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Document Title

Summary of the fate and behaviour in the environment for Deltamethrin

Data Requirements

EU Regulation 1107/2009 & EU Regulation 283/2013

Document MCA
Section 7: Fate and behaviour in the environment

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

Date

2015-12-02

Author(s)

[redacted]

Bayer CropScience

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Version history

Date	Data points containing amendments or additions[1] and brief description	Document identifier and version number
2015-12-02	CA7 requested documents M-533554-02-1 and M-539732-01-1 added.	M-480234-02-1

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

Additions to the document after the Completeness Check are highlighted in yellow. Content not necessary anymore is crossed out.

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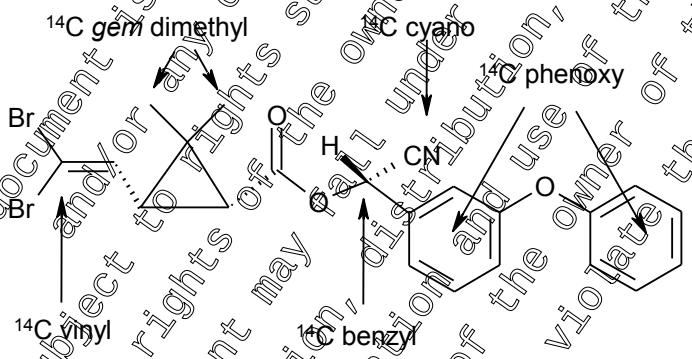
CA 7 FATE AND BEHAVIOUR IN THE ENVIRONMENT

Data on the fate and behaviour of deltamethrin 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 deltamethrin presented here only those environmental fate studies are described in sections 7.1 to 7.5, which were not submitted within the Baseline Dossier. However, for a better understanding of the behaviour of deltamethrin in soil, water and sediment, and air, short summaries including the results of all environmental fate studies which were considered relevant during the first EU evaluation (compare EU Monograph Annex B7) are given additionally in this summary in sections CA 7.1, CA 7.2 and CA 7.3. To differentiate between studies already evaluated during the last Annex I listing and new studies, the references or author(s) given in tables are written in grey for studies already evaluated and in bold black for new studies.

The proposed residue definitions for each compartment are given in CA 7.4.

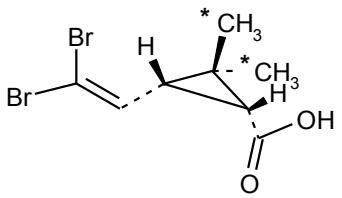
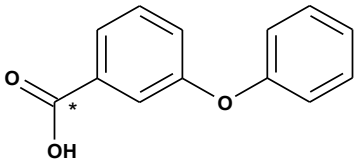
The results from monitoring studies published in literature, which were regarded relevant for the EU, are summarized in CA 7.5. Generally they well confirmed the knowledge about fate and behaviour of deltamethrin in the environment.

The studies concerning the fate and behaviour of deltamethrin in the environment were conducted using different radiolabel positions (vinyl-, gemi dimethyl-, benzyl-, cyano- and phenoxy- ^{14}C-label), as well as unlabelled deltamethrin. These radiolabel positions are sufficient to define the route of degradation of deltamethrin. The structure of deltamethrin and the positions of the different radiolabels are as follows:



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

In addition, studies have been performed with the radiolabelled and unlabelled major degradation products Br_2CA (AE F108565, cis) and mPBacid (AE F109036):

Structural formula of Br_2CA (AE F108565, cis): gemi dimethyl-^{14}C-labeling position was used, indicated by *	
Structural formula of mPBacid (AE F109036): benzyl-^{14}C-labeling position was used, indicated by *	

In original reports study authors may have used different names or codes for degradation products of deltamethrin. In this summary, a single name or a single code is used for each degradation product. If not otherwise noted, the name Br_2CA is referring to the cis-isomer, always. A full list containing structural formula, various names, short forms, codes and occurrences of degradation products is provided as Document N3.

Upon request by the RMS UK the notifier Bayer CropScience has prepared the two position papers M-533554-02-1 and M-539732-01-1 providing a comparison of the metabolic pathway in rat with those in plants, goats and the environment. The document M-539732-01-1 also includes a table of all significant metabolites identified in the different compartments and their quantitative occurrence.

CA 7.1 Fate and behaviour in soil

Deltamethrin is well degraded in aerobic soil to the final degradation product CO_2 (36% - 70% at day 64 to 90 depending on ^{14}C-label) and the substance is not expected to accumulate in soil. In parallel to mineralization, indicating a complete degradation of the molecule, non extractable residues (NER) ranged from 18 to 48% of the total radioactivity applied. The bound residues are mainly associated with the humin and fulvin acid fractions of humus, and the major part of this humus bound residues consists of bound degradation products. Degradation of deltamethrin in soil is a microbial process and the main degradation pathway in soil can be described by ester cleavage followed by oxidation leading to the formation of Br_2CA (AE F108565; cis) and mPBacid (AE F109036). Only Br_2CA was identified at levels >10%, at a maximum of 23% of applied radioactivity. No other metabolites exceeded 10% of applied radioactivity although the metabolite mPBacid was detected at >5% on at least 2 consecutive occasions.

A minor route of transformation, which was observed only in some of the soil degradation studies, is the oxidation of the nitrile group of deltamethrin resulting in deltamethrin-amide (D-$CONH_2$, AE 0035077), followed by further oxidation to deltamethrin-carboxylic acid (D-COOH, AE 0035100), which was also rapidly degraded by ester cleavage, oxidation and mineralization to CO_2.

