpose is soil under aerobic conditions in the dark in the laboratory ranged from 1 4 to 2.8 days in the tester soils. The formation fractions of FOEthiadone formed from flufenacet ranged from 0.405 to 0.913.

The calculated half-lives of FOE 3043-trilluoroethanesultonic acid for modeling purpose in soil under aerobic conditions in the dark in the laboratory ranged from 45 to 22.5 days in the tested soils. The formation fractions of FOE 5043-triftdoroethanesulfonic 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 aboratory were >1000 days to 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 ROE-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 aboratory given in section CA 7.1.2.1.





### CA 7.1.2.1.3 <u>An</u>aerobic degradation of the active substance

<u>An</u>aerobic 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 <u>an</u>aerobic conditions in the dark in the laboratory is now newly addressed by two studies, which are submitted within this Supplemental Dessier 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 Daboratory 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;C.;D.(M.; 1995)Title:Anaerobic Soil Metabolism of Phenyl-C ¹⁴ C]EOE 50430Report No:MR106645Document No:M-002162-01-1Guidelines:• OECD Test Guideline No. 307• OCSPP Test Guideline No. 835.4100/4200GLP:yes		
Report No:       MR106645         Document No:       M-002162-01-1         Guidelines:       • OECD Test Guideline No. 307         • OCSPP Test Guideline No. 835.4100/4200       • O	Report:	KCA 7.1.2.1.3 /01; , C.; , D.M.; 1995 (C.)
Report No:       MR106645         Document No:       M-002162-01-1         Guidelines:       • OECD Test Guideline No. 307         • OCSPP Test Guideline No. 835.4100/4200       • O	Title:	Anaerobic Soil Metabolism of Phenyl- U ¹⁴ C]EOE 50430
Guidelines:       • OECD Test Guideline No. 307         • OCSPP Test Guideline No. 835.4100/4200	Report No:	MR106645
• OCSPP Test Graideline No. 835.4100/4200	<b>Document No:</b>	M-002162-01-1
• OCSPP Test Graideline No. 835.4100/4200	Guidelines:	• OECD Test Guideline No. 307
		• OCSPP Test Guideling No. 835.4100,4200 v v
	GLP:	

#### **Executive Summary**

The degradation data as reported in study KO 7.1  $\frac{12}{\sqrt{9}}$ /01 were kinesically evaluated as part of the study to derive trigger endpoints.

The calculated half-life of flufe facet unter an aerobic conditions was 240 days, assuming first order kinetics.

### SI. MATERIALS AND METHODS

Details on the study conduct and is results are summarized under KCA 7.1.1.2/01.

The residue data for the ten item from the <u>an</u>aerobic study phase were evaluated using first order kinetics. Model input datasets were the residual amounts of flufenacet found at each sampling interval of the <u>an</u>aerobic study phase. See able 1.1.2- for input values.

### II. RESULTS AND DISCUSSION

The amount of flutenacet was decoming during the aerobic as well as during the <u>an</u>aerobic incubation phase. The half-life of flutenacet in the tested soil was 240 days under <u>an</u>aerobic conditions in the dark in the boratoey. The correlation coefficient ( $r^2$ ) for the fit was 0.95.

 Table 7.1.2.1.3-1: ADegradation 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 <u>an</u>aerobic conditions in the dark in the laboratory. Its calculated half-life under <u>an</u>aerobic conditions was 240 days in the tested so

	* * * * *	S	. ©`	$\bigcirc^{\prime}$	Ŵ
Report:	KCA 7.1.2.1.3 /02; , O.; 2012				<u></u>
Title:	Amendment No. 2 to [thiadiazole-5-14CFOE 504	S: Anaé	pobic 🔗		F
	Degradation/Metabolism in Two European Soils	, North	í K	<u>`</u>	
<b>Report No:</b>	MEF-11/908	u S	~ Ø		0
<b>Document No:</b>	M-437443-03-1	ŵ.	S 4	y r	Ű
<b>Guidelines:</b>	• OECD Test Guideline No. 307	0	), (C		¥
	• OCSPP Test Guideline No. 835.4100 4200	, L	<u>ه</u>	- C	
GLP:	yes Q y y	×	<u>Ö</u>	QŮ av	

#### **Executive Summary**

The degradation data as reported in study KCA 7(1.1.2/0) were kinetically evaluated according to FOCUS (2005)² as part of the study to derive best this for prigger endpoint determination. The experimental data could be well described by a double first other in parallel kinetic model for both soils. The calculated half-lives of fluctuated under anarrobic 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 by the environment.

MATERIALS AND METHODS

Details on the study conduct and is results are summarized under KCA 7.1.1.2 /02.

The residue data for the test item from the macrobic study phase were evaluated according to the FOCUS guidance document, on degradation kinetics using the software KinGUI 2 to derive the  $DT_{50}$  and  $DT_{90}$  values for flutence.

Model input tatasets were the residual amounts of the enacet 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 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 7.1.2.1.3- 2 and Table 7.1.2.1.3- 3 summarize the degradation of [thiadiazole- $5^{-14}$ C]flufenacet as a function of time.



Degradation of flufenacet in Soil Hoefchen am Hohenseh under Anaerobic Conditions Table 7.1.2.1.3- 2: (expressed as percent of applied radioactivity; single values)

		DAT	0 ¹	15 ²	15 ³	17	21	29	35	48	<i>7</i> 7	105	135
Rep	licate	DASF	N	/A	0	2	6	14	20	33	62 🖘	°90 🖌	
	А		97.0	29.6	43.7	38.9	34.3	25.4	21.6	100	12.9	10.2	6.5
	В		95.8	32.1	41.9	38.7	32.4	25.6	23.3	Q17.5	19.0	Ø.3	<b>5</b> 2

¹ Material balances at DAT-0 were 97.8% AR for replicate A and

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 Anacrobic Condition (expressed as percent of applied radioactivity; single values)

DAT         0 ¹ 15 ² 15 ³ 47         21         29         35         48         77         105         135           Replicate         DASF         N/A         0         2         6         14         20         33         6         90         120           A         92.9         42.5         46         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         26.7         187         19.9         12.1         4.5         3.1						A	¥	<u>d</u> ()	$\langle \mathcal{O} \rangle$	$\sim$		~		
Replicate         DASF         N/A         0         2         6         14         20         33         62         90         120           A         92.9         42.5         46         28.9         22.8         17.6         17.8         10.9         31         4.4         3.1			DAT	0 1	15 ²	15 ³	17	21	29	35	<b>48</b> ,0	[°] 77 [°]	[°] 105	135
A 92.9 42.5 4 6 28 9 22.8 17 5 17.8 10.9 3.1 4 4.4 3.1		Replicate	DASF	N	Ά	0	2 Ø		14	<b>20</b>	1 A	$(C \cap )$	90	120
B 93.3 45.8 ⁽¹⁾ 36.1 ⁽²⁾ 25.1 23.7 18 ⁽⁷⁾ 19 ⁽⁹⁾ 10.3 12.1 4.5 3.1	Ī	А		92.9	42.5	<b>4</b> .6 2	N 2	2.8	17.6		910.9	0 7	4.4	3.1
		В		93.3	45.8 🔇	36.1	0	<b>3</b> .7	187	139	10.Ĵ		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 inclustation plase)

³ after soil flooding (anaerobic@cubationphase)

⁴ Material balance of replicate A at D. 477 was wit in the acceptable lange between 90 and 110% AR - thus, results are not considered for kinetie evaluation

The chi² error values of the fits of att investigated kinetic models were  $\leq 10$  and the visual assessment of the regression ourves gave acceptable or good results (see Table 7.1.2.1.3-4 for details). The degradation of fufenacet followed DEOP kinetics in both soils, according to the lowest chi² error values.

The amount of flutenacet was declining during the aerobic as well as during the anaerobic incubation phase. The half lives of fufenace under an aerobic conditions in the dark in the laboratory were 23 and 15 days in soil Hortchen am Hoberseh and Dollendorf II, respectively.

#### Degradation kinetics of Hufenacet in soil under anaerobic conditions for trigger Table 7.1 evaluation L.

(Soil Type)	Kinetic Model ¹	DT50 [d]	DT90 [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 <u>an</u>aerobic conditions in the dark in the laboratory. Its calculated half-lives under <u>an</u>aerobic conditions were 23 and 15 days in the tested soils Hoefchen am Hohenseh and Dollendorf II.

Report:	KCA 7.1.2.1.3 /03; , G.; , S.; 2014
Title:	Kinetic Evaluation of the Degradation of Flutenacet and its Degradation
	Products under Anaerobic Soil Conditions in Laboratory According to FOCUS
	Kinetics Using the KinGUI 2 Top 🖉 🧳 🧬 🖉
<b>Report No:</b>	EnSa-13-0971
<b>Document No:</b>	EnSa-13-09/1 M-478213-02-1
<b>Guidelines:</b>	• FOCUS kinetics (2006, 20 $\mathbb{N}$ ) ^{3,4} $\mathbb{N}$
GLP:	no & P P P P

#### **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 3 /04) and M-437443-029 (Supplemental Dossier; KCA 7.1.2.1.3 /02) was performed with the software KinGU 2 according to FOCUS kinetics (2006, 2011)^{3, 4} to derive half-lives for flufenacet and its degradation products FØE 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 flufenacet and its degradation products for the degradation products.

The single first order of the double first order parallef were the most appropriate kinetic models to describe the degradation of flufenace for modeling purposes in the three tested soils under anaerobic conditions in the datk in the aboratory at  $20^{24} + 2^{\circ}$ 

The double first order parallel was the most appropriate kinetic model to describe the degradation of flufenacet for frigger evaluation in the three tested softs under anaerobic conditions in the dark in the laboratory at  $20 \pm 2$  %.

The calculated half-lives of florenacet for modeling purposes were 224.9 days, 41.6 days¹³ and 59.7 days¹³ (all  $20 \pm 2$  ), flooded soil conditions).

The calculated half-lives of flufence for bigger evaluation were 229.6 days, 15.0 days and 22.7 days (all  $20 \pm 2$  °C, flooded soil conditions).

#### **METHODS**

Soil residue data from the macrobic soil degradation studies M-002162-01-1 (Supplemental Dossier; KCA 7.1.2.1.3 / (0) and M-437443-02-1 (Supplemental Dossier; KCA 7.1.2.1.3 / (0) were used. In these studies, the degradation of flufenacet was studied in a total of three soils (sandy loam, loam and silt loam) under anaecobic conditions in the dark in the laboratory at  $20 \pm 2$  °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  $\times$  LOD. If they became < LOD / n.d. for a second time the curve was cut off until a subsequent value > LOQoccurred. 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. RESULT

The single first order or double first order parallel were the post appropriate kinetic models to describe the degradation of flufenacet for modeling purposes in all tested soils. Table ₩3- 5 ړ summarizes the results of the kinetic analysis.

Table 7.1.2.1.3- 5:	Kinetic parameters for the degradat	ion of flufen	acet in soil i	inder <u>an</u> xe	robicconditions
	for modeling purpose according to F	`OÇÇÎŚ 🍃			L,

			0'''	
Kinetic	<b>DT56</b>	chi² error	≫t-test 🎧	🔊 Visual
Model ¹	[days]	S [%]		Assessment ²
SFO	224.9		y < 0. <b>00</b> 1	0
DROP	41.6	9.5~ ³	ka 0.002 °ka < 0.001	+
°∼ DFOP \$	59.7 °	<u></u>	$k_1 \ge 0.001$ $k_2 \ge 0.001$	+
	Model ¹ SFO	Model 1         [days]           SFO         224.9           DFOP         41.6           SFO         59.7 6	Model ¹ [days]         [%]           SFO         224.9         224.9         206         206         206         206         206         206         206         206         206         206         206         206         206         206         206         206         206         206         206         206         206         206         206         206         206         206         206         206         206         206         206         206         206         206         206         206         206         206         206         206         206         206         206         206         206         206         206         206         206         206         206         206         206         206         206         206         206         206         206         206         206         206         206         206         206         206         206         206         206         206         206         206         206         206         206         206         206         206         206         206         206         206         206         206         206         206         206         206         206         <	Model 1         [days] $[9'_{6k}]$ SFO         224.9 $[9'_{6k}]$ $[9'_{6k}]$ DFOP         41.6 $9.5$ $[a_{6}, 0.002]$ $b_{7}$ $59.7^{6}$ $a_{11} < 0.001$

acceptable

¹ SFO: single first order, DFOP double first order parallel

- 2  VA = visual assessment: +
- ³ sandy loam
- ⁴ loam
- 5 silt loam
- ⁶ calculated from DFC

The double first order parallel was the most appropriate kinetic model to describe the degradation of flufenacet for triggen evaluation in all tested soils. Pable 7.1.2.1.3- 6 summarizes the results of the 4 kinetic analysis.

Table 7.1.2.1.3 for trigger evaluation according to FOCUS

Soil O	Kinetic Model ¹	DT50 Odays]	DT90 [days]	chi ² error [%]	t-test	Visual Assessment ²
Howe, Indiana S	DFOP C	229.6	895.6	1.0	$k_1: 0.011$ $k_2: < 0.001$	+
Dollendorf II ⁴	DFÓP	15.0	111.1	9.2	$k_1: 0.049$ $k_2: < 0.001$	+
Hoefchen am Hohenset	DFOP	22.7	156.9	1.1	$\begin{array}{l} k_1: < 0.001 \\ k_2: < 0.001 \end{array}$	+

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 <u>an</u>aerobic 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 flutenacet and its major degradation products in soil in the laboratory given in section section (A 7, A, 2, 1).

### CA 7.1.2.1.4 Anaerobic degradation of metabolites, breakdown and reaction products

No separate <u>an</u>aerobic soil degradation studies were conducted for major degradation products of flufenacet.

However, when studying the route and rate of degradation of flutenacet in soil upder anaerobic conditions in the dark in the laboratory (see section CA7.1.2, 3) in both studies an acrobic 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 trifluoroethanes 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:	KCar 7.1.2 1.4 /01	, G.;	
Title:	Kinetic Evaluation of th	e Degradation of Flufena	cet and its Degradation
	Products under Anaeroc	x Soil Conditions in Lab	oratory According to FOCUS
	Kinetics Using the Kind EnSa-13-0991 M+478213-02-1	GUI 2 Fool	
Report No: 🍌 🦏	EnSa-13-0991	Q.	
Document No?	M-478213-02-1 Č		
Guideline	FOCUS kineties (200	2011	
GLP:		la da	
.4		×	

### Executive Summary

A kinetic analysis of soil tesidue data from two anaerobic soil degradation studies M-002162-01-1 (Supplemental Dossier; KCA, 1.2.1,3,01) and M-437443-02-1 (Supplemental Dossier; KCA 7, 2.1.3,02) was performed with the software KinGUI 2 according to FOCUS kinetics (2006, 2011) to derive hath-lives for fluteracet and its degradation products FOE oxalate, FOE sulfonic acid, FOE thadone, FOE 5043-triftuoroethanesulfonic 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 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 two¹⁵ tested soils under anaerobic conditions (flooded soil conditions) in the dark in the laboratory at 20 20 °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  $1.1 \times 10^{-6}$  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  $0.3 \times 10^{-7}$  and  $3.9 \times 10^{-7}$  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, 48 and 66.4 days for FOE 5043-trifluoroethanesulfonic acid and 471 2 and 762.7 days for trifluoroactic acid

METHODS

Soil residue data from the anaerobic soil degradation studies M202162-01-1 (Supplemental Dossier; KCA 7.1.2.1.3 /01) and M-437443-02 (Supplemental Dossier; KCA 7.1.2 3 /02) were used. In these studies, the degradation of flutenacet was studied in one ¹⁴ or in two ¹⁶ soils (sandy loam, loam and silt loam) under <u>an</u>aerobic conditions in the dark in the dark of 
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 (SEG), 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  $0.5 \times \text{LOD}$ . 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 DT₃₆ values were calculated from the resulting kinetic parameters.

### 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 one¹⁴ or in two¹⁵ tested soils under anaerobie conditions.

Table 7.1.2.1.4- 1, Table 7.02.1.4- 6, 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 7.1.2.04- 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-5-¹⁴C] flufenacet: formation of degradation products FOE-thiadone, FOE 5043-trifluoroethanesulfonic acid and trifluoroacetic acid.



Kinetic parameters for the degradation of FOE oxalate in soil under anaerobic Table 7.1.2.1.4- 1: conditions for modeling purpose according to FOCUS

				Ro		
Soil	FF	Kinetic	DT50	chi ² error	t-test	VA ²
		Model ¹	[days]		° (	
Howe, Indiana ³	1.0 ^a	SFO - SFO	48.8	×1.9		-Ô
					0	$\mathcal{O}_{1}$

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 FOP oxalate in soil under an aerobic conditions for trigger evaluation according to FOCLES 

Soil	Kinetic Model ¹	DT ₅₀	D(L)0	cbi ² error	t-test	VA ²
Howe, Indiana ³	DFOP - ŞFO		Q 474.4		00.081	0
	_~~	J. ()	57 K/	$\langle \rangle$		

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 supronic acid in soil under anaerobic conditions for modeling purpose according to FOCUS

Soil	<u> </u>	PF C		DT sa [day\$5]	chi ² error [%]	t-test	VA ²
Howe, Indiana ³	S.	$@.1 \times 10^{3}$	SIO - SFO	35¥.2	6.6	0.011	0

FF = formation fraction

¹ SFO: single first orde DFOP double first order partiel e acceptable

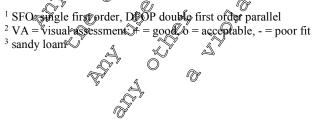
 $\bigcirc$ 

² VA = visual assessment ³ sandy loam

° Kinetic parameters for the degradation of FOE sulfonic acid in soil under anaerobic Table 7.1.2.1.4 conditions for trigger evaluation according to FOCUS

Soil		Konetic 🔊	DT50	DT90	chi ² error	t-test	VA ²
	s and a second s	Model O	[days]	[days]	[%]		
Howe, Indiana ³	0	≥ ØFOP X SFO	352.3	> 1000	6.6	0.295	0

1 P





#### Document MCA: Section 7 Fate and behaviour in the environment Flufenacet

Kinetic parameters for the degradation of FOE-thiadone in soil under anaerobic Table 7.1.2.1.4- 5: conditions for modeling purpose according to FOCUS

<b>C H</b>	DD	<b>T</b> 71 /1	DT			<b>X</b> 7 4 2
Soil	FF	Kinetic	DT50	chi ² error	t-test	VA ²
		Model ¹	[days]		0	
Dollendorf II ³	0.425 a	DFOP - SFO	33.9	×3.6	×0.00	tô
Hoefchen am Hohenseh ⁴	0.425 a	DFOP - SFO	97.0	S 5.0 ≪	< 0.001	, Ø
FF = formation fraction ¹ SFO: single first order, DFOP double ² VA = visual assessment: + = good, o ³ loam ⁴ silt loam						L [°]

Table 7.1.2.1.4- 6: Kinetic parameters for the degradation of FOE-thiadone in soil under anaeropi conditions for trigger evaluation according to FQCUS L R ,Û

Soil	Kinetic 🔗 Model 1	DA50 [days]	DT90 Q[days]	chi ² error	Opest	VA ²
Dollendorf II ³	DFOP - SFO	$\bigcirc$ $^{\prime}$ 23.9 $\bigcirc$		ي 2.6	√ < 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 paralle

² VA = visual assessment: + = good, o = acceptable,

³ loam

⁴ silt loam

#### Kinetic parameters for the degradation of FØE 5043 trifluoroethanesulfonic acid in soil Table 7.1.2.1.4- 7: under maerobic conditions for modeling purpose according to FOCUS

, O^v A

Soil	F.	F Kinetio Model	DT50 [days]	chi ² error [%]	t-test	VA ²
Dollendorf II ³		- <u>.</u>	1.8	30.6	< 0.001	0
Hoefchen am Hohenseh 4	1.00	0 ST DEOP - SFC	16.4	22.2	< 0.001	-

FF = formation

¹ SFO: single first order DFOP double first order parafiel

² VA = visual assessment: = pook fit good, o : acceptable;

 3  loam

⁴ silt loam

^a formed from F

Kinetic parameters for the degradation of FOE 5043-trifluoroethanesulfonic acid in soil Table 7.0 under anaerobic conditions for trigger evaluation according to FOCUS

Soil Soil	Kinetic Model ¹	DT ₅₀ [days]	DT90 [days]	chi ² error [%]	t-test	VA ²
Dollendorf II ³	DFOP - SFO	1.8	6.0	30.6	< 0.001	0
Hoefchen am Hohensen	DFOP - SFO	16.4	54.4	22.2	< 0.001	-

Ø ¹ SFO: single first order, DFOP double first order parallel

 2  VA = visual assessment: + = good, o = acceptable, - = poor fit

³ loam

⁴ silt loam

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### **Document MCA: Section 7 Fate and behaviour in the environment Flufenacet**

 Table 7.1.2.1.4- 9:
 Kinetic parameters for the degradation of trifluoroacetic acid in soil under <u>an</u>aerobic conditions for <u>modeling purpose</u> according to FOCUS

				<u>(A</u>		1
Soil	FF	Kinetic	DT 50	chi ² error	t-test	<b>VA</b> ²
		Model ¹	[days]		0 (°	
Dollendorf II ³	$\begin{array}{c} 0.575^{\text{ a}} \\ 6.3 \times 10^{\text{-7 b}} \end{array}$	DFOP - SFO	471.2	\$ ^{3.8}	0.00	Î
Hoefchen am Hohenseh ⁴	$\begin{array}{c} 0.575^{\ a} \\ 3.9 \times 10^{\text{-7 b}} \end{array}$	DFOP - SFO	≈762.7 √	2.9	Q.026	20 +
FF = formation fraction ¹ SFO: single first order, DFOP double ² VA = visual assessment: + = good, o ³ loam ⁴ silt loam ^a formed from flufenacet ^b formed from FOE-thiadone						Ŷ

 Table 7.1.2.1.4- 10:
 Kinetic parameters for the degradation of willuoroacetic acid in soil under an aerobic conditions for trigger evaluation according to FQCUS

Soil	Kinetic Models	DT 50 {days]	DT90 %		t-test	VA ²
Dollendorf II ³	DFOP - SFO	×471.2 (	/ >1000	~3.8	0.004	0
Hoefchen am Hohenseh ⁴	DFOR, SFO	, 762 <b>J</b>	>_000	2.9	0.026	+

¹ SFO: single first order, DFOP double first @der parallel

² VA = visual assessment:  $+ = g_{0}$  , o = a e p table = poor fit

- ³ loam
- ⁴ silt loam



The calculated half-lives for the degradation products for modeling purposes in soil under <u>an</u>aerobic 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 frifluoroacetic 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 sulforic 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  $6.3 \times 10^{-7}$  and  $3.9 \times 10^{-7}$  for trifluoroacetic acid.

The calculated half lives for the degradation products for trigger evaluation in soil under <u>an</u>aerobic 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 52.7 days for trifluoroacetic acid.

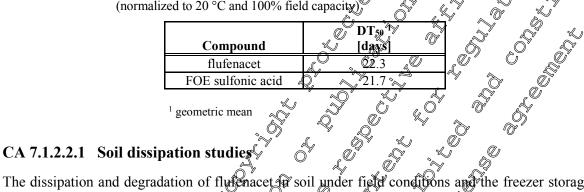
The results are included in the summary of the degradation rates of flufenacet and its major degradation products in soil in the laboratory given in section CA 7.1.2.1.



#### CA 7.1.2.2 **Field studies**

The dissipation and degradation of flufenacet was investigated in 16 field tigals 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 FQE sulfonic acid in soil under field conditions for modeling purpose are summarized in value 79.2.2-

#### Overall summary of DT50 values for degradation of flutenacet and its major degradation Table 7.1.2.2- 1: product FOE sulfonic acid in soils under field Conditions for modeling parpose (normalized to 20 °C and 100% field capacity)

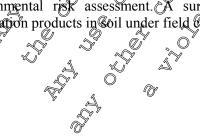


# The dissipation and degradation of flyenacet for soil under field conditions and the freezer storage of

flufenacet and its degradation products were evaluated during the Aprnex I beclusion 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		Authôr(s)	Year	Document No
KCA 7.1.2.2.1 /01 🖉	Ó Ò	, H.	1995	M-002175-01-2
KCA 7.1.2.2.1 /0			1995	M-002171-01-2
KCA 7.1.2.2.1 🖓 3 🔗 🗡	L L	)H. N	1995	M-002169-01-2
KCA 7.1.2.2 /04		, H. 🖉	1995	M-002172-01-2
KCA 7.1,2.2.2 /01	The second secon	, D. L., , P. S.	1995	M-002201-01-1
KCA 74, 2.2.2 (02)		Ĥ.,  D. L	1995	M-002199-01-1
		l de la companya de la compa		

No additional studies are submitted within this Sapplemental Dossier for the flufenacet renewal of approval. However, updated kipetic evaluations of the degradation behaviors of flufenacet and its major degradation product, FOE sulfonic acc in soil under field conditions have been performed according to FOCUS kinetics (2006)³ 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; , K.; 2008
Title:	Kinetic evaluation of the dissipation of flufenacet and its metabolite flufenacet
	- sulfonic acid in soil based on field studies
<b>Report No:</b>	MEF-08/266
<b>Document No:</b>	M-306683-01-1
<b>Guidelines:</b>	• FOCUS kinetics (2006) 3
GLP:	no V A X

#### **Executive Summary**

A kinetic analysis of soil residue data from the field dissipation studies M-002175-012 (Baseline Dossier, KCA 7.1.2.2.1 /01), M-002171-01-2 (Baseline Dossier, KCA 7.1.2.2.1 /02), M-002172-01-2 (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 pormalized half-lives (20 °C and 100% field capacity) for flufencet 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 flufenace 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 5.0 to \$1.1 days (geometric mean 22.3 d) for flufenacet and from 14.1 to 41.4 days (geometric mean 21.7 d) for FQE sulfable acid.