Deltamethrin is extensively degraded in soil under anaerobic conditions as well. However, degradation is somewhat retarded in comparison with aerobic degradation (DT_{50} ranges from 32 to 105 days, n = 5). The principal degradation pathway under anaerobic conditions is the same as observed under aerobic conditions. Since degradation is lowered down the main metabolite Br_2CA was found at a maximum level of 52 % of the radioactivity applied at day 59.

Photolysis will not significantly contribute to the degradation of deltamethrin in soil since extensive transformation was observed also in the dark control. Photo induced R/S epimerisation forming the alpha-R-isomer of deltamethrin and ester cleavage leading to mPBacid and *cis*-Br_2CA, respectively, was observed. The *trans*-Br_2CA was formed as a minor metabolite by photo induced opening of the cyclopropane ring of *cis*-Br_2CA and subsequent recombination to the trans-isomer.

The kinetics evaluation of the laboratory rate of degradation studies resulted in overall best fit trigger DT_{50} values of 5.3 to 59.3 days for deltamethrin. The DT_{50} values normalised to 20 °C and pF2 were calculated to range between 12.5 and 231 days, and modelling endpoint geometric mean DT_{50} of 54.8 days for deltamethrin.

Both major soil metabolites of deltamethrin, Br_2CA and mPBacid, degrade very rapidly in soil. The DT_{50} values of Br_2CA normalised to 20 °C and pF2 were calculated to range between 3.2 to 16.8 days, (geometric mean of 5.0 days), that of mPBacid ranged from 6.9 to 9 hours (geometric mean of 7.5 hours). only More details for the route and rates of degradation of deltamethrin and its major degradation products in soil are given in section CA 7.1.1 and section CA 7.1.2, respectively.

Field soil dissipation studies conducted in Minnesota (US) and at four sites in Germany confirmed that Deltamethrin shows a relatively fast to moderate dissipation from soil under field conditions with field DT_{50} ranging from 8 to 28 days (SFO, n = 5) and DT_{90} between 25 and 94 days, even after multiple application of exaggerated doses. Deltamethrin residues were mainly confined to the upper 15 cm of

soil. Br_2CA was not detected above the limit of quantification (LOQ = 0.01 mg/kg soil) under field conditions.

Deltamethrin and its major degradation products are strongly to weakly adsorbed in soil, more details for the adsorption and desorption in soil of deltamethrin and its major degradation products are given in section CA 7.1.3.1.

CA 7.1.1 Route of degradation in soil

The route of degradation of deltamethrin in soil has been investigated in a comprehensive series of laboratory studies using different soils and radio-labels (e.g. vinyl-, gemi dimethyl-, benzyl-, cyano- and phenoxy- ^{14}C-label). The proposed degradation pathway in soil is shown in Figure 7.1.1- 1.

Deltamethrin is well degraded in aerobic soil to the final degradation product CO_2 (36% - 70% at day 64 to 90 depending on ^{14}C-label) and the substance is not expected to accumulate in soil. In parallel to mineralization, indicating a complete degradation of the molecule, non-extractable residues (NER) ranged from 18 to 48% of the total radioactivity applied. The bound residues are mainly associated with the humin and fulvin acid fractions of humus, and the major part of this humus bound residues consists of bound degradation products. Degradation of deltamethrin in soil is a microbial process and the main degradation pathway in soil can be described by ester cleavage followed by oxidation leading to the formation of Br_2CA (AE F108565, cis) and mPBacid (AE F109036). Only Br_2CA was identified at levels >10%, at a maximum of 23% of applied radioactivity. No other metabolites exceeded 10% of applied radioactivity although the metabolite mPBacid was detected at >5% on at least 2 consecutive occasions.
A minor route of transformation, which was observed only in some of the soil degradation studies, is the oxidation of the nitrile group of deltamethrin resulting in deltamethrin-amide (D-$CONH_2$, AE 0035077), followed by further oxidation to deltamethrin-carboxylic acid (D-COOH, AE 0035100), which was also rapidly degraded by ester cleavage, oxidation and mineralization to CO_2.

Deltamethrin is extensively degraded in soil under anaerobic conditions as well. However, degradation is somewhat retarded in comparison with aerobic degradation (DT_{50} ranges from 32 to 105 days, n = 5). The principal degradation pathway under anaerobic conditions is the same as observed under aerobic conditions. Since degradation is slowed down the main metabolite Br_2CA was found at day 59 at a maximum level of 52% of the radioactivity applied. Levels of other metabolites found in the anaerobic soil studies (D-COOH, mPBacid, mPBalcohol, D-$CONH_2$) were much lower (maximum 4%).