METHODŚ

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Soil residue data from the field dissipation studies M-002175-0V-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 flufenaced was trudied at sites Breitenfielde (Germany), Kirchlauter (Germany), Monheim (Germany), Burscheid (Germany), Fresne-ØArcheveque (France), Fresne-L'Archeveque (France), Landun (France), St. Etienne du Gres (Erance), Saussay La Campagne (France), Fresne-L'Archeveque (France), Ravenna (Italy) and S. Romualdo (Italy) under field conditions covering a period of at least 31 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 (DFOR). 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 (DT₅₀) 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 DT₅₀ 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 010 = 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 secto 0.5 x LOD for samples after, before or deeper as a value LOD, or for samples between values 2000. 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 DOE sufform and hor the third on for the 20 - 30 cm soil layer), i.e. all values < LOD were set to 0.5 LOD, the section 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 sol 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 teclorically 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. Accessary driving variables for such a model are rainfall and potential evapotranspiration. On the field dissipation studies, rainfold 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 data given in the field dissipation studies were used to calibrate the MARS data.



Single first order (SFO) was used as kinetic model to describe the degradation of flufenacet and FOE sulfonic acid for modeling purposent all sites. The fixed formation fraction of FOE sulfonic acid did hardly change the results for flutenacet 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.



			Ro	
Trial number	Site	Texture	DT _{50 flufena}	DT ₅₀ flufenacet
That humber	Site	(0 – 30 cm depth)	[days	o [days]
30159/0	Breitenfelde (Germany)	sandy loam	17.17	
30162/0	Kirchlauter (Germany)	sandy loam	K K	19.8 Ø
30163/9	Monheim (Germany)	sandy loam	Ø1.8 🔊 🕅	20.5
30164/7	Burscheid (Germany)	silt loam	× 11.4	n.a
30248/1	Fresne-L'Archeveque (France)	silt loan		√ 1,85¥
30250/3	Fresne-L'Archeveque (France)	silt loam 🔬 🤇	) 3219 ~	20.8
30251/1	Laudun (France)	l@m 🛒	<b>2</b> 4.7 S	"An.a. 🔊
30253/8	St. Etienne du Gres (France)	Noam 🔊	37.6	O 19.6 S
30254/6	Saussay La Campagne (France)	silt loam	<i>€.</i> ₽	na
30455/7	Fresne-L'Archeveque (France)	🖉 silt koam 🗞	7.1	jy <b>B</b> yà.
30499/9	Burscheid (Germany)	, sih@am 📈	<b>8</b> .5	29.8
30500/6	Monheim (Germany)	sandy loam	% ⁰ 14.7	n.a.
40163/3	Laudun (France)	clay loam	45.30	<i>©</i> 21.8
40164/1	St. Etienne du Gres (France)	silt loan	<u>41</u> ,9	25.0
40494/2	Ravenna (Italy)	🔍 siltdoam 🎧	×36.2 Ø	41.4
40495/0	S. Romualdo (Itak) 🦉 🔬	🛛 🕺 silty clay 🖉	<u>\$</u> \$1.1 \$	14.1
Geometric mean			22.3⊳	21.7

n.a.: not applicable

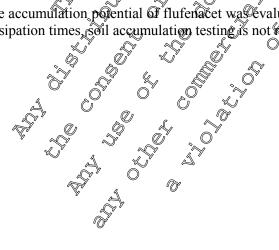
#### SFO of flufenacet (DT50FFA) and FOE sulfonic acid (DT50FOE SA) referenced to 20 °C Table 7.1.2.2.1- 1: and 100% field capacity

### COŅCĽUSľÒŇS

The calculated normalized half fives (20, C and 00% field capacity) for modeling purpose for the degradation in soil under field conditions ranged from 6.0 to \$1.1 days (geometric mean 22.3 d) for flufenacet and from 41.4 day & geometric mean 21.7 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 either¹⁴C-labeled of unlabeled test items. Adsorption and desorption isotherms were calculated by linear repression analysis of the adsorption or desorption data according to the Freundlick 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 coefficience of futenacet and its major degradation products are listed in Table 7.1.3.1- Q to Table 7.1.3.1- 6 an overal Osummary is given Table 7.1.3.1-1.

Table 7.1.3.1- 1:	Overall summary of adsorpti	on constants Koe	_{ads)} in soils of first	enacet and its major
	degradation products 🔬	Ô U	Å. Å	, O

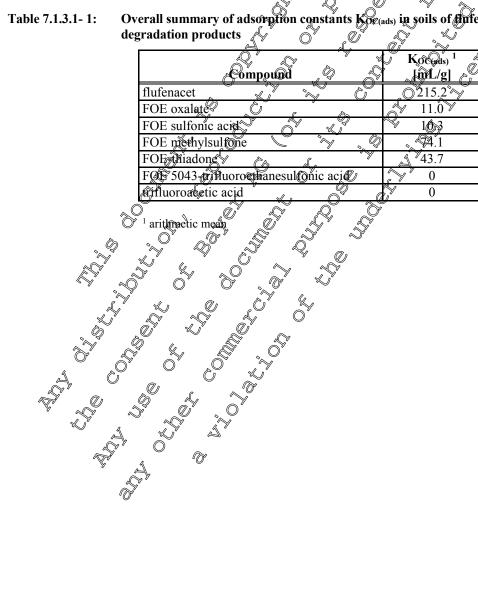




Table 7.1.3.1- 2:	Overall summary of adsorption constants and correlation coefficients in soils of
	flufenacet

				<u> </u>		
Soil	Texture	pН	Annex Point /	KF(age)	1/n	KOC(ads)
	(USDA)		Reference No	[ml/g]	0	_[mL/g]
# 307, Stanley, KS	silt loam	5.9		3.2	0.84 ¹	∑ [×] 190 ¹⊘
# 396, Vero Beach, FL	sand	5.0		©≫0.972≪	0.98 4 2	588 Ø
# 318, Hagerstown, MD	clay loam	6.4	KCA 7.43.3.1.1 /0 K	2,70	0.90	$211^{-1}$
# 395, Howe, IN	loamy sand	6.4	KCA /	1.6/2	0.87 1,2	<b>696</b> ^{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		40	000	
Brantford Silt Clay, St. George, Onatrio	silt loam	7.3		4.0	0.86	144
Ibaraki Ushiku, Japan	sandy loam	5.6	KORA 7.1. Q. 1 /04 O	6.92	0.85	160.8 ³
Hokkaido Kamikawa, Japan	loam	~ <b>4</b> ?9		8.96	09%	426.5
Laacherhof AXXa	loamy sand 🗞	5.8		<u>\$.56</u>	0.93	161.6
Hoefchen am Hohenseh	silt loam 🏑	6.5		ي 3.28 🕻	0.93	205.0
Hanscheiderhof	silt loam	5.3	K&A 7.1.3.4.1 /03	5.10	0.93	188.9
Dollendorf II	loamÕ	4		7.60	0.90	178.5
Wurmwiese	sandy 🖗 am 🏻	5.1		s \$32	0.98	195.2
			arithmetic mean	4.7	0.92	215.2
		Å,	ò Q',			

T

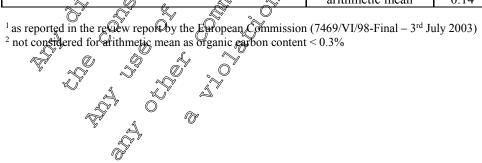
¹ as reported in the review report by the European Commussion (7469/VI/98-Final – 3 Duly 2003) ² not considered for arithmetic mean as less than 20% of the test them were adsorbed ³ not considered for arithmetic mean as it is a volcanic ash soil, not representative for European agricultural soils

### Overall summary of adsorption constants and correlation coefficients in soils of FOE Table 7.1.3.1- 3:

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Soil	Texture (VSDA)	pH~	Africe Point / Beference No	K _{F(ads)} [mL/g]	1/n ¹	K _{OC(ads)} ¹ [mL/g]
Winder Vero Beach, FL	& sand	<b>\$</b> .8		0.06 ²	1.42 1, 2	23 ^{1,2}
Shipshe, Howe, 🖗	🔍 sandy 🖗 am 💊	6.3	KCA 7.1.3.1.2 /01	0.10	0.93 1	13 ¹
Drummer, Champargn, II	silty 🗛 loan	6.6	KCA /.1.3.1.2/01	0.15	0.82 1	7 ¹
Oska-Martin 🕬 well, KS	suity clay	6.0		0.16	0.98 1	13 ¹
		\$	arithmetic mean	0.14	0.91	11.0





#### Table 7.1.3.1- 4: Overall summary of adsorption constants and correlation coefficients in soils of FOE sulfonic acid

Soil	Texture (USDA)	рН	Annex Point / Reference No	KF(a@)	1/n ~	KoC(ads) [mL/g]
Winder Vero Beach, FL	sand	5.8		Q 05 ²	0.86 ^{1,2}	^{1, 2}
Shipshe, Howe, IN	sandy loam	6.3	VCA 7 1 2 1 2 /01	o≫0.11 ≪	$1.00^{1}$	15®
Drummer, Champaign, IL	silty clay loam	6.6	KCA 7.1.3.1.2 /01	0.200	0.93	101
Oska-Martin Stilwell, KS	silty clay	6.0	ð v	0.07	.1Ø ⁸¹	. ≪ĭ6 ¹
Laacherhof AXXa	sandy loam	6.3	KCA7.1.3.2001	©12 ³	≫- ³ √	× 8 ³
Laacherhof AIII	silt loam	6.8	KCA97.1.3.2001	0.12 3	- ³ Ø	13 ³ °
			arithmetic mean C	0.12	1.04	10.4
					A.	$a^{\gamma}$

¹ as reported in the review report by the European Commission (7469/Vk/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 Ereundlich equation was established and K_d and K_d, oc values are reported.

Table 7.1.3.1- 5:	<b>Overall summary</b>	of adsorption	constants and	correlation	coefficients in soils of FOE
	methylsulfone	Ó, ×	~~ ·~ ·	«ĭ ~0'	1 Ca

meeny		A S		<u>a</u> ř		
Soil	Texture ?	рН	Annex Point	Kr (ads)	1/n	KOC(ads)
	(USDA) 🔨		Reference No	]mL/g]		[mL/g]
Wurmwiese	° Noam	5,B	Ô, Ô,	0.66	0.89	37.4
Hoefchen am Hohenseh	silt loam	<u>`</u> ©6		1.28	0.89	52.9
Dollendorf II	clay loam	7.3	KCA 2 .3.1.2	1.57	0.90	33.2
Guadalupe	🖉 sando loam 🕑	6.7 🗸		0.53	0.91	75.0
Springfield	🖇 🕺 stat Ioam 🕅	6.6		2.92	0.86	171.8
Õ	K	$\checkmark$	Qurithmette mean	1.39	0.89	74.1
~0		L.Y	<u>40</u>			

### S Overall summary of adsorption constants and correlation coefficients in soils of FOE-Table 7.1.3.1- 6:

Soil Soil Texture pH (USDA)	مریاتی Annex Point / Reference No	K _{F(ads)} [mL/g]	1/n	Koc(ads) [mL/g]
Winder Vero Beach, E		0.12 ²	0.78 1,2	43 ^{1, 2}
Shipshe, Howe, IS sandy logm 3.3	KCA 7.1.3.1.2 /01	0.33	0.81 1	44 ¹
Drummer, Champargh, IL Silty clay loam 6.6	KCA /.1.3.1.2/01	0.61	0.67 ¹	29 ¹
Oska-Martin Stilwell, KS Sifty clay 🌜 6.0		0.71	0.80 1	58 ¹
	arithmetic mean	0.55	0.76	43.7

¹ as reported in the review reported in the European Commission (7469/VI/98-Final – 3rd July 2003)

 2  not considered for anthmetic spean 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 –  $3^{rd}$  July 2003). The following studies are included in the Baseline Dossier:

Annex Point / Reference No	Author(s)	Vear Document No
KCA 7.1.3.1.1 /01	, I. V.; , S.	1992 MQ002202=01-1
KCA 7.1.3.1.1 /02	, K. P.; , X.	\$ ¹⁹⁹⁴ M-002\$86-01-1

Two additional studies have been performed for flufenacet and are submitted within the Supplemental Dossier for the flufenacet renewal of approval.

Report:	KCA 7.1.3.1.1/04;
Title:	[phenyl-UL- ¹⁴ C]flufenacer. Adsorption of Two Japanese Soils
<b>Report No:</b>	MEF-10/534
<b>Document No:</b>	M-387572-01-1
<b>Guidelines:</b>	• Japanese MAFFONew Test Guidelines 12 Nousan 8147
	• OECD Test Guideline No. 106 20 20 20
GLP:	yes & the yes

#### **Executive Summary**

The adsorption/desorption behavior of [phenyl-UL ¹⁴C]flufenacet was studied in two different soils in the dark in the laborator  $325 \pm 3^{\circ}$ C using the bach equilibrium method:

Soil	<u> </u>		Source			exture (USDA)	pН	OC [%]
	Č L	A set of A	4 191		A C	sandy loam	5.6	4.3
Hokkaido Kamik	awa 🐧 🔘 '	Hokkaid			Ş	loam	4.9	2.1
	.~~			N a	7,			

The adsorption phase of the study was carried out using air-dried soils pre-equilibrated in aqueous 0.01 M CaCl₂ 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,  $0 \ge 0.1$ , 0.03 and 0.01 mg/L in aqueous 0.01 M CaCl₂. The adsorption step was carried out for 24 hours under continuous agitation.

Flufenacet was sufficient able thoughout the study. The parental mass balances were 103.8 and 104.8 % of appred 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.

#### **MATERIALS AND METHODS** I.

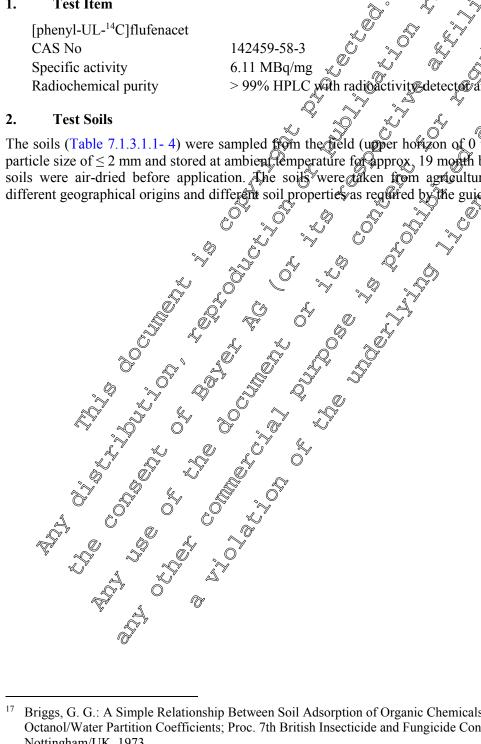
#### **MATERIALS** A.

#### 1. **Test Item**

[phenyl-UL-¹⁴C]flufenacet



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  $\leq 2$  mm and stored at ambient temperature for approx, 19 month before study start. The soils were air-dried before application. The soils were daken 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	Kampikawa gun				
State	Ibaraki pref. 🔬 🔊	Kokkaido(island				
Country	Japan	Japan y				
Soil Taxonomic Classification (USDA)	no informati	on available				
Soil Series	volcanic ash OECD type 2	© OECD type 4				
Textural Class (USDA)	sandy Qam 🔨 😪	ja j				
Sand [%] [50 $\mu$ m – 2 mm]	2 ⁶³ \$ 6	49 J				
Silt [%] $[2 \ \mu m - 50 \ \mu m]$		320				
Clay [%] [< 2 μm]						
pH - in CaCl ₂ (soil/CaCl ₂ 1/2) - in water (soil/water 1/1)	5.6 5.9 5.9 5.2 5.2 5.2 5.2 5.2 5.2 5.2 5.2 5.2 5.2	4.9 5.3				
- in KCl	5.2 V (	4.4				
Organic Carbon [%] Organic Matter [%] ¹	$\gamma^{*}$ $\gamma^{*}$ $\gamma^{*}$ $\gamma^{*}$ $\gamma^{*}$ $\gamma^{*}$ $\gamma^{*}$	2.1 3.6				
Cation Exchange Capacity [meq/100 g]		12.2				
Water Holding Capacity 5 at 0.33 bar (pF 2.5) [25]	× × × 41.9	36.5				
Bulk Density (disturbed)	0.78 5	0.97				

¹ calculated as: M[%] = OC[%] 1.724 USDA: Upited States Department of Agriculture

## B. STUDY DESIG

## 1. Experimentations

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-tosolution 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 CaCl₂ 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 CaCl₂ solution. The adsorption step was carried out for 24 hours in the dark at  $25 \pm 1$  °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 (FOD) and limit of quantitation (EOQ) 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 TESTITEM

Flufenacet was sufficient stable throughout the tudy. The parental mass balances were 103.8 and 104.8% of applied radioactivity [% AR] for soil @baraki Ushiku and Hokkaido Kamikawa, respectively

## C. FINDINGS

At the end of the adsorption phase, 53% - 71.8% AR was adsorbed to soil Ibaraki Ushiku and 57.4 - 63.8% AR to soil Heckaido Kamikawa. The adsorption constants  $K_{F(ads)}$  of flufenacet calculated based on the Freundlich sotherms 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 is 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	



		Adso	rption	Ô	Þ
Soil	K _F	1/n	R ²	Kec	- 0 6
ID	[mL/g]			[mL/g]	
Ibaraki Ushiku	6.916	0.8479	0.9996	<b>60.8</b>	Ŭ, Ţ, Ŏ
Hokkaido Kamikawa	8.956	0.9583	。0.9973 [@]	426.5	
Mean	7.936	0.903	0.9984	293,6	
		×,	Ő		
		<u> </u>	$\sim$	\$~ ^	Y Q

### Table 7.1.3.1.1-3: Adsorption constants and correlation coefficients of flufenacet in soil at 25 °C

 $\begin{array}{ccc} \text{III.} & \textbf{CONCLUSIONS} & & & & \\ \text{The adsorption constants } K_{F(ads)} & \text{of flufenacet ranged from 6.916 & 8.956 mL/g (arithmetic mean: \\ \end{array}$ 7.936 mL/g); the respective normalized adsorption constants Kocing ranged from Co.8 to 26.5 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 93; K. Ma 2012 S
Title:	[thiadiazole-5- ¹⁴ C]FOF 5043 (flufenacet): Adsorption Desorption on Five Soils
<b>Report No:</b>	EnSa-12-0597
<b>Document No:</b>	M-439282-01-1 2 4 5
<b>Guidelines:</b>	• OFCPATest Condeline No. 106 0 49
	• US EPA OC SPP Test Guideline No. 835.1230
	• Conadian PMRA Guideling DAC @ 8.2.4 2 *
GLP:	$\gamma e^{s}$ $$ $$ $$ $$

## Executive Summary

The adsorption desorption behavior of an adiazone-5-14 [flufenacet was studied in five different soils in the dark in the laboratory at  $20 \pm 2$  % using the batch equilibrium method:

Sời	Søurce	Texture (USDA)	pН	OC [%]
Laacherhof AXXa 🔍	Mortheim, Germany	loamy sand	5.8	2.2
Hoefchen am Hoßenseh 🗸	Burscheid Germany	silt loam	6.5	1.6
Hanscheider Hof 🌾	Burscheid Germany	silt loam	5.3	2.7
Dollendørf II	Blankenhøim, Germany	loam	7.3	4.4
LancherhotWurmwiese	O Monneim, 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 CaCl₂ solution containing HgCl₂ (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^vin aqueous 0.01 M CaCl₂. The desorption phase was performed by supplying preadsorbed soil samples with fresh aqueous 0.01 M CaCl₂ solution containing HgCl₂ (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, Dobendorf and Daacherhof Wurmwiese, respectively.

The adsorption constants  $K_{F(ads)}$  of flufenacet calculated bases on the Freundhich 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: OS.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  $K_{(O(des))}$  were 1.6 to 1.7 times higher than the  $K_{OC(ads)}$  values, indicating a strengthened binding of the test tem once adsorbed to the soil.

No correlation between the pH of the soils and the adsorption behavior of the test icm was observed.

According to Briggs ¹⁷, flufenacet can be classified as low mobile for absorption and for desorption in all tested soils.

I., 🖗 MATERIALS AND METHODS ^

## A. MATERIALS

1. Test Item

## 2. Test Soils

The soils (Table 7.1.3.17-4) were sampled freshly from the field (upper horizon of 0 to 20 cm), sieved to a particle size of  $\leq 2$  from and forced refrigerated at  $\leq 8$  °C for a maximum period of 6 months before study start. The soils were aid aried before application. The soils were taken from agricultural areas representing different geographical origins and different soil properties as required by the guidelines.



Parameter			Results / Units	Ĉo	
Soil Designation	Laacherhof	Hoefchen am	Hanscheider	Dollendorf II	Laacherhof
6	AXXa	Hohenseh	Hof		Wurmwiese
Geographic Location			,	D' Q	O' Q
City	Monheim	Burscheid	Burscheid	Blankenheim	Monheim
State	North-Rhine	North-Rhine	North-Rhipe	North-Rhine	North-Rhine
	Westphalia	Westphalia	Westphalia	Westphałia	Westphalia
Country	Germany	Germany 🐇	Germany	Germany	Germany
GPS Coordinates	N 51° 04.6	N 51° 0400	N 51° 04.5	N 50° 22. 9'.C	N 5 K 04.9'
	E 006° 53.5'	E 007 06.3'	1007° 08.4'	E @ 6° 43 @	E 066° 55.3'
Soil Taxonomic Classification	sandy,	loamy,	loanny-	fine-loamy,	Soamy,
(USDA)	mixed, mesic	Qixed,	skeletal,	mixed,	Winixed,
	Typic Cambudoll 😞	mesic, Typic	mixed, semi		
		Argudalf	active, mesic Dystric	َلَّ Yypic Futrude	Argudalf
		1. Č	Eutrudept	Ø	
Soil Series	<u> </u>		nformation avai	lable 🔗	
Textural Class (USDA)	loamy sand	S silt loam	Vilt loam	Noam	sandy loam
Sand [%] [50 $\mu$ m – 2 mm]	079			© 37	53
Sult [%] $[2 \ \mu m - 50 \ \mu m]$		°≫70 Ô		40	30
Clay [%] [ $< 2 \mu m$ ]		L 15 Ø		23	30 17
			13	23	17
pH - in CaCl ₂ (soil/CaCl ₂ 1/2)				7.2	<b>5</b> 1
- in water (soil/water 1/1)	0, 5.8 G	6.5		7.3	5.1
	0 ³ 6.4	0.6.7		7.5	5.4
- in water (saturated paste)	6.0	6.8	5.8	7.4	5.5
- in KCl	<b>\$</b> .7 ~~		<b>9</b> 4.9	7.0	4.7
Organic Carbon [%]	0 ⁷ 3.8	్ల సి. శి	4.7	7.6	2.9
Organic Matters [ ] 1		[∞] 1.6	2.7	4.4	1.7
Cation Exchange Capacity ( [meq/100 g) O	2 ^{9.0}		9.6	19.2	9.9
Water Holding Capacity	Ø Ö	×.			
maximum 🗸 🖉 🌋	S 49.91	© 55.9	61.3	78.5	61.9
[g H ₂ O ad 100 g soil JW]					
at 0.1 bar (p) 2.0) [5]	§7.2 O	31.7	36.7	41.1	20.1
Bulk Density (disturbed)	0 1.20	1.11	1.04	0.98	1.08
¹ calculated as? OM [%] = OC 405 · :	1.724				
DAT: days after treatment	2	GPS: global pos	sitioning system		
	<u>^</u>	LICDA II in 1	0 D		

### Table 7.1.3.1.1-4: Physico-chemical properties of test soils

DW: dry weight

GPS: global positioning system USDA: United States Department of Agriculture

## 1. Experimental Conditions

Ø

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-tosolution 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 CaCl₂ solution containing HgCl₂ (approx. 50 mg/L) with a soil-to-solution ratio of 1.40(5 g soil dry wath/20 mL solution). Flufenacet was applied at nominal concentrations of 1.003, 04, 0.03 and 0.01 M CaCl₂ in aqueous 0.01 M CaCl₂ solution. The desorption phase was performed by supplying pre-adsorbed soil samples with fresh aqueous 0.01 M CaCl₂ solution containing HgCl₂ (approx. 50 mg/L) for all test concentrations. For the highest test concentration (1.0 mg/L) two additional desorption excles were performed likewise. The adsorption and desorption steps were carried out each for 24 hours in the dark at  $20 \pm 2$  °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 are the supernatants was analyzed by light d 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 (sotherm) were calculated by linear regression analysis of the adsorption or desorption data according to the Feundlish equation.

## A. MATERIAL BALANCE

Mean material balance, were 401.8, 903, 959, 97.4 and 97.3% of applied radioactivity [% AR] for soil Laacherhof AXXa, Hoefchen an 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. DÉGRADATION 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 paacherhof 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).

8			×1	S	E.	$\cap$	ž (		d,	
			Ś	Test (	Concent	ration [	mg/L]	Č	Ď	
		Ad	sorptio	n 18	$\mathcal{Q}$	,	್ಷಿಯಿ	sorptio	n ²	
Soil	1.0	0.3	0.1	/ 0.03 _@	<b>0.01</b>	<b>1.0</b>	0.3	<b>Ø</b> ,1	0.03	0.01
Laacherhof AXXa	47.1	54-6	53.3	55 🔏	55.8Ø	40.7	¥37.2	\$5.5	33.7	35.0
Hoefchen am Hohenseh	44.3	<b>\$9</b> .0	<b>\$4</b> .6	52.8	53	40,4	37.4	° 33.5	34.3	34.3
Hanscheider Hof	57.1 🕻	J 60.8%	62.0	\$5.4	<u>6</u> 4.9	-300:0	27 <b>0</b>	26.6	25.0	24.2
Dollendorf II	67.2	71,∜	″72.8°ື	¢ 75.4	©76.9	Q2.7 /	19.9	18.5	16.7	15.8
Laacherhof Wurmwiese	° <b>44</b> .6	47,3	47.2	48	46.4Ô	41.1	38.2	38.8	37.6	40.0
		Ø.0	@¥							

Table 7.1.3.1.1- 5:	Percentage of adsorbed and	desorbed	l flufenac	et in soils:	(mean v	alues)
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¹ end of adsorption phase, mean xatues expossed 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/desor	ption consta	ints and coor	elation coefficien	ts of flufenacet in soil at
	20	' L ~ ~	j _O`	s,Oʻ	

		. W //		))	1			
	م م ا	Adso	rption	, S		Desor	rption	
Soil?	K	171	<b>A</b> A	Koc	K _F	1/n	R ²	K _{OC}
	[mL/g]		$\searrow$ $$	[mL/g]	[mL/g]			[mL/g]
Laacherhof AXXa	<b>Q</b> .555	90.9285	0.9991	161.6	5.580	0.9440	0.9988	253.6
Hoefchen am Hohensek	3.28	0.920	0.9965	205.0	5.637	0.9426	0.9980	352.3
Hanscheider Hof	5.101	0, <b>92</b> 65	0.9992	188.9	8.488	0.9374	0.9996	314.4
Dollendorf II	7.495	@9033	<b>@</b> .9994	178.5	11.707	0.9081	0.9996	278.7
Laachernof Wurnwiese	\$3.319	0.9797 0	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
A A B	L	~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~						
		Ő	CONG					
W a .n	S .4	≫ĨII.	CONC	LUSION	S			

The adsorption constant  $K_{F(adc)}$  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 Antex I Inclusion and was accepted by the European Commission (7469/VI/98-Final –  $3^{rd}$  July 2003). The following study is included in the Baseline Dossier:

		0.	~	Y	, <b>O</b>
Annex Point / Reference No	Au	ithor(s)	\$ 4		Document No
KCA 7.1.3.1.2 /01	, M. R.;	, P. ¥.;	, V. 🗛	1994	M-092185-01-1
			1 "0"	$\sim$	

The newly identified major degradation product FOE-thiadone was already characterized within the study M-002185-01-1_(Baseline Dossier, KCA 7.1.3.1.2001) which was summadized in the Baseline Dossier with regard to the major degradation products FOE oxalate and POE sufforic 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 fufenacet renewal of approval

Report:	KCA 7.1.3, 1.2 /01,
Title:	Soil Adsorption Desorption of FOE 5043 Degradates: FOE Sulfonic Acid, FOE
	Methy Sulfox de, FOE Oxalate, FOE Alcohol, and Thiadone
<b>Report No:</b>	MR 6598 O C C
<b>Document No:</b>	M3902183-01-1 %
Guidelines:	EPA Ref: 163 4, Adsorption/desorption
GLP:	yes have a second secon
~	

## Executive Summary

The adsorption desorption behaviors of the degradation products FOE methylsulfoxide, FOE sulfonic acid, FOE oxalate, FOE alcohol and FOE thradone were studied in four different soils in the dark in the laboratory at  $\frac{23}{5} \pm \frac{1}{5}$  °C using the bach equilibrium method:

Soil O	Source	Texture (USDA)	pН	OC [%]
O Winder	Vero Beach, USA	sand	5.8	0.27
A Shipshe	Howse USA	sandy loam	6.3	0.75
Drummer Ø	Champaign, USA	silty clay loam	6.6	2.13
🛇 🔍 Qska-Martin	Stilwell, USA	silty clay	6.0	1.21
	× X			

The adsorption phase of the study was carried out using air-dried soils and aqueous 0.01 M CaCl₂ 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 CaCl₂ (containing max. 0.5% acetonitrile). The desorption phase was performed by supplying pre-adsorbed soil samples with fresh aqueous 0.01 M CaCl₂ 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% applied radioactivity  $\mathcal{P}$  AR for soil Winder, Shipshe, Drummer and Oska-Martin, respectively  $\mathcal{P}$ 

The adsorption constants  $K_{F(ads)}$  of FOE-thiadone calculated based on the Freundtich 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  $\sqrt{9} - 62.2\%$  of the initially accorbed radioactivity was desorbed from the respective soils The desorption constants  $K_{OC(ac)}$  were 2 to 4 times higher than the  $K_{OC(ads)}$  values.

The results indicate that the adsorption behavior of FOE-thadone 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.

. MATERIALS AND METHODS

## A. MATERIALS

1. Test Item 3FOE-thiadono BAS No 3Specific activity 6Radiochemical purity 99.76 99.76 99.76 99.76 99.76 99.76 99.76 99.76 99.76 99.76 99.76 99.76 99.76 99.76 99.76 99.76 99.76 99.76 99.76 99.76 99.76 99.76 99.76 99.76 99.76 99.76 99.76 99.76 99.76 99.76 99.76 99.76 99.76 99.76 99.76 99.76 99.76 99.76 99.76 99.76 99.76 99.76 99.76 99.76 99.76 99.76 99.76 99.76 99.76 99.76 99.76 99.76 99.76 99.76 99.76 99.76 99.76 99.76 99.76 99.76 99.76 99.76 99.76 99.76 99.76 99.76 99.76 99.76 99.76 99.76 99.76 99.76 99.76 99.76 99.76 99.76 99.76 99.76 99.76 99.76 99.76 99.76 99.76 99.76 99.76 99.76 99.76 99.76 99.76 99.76 99.76 99.76 99.76 99.76 99.76 99.76 99.76 99.76 99.76 99.76 99.76 99.76 99.76 99.76 99.76 99.76 99.76 99.76 99.76 99.76 99.76 99.76 99.76 99.76 99.76 99.76 99.76 99.76 99.76 99.76 99.76 99.76 99.76 99.76 90.76 90.76 90.76 90.76 90.76 90.76 90.76 90.76 90.76 90.76 90.76 90.76 90.76 90.76 90.76 90.76 90.76 90.76 90.76 90.76 90.76 90.76 90.76 90.76 90.76 90.76 90.76 90.76 90.76 90.76 90.76 90.76 90.76 90.76 90.76 90.76 90.76 90.76 90.76 90.76 90.76 90.76 90.76 90.76 90.76 90.76 90.76 90.76 90.76 90.76 90.76 90.76 90.76 90.76 90.76 90.76 90.76 90.76 90.76 90.76 90.76 90.76 90.76 90.76 90.76 90.76 90.76 90.76 90.76 90.76 90.76 90.76 90.76 90.76 90.76 90.76 90.76 90.76 90.76 90.76 90.76 90.76 90.76 90.76 90.76 90.76 90.76 90.76 90.76 90.76 90.76 90.76 90.7690.

## 2. Test Soils

The soils (Table 75.3.1.27) were sieved to a particle size of  $\leq 2$  mm. The soils were taken from agricultural areas representing different geographical origins and different soil properties as required by the gridelines.



Parameter		Results	/ Units	
Soil Designation	Winder	Shipshe	Drummer	Oska-Martin
Geographic Location			2 A	
City	Vero Beach	Howe	Champaign 🔬	Stilwell
State	Florida	Indiana	Winois O	<b>A</b> ansas
Country	USA	USA	USA	O USA
Soil Series		no informati	on available	r k
Textural Class (USDA)	sand	sandy loam	silty clay loam	sitty clay
Sand [%] [50 $\mu$ m – 2 mm]	92.5	68.5	11.1	⁰ 3.1 ⁵
Silt [%] $[2 \ \mu m - 50 \ \mu m]$	1.3	17.6	<u></u> 54,∦	475
Clay [%] [< 2 μm]	6.3	13.9	34.8	× 49.8
pH in water (soil/water 1/1)	5.8 🐇		6.6	6.0
Organic Carbon [%]	0.27	Q0.75	×× 2.13	1.21
Organic Matter [%] ¹	0.5	L 1.3	‰ <u>3</u> .♥	2.1
Cation Exchange Capacity [meq/100 g]			22.4	29.3
Water Holding Capacity	5.0 0	8.3	24.8	28.1
at 0.33 bar (pF 2.5) [%]		× Ö		

### Table 7.1.3.1.2-1: Physico-chemical properties of test soils

¹ calculated as: OM [%] = OC [%]  $\cdot$  1.724  $\bigcirc$  SDA: United States Department of Agriculture

## B. STUDY DESIGN

## 1. Experimental@onditions

The test system for adsorption and desorption in batch equilibrium experiments consisted of glass centrifuge tubes closed with Teflore 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-tosolution 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 CaCl₂ solution with a soil-to-solution ratio of 3:10 (6 g soil dry weigh 20 mL solution). FOE-thiadone was applied at nominal concentrations of 50, 1.0, 0.2 and 0.04 mg/L in aqueous 0.01 M CaCl₂ solution (containing max. 0.5% acetonitrite). The desorption phase was performed by supplying pre-adsorbed soil samples with fresh aqueous 0.01 M CaCl₂ 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  $23.5 \pm 1.5$  °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 [9, 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 HPL Adiodetection 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 1.3 to 28.6% AR to soil Oska-Martin. The adsorption constants  $K_{F(ads)}$  of FOE-thadone calculated based on the Freundlich isotherms of the four test soils ranged from 0.12 to 0.71 ph/g and the normalized adsorption constants  $K_{OC(ads)}$  (normalized to organic carbon content franged from 29 and 58 mL/g. The Freundlich exponents 1/n were in the range of 0.673 to 0.80% indicating that the concentration of the test item affects its adsorption behavior in the examined concentration range (see Table 7.1.3 0.2-3).

At the end of the first desception phase, 134 to 622% (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, Brummer and Oska-Martin, respectively. The desorption constants  $K_{F(des)}$  frange 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 adsorbe	ed and desorbed FOE-thiadone in soils	(ranges of triplicates)
			( · · · · · · · · · · · · · · · · · · ·

, *	, O ^v	0 ,0	T∕¢″, °C	est Concent	ration [mg/l	L]			
A	A O Adsorption				Desorption ²				
Soil	_@ ,5.0 👸		~0.2	0.04	5.0	1.0	0.2	0.04	
Winder 🔗	Q2.1−3.£	1.6 <b>4</b> .4	s <b>28</b> − 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 2 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	0.9 - 16.2		35.5 - 36.7		13.8 - 17.1	1.5 - 4.0	6.0 - 10.1	
Oska-Martin	11.5 - 13.3	19.4 – 20.0	24.2 - 25.5	27.2 - 28.6	-5.68.7	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

									1
		Adso	rption			Deso	rpti		
Soil	K _F	1/n	R ²	Koc	K _F	1/n ·	$R^2 =$	[°] Koc K	
	[mL/g]			[mL/g]	[mL/g]	, K	¢ _0	[mL/g]	, O
Winder	0.12	0.782	0.975	43	0.35	0.705	0.958	128	× 1
Shipshe	0.33	0.807	0.999	44	1×12°	0:876	0.998	Å <b>1</b> 89 s	
Drummer	0.61	0.673	0.999	29	<i>_</i> <b>%</b> 56	0.654	<b>, 0</b> .995 ≪	ັ 73 🔊	
Oska-Martin	0.71	0.798	0.998	58	≥ <u></u> 2.10 (	D ^v 0.888	0.9280	174	0
				Ŵ			S	Ś	۔ ا

## 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 Freendlick exponents 1/n were in the range of 0.673 to 0.807, indicating that the concentration of the test arem 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.

	$\mathcal{O}$ $\mathcal{O}$ $\mathcal{O}$ $\mathcal{O}$ $\mathcal{O}$ $\mathcal{O}$ $\mathcal{O}$
Report:	KCA 7.1.3 <b>4</b> ,2 /03; <b>W</b> ² ; 2011 <b>C</b>
Title:	[Phenyl-UD-14C] BCS-CO62475: Adsorption/Desorption in Five Different
	Soils of the second sec
Report No:	AS15
<b>Document No:</b>	M-441141-00-1 S & A
Guidelines:	• QECD Test Guideline No. 106
	US EPA OCSEP Test Suideling No. 839.1220
	• Canadian PMRA Guideline DACO \$2.4.2
l la	• Commission Directive 95/36/EC amending Council Directive 91/414/EEC
GLP:	yes a contraction of the second
<u> </u>	
Executive Summa	

The adsorption desorption behavior of [phenyl-UL-¹⁴C]BCS-CO62475 ( $\triangleq$ [phenyl-UL-¹⁴C]FOE methylsulfone was studied in five different soils in the dark in the laboratory at 20 ± 2 °C using the batch equilibrium method:

Søil a	Source	Texture (USDA)	pН	OC [%]
Wyrmwiese A	Monheim, Germany	loam	5.3	1.8
Hoefeben am Nohensel	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 CaCl₂ 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 CaCl₂. 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 plass balances after 96 h were 93.7, 93.8, 90.5, 92.6 and 94.8% AR for soil Wurmwiese, Hoefchen and Hohenseh, Dollendorf H, Guadalupe and Springfield, respectively.

Material balances ranged from 97.9 to 103.4 % of applied raffoactivity [% AR] for Soil Wurmwiese, from 93.3 to 98.7% AR for soil Hoefchen am Hohenseh, from 96.6 to 99.5% AR for soil Dollendorf II, from 96.9 to 99.7% AR for soil Guadalupe and from 86.4 to 98.6% AR for soil Springfield.

The adsorption constants  $K_{F(ads)}$  of FOE methylsulfon calculated based on the Freundhich 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 1710 mL/g (mean: 4.1 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  $K_{QC(ads)}$  were 1.1 to 2.2 times higher than the  $K_{OC(ads)}$  values.

According to Briggs ¹⁷, FOE methylsulfore can be classified as low mobile or mobile in the tested soils.

- A. MATERIALS

## 2. Test Soils

The soils (Table 7.1.2.4) were sampled from the field (upper horizon of 0 to 20 cm or 0 to 6 inches), sieded to a particle size of  $\geq 2$  mm and stored for a maximum period of 25 months before study start. The soils were air-dred before application. The soils were taken from agricultural areas representing different geographical origins and different soil properties as required by the guidelines.



Parameter	Results / Units						
Soil Designation	Laacherhof	Hoefchen am	Dollendorf II	Guadalupe	Springfield		
	Wurmwiese	Hohenseh		$\sim$ $\sim$	L.		
Geographic Location			Ĺ	d' d'	0		
City	Monheim	Burscheid	Blankenheim	[®] Guadalupe.	Springfield		
State	North-Rhine	North-Rhine	North-Rhine	Cât/fornia	Nebraska		
Country	Westphalia Germany	Westphalia @ Germany	Westphalia Germany	USA	USA		
GPS Coordinates	N 51° 04.9' E 006° 55.2'	N 51° 0 <b>€0'</b> E 007≪96.3'	N 50° 22. 6 006° 43.0'	N 35° 01' WO20° 36C	∑N 96%15' W 44⊊03'		
Textural Class (USDA)	loam	silt Ioam 👡	clay toam	sandy loam	sitte loam		
Sand [%] [50 µm – 2 mm]	51	Q27 🔊	ે~31	560	<b>12.7</b>		
Silt [%] $[2 \ \mu m - 50 \ \mu m]$	28	× 54\$	8 38	ð <b>2</b> .6	ζ 60.8		
Clay [%] [< 2 $\mu$ m]	21	× 10	Ø 31 V	≥ 11.4 <i>S</i>	26.5		
pH	۲.	L, Ô		Ø a			
- in CaCl ₂ (soil/CaCl ₂ 1/2)	5.3	© [*] 6.6 , © [*]	A.3 S	67	6.6		
- in water (soil/water 1/1)	59	C 6 <u>.</u> 8	<b>∞</b> 7.4~Q	<b>\$</b> .8	7.2		
Organic Carbon [%]	ĈI.8 🗞	, 2,4 C	× 4.6×	٥.7	1.7		
Organic Matter [%] ¹	§ 3.1 ∜	°≈y¥.1 Ŭ	Q.9 ~	1.1	2.9		
Cation Exchange Capacity [meq/100 g]			\$21.9 J	16.1	16.1		

 Table 7.1.3.1.2-4:
 Physico-chemical properties of test soils

USDA: United States Department of Agriculture ¹ calculated as: OM [%

#### B. STUDY DE

#### 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 diplicate Oexperiments were performed in duplicate, O

In preliminary dests, the adsorption of the test item to the test system surface, the optimal soil-tosolution ratio, the appropriate adsorption an desorption equilibration times and the stability of the test item were determined.

O The adsorption phase was calried out using air-dried soils equilibrated in aqueous 0.01 M CaCl₂ solution with a soil-to-solution ratio of 1:2 (10 g soil dry weight/20 mL solution) for soils Wurmwiese, Hoefchen am Hohenseh auf Dollendorf II, 1:1 (20 g soil dry weight/20 mL solution) for soil Guadalupe and 1:10 (2 g sold dry weigh 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 CaCl₂ solution. The desorption phase was performed by supplying pre-adsorbed soil samples with fresh aqueous 0.01 M CaCl₂ 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  $20 \pm 2$  °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 lost 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 operation only due to the stability of the test item demonstrated by the parental mass balance. After the desorption steps, the soil was naxed 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 cabulated 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 193.4% of applied radioactivity [% AR] for soil Wurmwiese, from 93.3 to 98.7% AR for soil Hoeffben am Plohenseh, 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 complete material balances found for al Casoils and concentrations demonstrated that there was no significant loss of radioactivity desipated from the test systems of during sample processing.

## B. DEGRADATION OF TESTITEMS

FOE methylsulfone was sufficient stable proughout the study. The parental mass balances after 96 h were 93.7, 93.8, 90.5, 92.6 and 94.8% AR for soil Wurnewiese, Hoefchen am Hohenseh, Dollendorf II, Guadalupe and Spring field, 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 Hoefcher am Hoberseh, 43.1 to 56.2% AR to soil Dollendorf II, 34.4 to 44.9% AR to soil Guadalupe and 22.7% 36.9% AR to soil Springfield.

O

The adsorption constants  $K_{F(ads)}$  of FOE methylsulfone calculated based on the Freundlich isotherms of the five test soils ranged from 0.5233 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 sojk/n	(mean values)
------------------------------------------------------------------------------------	---------------

						·		·	
	Test Concent					ration [mg][2]			
Adsorption ¹				Desorption ²				. Oʻ	
1.0	0.3	0.1	0.03	0.01	1.0	0.3	<b>0.</b> 1	<b>0.03</b>	<b>0.0</b> 1
24.2	28.5	31.7	34.0	379	47.5	44.9	42.4	¥42.2√	40.7
39.5	44.0	48.0	50.6	<b>83</b> .1	£\$.7	321	30%.8	28. Ty	27.9
44.4	48.8	51.7	چ 55.3	[∞] 56.2 _∞	©31.6 «	28.0	29.0	25.2	25.7
34.4	38.2	40.9	43. <b>Ø</b>	44.7	33.0	\$32.7	31.1	29.0	<b>27</b> .1
23.0	26.6	29.8	34.0	3,607	59.7	59 <b>J</b> C	57.4	53.0	\$51.7
	24.2 39.5 44.4 34.4	1.00.324.228.539.544.044.448.834.438.2	1.0         0.3         0.1           24.2         28.5         31.7           39.5         44.0         48.0           44.4         48.8         51.7           34.4         38.2         40.9	Adsorption 1           1.0         0.3         0.1         0.03           24.2         28.5         31.7         34.0           39.5         44.0         48.0         50.6           44.4         48.8         51.7         55.3           34.4         38.2         40.9         43.2           23.0         26.6         29.8         24.0	Adsorption 1           1.0         0.3         0.1         0.03         0.01           24.2         28.5         31.7         34.0         36.9°           39.5         44.0         48.0         50.6         \$3.1           44.4         48.8         51.7         55.3         56.2           34.4         38.2         40.9         43.2         44.2	Adsorption         1         0.3         0.1         0.03         0.01         1.0           24.2         28.5         31.7         34.0         34.9°         47.5°           39.5         44.0         48.0         50.6         53.1         55.7           44.4         48.8         51.7         55.3         56.2         31.6           34.4         38.2         40.9         43.2         44.7         33.0           23.0         26.6         29.8         34.0         36.07         59.7	Test Concentration [mg/L]           Adsorption ¹ D           1.0         0.3         0.1         0.03         0.01         1.0         0.3           24.2         28.5         31.7         34.0         399         47.5         44.9           39.5         44.0         48.0         50.6         \$3.1         \$5.7         32.7           44.4         48.8         51.7         55.3         56.2         31.6         \$28.0           34.4         38.2         40.9         43.2         44.7         33.0         32.7           23.0         26.6         29.8         \$4.0         36.7         59.7         59.7	Adsorption 1       Desorption         1.0       0.3       0.1       0.03       0.01       1.0       0.3       0.1         24.2       28.5       31.7       34.0       34.9       47.5       44.9       42.4         39.5       44.0       48.0       50.6       33.1       35.7       32.7       36.8         44.4       48.8       51.7       55.3       56.2       31.6       28.0       29.0         34.4       38.2       40.9       43.2       44.7       33.0       32.7       31.1         23.0       26.6       29.8       24.0       36.7       59.7       59.7       57.4	Test Concentration [mg/L]           Adsorption 1         Description 2           1.0         0.3         0.1         0.03         0.01         1.0         0.3         0.1         0.03           24.2         28.5         31.7         34.0         3.9°         47.5         44.9         42.4         42.2           39.5         44.0         48.0         50.6         \$3.1         \$5.7         32.7         36.8         28.7           44.4         48.8         51.7         55.3         56.2         31.6         28.0         29.0         25.2           34.4         38.2         40.9         43.2         44.7         33.0         32.7         31.1         29.0           23.0         26.6         29.8         34.0         3607         59.7         59.7         57.4         53.0

¹ end of adsorption phase, mean values expressed as percentage of applied radioactivity

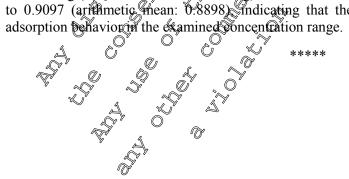
² end of first desorption phase, mean values expressed as percentage of the initially adsorbed amount

Table 7.1.3.1.2- 6:	Adsorption/desorption	constants	andcor	relation	coefficie	ents 🌮	OE methylsulfone	in
	soil at 20 °C		L	64	$\ll$	Ũ	•••	

		Å				$\ll$	. 0	
		Actso	rption	- S		Deso	phon	
Soil	K _F	Ph.	$OR^2$	¢K₀c ∕	$K_{F}$	y 1/n 🦉	R ²	Koc
	[mL/g]		$\langle \rangle$	mL/g	[mL/g	. ~		[mL/g]
Wurmwiese	0.6582	0.891	0.9990	37.4	0.2693	0.8980	0.9992	43.7
Hoefchen am Hohenseh	1.2797	0.88875	0.0997	s, [∞] <b>5</b> 2.9	Q	<b>9</b> .8931	0.9997	60.6
Dollendorf II	\$\$688	\$.9001 s	0.9996	33.2	1.8200	0.9124	0.9993	38.6
Guadalupe	ð.5253	≶0.909€	0.998	750	0.5671	0.9050	1.0000	81.0
Springfield	2.926	0.8602	0.9999	177.8	3.5944	0.8833	0.9994	211.4
Mean 🔊	1.3904	0-8898	0,9996	Q74.1	1.6435	0.8984	0.9995	87.1
Ô,	Ê.			1 5	¥.			