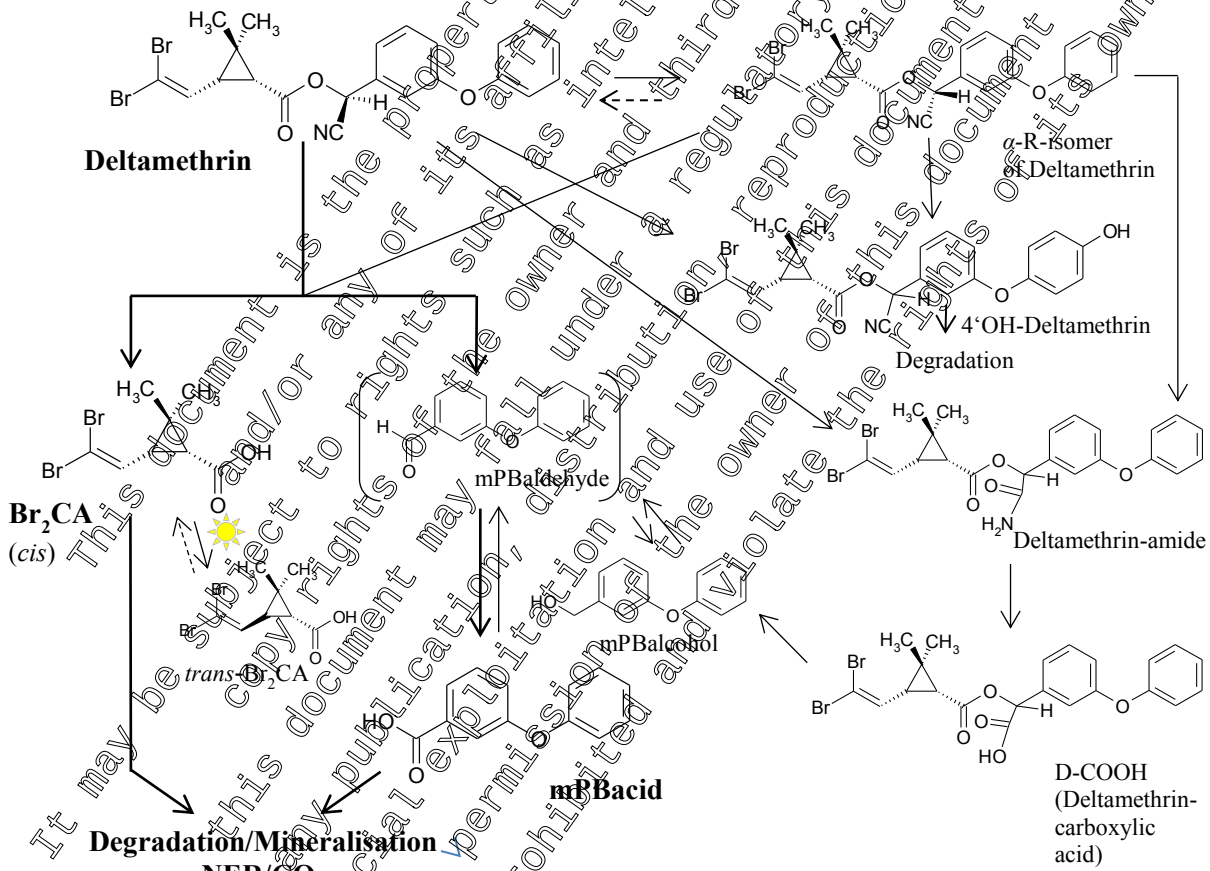
Photolysis will not significantly contribute to the degradation of deltamethrin in soil since extensive transformation was observed also in the dark control. Photo induced R/S epimerisation forming the alpha-R-isomer of deltamethrin and ester cleavage leading to mPBacid and cis-Br_2CA, respectively, was observed. *Trans*-Br_2CA was formed as a minor metabolite by photo induced opening of the cyclopropane ring of *cis*-Br_2CA and subsequent recombination to the trans-isomer.

The maximum occurrences of degradation products in percentage of applied radioactivity [% AR] are given as means of duplicates (see Table 7.1.1- 1). Normal written values were taken from the List of Endpoints (SANCO/6504/VI/99-final, 17 October 2002). The <u>underlined</u> figures are not new and were part of the EU Monograph Annex B7 already, but had not been listed in the above-mentioned List of Endpoints. Due to new EU-requirements to address metabolites >5% on two sequential sampling dates, the mPBacid is newly addressed as a major soil degradation product in this Supplemental Dossier.

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

Compound	Aerobic Soil [% AR]	Anaerobic Soil [% AR]	Photolysis [% AR]
Br_2CA (AE F108565; cis)	23.0	52	54 (dark controls)
mPBacid (AE F109036)	5.6	4.3	11 (in a pre-test)
Carbon dioxide	70	71	9 (dark controls)
Non-extractable residues	48	28	35

Figure 7.1.1- 1: Proposed degradation pathway of deltamethrin in soil (major metabolites are highlighted in bold writing)



CA 7.1.1.1 Aerobic degradation

The route of degradation of deltamethrin in soil under aerobic conditions in the laboratory was evaluated during the Annex I inclusion (compare EU Monograph Annex B7) and was accepted by the European Commission (SANCO/6504/VI/99-final, 17 October 2002). The following four of six studies included in the Baseline Dossier were regarded as relevant during the Annex I inclusion:

Author(s)	Year	Document No.
[redacted]	1991	M-136659-01-1
[redacted]	1979	M-149530-01-1
[redacted]	1979	M-149541-01-1
[redacted]	1978	M-063775-01-1

No additional studies are submitted within this Supplemental Dossier for the deltamethrin renewal of approval. The degradation product mPBacid (AE F109036) is newly addressed as major soil degradation product in this Supplemental Dossier because it was formed above the new identification triggers in aerobic soil degradation studies (see Table 7.1.1- 1).
A summary of the route of degradation of deltamethrin in soil is given in section CA 7.1.1 and Figure 7.1.1- 1.

CA 7.1.1.2 Anaerobic degradation

The route of degradation of deltamethrin in soil under anaerobic conditions in the dark in the laboratory was evaluated during the Annex I inclusion and was accepted by the European Commission (SANCO/6504/VI/99-final, 17 October 2002). The following two of three studies included in the Baseline Dossier were considered as relevant during the Annex I inclusion:

Author(s)	Year	Document No.
[redacted]	1991	M-136665-01-1
[redacted]	1980	M-149538-01-1

No additional studies are submitted within this Supplemental Dossier for the deltamethrin renewal of approval. A summary of the route of degradation of deltamethrin in soil is given in section CA 7.1.1 and Figure 7.1.1- 1.

CA 7.1.1.3 Soil photolysis

The route of degradation of deltamethrin in soil under photolytic conditions in the laboratory was evaluated during the Annex I inclusion and was accepted by the European Commission (SANCO/6504/VI/99-final, 17 October 2002). The following one of two studies included in the Baseline Dossier was considered as relevant during the Annex I inclusion:

Author(s)	Year	Document No.
[redacted]	1991	M-136671-01-1

No additional studies are submitted within this Supplemental Dossier for the deltamethrin renewal of approval. A summary of the route of degradation of deltamethrin in soil is given in section CA 7.1.1 and Figure 7.1.1- 1.