## CONCLUSIONS

The adsorption constants  $K_F(a_s)$  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: 70%1 mL/g). The Feundlich 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 rehavior in the examined concentration range.





Report:	KCA 7.1.3.1.2 /04; , M.; 2013
Title:	Determination of the Adsorption/Desorption Behavior of FOE 5043-trifluoro-
	ethanesulfonic Acid in Five Soils
<b>Report No:</b>	S11-03923
<b>Document No:</b>	M-449893-01-1
<b>Guidelines:</b>	• OECD Test Guideline No. 106
	• US EPA OCSPP Test Guideline No. 835.1230
GLP:	yes $\mathcal{D}^{\circ}$ $\mathcal{A}$ $\mathcal{D}^{\circ}$ $\mathcal{L}^{\circ}$

## **Executive Summary**

The adsorption/desorption behavior of BCS-CU62474 (2,2,2 prifluoroethanesultonates) report name: FOE 5043-trifluoroethanesulfonic acid) was studied in five different soils in the laboratory at  $20 \pm 2$  °C using the batch equilibrium method:

	× an	A. S.	Ň	Ø
Soil	Source S	Texture (USDA)	<b>ФН</b>	ØC [%]
Laacherhof AXXa	Monheim, Cormany 🖓	Joamy sand	6.4 ⋒	1.8
Dollendorf II	Blankenheinn, Germany	🔊 letam 🖉	7.4	5.0
Hoefchen am Hohenseh	Bursche d, Germany	🕺 sitt loam 🔍	6 ^g	1.8
Hanscheider Hof	Burscheid, Germany	🔬 silt loam	£.0	2.8
Laacherhof Wurmwiese	Montheim, Germany Ø	Sandy loam	<b>©</b> 5.2	1.9

The adsorption phase of the study was carried out using air-dried soils pre-equilibrated in aqueous 0.01 M CaCl₂ solution with a soil-to-solution ratio of 1.1 (50 g soil DW)/ 50 mL solution). Unlabeled BCS-CU62474 (2,2,2-trifluoroethane) was applied a nominal concentrations of 1.0, 0.3, 0.1, 0.03 and 0.01 mg/L in aqueous 0.01 M CaCl₂. The adsorption step was carried out each for 96 hours under continuous agitation.

FOE 5043-trifluoroethanesulfonic acid was sufficient stable broughout the study. The parental mass balances after 96 to were 98.3, 102.4, 93 1, 103 to and 704.6% AR for soil Laacherhof AXXa, Dollendorf II, Hoefchen and Hoherseh, Hanscheider Hof and Laacherhof Wurmwiese, respectively.

Only low to variable 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 cosumed that FOE 5043-trifluoroethanesulfonic acid has a high mobility in the tested coils.

MATERIALS AND METHODS

## A. MATERIALS

## 1. Test Item

unlabeled BCSU62474 (sodium 2,2,2-trifluoroethanesulfonate; report name 1:FOE 5043-trifluoroethanesulfonic acid)Batch IDNLL8865-4-1Certificate No.MZ 00482Chemical purity99.4%, ¹⁹F-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  $\leq 2$  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.

Parameter			Results / Units		
Soil Designation	Laacherhof	Dollendorf I			Laacherhof
Son Designation	AXXa		Hohenseh		Wurnawiese
Geographic Location		K,		б, _. О [°]	<u>A</u>
City	Monheim	Blankenheim	Burscheid	Burscheid	Monheim
State	North-Rhine	North-Rhife	North/Rhine	North-Rhine	Worth-Rhine
	Westphalia	Westphalia	Westphalia	Westphalia	Westphalia
Country	Germany	Germany	Germany	Germany	Germany
GPS Coordinates	N 51° 04.6	N 50° 22. 9'	≫N 512 04.0'	N 51° 04.5'	N 51° 04.9'
	E 006° 53 5	E@06° 43.@	E 007 06.3	E 007 208.4'	E 006° 55.3'
Soil Taxonomic Classification	Q,	no in	nformation wail	able	
(USDA) Soil Series		N ^Y CA	Dormation avail		
Textural Class (USDA)				$\sim$	
Sand [%] $[50 \ \mu\text{m} - 2 \ \text{mm}]$	doamy sand	loam	silt Ioam	r″silt loam 27	sandy loam
Silt [%] $[30 \ \mu m - 2 \ mm]$ Silt [%] $[2 \ \mu m - 50 \ \mu m]$	ľ de l	$\cap$ ''''		27 56	55 30
Clay [%] $[< 2 \mu m]$		<b>3%</b> €27 [°] ∕		56 17	30 15
		0.0	Å.	17	15
pH - in CaCl ₂ (soil/CaCl ₂ 12)		7 4 9	ST (5	5.0	5.2
			6.5	5.0	5.2
- in water (soil/water (1) - in water (saturated paste)	A 6.6		<b>6</b> .7	5.3	5.4
- In water (saturated paste)	6.7	~~~/.4 ~~ 0 - 1	6.8	5.4	5.5
	× 64×	× 7.10	6.1	4.7	4.8
Organic Carbon [%]		\$ 5.8	1.7	2.8	1.9
Organic Matter [%]	3.1	8.6	2.9	4.8	3.3
Cation Exchange Capacity	G 9.6	© [*] 21.5	11.5	10.1	11.0
[meq/100 g] Water Holding/Capacity		8			
		84.6	54.3	63.7	57.4
$[g H_2 Q^2 u d \ 100 g \text{ soil DW}]$	$\bigcirc +3.4 \checkmark$	04.0	54.5	03./	57.4
$a_1 \cup a_2 \cup a_1 \cup a_1 \cup a_2 $	15.9	43.1	27.9	29.1	21.2
at 0.83 bar (pt 2.5) [55]	<b>D</b> .6	33.5	20.6	22.9	17.0
Bulk Density (disturbed)	<u>گ</u> 1.27	1.00	1.10	1.04	
	1.27	1.00	1.10	1.04	1.13
	0 [°]	l	l		

¹ calculated as: OM [% OC [%] · 1.724 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 glass flasks (volume 100 mL) closed with PTFE sealed screw caps. The experiments over performed in duplicate.

In preliminary tests, the adsorption of the test item to the test system surface, the optimal soil-tosolution 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 equeous 0.01 M CaCl₂ solution with a soil-to-solution ratio of 1:1(50 g soil drys reption / 50 mL solution). Unlabeled BCS-CU62474 (2,2,2-trifluoroethanesulfonate) was applied at nominal concentrations 0.1.0, 0.3, 0.1, 0.03 and 0.01 mg/L in aqueous 0.01 M CaCl₂ solution. The adsorption step was carried out for 24 hours in the dark at  $20 \pm 2$  °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 wher (1:20, v/v) before the amount of FOE 5043-trifluoroethanesulfonic 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 (LOO) was determined as 04 ng/oL and the limit of detection (LOD) was set to 1/5 LOQ, equal to 0.02 ng/mL. At this level the stand to noise ratio was  $\geq$  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 frem, 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 supermatant only due to the stability of the test item demonstrated by the parental mass balance.

The HPLC-MS/MS method was calidated 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 CaCl₂ solution diluted with water (1:10, v/v), as the observed matrix effects were in  $\leq 10\%$  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.



#### П. **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 for tification 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.

#### **DEGRADATION OF TEST ITEM** B.

FOE 5043-trifluoroethanesulfonic acid was sufficient stable throughout the study. The parental mass balances after the total incubation time of 96 hours (24 P adsorption  $+2^{9}x$  24 h desorption) were 98.3, 102.4, 93.1, 103.0 and 104.6% AR for soil Lancherhol 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 Tifluotoethanes for 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 conceptrations

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 (KF-value and On) well determined.

## CONCLUSIONS

Only low to virtually no adsorption of the test tem BCS-CU62474 (2,2,2-trifluoroethanesulfonate) was measured for all soils and all test concentrations. Mowever, using this data it was not possible to calculate any reasonable Freundlich Sothermand therefore no data describing the Freundlich isotherm < (K_F value and 1/n) were determined. O

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; , M.; , W.; 2011
Title:	[1-14C] BCS-AZ56567: Adsorption/desorption in five different soils
<b>Report No:</b>	AS155
<b>Document No:</b>	M-406740-01-1
<b>Guidelines:</b>	• 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 61/414/REC
GLP:	yes yes

## **Executive Summary**

The adsorption/desorption behavior of  $[1-^{14}C]BCS-AZ5656$  ( $\triangleq [15]C]$ triftuoroacetate, report name: trifluoroacetic acid) was studied in five different sols in the dark in the laborator at 20 + 2 °C using the batch equilibrium method:

				/N
Soil	Source	Dexture (USDA)	🏷 рН 🕅	ŐC [%]
Wurmwiese	Monheim, Germany	koam 🖉	5Ø)	1.8
Hoefchen am Hohenseh	Burscheid, Germany 🄏	🛿 🕅 loam 🕎	<b>@</b> 6	2.4
Dollendorf II	Blankenheim Germany	elay loan	⁷ .3	4.7
Guadalupe	Guadalupe, USA	Sandy to am	6.7	0.7
Springfield	Springfield, USA	🔰 siltQoam 🔊	6.6	1.7

The adsorption phase of the study was carried out using air dried so is pre-equilibrated in aqueous 0.01 M CaCl₂ solution with a soll-to-solution ratio of 1.1 (20 g soil  $_{dry weight}/20$  mL solution). [1-¹⁴C]BCS-AZ56567 was applied at normal concentrations of 1.0, 0.3, 0.1, 0.03 and 0.01 mg/L in aqueous 0.01 M CaCl₂. The desorption phase was performed by supplying pre-adsorbed soil samples with fresh aqueous 0.01 M CaCl₂ solution for all test concentrations. The adsorption and desorption steps were carried our each for 24 hours under continuous agriation.

Trifluoroacetic and was sufficient stable broughout the study. The parental mass balances after 48 h were 93.9, 93 4 92.5, 99.2 and 91.8% R for soil Wurnwiese, Hoefchen am Hohenseh, Dollendorf II, Guadalupe and Springfield, Ospectively.

Material balances ranged from 899 to 98-7% AB in soil Wurmwiese, from 96.2 to 98.2% AR in soil Hoefchen am Hohensen, from 97.4 to 1003.1 in soil Dollendorf II, from 97.8 to 100.5 in soil Guadalupe and from 96.1 to 98.2% 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 (Ko-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**

		, O`
1.	Test Item	bacetate sodium salt; report name ¹ : tritheoroacetic acid) KML9027 3.48 MBq/mg > 98% HPLC with radioactivery-detector e sampled from the field (upper horizon of 0 to 20 cm or 0 to 6 $f \le 2$ mm and stored for a maximum period of 20 months before
	[1-14C]BCS-AZ56567 (trifluoro	bacetate sodium salt; report name ¹ : tripproroacetic acid
	Sample ID	KML9027
	Specific activity	3.48 MBq/mg
	Radiochemical purity	> 98% HPLC with taenoactivity-detection
2.	Test Soils	
The	soils (Table 7.1.3.1.2- 8) were	e sampled from the field (uppet horizonly of 0 to 20 cm or 0 to 6
incl	nes), sieved to a particle size of	$f \le 2 \text{ mm}$ and stored for a maximum period of 20 months before
repi	esenting different geographical of	d before application. The soils were taken from agricultural areas origins and different soil properties as required by the guidelines.
- 1-		
	~	
	K	
	A O	
	Ë ^	
		$f \leq 2$ mm and stored for a maximum period of 20 mm/ths before d before application. The soils were taken from agricultural areas origins and different soil properties as required by the guidelines.
	× A	



Parameter	Results / Units					
Soil Designation	Wurmwiese	Hoefchen am	Dollendorf II	Guadalupe	Springfield	
		Hohenseh		$\sim$	L.	
Geographic Location			Ĺ	o" "O`	O' ĝ	
City	Monheim	Burscheid	Blankenheim	Guadalupe.	Springfield	
State	North-Rhine	North-Rhine	North-Rhine	California	Nebraska	
Country	Westphalia	Westphalia				
Country	Germany	Germany	Gennany	USA	ي USA	
GPS Coordinates	N 51° 04.9'	N 51° 0∉Ø'	N 50° 22.	N 35 01'	© [™] N 96%15'	
	E 006° 55.2'	E 007 06.3'	∕ <b>€</b> 006° 43.0'	W020° 360	) [∞] W 44⊊°03'	
Textural Class (USDA)	loam	silt Ioam 👡	clay toam	sandy loam	sitte loam	
Sand [%] [50 $\mu$ m – 2 mm]	51	Q27 ~	°~ <b>3</b> 1	× 560	<b>12.7</b>	
Silt [%] [2 μm – 50 μm]	28	K 54 X	× 38 ×	æ <u>2</u> .6	ζ 60.8	
Clay [%] [< 2 $\mu$ m]	21	× 10		≥ ^{11.4}	) 26.5	
pH	² ²	l, Ô	× 40 .	Ũ .		
- in CaCl ₂ (soil/CaCl ₂ 1/2)	5.3	0 [°] 6.6 °	₹.3 ×	6	6.6	
- in water (soil/water 1/1)	59	<b>6</b> .8 [°]	≪ 7.4 <b>°</b>	\$	7.2	
Organic Carbon [%]	ČI.8 📎	24 Č	× 40×	٥.7	1.7	
Organic Matter [%] ¹	رُي 3.0 ⁽	°≈y4.2 Û	<u>8</u> .1	× 1.1	2.9	
Cation Exchange Capacity [meq/100 g]	× 140.98		^Q 21.9	16.1	16.1	

### Table 7.1.3.1.2- 8: Physico-chemical properties of test soils

¹ calculated as: OM [%] = OC (3 + 1.72) USP : 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 flem to the test system surface, the optimal soil-tosolution 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 CaCl₂ solution with a soil-to-solution ratio of 1:1 (20 g soil _{dry weight}/20 mL solution). [1-¹⁴C] 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 CaCl₂ solution. The desorption phase was performed by supplying pre-adsorbed soil samples with fresh aqueous 0.01 M CaCl₂ solution for all test concentrations. The adsorption and desorption steps were carried out each for 24 hours in the dark at  $20 \pm 2$  °C under continuous agitation.

## 2. Analytical Procedures

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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 soft Wurmwlese, from 96 7 to 98.2% AR in soil Hoefchen am Hohenseh, from 97.4 to 103.1 in soil Doffendorf J, 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 discipated from the test systems or during sample processing.

## B. DEGRADATION OF TES®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% At for sold Wurnwiese, Høefchen 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 and Hohefseh, -9.6 to 8.2% AR to soil Dollendorf II, -3.2 to -1.3% AR to soil Guadanipe 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 ported.

**]]** 

## CONCLUSIONS

Virtually no adsorption and to some extend negative adsorption for the test item  $[1-{}^{14}C]BCS-AZ56567$ ( $\triangleq [1-{}^{14}C]$ trifluor acetate was measured. However, using this data it was not possible to calculate any reasonable Freundlich isotherm and therefore no data describing the Freundlich isotherm (KF-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; , E.; 2003	
Title:	Time-dependent sorption of FOE5043-sulfonic acid in solv $\sim$ $^{\circ}$ $\mathcal{K}$	~
<b>Report No:</b>	MEF-229/03	Į.
<b>Document No:</b>	M-111445-01-1	
<b>Guidelines:</b>	• 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 sulfonie 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 CaCl₂ 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 Dacherhof 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 soiDLaacherhof 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 acherhof AXXa and Laacherhof AXXa and Laacherhof AXXa and Laacherhof AXXa and Laacherhof AIII, respectively. Despite that observed increase of sorption with ageing time FOE salfonic 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 onder acrobic 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).

## 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 solutionic acid in ambient soil extracts) in relation to the amount of FOE solution.

## **©**RESULTS AND DISCUSSION

## A. DATA

Table 7.1.3.2- F and Table 7.1.3.2- 2 summaries the time-dependent sorption behavior of [phenyl-UL- 14 C]FOE sulfonic action 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.

				DAT	Č	'n	
Replicate	0	3	7	14	28	56	100
1	0.110	0.104	0.103	0.094	0.077	9,059	029
2	0.108	0.105	0.101	0.095	05080	<u>%0</u> .064	0.028
1	0.0120	0.0177	0.0159	_0.0166(	0.0164	0.014	0.0001
2	0.0145	0.0166	0.0160	0.0150	0.0146	0.0110	0.0068
mean	0.12	0.16	006	s.0 <del>9</del> 17	¢ 0.20 /	0.18	0.23
mean	8	11	×11	\$11 ⁽	گ 13	126	16
mean	2				- S	Ö A	Ű
	1 2 1 2 mean mean	1         0.110           2         0.108           1         0.0120           2         0.0145           mean         0.12           mean         8	1         0.110         0.104           2         0.108         0.105           1         0.0120         0.0177           2         0.0145         0.0166           mean         0.12         0.16           mean         8         11	1         0.110         0.104         0.103           2         0.108         0.105         0.101           1         0.0120         0.0177         0.0159           2         0.0145         0.0166         0.0166           mean         0.12         0.16         0.166           mean         8         11         11	Replicate         0         3         7         14           1         0.110         0.104         0.103         0.094           2         0.108         0.105         0.101         0.095           1         0.0120         0.0177         0.0159         0.0166           2         0.0145         0.0166         0.0160         0.0150           mean         0.12         0.16         0.066         0.0150           mean         8         11         11         11	Replicate         0         3         7         14         28           1         0.110         0.104         0.103         0.094         0.077           2         0.108         0.105         0.101         0.095         0.080           1         0.0120         0.0177         0.0159         0.0166         0.0164           2         0.0145         0.0166         0.0166         0.0159         0.0166         0.0164           2         0.0145         0.0166         0.0166         0.0150         0.0146           mean         0.12         0.16         0.06         0.0177         0.0150         0.0146           mean         8         11         11         13         11         13         11	Replicate         0         3         7         14         28         56           1         0.110         0.104         0.103         0.094         0.077         0.059           2         0.108         0.105         0.101         0.095         0.080         0.064           1         0.0120         0.0177         0.0159         0.0166         0.0164         0.0144           2         0.0145         0.0166         0.0160         0.0150         0.0146         0.0144           2         0.0145         0.0166         0.0160         0.0150         0.0146         0.0144           mean         0.12         0.16         0.066         0.0177         0.0150         0.0146         0.0114

 Table 7.1.3.2-1:
 Time Dependent Sorption of FOE sulfonic acid in Soil Laacherhof AXXa

¹ Concentration of test item in desorption solution from soil bately equilibrium shaking test

² Concentration of test item in soil after 24 h desprouten phase (sum of test item in ambien (soil extracts)

³ Time-dependent sorption factor K_d (DAT-100)  $(K_d (DAT-9) = 2)$ 

Table 7.1.3.2- 2: Time Dependent Sometion of FOE suffonic acid in Soil acheroof AIII

	Ĩa	, s		Ô	DØT	$\sim$		
Parameter	Replicate		<b>3</b>	<i>_©</i> _7	Q14	28	56	100
$a \dots \int u a / m I 1^{1}$		Ø.113 ×	_0.107 %	/ ~ ~	0.099	0.084	0.062	0.027
$c_{desorbed} [\mu g/mL]^{1}$		V 0.109	0.105	0.102	0.095	0.081	0.060	0.030
c extracted [µg/g] ²		0.0125	0.0952	0.0145	0.0131	0.0129	0.0096	0.0069
0	2	6,0137	×0/.0149	0.0145	1	0.0125	0.0093	0.0028
K _d [mL/g]	genean 🖉	0.12	0.14	0.14	0.15	0.15	0.15	0.18
K _{oc} [ml 🎝] 🐁	O mean O	135	Ŕ	16	17	17	18	20
Time-dependent Sorption factor	nkean	01.5		Ţ,				

¹ Concentration of test item in desorption solution from sol batch equilibrium shaking test

² Concentration of test item in son after 24 desorption phase (sum of test item in ambient soil extracts)

³ Time-dependent sorption factor  $K_d (DAT-0) = 2$ 



During the entire ageing period of 400 days the sorption values (K_d) increased by a factor of 2 (0.12 to 0.23 mL/g) and  $45^{\circ}$  (0.1200 0.18 mL/g) in soils Laacherhof AXXa and Laacherhof AIII, respectively.

However, the overall tesults 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-trifluoroethenesulfonic 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 flufenaeet degradation products derived from laboratory studies

	2	ð	<u> </u>	i i i i i i i i i i i i i i i i i i i	× ï
Degradation Pro	duct	Ø "k	UF 🔊	×,	°~
FOE sulfonic acid	×.	٥ ١ ٥	0.46	, O	L'
FOE methylsulfone	a)	<u></u> 1	.31	S a	y do
FOE 5043-trifluoroethanes	ulfonicacid		.36	ñ "O"	- A
trifluoroacetic acid	á .	V (	Ø39 _ Ø	″ Ü	
		Y of			a l'

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;
Title:	Amendment No. 1 to Final Report - Determination of the Plant Uptake Factor of
	FOE methylsulfone FOE soffonic acid and trifluor phanesulfonic acid in Wheat
<b>Report No:</b>	EnSa-12
<b>Document No:</b>	M-434257-02-5 3 4
<b>Guidelines:</b>	none $\mathcal{O}^{\vee}$ $\mathcal{O}^{\vee}$ $\mathcal{O}^{\vee}$ $\mathcal{O}^{\vee}$
GLP:	yest y a a a a a a a a a a a a a a a a a a

## Executive Summary

The plant uptake factors (PUFs) of the degradation products FOE sulfonic acid, FOE methylsulfone and FOE 5043-trifluoroethanesulfonic acid in when were determined in a greenhouse climatic chamber over a study duration of 8 days under controlled temperature, humidity and light conditions (temperature:  $18 \pm 21$  °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  $\mu$ g/L for FOE sulfonic acid, 7.86  $\mu$ g/L for FOE methylsulface and  $O.89 \mu$ g/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, 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.



#### MATERIALS AND METHODS I.

#### A. MATERIALS

#### 1. **Test Items**

A. MATERIALS	Ũ
. Test Items	
unlabeled AE 0841914 (FOE5043-s	sulfonic acid sodium salt; report name $FOF$ sulfonic acid) $\sqrt[4]{}$
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 na	AZ15999 BCS CO62475-00-01
Certificate of Analysis:	AZ15999 ~ ~ ~ ~ ~ ~ ~ ~ ~
Batch Code:	BCS_C062475-00-01 & 0 ⁹ 0 ⁹
Chemical Purity:	
unlabeled BCS-CU62474 (sodium 2	2,2,2 Tifluoroethanesulfonate report name 1 TOE 5043-
trifluoroethanesulfonic acid) Certificate of Analysis:	MZ00482 2 5 5 2 5
Batch Code:	BC\$CU62474-01-00 ~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~
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 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. STUDÝ DESDŐN

#### 1. Experimental Conditions

The hydroponic test systems for the plant uptake factor (PUF) experiments consisted of brown glass bottles (volume 1000mL), filled with 800 mb test solution and ten wheat plants/test vessel. The plants were fixed with the stome 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 contral 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  $\Delta DAT-8$ 

## 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  $\triangleq$  DAT-8).

The mass selective detector was operated in the electrospray fonization 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 HPLQ-MS/MS method was tested over a concentration range from 0.3 to 45.0  $\mu$ g/L for FOE sulfonic acid, from 0.07 to 10.50  $\mu$ g/L for FOE methylsulfone and from 0.15 to 22.50  $\mu$ g/L for FOE 5043-trifluoroethanesulfonic acid. The correlation coefficient (R²) of the external multi-point calibration curve was 0.9999 for FOE sulfonic 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 methylsulfore 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:

$\frac{\ln\left(\frac{m_{DAT-8}}{m_{DAT-0}}\right)}{\ln\left(\frac{m_{DAT-8}}{m_{DAT-0}}\right)}$	
$\ln\left(\frac{m_{\rm part}}{m_{\rm part}}\right)$	
$Q^{*} \qquad QUF \neq VIF \neq VIII = VIIII  = VIIII = VIIIII I = VIIIIII = VIIIIIII = VIIIIIIII$	
A $A$ $A$ $A$ $A$ $A$ $A$ $A$ $A$ $A$	
with:	
	[a]
mDAtor puttal amount of togritem intest solution	[µg]
mp _{AT-8} () amount of test new in test solution at study end (DAT-8)	[µg]
$V_{\text{DAT-0}} = \text{initial volume of test solution}$	[L]
$\sqrt{y}_{DAT-8}$ = volume of test solution at study and (DAT-8)	[L]
RESULTS AND DISCUSSION	

## A. FINDANGS

The transpiration, plume 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  $\mathbb{KOE}$  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.

# **Bayer CropScience**

### **Document MCA: Section 7 Fate and behaviour in the environment** Flufenacet

ethane	sulfonic acid	l in Wheat	t			\$		
Test	Replicate		DAT-0	_		DAT 8	_	PUF
Item		V	c	m	V	. ~ <b>\$</b>	ണ	r
		[L]	[µg/L]	[µg]	[L]	prg/L]	[µg] 🦂	Y ô
FOE sulfonic acid	1	0.80	34.27	27.42	0.66	<b>39.28</b>	25.92	0,20
	2	0.80	34.58	27.66	0.67Ø	37.90	25.45	Q 47
	3	0.80	34.47	27.58	0.70	36,24	\$.37	∞0.63
	Mean	0.80	34.44					¥ 0.46
FOE methylsulfone	1	0.80	7.86	_ <b>(6</b> .29 _{&gt;}	0.69 🌾	7.66	5.2%	1.17
	2	0.80	7.91 🦼	© 6.33 🗶	× 0.69	7.4D	545	<b>X:3</b> 9
	3	0.80	7.82	6.260	0,72	7,52	5.41	<b>1.37</b>
	Mean	0.80	7.86		A	~		1.31
FOE 5043-trifluoro-	1	0.80	15.78	12.62	م مراجع 🔊 🔊	15.53	10.73	1.11
ethanesulfonic acid	2	0.80	≪1⁄5.94 🧋	¥12.75	0.72	15.20	10.95	1.44
	3	0.80 👸	¥15.96Q	12,7	0.74	<b>\$</b> \$,00	0.65	1.52
	Mean	0.80 🗡	15.89	<u>Š</u> ^v	$\overset{\sim}{\sim}$	Ű.	0	1.36

### Table 7.1.4- 2: Plant Uptake Factors of FOE sulfonic acid, FOE methylsulfone and FOE 5043-trifluoro-

DAT: days after treatment V: volume of test solution m: mass of test item in test solution ant uptake factor

concentration of test item in

## ONCLUSIO

The plant uptake factors in when were determined as 0.46 for FOE sulfonic acid, 1.31 for FOE methylsulfone and 1.36 for FOF 5043-triffuoroethanesulfonic actd.

K) Õ The plant uptake factor of FOE sufferic act indicates a Dight inhibition of the plant uptake, due impermeability of the cell walls for polar compounds. The plant uptake factors of FOE methylsulfone and FOE 5043-tralluoroethanes atonic acid demonstrates a good plant uptake behavior of these test items.

Report: KC 7.1.4 02; , R.; 2013
<b>Title:</b> Agendment No 200 Determination of the Plant Uptake Factor of trifluoroacetic
acid (TFA) in Wheat
<b>Benort No:</b> $\mathcal{P}_{i}^{*}$ EnSa-13-035 $\mathcal{T}_{i}$ $\ll i$
<b>Document No:</b> $M-4$ 56754-03-1 $\sim$
Guidelines, none of o
GLP: Wayes we average and the second se
Executive Summary a O

## **Executive Summary**

The plant uptake factor (PUFs) of [1-14C]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  $\mu$ g/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 ar 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% continuing the reliability of the plant uptake experiment.

PUFs were calculated from the amount of the respective test mem 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

[1-14C]trifluoroacetate (sodium salt; report name 1: trifluoroacetic acid)

Batch Code: Specific Activity: Radiochemical Purity

KNIL 9494 0.08 MBq/mg $5 \ge 98\% (HPLC/radiodetection)^{7}$ 

## 2. Test Plants

Wheat plants (variety. Thasos) were pre-grown up to BBCH growth stage 15 on soil in a greenhouse under controlled temperature, humdity 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 gentle water shower. Afterwards the plants were transferred to the test vessels.

## B. STUDY DESIG

## 1. Experimental Conditions

The hydroponic test systems for the plant uptake factor (PUF) experiments consisted of brown glass bottles volume 1000 mP), filled with 800 mL test solution and ten wheat plants/test vessel. The plants were fixed with elastomer form 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  $\mu$ g/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

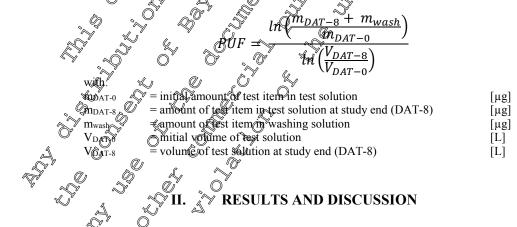
At each sampling interval aliquots of 1 mL each were taken from each test system. The initial and final test solution volume was determined at DATO and DAT-8, respectively. Additionally, at study end (DAT-8) the roots of each bunch test plants and the respective test vessel were washed with 200 mL acetonitrile/water (1/1, v/v). Afterwards, the wheat plants of each test systems over combined, weighed and homogenized.

Test and washing solutions were characterized by fiquid 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 initian 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:



## A. FINDINGS

The transpiration volumes 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%.



# **Document MCA: Section 7 Fate and behaviour in the environment Flufenacet**

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.

Replicate		DAT-0		DAT-8 V VUF
	V	c	m	V @ m mwash
	[L]	[µg/L]	[µg]	
1	0.80	75.5	60.4	0.26 100.9 26.2 6.5 954
2	0.80	75.3	60.2	0.27 103 27.9 65 0.51
3	0.80	75.4	60.3	0.40 82.2 29.5 24.1 $0.69$
4	0.80	75.5	60.4	<b>2</b> 928 1695.1 29.4 ∞ 5.7 , 0.52
5	0.80	76.5	61.2	0.37 86.9 32.1 4.5 0.00
Mean	0.80	75.6	~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~	

DAT: days after treatment V: volume of test solution m: mass of test item in test solution O, mwast mass of test item in washing Solution

III CONCLUSIONS

The plant uptake factors of [1-¹⁴C]tribuoroacetate (report name: tribuoroacetic 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: XXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXXX
<b>Title:</b> Determination of the Plant Uptake Factor of TFA (trifluoroacetic acid) in Wheat,
∫ Corn and Tomators O
<b>Report No:</b> $\mathcal{P}$ EnSa-12-058 $\mathcal{P}$ $\mathcal{P}$
Document No: M-440106-01-1
Guidelines: C none y y GLP: y no ~ y
GLP: no no r

## 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  $\mu$ g/L for wheat, 711.8  $\mu$ g/L for tomatoes and 769.1  $\mu$ g/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 tomates 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, 0,8 and 1 (only corn) days after treatment (DAT).

PUFs were calculated from the amount of the respective test 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 wallo whereas the plant uptake in corn was not restricted.

## I. MATERIALS AND METHODS

## A. MATERIALS

## 1. Test Items

[1-¹⁴C]trifluoroacetate (sodium salt; report name ¹: trifluoroacetic acid) Batch Code: KML 9072 (used for wheat and corn) KML 9241 (used for tomatoes)

Specific Activity: Radiochemical Purit

## 2. Test Plants

Wheat plants (variety: Trasos), 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 Got system by watering and washing with a gentle water shower. Afterwards the plants were transferred to the test vessels.

(HPDC/radiode

MBq/mg

## 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), fined with 800 mL test solution and either ten wheat plants/test vessel or one corn of romato 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  $\mu$ g/L for wheat, 711.8  $\mu$ g/L for tomatoes and 769.1  $\mu$ g/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 17 (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-89 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.

	$V_{DAT-x}$	
	$\sim \sqrt{2}$ $O$ $\left[ ln\left(\frac{Dn}{V}\right) \right] \sim \sqrt{2}$	
	V = V = V = V = V = V = V = V = V = V =	
with:		
mdat-0	= initial amount of test item in test solution	[µg]
mdat-x	= amount of test item in test solution at study end (DAT-gor DAT-11)	[µg]
mwash	= amount of test from in washing solution	[µg]
VDAT-0	= initial volume of test solution	[L]
VDAT-x	= volume of test solution at study end (DA) $-8$ or DAT $-11$ )	[L]

## **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.



Replicate		DAT-0			DA	T-8	\$	PUF
	V	c	m	V	c	m	magash	
	[L]	[µg/L]	[µg]	[L]	[µg/L]	[µg]	fugl	0
1	0.800	767.8	614.3	0.550	854.1	469.8	<b>9</b> .1	0.66
Mean	0.80	767.8				Ó		0,66
					@ °	d a	~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~	Į,
DAT: days a	fter treatme	ent		olant uptake	$(\alpha)$	·¥	.∼″	,0 [×] .
V: volume o	f test soluti	on			f test item i	n test solut	ion	
m: mass of to	est item in t	est solution	mwash: 1	mass of tes	t ûtem in wa	shing solut	ion 🕎	Q
				×.		, O	Š	O'Y
				0	, Ö	a O	,Ű	Û,
1.4- 5:	Plant Upt	ake Facto	rs of trifluo	oroacetic	açið in To	mato	× &	, Õ
Replicate		DAT-0	~		Q ^y da	ZT-8	Appl 9.1 0.7 0.7 0.7 0.7 0.7 0.7 0.7 0.7	<b>P</b>
	V	c	m 🔨	v 🍣	c _a	(m)		65
	[L]	[µg/L]	[µg]Ô	[Lĵ [≫]	[µØĽ]	[µǧ]	Qug	°
1	0.800	700.9	560,7	0,535	\$06.5	¥31.5 🔬	6.0	0.62
2	0.800	722.7	<b>\$</b> ₹8.2	0.585 /	C 742.2 🖉	× 434.2	7. <b>\$</b>	0.86
Mean	0.80	711.8			₹ ₹			0.74
V: volume o		on 🦄	c: conç		fstest itenoj			
m: mass of to	f test soluti est item in t	on $\sqrt[n]{}$	e: conç m _{wash} G	entration of mass of tes	ftest iten t item in wa	ishing Solut		
m: mass of to	f test soluti est item in t	on Solution	se: conc mwash	entration of mass of tes	titest iten titem in wa	ishing Solut		
m: mass of to	f test soluti est item in t	on est solution akerfactor	se: conç m _{wash} G	entration of mass of tes	ftest iten t item in wa	rn T-11	ion	PUF
m: mass of to	f test soluti est item in t	on Solution est solution cake factor DAT-0	G: conç m _{wash} rs of trifluc	entration of mass of tes	titem in wa	rn T-11 m	ion m _{wash}	PUF
m: mass of to	f test soluti est item in t Plant Opt	on est solution take factor DAT-0 c [µg/0]	Se: conç m _{wash} G rs of trifluc	entration of mass of fees	Etest iten t item in wa acid in Co	ishing Olut Tn T-11 m [µg]	ion m _{wash} [µg]	
m: mass of to	f test soluti est item in t Plant Opt	on $\sim$ est solution cake Factor DAT-0 c [ $\mu$ g/D] 762.0	rs of trifluc more free free free free free free free f	entration of mass of test proacetic V V V V V V V V V V V V V V V V V V V	titem in wa acid in Co part free free free free free free free fr	ishing Out 7n T-11 [μg] 480.1	ion <b>m</b> _{wash} [μg] 3.6	1.04
m: mass of to	f test soluti est item in t Plant opt V [L] 0.800 20800	on $\sim$ est solution <b>ake Factor</b> <b>DAT-0</b> c $\mu g/D $ 762.0 $\sim$ 772.6 $\sim$	C: conc mwash rs of trifluo m by by by by by by by by by by by by by	entration of mass of test proacetic <u>PL</u> 0.640 @ 0.672	titem in wa cid in Co part in Co	ishing Out π T-11 m [μg] 480.1 509.5	ion m _{wash} [μg] 3.6 4.4	1.04 1.06
m: mass of to	f test soluti est item in t Plant Opt V [L] 0,800 0,800	on est solution <b>DAT-0</b> <b>C</b> [µg/0] 762.0 772.6 772.8	C: conç mwash rs of trifluc 1921 009.6 0 618.0 618.0	entration of mass of test proacetic PL 0.640 ( 0.675	titem in wa acid in Co part free free free free free free free fr	ishing Out 7n T-11 [μg] 480.1	ion <b>m</b> _{wash} [μg] 3.6	1.04 1.06 0.86
m: mass of to	f test soluti est item in t Plant opt V [L] 0.800 20800	on $\sim$ est solution <b>ake Factor</b> <b>DAT-0</b> c $\mu g/D $ 762.0 $\sim$ 772.6 $\sim$	C: conc mwash rs of trifluo m by by by by by by by by by by by by by	entration of mass of test proacetic <u>PL</u> 0.640 @ 0.672	titem in wa cid in Co part in Co	ishing Out π T-11 m [μg] 480.1 509.5	ion m _{wash} [μg] 3.6 4.4	1.04 1.06
m: mass of to	f test soluti est item in t Plant $\overline{V}$ V [L] 0.800 0.800 0.800 0.800 0.800	on est solution ake Factor DAT-0 c [µg/0] 762.0 772.6 772.8 772.8	C: conc mwash rs of trifluo (09.6 618.0 618.7 618.7	entration of mass of test proacetic PL 0.640 ( 0.675	titem in wa titem in wa acid in Co pA pA pA pA pA pA pA pA pA pA	ishing Out π T-11 m [μg] 480.1 509.5	ion m _{wash} [μg] 3.6 4.4	1.04 1.06 0.86
m: mass of to 1.4- 6: Replicate 1 3 3 Mean	f test soluti est item in t Plant Opt V [L] 0.800 0.800 0.800 0.800 0.800 0.800 0.800	on est solution DAT-0 C 1µg/01 762.0 772.6 772.8 772.8 77901	E: conç m _{wash} rs of trifluc 102 09.6 0618.0 618.0 9 018.0 9 018.0 9 018.0 9 018.0 9 018.0 9 018.0 9 018.0 9 018.0 9 018.0 9 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0	entration of hass of test proacetic PL 0.640 ( 0.675 0.670	titem in wa titem in wa acid in Co pA pA pA pA pA pA pA pA pA pA	ishing Out <b>π</b> <b>T-11</b> <b>m</b> [μg] 480.1 509.5 526.5	ion <b>m</b> wash [µg] 3.6 4.4 4.3	1.04 1.06 0.86
m: mass of to 1.4- 6: Replicate 1 3 Mean DATE gays a	f test soluti est item in t Plant Opt V [L] 0.800 0.800 0.800 0.800 0.800 v 0.800 v 0.800 v 0.800 v 0.800 v 0.800 v 0.800 v 0.800 v	on est solution <b>DAT-0</b> <b>C</b> <b>DAT-0</b> <b>C</b> <b>DAT-0</b> <b>C</b> <b>762.0</b> 772.6 772.8 <b>7692</b> <b>7692</b>	E: conç mwash rs of trifluc 1923 009.6 0 618.0 618.0 618.0 9 0 618.0 9 0 618.0 9 0 9.0 0 618.0 9 0 618.0 9 0 9.0 0 618.0 9 0 90.0 0 618.0 0 0 90.0 0 br>0 90.0 0 0 90.0 0 0 90.0 0 0 90.0 0 0 90.0 0 0 90.0 0 0 90.0 0 0 90.0 0 0 0 90.0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0	entration a mass of test proacetics <u>PLI</u> 0.670 0.670 0.670 0.670 0.670 0.670	titem in wa titem in wa cid in Co pA pa pa pa pa pa pa pa pa pa pa	rn T-11 m [µg] 480.1 509.5 526.5 n test soluti	ion m _{wash} [µg] 3.6 4.4 4.3 ion	1.04 1.06 0.86
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The plant uptake factors of  $[1-{}^{14}C]$ trifluoroacetate (report name: trifluoroacetic acid) were determined as 0.66 in wheat, as 0.24 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.

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Report:	KCA 7.1.4 /04; , 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
<b>Report No:</b>	EnSa-13-0545
<b>Document No:</b>	M-468684-01-1
<b>Guidelines:</b>	• EFSA PPR-panel on the use of the Plant Uptake Factor in exposure models
	$(2013) \qquad
GLP:	

#### **Executive Summary**

The EFSA PPR-panel (2013) has recognized in an opinion that plant uptake is roop 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 accurrence of the process is demonstrated.

Evidence for the occurrence of plant uptake of the degradation product trifluomacetic acid has been demonstrated consistently in crop specific plant uptake studies and supportive confinest 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.

## . MATERIAL AND METHODS

Evidence on the occurrence of trifluoroacetic acid/uptak@by plants was provided by confined rotational crop studies on wheat, turing, swiss chard, radish and lettice using TFA-precursor as well as the two plant uptake studies KC/ $\sqrt{1.4}$  / $\sqrt{2}$  and K $\sqrt{A}$  7.1  $\sqrt{4}$ /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, radion and lettuce. Transfer from soil into plant matrices was clearly shown as significantly high esidues 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 PVF 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  $c_{uptake} = \frac{m_{uptake}}{V_{Uptake}}$ and with: PUF = plant uptake factor = test item concentration in plants Cuptake = test item concentration in porewate cporewater = amount of test item taken up by bants muptake = volume of test solution taken up by plants Vuptake S to gateulate the amount of Leaching models (e.g. PEARL and PELMO) use the PDF compound taken up by a plant with the transpiration stream in each time step according to: equation 2 with: = amount of test item taken up by plants muptake = test item concentration in porewater cporewater = volume of test solution taken up by plants Vuptake PUF = plant uptake factor

The EFSA PPR-Panel (2067) 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) outpres a thered approach  $\sim$ 

- 1 Briggs' formula estimating grop independent uptake factors based on the K_{oc} (FOCUS, 2000)
- 2 Plant uptake experiments with tagget 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 (TSCK) 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 ¹⁴C tabelled 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 to the test solution at the start and at the end of the study (reduced volume of the remaining test solution) adjows at indirect estimate of the plant uptake factor of the test item through the following calculation.

	1. (minal + mwash of some of the second
	$PUF = \bigcirc $
	The final is in the second sec
	$\mathcal{O}$ $\mathcal{O}$ $\mathcal{O}$ $\mathcal{O}$ $\mathcal{O}$ $\mathcal{O}$
with:	
m _{DAT-0}	= initial amount of test item in test solution $\Im$ [µg]
$m_{\text{final}}$	= amount of test item in test solution at study end $[\mu g]$
mwash	= appount offest item in wash solution at study and [µg]
V _{DAT-0}	= $\frac{1}{\sqrt{2}}$ $\frac$
$V_{\text{final}}$	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 trifluoroactic acid taken up by the plant from the test solution in the PUF experiment.

A supportive study KCAS. 1.4 by on the plant what of trifluoroacetic acid on the target crop wheat and additionally on com and tomatoes was also conducted.



## 1. Confined Rotational Crop Studies

In the first control 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  $2^{nd}$  rotation and a decline was noted from the material of the  $3^{rd}$  rotation. This is explained by the formation of the trifluoroacetic acid metabolite in soil over time followed by significant plant uptake in the  $2^{nd}$  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 when, radish and lettuce the transfer of trifluoroacetic acid from soil into the plant matrices was clearly mown 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 trifluotoacetic 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<br/>(rest period: % days, single values)

	[^>`[L] 🔬	µg/L	mpágo Úggi	DAT-8	СDAT-8 / [µg/L]	m _{DAT-8} [μg]	m _{DAT-8} [μg]	PUF
1	0.800	7\$s/5	Q60.4	⊁ 0.260≶	100.9	26.2	6.5	0.54
2 **	0,890	95.3	⁰ 60.2	0.270	103.4	27.9	6.5	0.51
3	0,800	() 75.4 ()	60 Ô	0.420	82.2	34.5	4.1	0.69
4	×0.800 ×	₹ 75,5	60/4	<b>@</b> .280	105.1	29.4	5.7	0.52
5 💊	0.809	76.5	£1.2 (	> 0.370	86.9	32.1	4.5	0.66
me	~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~	\$75.6		v .				0.59

DAT days after treatment V. Volume of test solution m: mass of test item in test solution

Additional recovery experiments demonstrate that the reduced test item amount in test solution at study end could be ecovered 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.

#### **CONCLUSIONS** III.

The EFSA PPR-panel (2013) has recognized in an opinion that plant uptake via goots is significant when calculating leaching exposure concentrations and has recommended the use of the Plant Uprake Factor (PUF) in exposure models, if evidence for the actual occurrence with process is the monstrated.

Investigations into the trifluoroacetic acid-specific paserve uptake in wheat determined an experimental evidence-based plant uptake factor (PUF) of 0.590 or trithroroacetic acid for use in higher tier environmental leaching model calculations. The transfocation of TFA from the test solution into the plant was further confirmed by a high recovery rate of trifluoroaceto acid of 92.6% in the combusted plant material.

Supportive experiments showed a trifluoroacetic acid ROF-factor of 0.66 for the targelerop 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 triftuoroace acid is demonstrated in confined rotational crop studies of in which increasing concentrations of trifluoroacetic acid in various crop matrices coincided with decreasingsoil residues of trifluoroacetic foid and the precursors.

Evidence for the occurrence of plant uptake of triflitoroacet 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  $> 0^{\circ}$  in environmental leaching models. For model assessment of plant protection products applied in wheat a trithroroacetic acid PUF of 0.59 is justified from study

Act under. Rene of plan a which increasing a sing soil residues of a plant uptake of trifford and b of a environmental leaching plant a trifford a trifford action a trifford a wheat a trifford action a trifford a triffo



### 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/96/Final 3rd July 2003). The following study is included in the Baseline Dossier:

Annex Point / Reference No	Author(s)	, Ö ^y		Document No
KCA 7.1.4.1.1 /01	, I. V.;	, S. )	1993	M-002198-04+1
	$\sim$	() and	Ŭ ()	$\bigcirc$ $\checkmark$

No additional studies are submitted within this Supplemental Dossier for the flutenacet 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 Possier

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Annex Point / Reference No	~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~		(Author's)	Q,	\$	Year	Document No
KCA 7.1.4.1.2 /01	)	Ő	, I. X,	øs.	Â,	1993	M-002198-01-1
<u> </u>			· · · · · · · · · · · · · · · · · · ·		$\sim$		

An additional study has been performed for trifluoroacetic acity to refine the results from the batch equilibrium experiments summarized in section CA 7 9.3.1 and is submitted within this Supplemental Dossier for the flufenacet renewal of approval.

Report: 5 M& 2014
Title: 1-14C]trifluoroacetate Soil Column Leaching
Report No: EnSa, 14-0050
Guidelines? CECI2 Test Gardeline No. 312
US IOA OCOPP Test Guideline No. 835.1240
GLP: yes 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 laboratory at 20.1 °C using two different soil column leaching experiments

Soil	Source	Texture (USDA)	pН	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



[1-¹⁴C]trifluoroacetate was used as test item. Additional soil columns were treated with [triazine-UL-¹⁴C]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. Dest 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 1938% 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 89.9 to 105.5% AR and between 96.8 to 104.3% AR, respectively, in all soil columns and bothgest 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 fourto to fifth leachate fraction of each soil column. 58.2 to 90.3% AR of the traced 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.

- soil columes. 7 - costigated!



The soil adsorption coefficients (K_d) for the reference item calculated according to Lambert²⁰, Hamaker²¹ and McCall²² 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 [1-¹⁴C]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 Ketelle²³ and Swoboda²⁴. 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 triffuoroacetic acid has a high mobility in the tested soils.

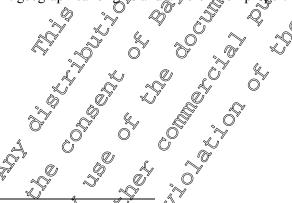
### A. MATERIALS

#### 1. Test Item

[1-¹⁴C]trifluoroacetate (report name): trifluoroacetic acid) CAS No Specific activity Radiochemical purity 3.48 MIBq/mg > 98% HPLC with adioacovity detect

#### 2. Test Soils

The soils (see Table 7.1 4 1.2- 1) were sampled Deshly from the field (upper horizon of 0 to 20 cm), sieved to a particle size of  $\leq 2$  mm and stored refrigerated at  $\leq 8$  °C for 18 days before study start. The soils were air-dried Defore application. The soils were taken from agricultural areas representing different geographical origins and different soil properties as required by the guidelines.



I.

- ²⁰ S. M. Lambert; Portem 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 W. 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; Proceedings 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.