CA 7.1.2 Rate of degradation in soil

Deltamethrin was degraded in soil under aerobic and anaerobic conditions in the laboratory (see section CA 7.1.1 before), as well as under field conditions. The kinetic models and DT_{50} values in soil of deltamethrin and its major degradation products used for modelling purpose and trigger evaluation (best-fit) as well as the formation fractions in soil for major degradation products are summarized in sections CA 7.1.2.1 and CA 7.1.2.2.

Modelling input values for the calculation of predicted environmental concentrations (PECs) of deltamethrin and its major degradation products in soil (PEC_{soil}), groundwater (PEC_{gw}) and surface water (PEC_{sw}) were derived from studies and kinetic evaluations (acc. to FOCUS kinetics (2006)[1]) summarized in sections CA 7.1.1, CA 7.1.2 and CA 7.2, and are submitted within this Supplemental Dossier for the deltamethrin renewal of approval.

The DT_{50} values and maximum occurrences / formation fractions in soil and aquatic systems of deltamethrin and its major degradation products used as modelling input values for the calculation of PECs are summarized in Table 7.1.2- 1 and Table 7.1.2- 2.

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

Modelling Input Parameter	Endpoint	Comment
deltamethrin		
DT_{50} in soil [days]	231	laboratory, normalised, worst case
maximum occurrence in soil [%]	100	worst case
Br2CA (AE F108565; *cis*)		
DT_{50} in soil [days]	16.8	laboratory, normalised, worst case
maximum occurrence in soil [%]	23.0	laboratory, aerobic soil, worst case
mPBacid (AE F109036)		
DT_{50} in soil [days]	0.38	laboratory, normalised, worst case
maximum occurrence in soil [%]	5.6	laboratory, aerobic soil, worst case

[1] 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, 434 pp.

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

Modelling Input Parameter	Endpoint	Comment
deltamethrin		
DT_{50} in soil [days]	54.8	geometric mean, laboratory, normalised
Br_2CA (AE F108565; *cis*)		
DT_{50} in soil [days]	5.0	geometric mean, laboratory, normalised
FF deltamethrin → Br_2CA in soil	1.0	worst case assumption
mPBacid (AE F109036)		
DT_{50} in soil [days]	0.31	geometric mean, laboratory, normalised
FF deltamethrin → mPBacid in soil	1.0	arithmetic mean field

FF: formation fraction

CA 7.1.2.1 Laboratory studies

CA 7.1.2.1.1 Aerobic degradation of the active substance

The rate of degradation of deltamethrin in soil under aerobic conditions in the laboratory was evaluated during the Annex I inclusion (compare EU Monograph Annex B7) and was accepted by the European Commission (SANCO/6504/VI/99-final, 17 October 2002). The following four of six studies included in the Baseline Dossier were regarded as relevant during the Annex I inclusion.

Author(s)	Year	Document No.
[redacted]	1991	M-136659-01-1
[redacted]	1979	M-149530-01-1
[redacted]	1979	M-149541-01-1
[redacted]	1978	M-063775-01-1

No additional "rate of degradation study for the active substance" is submitted within this Supplemental Dossier for the deltamethrin renewal of approval.

However, updated kinetic evaluations of the degradation behaviour of deltamethrin in soil under aerobic conditions in the dark in the laboratory have been performed according to FOCUS kinetics (2006) [1] to derive kinetic parameters suitable for modelling purpose and environmental risk assessment (see **Error! Reference source not found.** 2013, report M-462053-01-1, below).

A summary of the degradation rates of deltamethrin and its major degradation products in soil in the laboratory is given in Table 7.1.2- 1 and Table 7.1.2- 2 before.

Report:	**KCA 7.1.2.1.1 /10; [redacted]; 2013**
Title:	Deltamethrin: Kinetic Modelling Evaluation of Data from Aerobic Soil Degradation Studies to Derive Trigger and Modelling Endpoints
Report No:	VC/11/026A
Document No:	M-462053-01-1
Guidelines:	- EU Council Directive 91/414/EEC, as amended by Commission Directive 95/36/EC of July 1995, Section 5, Point 7 and Commission Regulation (EC) No 1107/2009 of 21 October 2009; - FOCUS kinetics (2006) [1]
GLP:	No (modelling calculation)

EXECUTIVE SUMMARY

A kinetics evaluation of the relevant aerobic soil degradation studies with the insecticide deltamethrin has been conducted using the computer program KinGUI2 according to FOCUS Kinetics guidance [FOCUS, 2006] [1]. The trigger and modelling endpoint DT_{50} values derived for deltamethrin can be used in environmental exposure assessments along with the modelling endpoint DT_{50} for the mPBacid and Br_2CA metabolites. However, the updated kinetics results for both the metabolites are summarized later, i.e. in the relevant section CA 7.1.2.1.2.

The resulting DT_{50} values and maximum occurences in soil of deltamethrin and its major degradation products used as modelling input values for the calculation of predicted environmental concentrations in soil (PEC_{soil}) are summarized in Table 7.1.2- 1, those for predicted environmental concentrations in groundwater (PECgw) in Table 7.1.2- 2.

I. METHODS

Laboratory degradation data for deltamethrin and the metabolites (see sections CA 7.1.1 and CA 7.1.2) were evaluated against the FOCUS Kinetics flowcharts for the determination of parent trigger/modelling and metabolite modelling endpoints. The chemical structures and names of deltamethrin and the metabolites mPBacid and Br_2CA are shown in section 2 of report. The used data on degradation of deltamethrin are shown in the following tables.