Parameter	Results / Units					
Soil Designation	Laacherhof AXXa	Dollendorf II	Hoefchen an Hohensch ~	Laacherhof ° Wurmwiese		
Geographic Location	MMa					
City	Monheim	Blankenheim	Burscheid	Monheim		
State	North-Rhine	North-Rhin	North-Rhite	North-Rhine		
State	Westphalia	Westphalia	Westphalia	Westphalia		
Country	Germany	Germany	Germany	Germany		
GPS Coordinates	N 51° 04.647	N 50022. 899	N 51 04.001	x \$1° 04 \$57'		
	E 006° 53.517'	E 006° 43.001	E 007° 06 3 7'	© 006° 5\$251'		
Soil Taxonomic Classification	sandy, mixed,	tine-loamy,	Joamy, mixed,	loamy mixed,		
(USDA)	mesic Typic	Qmixed, active, `~	🧷 mesic Typic 🖒	meste Typic		
	Cambudoll	frigi@Typic & Eutrudept		Argudalf		
Soil Series	<u> </u>	no information available of				
Textural Class (USDA)	L'					
Sand [%] [50 $\mu$ m – 2 mm]	78	~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~	19	57		
Silt [%] $[2 \ \mu m - 50 \ \mu m]$	.016	\$ 36 K	× 64.	28		
Clay [%] [< 2 µm]	6	م ^ع رية 25	S N	15		
pH						
- in CaCl ₂ (soil/CaCl ₂ 1/2)		√.7.4 ~~	6.5	5.3		
- in water (soil/water 1/1)	06.5	مُ ۲.5 م	6.7	5.5		
- in water (saturated paste)	6.60	l 7.4 🖉	6.8	5.5		
- in KCl	Ū ^{\$} 6.8 [°]	P g.1 j	6.1	4.9		
Organic Carbon [%]	Å1.8 🖉	5.2	1.6	1.9		
Organic Matter [%]	3.1	9.00	2.8	3.3		
Cation Exchange Capacity $\bigcirc^{\vee}$ [meq/100 g]		22.3	12.2	9.9		
Water Holding Capacity	NO N					
maximum [®] ^o	43.8	79.3	51.8	60.2		
[g H ₂ O <i>ad</i> 100 g(soil DW) at 0.1 bar (pF 20) [%]	S 133 C	38.2	26.5	20.9		
Bulk Density, disturbed	§1.22	1.01	1.12	1.13		
	0 ×					

#### Table 7.1.4.1.2-1: Physico-chemical properties of test soils

¹ calculated as: OM [%] = 6c [%] · 1.724 DAT: Mays after treatment DW: dry weight

GPS: global positioning system USDA: United States Department of Agriculture

## 1. Experimental Conditions

B.

ST

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 chamber at  $20 \pm 2$  °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  $\mu$ L of the respective application solution were applied from wise onto the soil surface of the respective soil columns

After application, a glass frit glued to be upside down glass funnel was placed onto the top of each soil column in order to avoid whirling op the soil during the feaching 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 peristatic purps 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 peristatic purps. A supernatant of approx. 10 20 mg was maintained above the soil layer throughout the experiment.

All experiments were performed in durficate 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 frigation 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 intervals 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 coumns were deep-frozen and cut each into 5 segments of approx. 6 cm height for further analysis (text 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 (c.g. the reference item) were calculated according to Lambert ²⁰ and according to Hamaker ²¹ / McCall²²; 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 and boween \$2.2 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 soll columns and both test designs.

### B. DEGRADATION OF TEST FIEM

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 62.000 97.00 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 90.32 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  $A_{\rm c}$  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 32.9% 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 7 to 9 of soil Laacherhof AXXa, in leachate fraction 7 to 9 of soil Laacherhof AXXa, in leachate fraction 9 of soil Laacherhof AXXa, 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 9 of soil Hoefchen am Hohenseh and in leachate fraction 9 of soil Hoefchen am Hohenseh and in leachate fraction 9 of soil Hoefchen am Hohenseh and in leachate fraction 9 of soil Hoefchen am Hohenseh and in leachate fraction 9 of soil Hoefchen am Hohenseh and in leachate fraction 9 of soil Hoefchen am Hohenseh and in leachate fraction 9 of soil Hoefchen am Hohenseh and in leachate fraction 9 of soil Hoefchen am Hohenseh and in leachate fraction 9 of soil Hoefchen am Hohenseh and in leachate fraction 9 of soil Hoefchen am Hohenseh and in leachate fraction 9 of soil Hoefchen am Hohenseh and in leachate fraction 9 of soil Hoefchen am Hohenseh and in leachate fraction 9 of soil Hoefchen am Hohenseh and in leachate fraction 9 of soil Hoefchen am Hohenseh and in leachate fraction 9 of soil Hoefchen am Hohenseh and in leachate fraction 9 of soil Hoefchen am Hohenseh and in leachate fraction 9 of soil Hoefchen am Hohenseh and in leachate fraction 9 of soil Hoefchen am Hohenseh and in leachate fraction 9 of soil Hoefchen am Hohenseh and in leachate fraction 9 of soil Hoefchen am Hohenseh and in leachate fraction 9 of soil Hoefchen am Hohenseh and in leachate fraction 9 of soil Hoefchen am Hohenseh and in leachate fraction 9 of soil Hoefchen am Hohenseh and in leachate fraction 9 of soil Hoefchen am Hohenseh and in leachate fracting hoefchen am Hohenseh and in leacha



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 with investigated soils (mean: 5.6 mL/g). The respective organic carbon normalized soil adsorption coefficients (K_o) were in the range of 120.4 to 337.1 mL/g (overall mean: 258.4 mL/g). According to the Briggs^{Fe@r!} Textmake 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 [1-¹⁴C]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" all soils.

Table 7.1.4.1.2- 2:	Adsorption coefficients of the	test tem a	and/referenc	e item- in s	oils 🖉
	(mean values of duplicate soil c	alumns) 🏯	Ş. X	. 64	a subscription of the second s

(internit variates of aup			60 °C	
Soil	[1- ¹ 65]triflu Ka mL/gl	iorøacetate koc fmL/g]	[triazine&L Ka [m]Z/g]	- ¹⁴ C <b>]@r</b> azine Koc [mL/g]
Laacherhof AXXa 🛛 🔇		0.0	~~ 5.1 C	281.3
Dollendorf II	0.0		6.34	120.4
Hoefchen am Hohenseh ¹		0.0	Ô5.4	337.1
Laacherhof Wurmwiese		0.0%	5.6	294.9
Overall Nean	<b>₹0.0</b> 0 [×]	Ø.0	5.6	258.4
	L L	0 .0		

¹ only one soil column was considered

A AII. CONCLUSIONS

The mobility of the test item [1, 14C]trifuoroacetate 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 is can be assumed that trifluoroacetic acid has a high mobility in the tested soits.



#### Lysimeter studies CA 7.1.4.2

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  $-3^{\text{rd}}$  July 2003). The following study is included in the Baseline Dossier: Q.

Annex Point / Reference No	Author(s) Year Document So
KCA 7.1.4.2 /01	, EO , 1996 , 1996 01-2
KCA 7.1.4.2 /02	JE. J. 1995 M-002192-01-2
KCA 7.1.4.2 /03	E. 5 1995 M-002195-01-P
KCA 7.1.4.2 /04	, E. 195 MO0219401-1
KCA 7.1.4.2 /05	EC _ @ _ @ _ @ _ 0021& 01-1

ssier for the flufenaget renewal of No additional studies are submitted within this Supplemental approval.

#### Field leaching studies CA 7.1.4.3

CA 7.1.4.3 Field leaching studies



### CA 7.2 Fate and behavior in water and sediment

The route and rate of degradation of flufenacet under aerobic conditions was Sudied in a number of aquatic test systems at different temperatures, using either [phenyl-UL-¹⁴C] or [thiadiazote-2-¹⁴C]-labeled flufenacet as test item. Flufenacet was stable to hydrolysis and photolysis in steffe aquatic systems, while degradation was observed in microbial active aquatic systems. Ike water/sediment systems and surface water. Under aerobic conditions flufenacet was degraded in water, sediment and the entire system to two major degradation products: FOF thiadone (max. occurrence \$4.3% of applied radioactivity [% AR], entire system) and FOE methylsubide (max. occurrence \$1.4% 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 5% AR) accompanied by the formation of non-extractable residues (2 to 46% OAR).

On request of the US environmental protection agency (EPA) the route of degradation of FOEthiadone under aerobic conditions was additionally studied in a number of aquatic test systems at different temperatures, using either [phenyl-bt-¹⁴C] or [thisdiazole-2-¹⁴C] 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, fortung carbon dioxide and carbon monoxide as final major degradation product.

In addition to the aerobic water/sediment studies in the Daboratory a microcosm study with 11 microcosm systems was performed in the Netherlands. Measurement of the disappearance of flufenacet from the water phase showed that under more realigne 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 wrobic aquatic systems (see Figure 7.2-1) was similar to that observed in action for sort (see Figure 7.1).

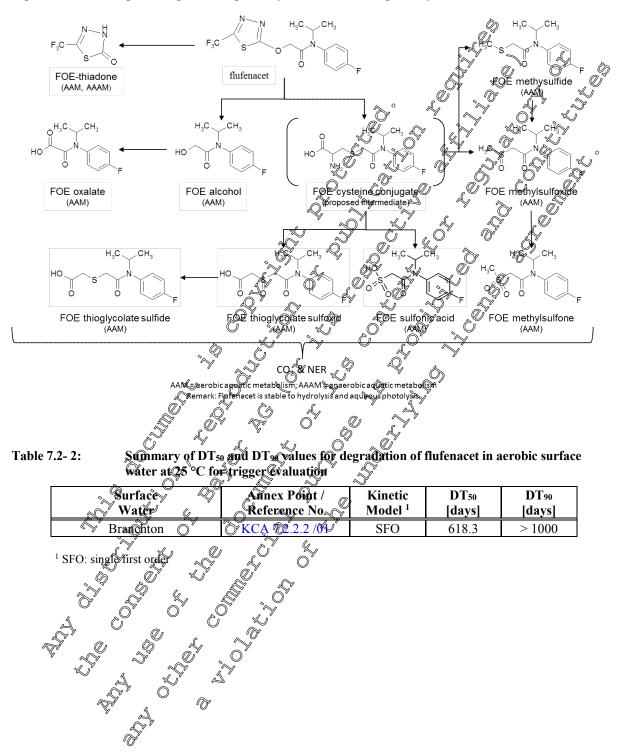
The kinetic models and  $DT_{50}$  values in aquatic systems of flufenacet used for modeling purpose and trigger evaluation (best-fit) are summarized in Table 7.2.2 to Table 7.2.3. For the major degradation products FOF methylsulfide and FOE-thiadone no half-lives for modeling purposes and trigger evaluation 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 summatized in Table 7. 22-3.

Table 7.2- 1:	Summary of maximum occurrences in aquatic systems of major flufenacet degradation
	<b>products derived from laboratory studies</b> (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- 3: Summary of DT₅₀ and DT₉₀ values for degradation of flufenacet in aerobic water/sediment systems at 20 °C for modeling purpose (non-normalized) and trigger evaluation Ô

		a.				
		Modeling l	Purpose	Trigge	r Evaluat	
Water/Sediment	Annex Point /	Kinetic	DT50	Kinetic	DT 50	
System	Reference No	Model ¹	[days]	Model ¹	[days]	[days]
Entire System			0	O NO	A	Z Z
Nelson Environmental Study Area (NESA)	KCA 7.2.2.3 /04	SFO	90.3	SFO SFO	90.3 ×	[≪] 300.1
Bayer Research Park (BRP)	KCA 7.2.2.3 /04	SFO 🔊	89.O	& SFO	° 89.0 ×	295.7
Nelson Environmental Study Area (NESA)	KCA 7.2.2.3 /04	SEQ	<b>19</b> .7	SFOS	187	65.3
Bayer Research Park (BRP)	KCA 7.2.2.3 /04	<b>,</b> §FO ∖ _∞	€ 38.1 «	SFO	38.1	126.6
Water				4 4		-
Nelson Environmental Study Area (NESA)	KCA 7.2.2.3 /04	s stor	\$8.7	SFO	<b>5</b> 357	195.1
Bayer Research Park (BRP)	KCA 7.2.2.3	, SFO ∅	≶ 40.%	DCOP	31.5	171.6
Nelson Environmental Study Area (NESA)	KCA 7.2.2.3 /04	SFOL	100	°≫SFO	17.0	56.4
Bayer Research Park (BRP)	KCA 7Q.2.3 /0⊕	SEO	23.8	DF DF	18.6	94.3
Sediment		N K				
Nelson Environmental Study Area (NESA)	KČA 7,2,37.3 /04	SFO	140.5	SFO SFO	140.5	466.8
Bayer Research Park (BRP)	KCA 2.2.3 /04	SPO 🗞	\$120.5	sFO	120.5	400.2
Nelson Environmental Stu	K 7.2.2 /04	^{SFO} ⊘	17,6	SFO	17.6	58.6
Bayer Research Park (BRP)	CA 7,2.2.3 /04	, SF6	A7.9	SFO	47.9	159.1
¹ SFO: single first ordee DFOP (0)	uble first order in ara	$\bigcirc$	<u>o</u>			

## Summary of DT50 and DT90 values for ordirect photochemical degradation of FOE-thiadone in serobic surface water at 25 °C for trigger evaluation Table 7.2- 4:

Surface Water Anne Poin Reference	No Model	DT50 (experimental) [days]	DT50 (natural conditions) [days]
Rome 5 %CA 7.25.3	/01 SFO	5.8	15.5 (Phoenix, USA) 24.0 (Athens, Greece)
'SFO: sprigle 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 ander sperile conditions in the dark in the laboratory were evaluated during the Annex I occlusion using [phenyle]1-146] labeled flufenacet, and were accepted by the European Commission (7460)VI/98 Final – 3rd July 2003). The following studies are included in the Baseline Dossier:

Annex Point / Reference No	Author(s) 🖉 🦼	🖉 🛛 🖉 Vear 🖉 Document No
KCA 7.2.1.1 /01	Ø., S. &	1992 M-00203-01-1

Two additional studies have been performed for FOE thiadone on request of the US Environmental Protection Agency (EPA) and are submitted within this Supplemental Possier for the flufenacet renewal of approval. A summary of the route and rate of degradation of flutenacet in water and sediment is given in section CA 7.2 and Figure 2-1.

Report:	KCA 7.2.1.17/03; J. K.; M. M. M. 1999
Title:	Hydrolysis Study of Thiadone (A Metabolite of FOE 5043)
<b>Report No:</b>	
<b>Document No:</b>	M-0
<b>Guidelines:</b>	• EPA Ref Subdivision N, Guideline Section 161-1
GLP:	NOS AV A A

### **Executive Summary**

The hydrolytic route and rate of degradation of [thadiazole-2-¹⁴C]FOE-thiadone were studied in sterile buffer solutions at pHO, 7 and 9 in the dark in the laboratory for 30 days at  $25 \pm 1$  °C.

A test item concentration of 0.5 mg/L ( $\triangleq 0.5 \text{ ppm}$ ) was applied.

Ø

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-2-14C]FOE-thiadoneLot No:97B0Specific Activity:10.88Radiochemical Purity:97.79

97B064-130 10.88 MBq/mg (50 mCi/mmol: \$2,680 dpm/µg) 97.7% (stated) and 95.5% measured af DAT

#### 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 diagdrogen phosphate with sodium hydroxide and the pH 9 buffer was prepared from potassium chloride/berc 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 ( $\triangleq$  0.5 ppm)

The application solution was prepared in acetonitrile. 680  $\mu$ L 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 viate, which were then capped.

The test systems were incubated in the tark for 30 days at  $25 \pm 1^{\circ}$ C in an environmental chamber.

### 2. Sampling²

Six sampling intervals were distributed over the entire incubation period of 30 days. Duplicate samples were processed and analyzed 3, 7, 14, 21 and 30 days after treatment (DAT).

Sterility of the test Solutions was specked at DAT-0 and DAT-30 for each of the three buffers.

## 3. Analytical Procedures

At each sampling interval, diplicate 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.



#### П. **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 [thiadiace] OE-thiadone, as a function of time.

#### Degradation of FOE-thiadone in Buffer at puts Table 7.2.1.1- 1: (expressed as percent of applied radioactivity, single values)

			<i>R</i> ⁿ	$\sim$ $\bigcirc$	l V	[*] 0	- Ro	_
Compound	Mean	0%	7 3	<b>D</b> A 7		521	30	
FOE-thiadone	А	262	<b>25</b>	954	95.8 [®]	96.1 [©]	96.0	$\mathbb{Q}_{n}$
	В	~ <b>Q</b> 5.7	~95.7	96.0	<u>9</u> 5.7	96 <b>0</b> 2″	96 Ø	7
Unidentified Radioactivity ¹	A 🔬	, 3.9 🛸	Q4.4	4.1	<b>4</b> .2	3.9	<b>4</b> ,0	
	B	4.3	4.3	4.0%	4.3	3.9	<b>Ô≸</b> .6	
Material Balance ²	mean	100.0	999	100.6	100,9	98.4 ⁽ (	<b>97.9</b>	
	e /	AL /		$\sim$		0		

DAT: days after treatment

mpurities in the fortification solution ¹ More than one component - due to

² Mean values of duplicates.

Table 7.2.1.1- 2: Degradation of FOE-thudone in Buffer at pH

(expressed as percent of applied radioactivity; single valued

		- N	- Q	`~₽́A	T		
Compound Q	Replicate	<i>≪</i> y0	3		14	21	30
FOE-thirdone	A	95.6 ĝ	97.0	C96.2	96.7	96.9	97.8
	§ в,≪	95 2	97,3®	° 97.3	96.4	97.2	97.1
Unidentified Radioaetivity		A A	30	3.8	3.3	3.1	2.3
		A.8	<b>2</b> .7	2.7	3.6	2.8	2.9
Material Balance	mean	<b>∛100.0</b> ⊘	<b>, 99.1</b>	99.3	101.1	<b>98.7</b>	97.8
	$\sim$						

DAY: days after treatment ð Ø

¹ More than one component - due to the impurities in the fortification solution. ² Mean values of duplicates

## Degradation of FQE-thiad ore in Buffer at pH 9

Dexpressed as per ont of applied radioactivity; single values)

Į Į		<u></u>			DA	Т		
T,		[≫] Mean	0	3	7	14	21	30
	FOE-thiademe ~	A	95.3	96.5	97.2	97.1	96.8	97.2
		В	96.0	97.1	96.6	97.4	96.6	97.4
	Unidentified Radioactivity 1	А	4.7	3.5	2.8	2.9	3.2	2.9
		В	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	<b>99.7</b>

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 potion of radioactivity dissipated from the vessels or was lost during processing of the 

#### С. **STERILITY**

The sterility of the samples was maintained throughout the

#### **DEGRADATION OF TEST ITEM** D.

FOE-thiadone was stable to hydrolysis under the tested condition

#### ¢ŏncki¥si( III.

s concluded that FOE-FOE-thiadone did not degrade during the study period of 30 hays. thiadone is stable to hydrolysis at pH 5, 7 and 9 at 25°

Report:	KCA 7.2.1.1 (92;
Title:	[thiadiazoles-14C]FOE5043-thiadore (BCSOAA41715): Hydrolytic Degradation
<b>Report No:</b>	M-358419-01-1 0 0 0
<b>Document No:</b>	MEF-0.90/308
<b>Guidelines:</b>	• OE Test Quideline No. 14
	• Commission Directives 94/37/EC and 95/36/EC amending Council Directive
	94/414/ÉĚC 4 ~ O ~ O
GLP:	Bes A A A A

### **Executive Summary**

The hydrolytic route and rate of degradation of [thradiazole-2-14C]FOE-thiadone were studied in sterile buffer solutions at pH 4, 7 and 9 in the dark in the laboratory for 7 days at  $50 \pm 1$  °C. (1) I

A test item concentration of 1.0 mg/L was applied.

Duplicate test systems were processed and malyzed 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- Supplemental Possier, 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-2-14C]FOE-thiadoneBatch No:KATH 6249Specific Activity:4.28 MBq/mRadiochemical Purity:> 99 (HPLC/

4.28 MBq/mg > 99 (HPLC/radiodetection and TLC/radiodetection

#### 2. Test Buffers

The following three 0.01 M buffers were used: an acctate buffer for \$415, a FRIS buffer for \$477 and a borate buffer for pH 9. All buffer solutions were perilized 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 volatile were for used as test systems.

The study application rate (SAR) of FOE thadone was approximately 1.0 mg/L.

The application solution was prepared in aceton trile.  $423 \ \mu L$  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 (whe vials, which were then capped.

The test systems were incubated in the dark for 7 days at  $50 \pm 10^{\circ}$ 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 of and DAT-7 for each of the three buffers.

## 3. Analytical Procedures

At each sampling miterval, 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]FOE-miadone as a function of time.

### Table 7.2.1.1- 4: Degradation of FOE-thiadone in Buffer at place

(expressed as percent of applied radioactivity, mean values of duplicates)

			(Cn		(n V		i ca	6
Compound	0	0.1 ្ষ	0.25		2			
FOE-thiadone	98.6	100	99 <u>,</u> 5Ĉ	100.3	98.7 🔊	@93.5	92.6	
Unidentified Radioactivity	0.4	Q,	42×	04	0.1	0.4	° 0.3 (	Ũ
Material Balance	<b>99.0</b>	<b>101.4</b>	<b>200.</b> 7	100.4	<b>98</b> .8	93.9	92,9 [©]	7
	a C	×	$\sim$		$\langle \langle \rangle$	.0	6	

DAT: days after treatment

Table 7.2.1.1- 5:Degradation of FOE-thradone in Buffer at pH 7 (expressed as percent chapplied adioactivity; mean values of duplication)

			Ô	DAT			1
Compound 🦉	0رچ	0.1	0.25	A.	2	5	7
FOE-thiadone	999.2	¥00.2	<b>\$00.1</b>	100.0	100.4	98.5	99.7
Unidentified Rackoactivity	0.6	0.4%	0.7 0	ه 0.4	<b>©0.3</b>	0.8	0.1
Material Balance	<u>99.8</u>	100.6	100.8	100.4	100.6	99.2	<b>99.8</b>
		No.	(A) n				

DAT: days after treatmer

Degradation of EQE-thiatone in Buffer at pH 9

(expressed as percent of applied radioactivity, mean values of duplicates)

		, ~(	Ş.	DAT			
K Kompound		0.1K)	0.25	1	2	5	7
	29.5	100.5	100.1	101.5	99.7	100.1	99.8
Unidentified Radioact	ivity 0.5	0.3	0.6	0.2	0.9	0.4	0.2
🖉 MateGal Balance		100.9	100.6	101.6	100.6	100.5	100.0
	S S						

## B. MATERIAL BALANCE

s after treatment

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% ÅR 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

Table 7.2.1.1- 6:

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 year at pH 4, pH 7, and pH 9, and therefore at 25 °C as well.

Considering the hydrolytic stability determined under environmental phyconditions 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 flurenacet in sterile buffers in the laboratory was evaluated during the Annex I inclusion using [phenyl-UL-16] -labeled flurenacet and was accepted by the European Commission (7469/VI/98-Kinal – 39 July 2003). The following studies are included in the Baseline Dossier:

Annex Point / Reference N	0	Ô.		utthor(s)	, O ^v	Å,	Year	Document No
KCA 7.2.1.2 /01	, Ô	)		M.;	, B,	Å. ^	1995	M-002206-01-1
KCA 7.2.1.2 /02	Ŷ	N.	<i>a</i>		, E. 🦓	Ő	1993	M-002208-01-1
	Ś	0	S	°≈∕	Ô.	. <i>Q</i>		

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; N. R.; A. M.; 1999
Title: Aqueou photol is of Thiadone (a metabolite of FOE 5043)
Report No: $\sqrt[9]{108729}$
Document Nov M-077985-07-1 ~ O
Guidelines A Ref. Subdivision N. Guideline Section 161-2
GLP: Star Contraction of the second s

## Executive Summary

The photolythe route and rate of degradation of [thiadiazole-2-¹⁴C]FOE-thiadone were studied in sterile aqueous buffer at pH under exposure to simulated sunlight (12 h light/12 h dark cycle) in the laboratory for 30 days at  $25 \pm 2$  °C.

A study application rate of 0.49 mg/L ( $\triangleq 0.49$  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.



#### Document MCA: Section 7 Fate and behaviour in the environment Flufenacet

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-2-¹⁴C]FOE-thiadone Batch No: C-784 Specific Activity: Radiochemical Purity:

10.88 MBq/mg (50 mQi/mmol;@52 95.3% (HPLC/radiodetection),

#### 2. **Test Buffer**

A 50 mM phosphate buffer with a pH of was used for the study. FOE chiadone was found to be hydrolytically stable at this pH value. The buffer solution was sterfized before use

#### В. **STUDY DESIGN**

#### 1. Experimental Condition®

Static test systems were used, consisting of flint glass sample jars (volume 59 mL) filled with 10 mL buffer and equipped with graque seven caps fitted with Terlon 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 not oss of radioactivity from the pH 7 test systems, no trapping System was employed for volations in the definitive study.

The study application rate (SAR) of FQD thiad  $\frac{1}{2}$  was 0.49 mg/L ( $\triangleq 0.49$  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 asetonitrile. 50  $\mu$ L 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 acetometrile concentration  $\leq 1\%$ ). 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  $25 \pm 2$  in a water bath placed in a solar simulator containing a Xenon lamp simulating natural sunlight. The light equission was filtered with a 290 nm cut-off UV-filter, which eliminated all wavelengths < 200 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  $25 \pm 2^{\circ}$ 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 sylinder 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/radiodetectron method was 1.5% (R.

The identity of the test item was elucidated by HPOC-MS

As only minimal degradation of the cest item was observed in sterile aqueous buffer (pH 7), no photolytic half-life was calculated.

## RESULTS AND DISCUSSION

## A. EXTRACTION AND QUANTITATION OF RADIOACTIVITY IN SOIL SAMPLES

Table 7.2.1.2- 1 summarizes the degradation of [thiadrazole  $2^{4}$ C]FOE-thiadone and the formation and degradation of ito degradation products as a function of time.

 Table 7.2.1.2- 1:
 Degradation of POE-thiadone in Aqueous Buffer (pH 7) under Photolytic Conditions

 (analysis obtained from the Integrated HRLC Chromatogram ¹; mean value of duplicates)

		$ \land \land$	<b></b>	$\sim$				
	KY RO OY	8 . V		Ž	DA	۸T		
	Compound	Mean	Ø	3	7	14	21	30
	FOE-thiadone	irradiated	Da.	98.6	99.3	99.8	100.0	100.0
	a vi v	dark	<b>97</b> .1	98.9	99.3	99.0	98.9	100.0
	Reg #1 (fortification imp@rity) (	oradiated	n.a.	0.9	0.4	n.d.	n.d.	n.d.
a		dark	1.2	1.1	1.0	1.1	1.1	n.d.
J.	$\operatorname{Reg} \#_2^{\mathcal{O}} = \mathbb{Q}_{\mathcal{A}}$	irradiated	n.a.	0.3	n.d.	n.d.	n.d.	n.d.
Apr.	(for fication mpurity)	dark	1.8	n.d.	n.d.	n.d.	n.d.	n.d.
v	Unidentified	uradiated	n.a.	0.3	0.3	0.2	0.0	0.0
	Radioactivity 🖉 🖉	ð 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
	Material Balances	dark	104.7	101.5	98.2	101.9	100.7	97.2

DAT: day@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 these samples.

#### C. **STERILITY**

The sterility of the samples was maintained throughout the stud

#### **DEGRADATION OF TEST ITEM** D.

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 1000% AR. Thus virtually no degradation of FOEthiadone was observed for the irradiated and dark control samples at any of sampling intervals 

Two minor degradation products were present in both the pradiated 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 of dark-on trol samples, neither

FOE-thiadone was stable to photodegradation under the test conditions

to sand see present in bo SAT 49 Since these anymore in the DAT. July CONCLUSIC to the to the test co tot to the test co to the test co to the test co to the test co to t



### 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; , H. P.; , M.; 2011
Title:	[thiadiazole-2-14C]BCS-AA41715 (FOE \$943-thiadone) Phototransformation in
	natural water
<b>Report No:</b>	MEF-09/506
<b>Document No:</b>	M-404931-01-1
<b>Guidelines:</b>	• EPA Ref: Subdivision N, Guidenne Section 16,52
	• Japanese MAFF New Test Guideline's 2 Nousan 814 Annex No. 2 2
	• Canadian PMRA Guideline DACQ 2.3.3.2 2
	• Commission Directives 24/37/EC and 9506/EC amendin@Council/Directive
	91/414/EEC
GLP:	yes y i i i i i i i i i i i i i i i i i i
L	

### **Executive Summary**

The photolytic route and rate of degradation of  $thiadia Ole-2-{}^{14}CJFOE-bhadone were studied in sterile, natural water from river Bhine under exposure to simulated studied in the laboratory for 14 days at <math>25 \pm 1$  °C.

A study application rate of 0.8 mg/L @as 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 otensity ander experimental conditions would match high intensive natural solar radiation found in Proenix, AZ, USA for 30 days in summer.

Mean material balances ranged from 92.6 @ 98.5% of applied radioactivity [% AR] for irradiated samples and from 99.6 to 100.2% AR for eark costrol samples.

The maximum amount of votatiles was 57.8% AR in irradiated samples at DAT-9. They were identified as carbon dioxide and carbon motoxide. Formation of other volatile organic compounds was not significant, as demonstrated by values being  $\leq 0.5\%$  AR at all sampling intervals. No formation of volatiles was observed in dark control samples.

The amount of FOE-thradon irradiated samples decreased from 98.5% AR at DAT-0 to 20.4% AR at DAT-14% Inder dark conditions TOE-thiadone was stable during the test period.

Beside the formation of carbon dioxide and carbon monoxide, one minor degradation product was observed in irradiated camples 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.



Document MCA: Section 7 Fate and behaviour in the environment Flufenacet

#### 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 MBa/mg > 99% (HPLC/radiodetection Radiochemical Purity:

#### 2. **Test Water**

Water from the Rhine River (see Table 7.2.1.3- 10 was sampled at a distance of bout 1 for from the river bank in a water depth of about 10-30 cm. The Rhive 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	ofstest soi	ils ^v
-------------------	------------------	------------	-------------	------------------

Parameter 📎 🔬 🔎	<b>Results</b> / Units
Water Designation	A Akhine River
Geographic Location	· · · · · · · · · · · · · · · · · · ·
km 🖉 Õ V V	717 - 718
City D D C C	Monheim
km City State	North-Rhine Westphalia
Country	Germany
$pH^1$ $O$ $Q$ $A$ $Q$ $A$	8.0
Suspended Sobjds [mg/P] 1 2 2	130
Total Evaporation Residues [mg/L] 1	370
Oxygen Saturation at 22.5 % [%]	95.3
Conductivity [jts cm]	529
Total Organic Carbon mg/L	2
Water Hardness [° du ]	10.5
Total Prosphorous [mg/Lf/	0.0815
TotakNitrite and Nitrate [mg/L]	3.1
¹ measure@after sampling	

#### B. STUDY DESIGN

#### Experimental Conditions 1.

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  $\mu$ L 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  $_{\pi}$  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 pradiated samples of main test 1, the irradiation experiment was repeated by exposing the dark control samples of main test 1 to kent (main test 2). For main test 2 all test systems were sealed with orimp caps to allow for investigation of the headspace by combustion.

The irradiated test systems were incubated under continuous pradiation for  $\frac{1}{2}$  days at  $25 \pm 1$  °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  $\frac{2}{2}$ 90 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 4 days in a climatic cabinet protected from light at  $25 \pm 1$  °C.

### 2. Sampling

Seven sampling intervals were distributed over the entree incubation period of 14 days.

Duplicate test systems of dradiated 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, applicate 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). DT₅₀ values were calculated from the resulting parameters. So kinetic evaluation was performed for dark control samples, as virtually no degradation of FOE-thiadone was observed over the whole study period.

#### RESULTS AND DISCUSSION II.

### EXTRACTION AND QUANTITATION OF RADIOACTIVITY IN SOIL SAMPLES A.

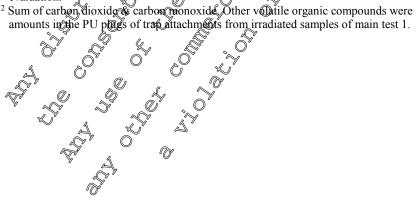
Table 7.2.1.3- 2 and Table 7.2.1.3- 3 summarize the degradation of thradiazole-2-14 CP OE-thiadone and the formation and degradation of its degradation products in irradiated and dark control samples as a function of time.

Table 7.2.1.3- 2:	Degradation of FOE-diadone in Natural Water under Photolytic Conditions
	(main test 2; mean values of diplicates and a set of the set of th

	<u> </u>	~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~		A Y	. 0		
Compound	l de la companya de l	  1	2	DQŤ	$\mathbb{N}_8$	9	14 ¹
Volatiles ²	p.a.	6.5	د 12.3 پ	40.5 C	<b>49.7</b>	53.2	18.7
FOE-thiadone	©98.5	l∽ 88.9 [≈]	79.j	45,8	37.4	34.9	20.4
Unknown #1	n.dØ	1.4	2.3	5.9	7.5	6.3	4.2
Unidentified/Diffuse S	0.0	0.0		∲0.4	0.5	0.7	1.1
Total Residues in Pest Solution	Ø98.5 🖉	90.0	<b>81.4</b>	52.1	45.4	42.0	25.7
Material Balances	98,5	96.5	93.7	92.6	95.2	95.2	44.4

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

¹ The drop of the material balance at DA Q14 was caused by a leak in the oxidizer. However, this loss did not influence the distribution of adioactivity in solution and thus, the results of DAT-14 were also used for the final evaluation. 2 Sum of carbon dioxide & carbon monoxide Other v@atile organic compounds were not detected in significant





ndf analvze

## **Document MCA: Section 7 Fate and behaviour in the environment Flufenacet**

## Table 7.2.1.3- 3:Degradation of FOE-thiadone in Natural Water under Dark Conditions<br/>(main test 1; mean values of duplicates)

				DAT		<u>9</u>	
Compound	0	1	2	5	64	8 0	14
Volatiles	n.a.	n.a.	n.a.	n.a.	n.a.	m.a.	m.a.
FOE-thiadone	100.0	100.1	99.6	99.6	000.2	×100.2 «	99.7
Unknown #1	n.d.	n.d.	n.d. 🔊	。n.d. 🦼	n.d.s	n.d.	n.dS
Unidentified/Diffuse Radioactivity	n.d.	n.d.	n.d.	n.d.	nd	tt.d.	°nyd.
Total Residues in Test Solution	100.0	100.1	99.6	°,99.6	\$100.2 ·	100.2	ه 99.7
Material Balances	100.0	100.1	99.6	&°99.6 ′	0100.2	100,2	99,7
			D C	.01	, Ŵ	Ô	, O'

n.d.: not detect

DAT: days after treatment

### **B. MATERIAL BALANCE**

### <u>Main Test 1</u>

For irradiated samples equipped with the solid rap attachments, the material balances were not sufficient due to formation of volatiles which were neither adsorbed by the polyarethane plug nor the soda lime. For irradiated samples sealed with rimp 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 camples anged from 99.6 to 100.2% AR. Thus, results from main test 1 were used for final evaluation of the dark control camples.

### 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 of 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 ost during processing of theses samples (except irradiated samples at DAT (14).

## C. STERILITY AND SXYGEN SATURATION

Sterility and oxygen saturation of the samples were maintained throughout the study (main test 1 and main test 2).

## D. VOLATILAZATION

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  $\leq 0.5\%$  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

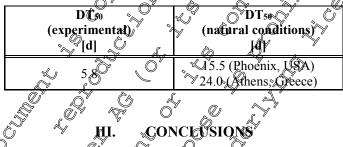
The amount of FOE-thiadone in irradiated samples decreased from 98.5% AR at DAT-0 to 20.4% AR at DAT-14.

Beside the formation of carbon dioxide and carbon monoxide, one minor degradation product was observed in irradiated samples with a maximum amount of 5% AR at DAT-18, 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. ). 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

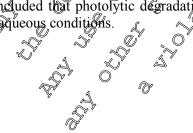


FOE-thiadone was opidly degraded in sterne, natural water under exposure to simulated sunlight in the laboratory. No degrad of the providence was observed in dark control samples.

The experimental half-fives in irradiated samples were calculated as 5.8 days, equal to 15.5 solar summer days at Phoenix, AZUSA @24.0.summer days at Athens, Greece.

Beside the formation of carbon dioxide and carbon monoxide, one minor degradation product was observed in irradiated camples with a Gaximum amount of 7.5% AR at DAT-8, rapidly declining to 4.2% at DAT-4.

4.2% at DATA4.





### 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 –  $3^{rd}$  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 nexts to be addressed. In case of flufenacet this data requirement will be met by the study KCA  $\frac{52.22}{01}$ , 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 QECD Test guideline No. 309 and demonstrates that the study KCA 7.2.2.2 /01 is suitable to address the fact of florenacet in open water a@required according to regulation (EC) No. 1107/2009. Additionally, a re-evaluation KCA 7.2.2.2 /02 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 (91; , M. J.; , P, P.; , S. L.; 1995
Title:	[phenyl-U- ¹⁴ ¢]FOE 5043 - Determination of Aerobic Aquatic Biotransformation
	at 25 °C C
<b>Report No:</b>	BR106901
<b>Document No:</b>	M-002210-01Q S S
<b>Guidelines:</b>	• Canadian Guidelines T-1-255
GLP:	y s o o

**Executive Summary** 

The degradation of [phenyl-UL-¹⁴C] furtheracet under derobic conditions was investigated in one natural pone vater under a standard daily lighting regime (16 h light, 8 h dark) in the laboratory for 368 days at  $25 \pm 1^{\circ}$ C:

Freshwater Pond	Dissolved Oxygen	pН
	[mg/L]	•
OBranchon Branchton Ontario, Canada	9.6	7.5

The test concentration of fluferacet 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  $\leq$  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 & 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 93.9% 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 sulforic acid (not detected up to DAT-188, max. 8.6% AR at DAT-368) and FOE alcohol (max 9.6% 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 furst order kinetics.

### A. MATERIALS

#### 1. Test Item

[phenyl-UL-¹⁴C]flufenacet Batch No Specific activity Radiochemical purity

I.

### 2. Test Water

Natural unfiltered water from a freshwater pond near Branchton/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.

MBq/mg (⇔ 66.5 maCi

For control samples an alignot 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
1 4010 /	i nysico chemicai	properties of test mater

Parameter	Water 🖉
Geographic location	
- city	Branchton /St. George
- state	Ontario de Contario de Cont
- country	Ontario, Canada O A
Total alkalinity as CaCO ₃ [mg/L]	
Total Hardness as CaCO ₃ [mg/L]	
Suspended solids [mg/L]	8.54
Dissolved oxygen [mg/L]	
pH	
Specific conductivity	
Microbial biomass [cfu/mL]	norsterile water sterile water
7 days prior study start	$\swarrow$ 5.9 x $\Re^3$ $\swarrow$ $\swarrow$ $\Re^5$ 0 $\swarrow$
DAT-35	$3.0010^5$ $n \Omega$
DAT-278	$3.3 \times 10^3 \times 3.0 \times 20^3$
DAT-368	$1.7 \times 10^3 / 3.8 \times 10^2$ $20 \times 10^2$
n.a. = not analyzed, n.d. = not detected	DAT: days after treament
cfu: colony forming units	

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 fasks (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 of non-sterile pond water.

The study application rate (SAR) was based on Osingle field application rate of flufenacet of 1 kg/ha, resulting in a SAR of O mg/L.

The application solution was prepared in acconitrile 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 application system.

The test systems were increased under a erobic conditions under a daily lighting regime of 16 hours light and 8 hours dark (light intensity ranged from 7.3 to 7.5 W/m²) for 368 days at  $25\pm1$  °C in a walk-in climatic character. 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 nonsterile 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 sprior to disconnecting them from the flow-through system. Afterwards, the test yessels were swirled gently and an aliquot was submitted for microbial enumeration, when applicable

The residual water was characterized by liquid scientilation counting asO as by HPLC/radiodetection. The amount of volatiles was determined by light scintillation counting at each sampling interval.

The identity of the test item and its degradation products was ended by GC-EI/MS either directly or after derivatization or by thermospray HPLOS-MS.

The residue data for the test item were evaluated assuming first order kinetics. Model input datasets were the residual amounts of flufenace found at each sampling interval. See Table 7.2.2.2-2 and Table 7.2.2.2-3 for input values.

## SULTS AND DISCUSSION

#### A. EXTRACTION AND QUANTITATION OF RADIOACTIVITY IN SOIL SAMPLES

Table 7.2.2.2- 2 and Table 7.2.2.2 summarizes the degradation of [phenyl-UL-¹⁴C]flufenacet and the formation and degradation of its degradation produces in non-sterile and sterile test systems as a function of time.

Table 7.2.2.2- 2:	Degradation of flutenacet in Non-storile Pour Water under Aerobic Conditions
	(expressed as percent of applied radioactivity, mean value of duplicates)

		() .*	J° 4	$\mathbb{Q}_{n}$						
Compound (replicate)										
сотропца (церисате)	۵×		, D	ts i	29	60	95	188 ¹	278	368
A S	∢ 100.0	A06.6	AØ7.5	\$4,03.5	105.0	104.0	88.0	<del>60.2</del> ¹	77.0	57.2
		108.5	107.3	D106.9	102.4	100.4	97.3	87.0	71.4	57.5
nem n	99.8	1075	1074	105.2	103.7	102.2	92.6	73.6	74.2	57.4
FOE oxalate	nd.	tad.	∘n.a.	n.d.	n.d.	2.1	4.9	5.9	13.8	24.0
FOE sulforme acid	n.d.	Ön.d.	Kn.d.	n.d.	n.d.	n.d.	n.d.	n.d.	6.5	8.6
FOE alcosol	n.d	n.d.	n.d.	n.d.	n.d.	2.8	3.6	2.7	3.5	4.4
Unidentified Rechoactivity ²	n.	n.D	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	1.2	n.d.
Residues in Water 🦼	<b>£</b> 99.8	108.4	107.8	105.4	103.7	107.6	101.1	96.9	100.1	97.8
Carbon dioxide	D n.a. 🕡	<b>0.0</b>	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				

DAT: days after treatment

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  $\leq 1.2\%$  AR at any sampling interval.



(expressed as percent of applied radioactivity; single values)										
Common d		DAT 🖉								
Compound	0	4	7	15	29	60	95	1 <b>88</b> °	278	368
flufenacet	98.9	105.3	107.3	103.2	105.2	107.2	101.9	<b>\$</b>	9\$ <u>9</u> 5	<b>2</b> 59
FOE oxalate	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	Sn.d.	⊿n.d.	Kn.d.
FOE sulfonic acid	n.d.	n.d.	n.d.	n.d.	n.đ	° n.d. 🖒	n.d	n.d.	n.d	n.d.
FOE alcohol	n.d.	n.d.	n.d.	n.d.	n.d.	nQ.	n.d/	4:5	4.8%	6.8
Unidentified Radioactivity 1	n.d.	n.d.	n.d.	n.d.		n.d.	&n.d.	~p.d.	@p.d.	<u> </u>
Residues in Water	98.9	106.0	108.2	103.2			0101.9	P104.3	101.6	102.0
Carbon dioxide	n.a.	0.0	0.0	0,0	0.0	0,0	0,20	0.6Ô	0.80	0.8
Volatile Organic Compounds	n.a.	0.0	0.0	~Q.0	<b>9</b> .0	°~9.0	0.6	0.0	Ø.1	0.0
Material Balance	98.9	106.0	108.2	103.2	105.2	/ 107 🕉 🄇	₽102.2 ⁴	0 [°] 105.0	102.5	102.8

Degradation of flufenacet in Sterile Pond Water under Aerobic Conditions

DAT: days after treatment

Table 7.2.2.2- 3:

n.a.: not analyzed

n.d.: not detected

¹ Minor degradation products were quantified if they aprounted \$1% AB and were summed up to unidentified radioactivity (unknown #1 + #2). The maximum amount of a single degradation product wa %1.3% AP at any sampling interval.

#### B. MATERIAL BALANCE

Mean material balances ranged from 96,8 to 109.6% of applied adioactivity (% AR) for non-sterile samples (mean of duplicates) and from 99.9 to 108.2% Are 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 WATE

Residues in water wayed nearly constant over the entire incubation period, ranging from 96.9 to 108.4% AR for pon-sterile samples and from 28.9 to 108.2% AR for sterile samples. See Table 7.2.2.2- 2 and Table 7.2.2.2- 3 for details,

### D.

The maximum amount of carbon dioxide forme on the test systems was 3.0% AR for non-sterile test systems and 08% AR for sterne test stems at study end. Formation of volatile organic compounds was insignificant in non-stepile and sprile test systems as demonstrated by values of  $\leq 0.3\%$  AR at all sampling intervals See als Table 2.2.2- 2 and Table 7.2.2.2- 3 for details.

#### ÁÐEGRADATRÓN OR TEST FEM E.

The amount of flufenacet in from-sterile test systems decreased from 99.8% AR at DAT-0 to 92.6% AR at DAT-95 and further to \$7.4% 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 Tethe 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-¹⁴C]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. 5.6% AR at DAT-368) and FOE alcohol (max. 5.6% AR at DAT-368).

The calculated half-life of flufenacet under aerobe was 358 days conditions in non-sterile test systems, assuming first order kinetics.

Report:	KCA 7.2.2.2 /02;
Title:	KCA 7.2.2.2 /02; EVALUATION OF Aerobic Evaluation of Study: [phenyl ] -14C]FOE 5045 Determination of Aerobic
	Aquatic Biotransformation at 25 °C 4 $\sqrt{2}$ $\sqrt{2}$
<b>Report No:</b>	EnSa-13-0268
<b>Document No:</b>	
<b>Guidelines:</b>	• Canadian Goidelines T-1-255
	• OECD Test Guideline Nov 309 2 A
	• Regulation (EG No. 107/2009
GLP:	no n

#### **Executive Summary**

The statement evaluates the essential experimental facts of the study "[Phenyl-U-¹⁴C]FOE 5043 -Determination of Aerobic Aquatic Brotransformation at 25°C" (see KCA 7.2.2.2 /01 for summary) in comparison to the requirements set by DECD Test guideline No. 309 "Aerobic Mineralization in Surface Water Simulation Biodegradation Test".

In study KCA 7.22 2 /01 the degradation of [phonyl-UL-¹⁴C]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  $25 \pm 1$  °C

One test concentration of 1,9 mg/L of flutenacet was used. Flow-through test systems, which permit the collection of rotatiles, 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 vest 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 tem.

The use of only one test item concentration is considered acceptable by the potifier as it covers a west 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/cm³ and thus, reflects also a worst case scenario referred to the kinetic behavior of the test item under the tested conditions ( $DT_{50}$  varies).

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  $DAT_{-}$  to meet also this guideline requirement (see KCA 7.2.2.2 /03 for summary).

### I. CONCLESIONS

Considering all results of this comparison, the notifier is of the opinion that the re-evaluated aerobic aquatic biotransformation study of flufenacet (see KCA 7.22.2 /03 for summary) is suitable to address the fate of flufenacet in open water as required according to regulation (EC) No. (1007/2009).

Report:       KCA 7.2.2,2403;       K, 2014         Title:       Kinetic Evaluation for Calculating Refined Half-life Times of [Phenyl-UL- ¹⁴ C]Flutenacet in Vatural Pond-Water According to FOCUS Kinetics Using the KinGU 2 Tool         Report No:       EnSa 13-0970         Document No:       M 4/8212-01-1         Guidelines:       OCUS kinetics (2006 2011) ³		
¹⁴ C]Flufebacet in Natural Pond-Water According to FOCUS Kinetics Using the KinGU 2 Tool         Report No:       EnSa 13-0970         Document No:       M 4/8212-01-1         Guidelines:       OCUS kinetics (2006 2011) 3         GLP:       Yo	Report:	KCA 7.2.2,2403; , G.; , K, 2014
Report No:       EnSe 13-0970         Document No:       M # 8212-01-1         Guidelines:       OCUS kinetics (2006 2011) 3         GLP:       Yo	Title:	
Report No:       EnSe 13-0970         Document No:       M # 8212-01-1         Guidelines:       OCUS kinetics (2006 2011) 3         GLP:       Yo		¹⁴ C]Flufenacet in Natural Pond-Water According to FOCUS Kinetics Using the
Document No: M478212-01-1 Guidelines: OCUS kinetics (2006-2011) 3 GLP: 00 0 4		KinGUNZ Took
Document No: M. 478212-01-1 Guidelines: OCUS kinetics (2006 2011) 3 GLP: 00 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0	<b>Report No:</b>	EnSe 13-0970 S O O
$GLP: \qquad	<b>Document No:</b>	M 478212 0I-1
	<b>Guidelines:</b>	• $OCUS \text{ kinetics} (2006, 2011)^{3}$
	GLP:	
	- Co	

Executive Summary 🔬

According to regulation (EC) no. 1 07/2009 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 01-255. 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 itom has started within the first 60 days of the study, the duration can be exceeded 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 (SFOD 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  $25 \pm 1$  °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  $25 \pm 1$  °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 paraflel (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 funcated at 95 days of incubation according to OECD test guideline No. 309 and based on statement (CA 7.2.2.2).

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 DT₅₀ values were calculated from the resulting kinetic parameters.

. 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 acrobic 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 fluttenacet in natural water test system under<br/>aerobic conditions according to FOCUS 1 2 2 2

Test System	Kinctic Model ²	DT50 Jaysj	DT ₂ [days]	chi ^{2%} error	t-test	Visual Assessment ³
Ontario lake pond-water system	ŠFO Š	6188.3	\$1000\$	2.4	k: <0.01	+

¹ The existing study was re-evaluated up to DAT 95, to meet the current guideline requirements

³ Visual assessment  $\mathcal{F} = good$ 

Ø

### II. CONCLUSIONS

The calculated half fife of furtherace in natural water sediment system (Ontario lake) in the laboratory under activitions at standard daily lighting regime (16 hours light and 8 hours dark) at  $25 \pm 1.5$  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 A 7.2.