Table 7.1.2.1.1- 1: Soil degradation study information - deltamethrin

Soil	Label	Rate	Temp. (ºC)	Moisture content	Texture (USDA)	Reference
Dubbs	Methylene	High	25	75% 1/3 bar	Sandy loam	[redacted] [1979] M-063775-01-1
Dubbs	Methylene	Exag'd	25	75% 1/3 bar	Sandy loam	
Dubbs	Vinyl	High	25	75% 1/3 bar	Sandy loam	
Dubbs	Vinyl	Exag'd	25	75% 1/3 bar	Sandy loam	
Hagerstown	Methylene	High	25	75% 1/3 bar	Silty clay loam	
Hagerstown	Methylene	Exag'd	25	75% 1/3 bar	Silty clay loam	
Hagerstown	Vinyl	High	25	75% 1/3 bar	Silty clay loam	
Hagerstown	Vinyl	Exag'd	25	75% 1/3 bar	Silty clay loam	
Dubbs	Cyano	High	10	75% 1/3 bar	Sandy loam	[redacted] [1979a] M-149530-01-1
Dubbs	Cyano	High	25	75% 1/3 bar	Sandy loam	
Dubbs	Vinyl	High	10	75% 1/3 bar	Sandy loam	
Dubbs	Vinyl	High	25	75% 1/3 bar	Sandy loam	
Dubbs	Cyano	Normal	25	75% 1/3 bar	Sandy loam	[redacted] [1979b] M-149541-01-1
Dubbs	Cyano	High	25	75% 1/3 bar	Sandy loam	
Dubbs	Phenoxy	Normal	25	75% 1/3 bar	Sandy loam	
Dubbs	Phenoxy	High	25	75% 1/3 bar	Sandy loam	
Memphis	Cyano	Normal	25	75% 1/3 bar	Silt loam	
Memphis	Cyano	High	25	75% 1/3 bar	Silt loam	
Memphis	Phenoxy	Normal	25	75% 1/3 bar	Silt loam	
Memphis	Phenoxy	High	25	75% 1/3 bar	Silt loam	
Casa Grand	Benzyl	High	25	75% 1/3 bar	Sandy loam	[redacted] [1991] M-136659-01-1
Casa Grand	Gem	High	25	75% 1/3 bar	Sandy loam	
Dollendorf	-	-	20	pF2	Clay loam	[redacted] **[2011] M-413119-01-1 (refer to MCA 7.1.2.1.2/02)**
Höfchen	-	-	20	pF2	Silt loam	
Wurmweise	-	-	20	pF2	Sandy loam	
Wurmweise	Gem	-	20	55% MWHC	Sandy loam	[redacted] **[2013] M-455519-01-1 (refer to MCA 7.1.2.1.2/01)**
AXXa	Gem	-	20	55% MWHC	Loamy sand	
Höfchen	Gem	-	20	55% MWHC	Silt loam	
Dollendorf	Gem	-	20	55% MWHC	Loam	

Table 7.1.2.1.1- 2: Deltamethrin residue data for study by [redacted] 1978, M-063775-01-1

Time	Methylene (benzyl)-label		Vinyl-label	
	High rate	Exaggerated rate	High rate	Exaggerated rate
(days)	(% AR)	(% AR)	(% AR)	(% AR)
Soil Dubbs				
0	92.52	91.20	101.54	97.61
4	52.95	60.85	62.33	70.11
8	37.15	47.61	43.31	44.78
16	26.38	32.37	29.42	30.21
32	17.22	19.65	18.70	20.80
64	10.57	11.33	13.71	12.46
Soil Hagerstown				
0	88.92	93.09	95.69	90.94
4	59.25	63.08	61.20	66.78
8	41.62	46.57	44.54	53.28
16	30.34	29.55	30.30	30.11
32	22.53	19.45	13.24	19.34
64	14.49	11.82	13.36	6.55

% AR = % of applied radioactivity

Table 7.1.2.1.1- 3: Deltamethrin residue data for study by [redacted] 1979, M-149530-01-1

Time	Cyano-label	Vinyl-label
(days)	(% AR)	(% AR)
Soil Dubbs, incubation temperature 10°C		
0	94.6	96.3
4	86.5	91.8
8	82.3	83.5
16	74.2	82.2
32	58.9	72.8
64	25.9	41.4
Soil Dubbs, incubation temperature 25°C		
0	94.6	96.3
4	74.5	74.1
8	60.4	63.7
16	33.3	50.7
32	25.2	38.8
64	9.2	13.9

% AR = % of applied radioactivity

Table 7.1.2.1.1- 4: Deltamethrin residue data for study by [redacted] 1979, M-149541-01-1

Time (days)	Cyano-label Normal rate (% AR)	Cyano-label High rate (% AR)	Phenoxy-label Normal rate (% AR)	Phenoxy-label High rate (% AR)
Soil Dubbs				
0	93.8	93.8	90.0	92.0
4	75.6	77.9	70.6	77.8
8	58.7	68.7	54.5	65.5
16	43.8	49.5	39.8	50.6
32	27.7	37.2	32.7	30.7
64	19.9	22.9	21.4	23.3
128	15.6	15.2	15.1	17.3
Soil Memphis				
0	91.6	101.6	98.0	93.8
4	78.8	77.2	77.0	78.6
8	70.1	74.2	63.9	68.4
16	55.5	53.3	55.4	53.0
32	40.7	33.5	32.3	36.0
64	25.1	20.2	21.3	20.6
128	12.9	13.8	15.6	17.2

% AR = % of applied radioactivity

Table 7.1.2.1.1- 5: Residue data for the study by Error! Reference source not found. 1991, M-136659-01-1