² SFO: single first order



### CA 7.2.2.3 Water/sediment study

The route of degradation of flufenacet in water/sediment systems under probic and <u>an</u>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:

		~ 0 .		
Annex Point / Reference No	Author(s		[≫] Year	Document No
KCA 7.2.2.3 /01	, N. C.;	, D. MS	¢ ¥995	M-002215-01-1
KCA 7.2.2.3 /02	, I. V.;	, ]	M& 1995	M-002213-01-4
KCA 7.2.2.3 /03	, P. P.	, <b>D</b> .W.	19 <b>2</b>	M-004595-01-1
	_O_	Ĉ		Č Oľ

No additional studies are submitted within this Supplemental Dossier for the Aufenace 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 (94; , G, G, 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 🔊 🕺
<b>Report No:</b>	EnSact 3-0972Q'
<b>Document No:</b>	M-4977845-09-1 6 6 4
<b>Guidelines:</b>	• FOCUS kinetics (2006, 2011) ^{3, O}
GLP:	
A.	

### 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 Kine UI 2 according to FOCUS kinetics (2006, 2011)^{3, 4} to derive halflives for flue for flue for 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 flufenator 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  $20^{\circ}\pm 1^{\circ}$ C.

The calculated half lives of fluferracet 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 fives 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  $20 \pm 1$  C.

The kinetic analysis was performed according to FOCUS kinetics  $(200\%/2011)^{10^4}$  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 fluctuacet 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 offit, 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 k 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 ampling 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  $\neq$  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 DOD. Whey 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, value and sediment were shifted, starting with sampling time t = 0 at the day of the maximum occurrence of DOE 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 knetic medel 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.

#### RESULTS

The single that order (SFQ) 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 ord 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.



#### Document MCA: Section 7 Fate and behaviour in the environment Flufenacet

Table 7.2.2.3- 1:	Kinetic parameters for the degradation of flufenacet in the <u>entire system</u> under aerobic
	conditions for modeling purpose according to FOCUS

Water/Sediment System	Kinetic Model ¹	DT50 [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⊗9.001≪	+
NESA ³	SFO	19.7	9.8	. <0.00 f	+ ~
BRP ⁴	SFO	38.1	4.90	k: <0:001	O K

¹ SFO: single first order

² visual assessment: + = good

³ Nelson Environmental Study Area (NESA) in Lawrence, Kansas

⁴ Bayer Research Park (BRP) in Stilwell, Kansas, USA

### Kinetic parameters for the degradation of flufenacet in the entire system under aerobic Table 7.2.2.3- 2: conditions for trigger evaluation according to FOCUS, O

Water/Sediment System	Best-Fit Kinetic Model ¹	DT ₅₀ [days]	DT90	Chi ² error	Ctest (	Visual Assessment ²
NESA ³	SFO	<b>20</b> 3	300.1		≫k: <0.001	+
BRP ⁴	SFO	<b>689</b> .0	295,7	3.8	k: 🔊 001	+
NESA ³	SFO	Õ 19.7	65,3	9.8~	_kØ.001	+
BRP ⁴	SFO	38.4	°126.6	$\mathbb{C}_{4,9}$	k. <0.001	+

¹SFO: single first order

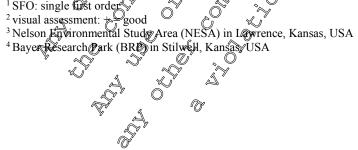
² visual assessment: + = good

³ Nelson Environmental Study Area (NESA) in Lawrence, Kansas, US ⁴ Bayer Research Park (BRP) in Gilwell, Kansas, USA Ę

#### Kinetic parameters for the degradation of florenacet in water under aerobic conditions Table 7.2.2.3- 3: for modeling purpose according to CUS

Water/Sediment System		DT50 0 [days]	chi ² error [%]	t-test	Visual Assessment ²
NESA ³	SFO SFO	>> 58 <del>7</del> 7 [™] ≈	4.9	k: <0.001	+
BRP ⁴	SFO SFO	49.9	6.8	k: <0.001	+
NESA ³	y Sto	17.0	6.8	k: <0.001	+
BRP ⁴	SFO 🗸	Q ² 23.8	12.5	k: 0.002	+

¹ SFO: single wst order





#### Document MCA: Section 7 Fate and behaviour in the environment Flufenacet

Table 7.2.2.3- 4:	Kinetic parameters for the degradation of flufenacet in <u>water</u> under aerobic conditions
	for <u>trigger evaluation</u> according to FOCUS

Water/Sediment	Best-Fit	DT50	DT90	chi ² error	t-test	Visual		
System	Kinetic Model ¹	[days]	[days]	[%]	~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~	• Assessment ²		
NESA ³	SFO	58.7	195.1	4.9	ks ₹0.001	O ^Y + Ô		
BRP ⁴	DFOP	31.5	171.6	3.9	05y: <0.062 © k ₂ : 0,001			
NESA ³	SFO	17.0	56.4	<u></u> 6.8	k:≪0.001 (			
BRP ⁴	DFOP	18.6	94.3	8.76	k120.185 (k12: 0.040)	~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~		
¹ SFO: single first order, DFOP: double first order in parallel ² visual assessment: + = good ³ Nelson Environmental Study Area (NESA) in Lawrence, Kapsas, USA ⁴ Bayer Research Park (BRP) in Stilwell, Kansas, USA								

#### Kinetic parameters for the degradation of florenacet in sediment under aerobic Table 7.2.2.3- 5: conditions for modeling purpose according to FOCUS *M*n

Water/Sediment System	Kinetic Model ¹	DT50	«shi² error [%]	t-test	Visual Assessment ²
NESA ³	SFO	C 1240,5 ×		≽ k; �.001	+
BRP ⁴	SFO 🔊	¥20.5 ×	9.5	∧k; 0.010	+
NESA ³	SFO 🦄	. ∼ 17.6 <i>L</i>	گ 7.3 D	k. ≤0.001	+
BRP ⁴	SFO	<u>مَ</u> 47, 90 م	77	∞ ⁰ k: <0.003	+

¹SFO: single first order

² visual assessment: + = good

³ Nelson Environmental Study Area (MESA) in Lawrence, Kansas

⁴ Bayer Research Park (BRP) in Stilwell, Kansas, USA

#### Ø Table 7.2.2.3- 6: Kinetic parameters for the degradation of Aufenacet in sediment under aerobic conditions for trigger evaluation according to FOCUS °~~/

L )

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Water/Sediment System	Best-Fit	DT 50 [days]	DAT %	chi ² Error [%]	t-test	Visual Assessment ²
NESA ³	SFO S	149.5	466.8	2.1	k: <0.001	+
BRP ⁴	SFO SFO	Ø20.5	400.2	7.5	k: 0.010	+
NESA ³	SFQ	17.6	58.6	7.3	k: <0.001	+
BRP ⁴ $\bigcirc$	SFO C	¥ 47.9	159.1	7.7	k: 0.003	+

¹ SFO: siggle first_order

² visual assessment.  $+ = g \cos^2$ 

³ Nelson Environmental Study Area (NESA) in Lawrence, Kansas, USA

Ø

⁴ Bayer Research Park (BRP) in Striwell, 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

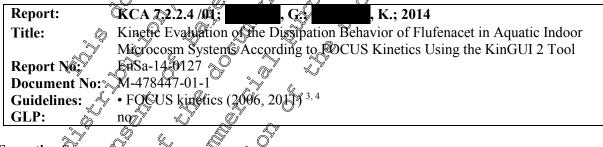
The route of degradation of flufenacet in a microcosm study was evaluated during the Annex I Inclusion and was accepted by the European Commission (746/VI/98 Final 3rd July 2003). The following studies are included in the Baseline Dossier:

	a		40	ſ	
Annex Point / Reference No	ÂQ.	thor(s)	2°L	Year 🖔	Document No
KCP 10.2.3/01	, Ě	E. M.C. , R.		1999	M-023412-01-1
				°())	

A short summary of the results of this microcosm studo is provided below:

In addition to the aerobic aquatic degradation studies in the laboratory on 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. DTS-values for flufenacet in the water phase of the microcosms ranged from 12, to 24(1) days (mean of 8.8 days).

An updated kinetic evaluation of the degradation behavior of flutenacet in water/sediment under aerobic conditions in the dark in indoor microcosms have been performed according to FOCUS kinetics (2006, 2011)^{3, 4} of deriver kinetic parameters suitable for modeling purpose and environmental risk assessment.



### Executive Summary

A kinetic analysis of residue data from the aerobic aquatic indoor microcosm dissipation study M-02341-01-12 (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 (SEO) 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  $\mu$ g/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  $\mu$ g 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 fractmatter 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  $\mu$ g/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 furfenace, 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 > LOO 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.

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 advatic indoor microcosm under aerobic conditions. Table 7.2.2.4-1 sommarizes the results of the kinetic analysis.

RESULTS

# Table 7.2.2.4-1: Kinetic parameters for the dissipation of flufenacet in aquatic indoor microcosm system under aerobic conditions for refined rists and exposure assessments according to FQCUS

		, C		0°		
Test Concentration	Kinetic	<b>D21</b> 50	<b>D</b> T90	[©] chi² error	t-test	Visual
[µg/L] 🔊	、 O'Model O'	a days]	[~] [days] [~]	[%]		Assessment ²
0.75 🔊 🐇	SFO (	18.3	[™] 60 <b>©</b>	5.0	k: <0.001	+
1.5	SFO O	19.4%	64.4	5.5	k: <0.001	+
3.0 \$	OSFO O	20,5	68.0	3.2	k: <0.001	+
6.0	≪ SFO⊘	Q4.5	48.0	2.5	k: <0.001	+
12.0 🔊	SFQ	17.7	₽ 58.7	3.9	k: <0.001	+
24.0	SPO S	21,2	70.6	7.7	k: <0.001	0
Geometrie i	nean 🖉 🖉	<u>,</u> 185				

¹SFO: singly first order

² visual seessment: + = good o = medium/acceptable

#### 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. Assummary of the route and rate of degradation of flufenacet in water and sediment is given in section CA 73 and Figure 7.2-1.

#### CA 7.3 Fate and behavior in air

Volatilization of flufenacet from plant and soil is not expected an therefore transfort 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  $\leq 2$  days.

### CA 7.3.1 Route and rate of degradation in ai

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/VØ)8-Final –  $3^{rd}$  July 2003). The following study is included in the Baseline Dossier:

	d()) *				
Annex Point / Reference No		Á Author(s)		🔨 Xear	Document No
KCA 7.3.1 /01	Ŭ ĵ		$\hat{o}$	¥	M-002236-01-1

No additional studies are submitted within this Supplemental Bossier for the flufenacet renewal of

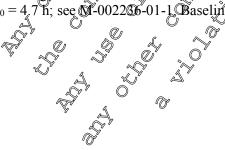
### CA 7.3.2 Transport via at

The volatilization behavior of Mufenacet from soil in field mal was evaluated during the Annex I Inclusion and was accepted by the European Composition (2469/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 P	, E.	1995	M-002237-01-2

### CA 7.3.3 Local and global effects

Local and stobal effects of flufence were not considered since its half-life in air is  $\leq 2$  days (DT₅₀ = 4.7 h; see 07-002206-01-1 Baseline Dossier, KCA 7.3.1 /01).





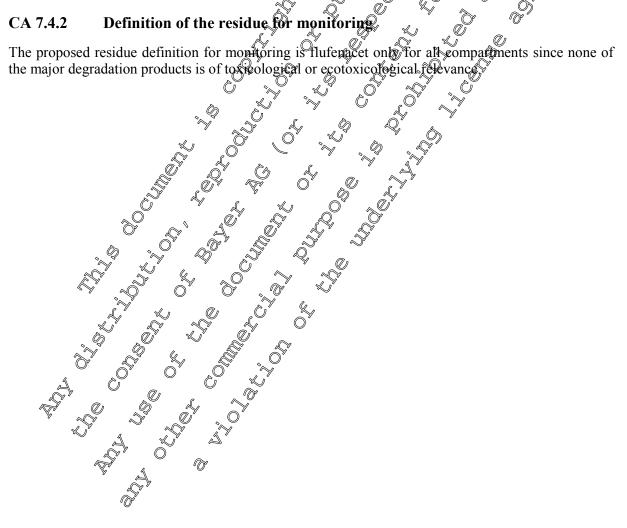
#### CA 7.4 **Definition of the residue**

#### 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 methylsolfone, 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

#### Definition of the residue for monitoring CA 7.4.2





### CA 7.5 Monitoring data

Flufenacet and some of its degradation products are frequently on the lise 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  $\mu$ g/L.

The detected concentrations of trifluoroacetic acid in Seean water indicate the beside anthropogenic sources also naturally sources for trifluoroacetate exist.

Literature:	KCA 7.5 /03; G.; B.; W. ; 2003
Title:	Entry of pesticides into surface waters new results of the Lanspringe run-off
	monitoring project 1999-200
Source:	Paar raviewed literature:
	Symposium Pesticide Chemistry, 12th, Pacenza Italy, June 4-6, 2003 (2003)
<b>Report No:</b>	not applicable is in the second se
<b>Document No:</b>	M-460945-01-1 0
<b>Guidelines:</b>	none
GLP:	no v v v v v

#### **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 period 2 (May 1999 until December 2001) in a maximum concentration of 0.07  $\mu$ g/L.

A. Material	IATORIAL AND METHODS
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	n/a
products):	
Temperature:	n/a
Precipitation:	n/a



#### **B.** Study design and methods



In investigation period 2 (1.05.1999-31.12.2001) flufenacet was detected in three water samples with a maximum value of  $0.07 \ \mu g/L$ .

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  $\mu$ g/L.

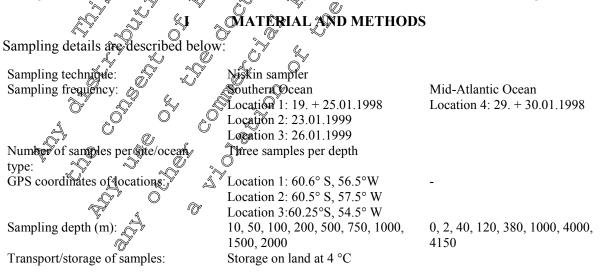
#### IV COMMENTS BY THE NOTIFIER

The detected concentrations of flufenacet in surface water in this study were always below the European Union drinking water and groundwater limit of  $0.1 \mu g/L$ . Thus, this study will not be further considered in the risk assessment.

Literature:	KCA 7.5 /02; ,H., ,E. H., , , , , , J.
	L.; 2002
Title:	Irifluoracetate in Ocean Waters
Source:	Peer-reviewed literature
	Environmental Science and Technology, 36, 1, p.12-15
<b>Report No:</b>	not applicable
<b>Document No:</b>	M-455778-01-1 🔗 🔗 🖉 🖓 🎲
<b>Guidelines:</b>	none $\tilde{U} \sim \tilde{V} \sim \tilde{V}$
GLP:	no lo

#### **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.



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  $\mu$ L sulfuric acid (98%). This solution was extracted with 1 mL methyl tert-butyl ether (MTRF) 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  $\mu$ C of L pentafluoro phenyl-diazoethane (8 vol % in MTBE), prepared from pentafluoro-acetophenore.

Artificial seawater samples (pure salts in deionised water) were spiked with sodium thiluoroacetate in deionized water to give calibration concentrations of 28 to \$39 ng/b trifluoroacetate. The final samples were examined by GC-MS with a limit of quantification of 32 ng/b and a primit of detection of 20 ng/L.

Blanks were analysed each sampling year for control For the sampling period 1998 about 400-yearold 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 & 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.

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.

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Table 7.5- 2:	Concentrations of	trifluorðace	etate/and	CEC-12 ages	of MichAtlan	tic seawater samples
	A 1	_0*	v v			r

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	Depth 🦂	Trifluoroacetate	e ^{a)}	± \$10 ^(a)	CFC-12 ^{b)}
	[m]	Q ng/L	, s	lng/L] ≈ 🆘	[year]
	0	Trifluoroacetate		5 10 L	< 5
	SFC 2 C	200	K O	. 8	-
	Depth [m] 0 SFC 2 40 120	200 210 205 210 210 205			< 5
		× 210 03 × 205 5 × 210		~ <b>3</b> %	< 5
	s, 380 °∼y	Q 21Q		, 6	12
	380 × 1000 × 4006 4006	(j. 205 r		16	46
	40.06 (			16	> 60
	4750	200	¢.	16	> 60
	a) n =	served CFGF2 conce	0 [°]		
	b) valculated wang ob	served CFQ 2 conce	pration		
			)°		
2	. O	0 ×			
, C					
	5 1 2	Y XY			
	~ 1	Ø			
	A A				
	A V				



Site (Sampling Date)	Location 1 (19. +	25.01.1998)	Location 2 (23. Location 3 (26.	01.1999) 01.1999)
Depth	trifluoroacetate ^{a)}	± SD ^{a)}	trifluoroacetate ^{a)}	$\circ \pm SD^{a}$
[ <b>m</b> ]	[ng/L]	[ng/L]		[nĝ/L] ⊘
10	195	22	<b>3</b> ,0 √	27@``
50	185	10	©220 、 O	
100	195	8 🔊	× 205 ×	22
200	195	6	Q 1.70 W	^2 <u>8</u>
50	205	10	0' v v v	
750	195	. V s	× ~190 ~	21 K
10	195		165	0 2 <b>8</b> S
50	200		205	<u></u>
100	200	Q 6	205	<u>Ø</u> Ž9
200	- ~	, ´ ^Q´ _×	∫	19
500	200		« <u> </u>	- K
750	200 🔬 🏷	≈22 .0	× 200 0	18
1000	205	6 Q V		-
1500	220		y x - Ø	-
2000	210~~		<u> </u>	-

 Table 7.5-3:
 Concentrations of trifluoroacetate and CFC-12 age of Southern Ocean water samples

SD: standard deviation  $^{a)} n = 6$ 

Independent of depth and location, existing trifluoroacetate revels 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 evealing 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 & 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 1990 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.

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Literature:	KCA 7.5 /01; B. F., R. W., K., A., A.,
	N., L., C., D. C. G.; 2005
Title:	Trifluoroacetate profiles in the Arctic, Atlantic, and Pacific Sceans.
Source:	Peer-reviewed literature:
	Environmental Science and Technology, 39, p. 6555-6560
<b>Report No:</b>	not applicable
<b>Document No:</b>	M-455832-01-1
<b>Guidelines:</b>	none
GLP:	no L S L S L
vecutive Summa	

#### **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 trifluoroace ate concentrations in the marine environment and to investigate possible natural sources of trifluoroaceta@. Profiles were also taken over underwater vents in the North and South Pacific and the Mediterranean Sea. At the profile sites or fluoroacetate values ranged from < 10 ng/L in the Pacific Ocean to greater than 150 ng in the Atlantic Ocean. Samples from the Canada Basin of the Arctic Ocean exhibited variable trichoroacetate concentrations (60-160 ng/L) down to 700 m. Below this depth, the trifluoroace are concentrations were constant (150 ng/L). Water from the Canadian Arctic had constant high trithuoroscetate 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 trifluoroacetate.

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	• N	(// //			

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		
L'A G G	duplicat (68 % of the samples had duplicates)		
Sampling depth (m):	site dependent; various depth down to 5300 m		
Transport/storage of samples:	Coopand dark storage during shipping; storage on land at 4 °C in		
	the dark		
The samples were processed and analyz	ed as summarized below:		
Sample protessing:	<ul> <li>Derivatization of the acid with 2,4-difluoroanaline in the presence of dicyclohexylcarbodiimide</li> <li>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.</li> </ul>		
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 80-405 % 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.

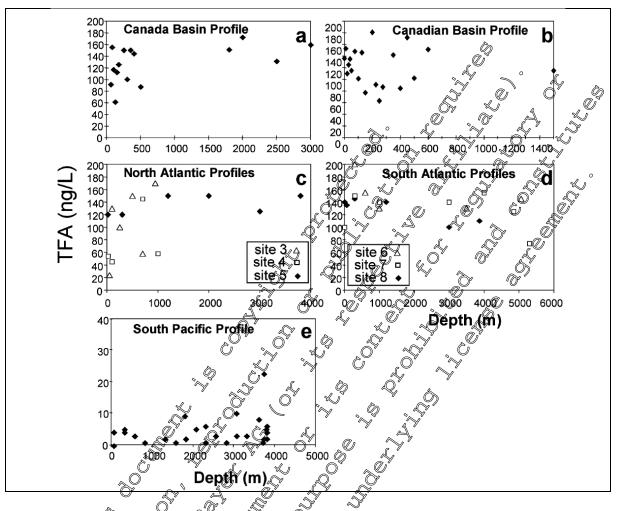
					7.
Site location	Site no.	max. mónitoring depth [m]	trifl@roacefate	Difference () between () Huplicates () [%g)	No. of samples
Canada Basin (Western Arctic)	1	1500	C 34-0781 🔪	j Q	20 ^{b)}
Canada Basin (Western Arctic)	2	30000	é∰-172 ,	<b>8</b>	15 ^{b)}
Nares Strait (Eastern Arctic)	30	~	20-170	Č 7	7 ^{b)}
Nares Strait (Eastern Arctic)	4	≪ي 579 ج	©120–1©°	ٌ∽∕ 5	8 ^{b)}
Nares Strait (Eastern Arctic)	\$	© 365	8-4245	≫ <u>2</u> 0	6 ^{b)}
North Atlantic	6 🚿	× 1900 🔬	28–190	27	6 ^{b)}
North Atlantic	1 70	947 °		38	7 ^{b)}
North Atlantic	251	a 3800 a	120-150	24	5 ^{b)}
South Atlantic		3875	⊘ 145≏∿00	12	6 ^{b)}
South Atlantic	ي 10	\$300	64,155	8	8 ^{b)}
South Atlanti	11	3053	200-130	6	6 ^{b)}
South Pacific 🔊	12	رت [*] 3830	<u>√</u> 1−150	-	16
South Pacific ^{a)} $\bigcirc^{\vee}$	03	S 2500	∾ 1–90	-	16
North Racific	≈⁄ 14	175/	1–25	12	13 ^{b)}
North Pacific 🖉 🖇	150	200	1–30	8	11 ^{b)}
North Paçifiç O	160°	<u>∞</u> 0°300 ₩	1–68	8	10 ^{b)}
North Pacific 🔬	@ <b>]</b> ,7	ر» 30 <b>%</b>	1-80	3	9 ^{b)}
North Racific	م چې 18 م	300	1–20	8	8 ^{b)}
North Pacific	19	300	2-50	10	11 ^{b)}
North Pacification	18 19 20	1000-2200	3-140	not stated	not stated
North Pacific ^a )	, M	3968	2-230	-	23
Mediterranean Sea ^a	⁰ 22 (	200	0.5-50	-	20

Table 7.5- 4:	Measured levels of trifluoroa	cetato in oceanic waters
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Measured trifluoroacetate levels franged 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<br/>depth (m) for (a) Canadian Basin at site 1, (b) Canadian Basin at site 2, (c) North<br/>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 the luoroacetate 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.

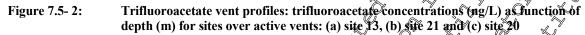
Profile data, from the two northern is cated Eastern Artic sample sites (nos. 3–4) reveal constant concentrations of trifluoroscetate throughout the water column at 150 ng/L with good agreement between duplicate samples (difference between duplicates < 7%). Results for the southern located Eastern Artic sample sites (no. 5) indicate high surface concentrations but significantly lower values down to depth of 250 to with fucreasing 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%).

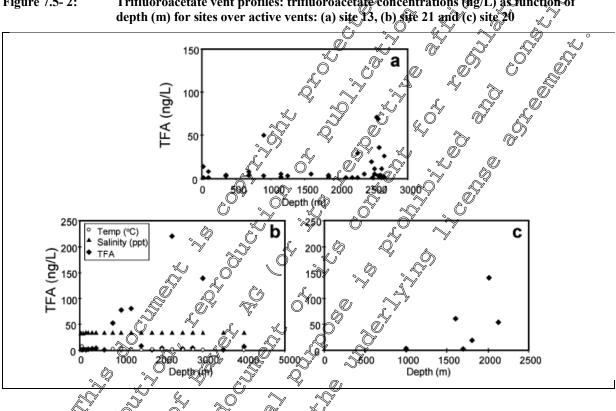
Two profiles (nos. 6–7) extending to depths of 1000 m were obtained at the North Atlantic Ocean sample sites with concentrations of trifluoroacetate between 17 to 190 ng/L. Lowest concentrations were measured in the upper 50 m. For deeper water layers the concentration of trifluoroacetate was about 150 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 depth (150-200 m), and < 10 ng/L below 300 m.





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 Deak 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).

#### Ш **CONCLUSIONS**

Oceanic trifluoroacetate depth profiles sampled over various sites reveal high spatial heterogeneity AS JURNE in their horizontal and vertical distribution. Higher trifluoroacetate level were beerved in the arctic Ocean and the North/South Atlantic (around 150 ng/L) whereas lower trifloor acetate levels X < 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 of direct exchange with apper water layers or the atmosphere, existing trifluoroacetate concentrations can be only the result of matural sources. Measurements of trifluoroacetate levels over active vents suggest that some deep-sea vents

This study provides screening data on the occurrence of trifleoroacetate 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