Time (days)	Benzyl-label Replicate 1 Deltamethrin (%AR)	Benzyl-label Replicate 2 Deltamethrin (%AR)	Gem-label Replicate 1 Deltamethrin (%AR)	Gem-label Replicate 2 Deltamethrin (%AR)
Soil Casa Grand				
0	92.61	94.62	85.94	97.23
1	91.28	93.04	94.31	95.50
3	78.34	82.89	84.30	86.57
7	62.63	67.87	79.20	81.08
14	50.33	49.80	48.45	54.20
30	33.71	30.39	31.94	35.42
59	15.51	12.50	19.35	20.83
90	9.04	8.10	12.30	11.39
120	5.80	5.63	9.47	9.82
181	4.06	3.38	6.66	8.99

% AR = % of applied radioactivity

Modelling strategy for data processing:

For time zero when metabolites are detected, the concentration was set to 0 and their detected concentration was added to concentration of parent. Values reported as <LOQ were set to ½ LOQ for the first occurrence and subsequent <LOQ values not used in the kinetics.

Optimisation model:

The sampling times and residue data (Table 7.1.2.1.1- 1 to Table 7.1.2.1.1- 5) were entered into KinGUI2 (compare Figure 1 and Figure 2 and section 4.2 of report) and optimisations carried out for deltamethrin (and the metabolites mPBacid and Br_2CA, see later) in a stepwise procedure according to

FOCUS Kinetics guidance for the determination of trigger and modelling endpoints (FOCUS, 2006; Flowcharts 7-1, 7-2, 8-5 and 8-6). Equations 1-4 describe the SFO, FOMC, DFOP and HS kinetics models used. The kinetic evaluations and the statistical calculations were conducted with KinGUI (v2.0) using iteratively re-weighted least-squares (IRLS) optimisation (for details on optimisation statistics see section 4.3 of report).

II. RESULTS

Table 7.1.2.1.1- 6 to Table 7.1.2.1.1- 9 summarise the optimised SFO, FOMC, DFOP and HS model parameters. The detailed KinGUI2 output files are shown in Appendix 8.1 of the report.

For the determination of trigger endpoints, the SFO, FOMC and DFOP model fits (Table 7.1.2.1.1- 6 to Table 7.1.2.1.1- 8) were evaluated according to Flowchart 7-1 (FOCUS, 2006) in order to determine the best-fit kinetic (Table 7.1.2.1.1- 10). For a number of soils, HS kinetics was determined to be the best-fit kinetic by expert judgement (case-by-case decision).
For the determination of modelling endpoints, the SFO, FOMC, DFOP and HS model fits were evaluated in order to determine the best-fit kinetic (Table 7.1.2.1.1- 11) according to Flowchart 7-2 (FOCUS, 2006). Two trials resulted in the selection of SFO as acceptable fits for modelling. Four trials were within the experimental DT_{90}, thus the modelling endpoint DT_{50} was derived as the best-fit biphasic kinetic DT_{90}/3.32 (two soils FOMC and two soils HS). The majority of trials resulted in the selection of the modelling endpoint DT_{50} based on the DFOP or HS slow-phase k2 degradation rate. Table 7.1.2.1.1- 12 shows the calculated FOCUS correction factors (g_{10} 2.58 and B-factor 0.7) for each soil. An overall geometric mean normalised (20°C and pF2) modelling endpoint DT_{50} of 54.8 days is calculated for deltamethrin (Table 7.1.2.1.1- 11).

Table 7.1.2.1.1- 6: Optimised SFO kinetic model parameters for deltamethrin

Soil	Label	Info	Kinetic	DT_{50} (days)	DT_{90} (days)	Chi^2 error (%)	t-test (-)	Visual fit
Dubbs	Methylene	Exag'd	SFO	11.6	38.7	11.7	0.006731	Poor
Dubbs	Methylene	High	SFO	7.9	26.3	16.7	0.016958	Poor
Dubbs	Vinyl	Exag'd	SFO	9.9	32.9	13.1	0.008436	Poor
Dubbs	Vinyl	High	SFO	8.5	28.1	15.4	0.014121	Poor
Hagerstown	Methylene	Exag'd	SFO	10.5	34.8	12.1	0.006708	Poor
Hagerstown	Methylene	High	SFO	11.7	38.9	15.8	0.027242	Poor
Hagerstown	Vinyl	Exag'd	SFO	11.4	37.9	7.2	0.000732	Good
Hagerstown	Vinyl	High	SFO	9.0	29.9	12.8	0.006150	Acceptable
Dubbs	Cyano	10°C	SFO	39.4	131	3.5	0.000171	Good
Dubbs	Cyano	25°C	SFO	13.6	45.3	7.9	0.00149	Acceptable
Dubbs	Vinyl	10°C	SFO	59.3	197	3.8	0.000857	Good
Dubbs	Vinyl	25°C	SFO	22.3	74.0	7.5	0.00182	Acceptable
Dubbs	Cyano	High	SFO	27.6	91.8	10.0	0.00369	Acceptable
Dubbs	Cyano	Normal	SFO	19.5	64.9	13.4	0.00948	Poor
Dubbs	Phenoxy	High	SFO	25.7	85.4	11.6	0.00662	Poor
Dubbs	Phenoxy	Normal	SFO	23.5	78.1	15.1	0.023765	Poor
Memphis	Cyano	High	SFO	23.0	76.3	9.8	0.00215	Poor
Memphis	Cyano	Normal	SFO	32.2	107	6.6	0.00043	Acceptable
Memphis	Phenoxy	High	SFO	27.0	89.8	9.7	0.00272	Poor
Memphis	Phenoxy	Normal	SFO	24.5	81.3	11.2	0.00477	Poor
Casa Grand	Benzyl	High	SFO	19.0	63.2	6.6	1.12e-11	Acceptable

Casa Grand	Gem	High	SFO	22.9	76.2	9.2	8.35e-09	Poor

Table 7.1.2.1.1- 7: Optimised FOMC kinetic model parameters for deltamethrin

Soil	Label	Info	Kinetic	DT_{50} (days)	DT_{90} (days)	Chi^2 error (%)	t-test (-)	Visual fit
Dubbs	Methylene	Exag'd	FOMC	8.4	84.9	1.0	-	Excellent
Dubbs	Methylene	High	FOMC	5.3	78.3	1.2	-	Excellent
Dubbs	Vinyl	Exag'd	FOMC	7.7	70.4	2.4	-	Excellent
Dubbs	Vinyl	High	FOMC	6.0	78.2	2.3	-	Excellent
Hagerstown	Methylene	Exag'd	FOMC	7.9	75.9	1.9	-	Excellent
Hagerstown	Methylene	High	FOMC	7.6	132	2.9	-	Excellent
Hagerstown	Vinyl	Exag'd	FOMC	9.8	53.7	3.3	-	Excellent
Hagerstown	Vinyl	High	FOMC	6.8	64.9	4.7	-	Very good
Dubbs	Cyano	10°C	FOMC	34.1	113	5.1	-	Very good
Dubbs	Cyano	25°C	FOMC	11.7	64.7	5.4	-	Very good
Dubbs	Vinyl	10°C	FOMC	52.1	174	4.8	-	Very good
Dubbs	Vinyl	25°C	FOMC	17.3	136	5.9	-	Good
Dubbs	Cyano	High	FOMC	19.8	216	2.2	-	Excellent
Dubbs	Cyano	Normal	FOMC	13.9	186	3.8	-	Very good
Dubbs	Phenoxy	High	FOMC	18.7	226	3.9	-	Very good
Dubbs	Phenoxy	Normal	FOMC	13.9	291	3.3	-	Excellent
Memphis	Cyano	High	FOMC	17.6	153	4.7	-	Very good
Memphis	Cyano	Normal	FOMC	25.2	192	0.9	-	Excellent
Memphis	Phenoxy	High	FOMC	20.3	205	2.9	-	Very good
Memphis	Phenoxy	Normal	FOMC	17.2	206	4.1	-	Very good
Casa Grand	Benzyl	High	FOMC	15.8	85.9	2.4	-	Excellent
Casa Grand	Gem	High	FOMC	19.0	111	6.3	-	Excellent

Table 7.1.2.1.1- 8: Optimised DFOP kinetic model parameters for deltamethrin

Soil	Label	Info	Kinetic	DT_{50} (days)	DT_{90} (days)	Chi^2 error (%)	k_2 t-test (-)	Visual fit
Dubbs	Methylene	Exag'd	DFOP	8.3	71.0	2.2	0.02523	Excellent
Dubbs	Methylene	High	DFOP	5.3	67.7	1.4	0.00773	Excellent
Dubbs	Vinyl	Exag'd	DFOP	7.5	86.3	4.3	0.15611	Excellent
Dubbs	Vinyl	High	DFOP	6.0	82.6	1.8	0.03006	Excellent
Hagerstown	Methylene	Exag'd	DFOP	7.8	80.0	0.5	0.00332	Excellent
Hagerstown	Methylene	High	DFOP	7.3	102	1.4	0.01286	Excellent
Hagerstown	Vinyl	Exag'd	DFOP	9.7	55.0	3.5	0.09334	Excellent
Hagerstown	Vinyl	High	DFOP	7.2	98.1	5.5	0.35090	Very good
Dubbs	Cyano	10°C	DFOP	39.4	131	4.4	0.03239	Good
Dubbs	Cyano	25°C	DFOP	11.5	68.0	5.8	0.22264	Good
Dubbs	Vinyl	10°C	DFOP	59.3	197	4.8	0.04907	Good
Dubbs	Vinyl	25°C	DFOP	18.8	85.7	3.2	0.00881	Very good
Dubbs	Cyano	High	DFOP	19.3	192	2.3	0.02473	Excellent
Dubbs	Cyano	Normal	DFOP	13.6	254	1.8	0.04306	Excellent
Dubbs	Phenoxy	High	DFOP	18.1	372	1.7	0.11369	Excellent
Dubbs	Phenoxy	Normal	DFOP	12.8	190	2.8	0.01213	Excellent
Memphis	Cyano	High	DFOP	17.9	188	5.0	0.25730	Excellent
Memphis	Cyano	Normal	DFOP	25.0	158	0.8	0.00089	Excellent
Memphis	Phenoxy	High	DFOP	20.5	528	1.7	0.29731	Excellent
Memphis	Phenoxy	Normal	DFOP	17.5	210	5.0	0.21500	Excellent
Casa Grand	Benzyl	High	DFOP	15.7	87.2	2.7	0.00051	Excellent
Casa Grand	Gem	High	DFOP	18.9	131	6.0	0.19300	Excellent

Table 7.1.2.1.1- 9: Optimised HS kinetic model parameters for deltamethrin

Soil	Label	Info	Kinetic	DT_{50} (days)	DT_{90} (days)	Chi^2 error (%)	k_2 t-test (-)	Visual fit
Dubbs	Methylene	Exag'd	HS	9.6	78.5	7.5	0.21873	Very good
Dubbs	Methylene	High	HS	5.6	66.6	4.9	0.05695	Excellent
Dubbs	Vinyl	Exag'd	HS	7.3	73.1	2.8	0.02211	Excellent
Dubbs	Vinyl	High	HS	6.2	74.5	4.2	0.04888	Excellent
Hagerstown	Methylene	Exag'd	HS	7.7	71.9	2.7	0.01985	Excellent
Hagerstown	Methylene	High	HS	7.1	93.1	1.6	0.00716	Excellent
Hagerstown	Vinyl	Exag'd	HS	9.8	55.7	2.5	0.01182	Excellent
Hagerstown	Vinyl	High	HS	8.5	24.4	8.7	0.50000	Acceptable
Dubbs	Cyano	10°C	HS	41.2	104	1.3	0.00343	Very good
Dubbs	Cyano	25°C	HS	11.3	67.3	3.1	0.03251	Very good
Dubbs	Vinyl	10°C	HS	57.0	155	2.9	0.02149	Very good
Dubbs	Vinyl	25°C	HS	19.1	85.2	3.2	0.00695	Very good
Dubbs	Cyano	High	HS	17.5	163	2.9	0.00672	Very good
Dubbs	Cyano	Normal	HS	13.7	201	3.6	0.03646	Very good
Dubbs	Phenoxy	High	HS	18.0	226	1.9	0.00613	Excellent
Dubbs	Phenoxy	Normal	HS	11.1	164	2.9	0.00330	Very good
Memphis	Cyano	High	HS	17.6	147	5.9	0.05617	Very good
Memphis	Cyano	Normal	HS	27.3	136	2.7	0.00128	Very good
Memphis	Phenoxy	High	HS	19.2	178	4.4	0.03393	Good
Memphis	Phenoxy	Normal	HS	17.9	178	6.4	0.08073	Good
Casa Grand	Benzyl	High	HS	17.2	88.6	4.5	0.00466	Excellent
Casa Grand	Gem	High	HS	19.0	129	6.1	0.01714	Excellent

Table 7.1.2.1.1- 10: Selection of optimised kinetic model parameters for deltamethrin – trigger endpoints

Soil	Label	Info	Kinetic	DT_{50} (days)	DT_{90} (days)	Chi^2 error (%)	t-test (-)	Visual fit
Dubbs	Methylene	Exag'd	FOMC	8.4	84.9	1.0	-	Excellent
Dubbs	Methylene	High	FOMC	5.3	78.3	1.2	-	Excellent
Dubbs	Vinyl	Exag'd	HS	7.3	73.1	2.8	0.02251	Excellent
Dubbs	Vinyl	High	DFOP	6.0	82.6	1.8	0.03016	Excellent
Hagerstown	Methylene	Exag'd	DFOP	7.8	80.0	0.5	0.00332	Excellent
Hagerstown	Methylene	High	DFOP	7.3	102	1.4	0.01286	Excellent
Hagerstown	Vinyl	Exag'd	HS	9.8	55.7	2.5	0.01182	Excellent
Hagerstown	Vinyl	High	FOMC	6.8	64.9	4.7	-	Very good
Dubbs	Cyano	10°C	SFO	39.4	131	3.5	0.00017	Good
Dubbs	Cyano	25°C	HS	11.5	67.3	3.1	0.03251	Very good
Dubbs	Vinyl	10°C	SFO	59.3	197	3.8	0.00086	Good
Dubbs	Vinyl	25°C	HS	19.1	85.2	3.2	0.00695	Very good
Dubbs	Cyano	High	FOMC	19.8	216	2.2	-	Excellent
Dubbs	Cyano	Normal	DFOP	13.6	254	1.8	0.04306	Excellent
Dubbs	Phenoxy	High	HS	18.0	226	1.4	0.00613	Excellent
Dubbs	Phenoxy	Normal	DFOP	12.8	190	2.8	0.01213	Excellent
Memphis	Cyano	High	FOMC	17.6	153	4.7	-	Very good
Memphis	Cyano	Normal	DFOP	25.0	158	0.8	0.00089	Excellent
Memphis	Phenoxy	High	HS	19.2	178	4.4	0.03393	Good
Memphis	Phenoxy	Normal	FOMC	17.2	206	4.1	-	Very good
Casa Grand	Benzyl	High	FOMC	15.8	85.9	2.2	-	Excellent
Casa Grand	Gem	High	HS	19.0	129	6.0	0.01767	Excellent

Table 7.1.2.1.1- 11: Selection of optimised kinetic model parameters for deltamethrin – modelling endpoints

Soil	Label	Info	DT_{50} derivation	DT_{50} (days)	DT_{50} 20ºC and pF2 (days)	Chi² error (%)	t-test (-)
Dubbs	Methylene	Exag'd	Slow-phase DFOP k_2	32.9	43.2	2.2	0.02523
Dubbs	Methylene	High	Slow-phase DFOP k_2	36.7	48.3	1.4	0.00773
Dubbs	Vinyl	Exag'd	Slow-phase HS k_2	36.1	47.4	2.8	0.02211
Dubbs	Vinyl	High	Slow-phase DFOP k_2	52.4	68.8	1.8	0.03016
Hagerstown	Methylene	Exag'd	Slow-phase DFOP k_2	47.4	62.2	0.5	0.00332
Hagerstown	Methylene	High	Slow-phase DFOP k_2	53.6	70.4	1.4	0.01286
Hagerstown	Vinyl	Exag'd	HS DT_{90}/3.32	16.8	22.0	2.5	0.01182
Hagerstown	Vinyl	High	FOMC DT_{90}/3.32	19.5	25.7	4.7	-
Dubbs	Cyano	10ºC	SFO	39.4	12.5	3.5	0.00017
Dubbs	Cyano	25ºC	Slow-phase HS k_2	26.9	35.3	3.1	0.03251
Dubbs	Vinyl	10ºC	SFO	59.3	18.8	3.8	0.00086
Dubbs	Vinyl	25ºC	Slow-phase HS k_2	28.5	37.4	3.2	0.00695
Dubbs	Cyano	High	Slow-phase DFOP k_2	96.5	127	2.3	0.02473
Dubbs	Cyano	Normal	Slow-phase DFOP k_2	176	231	1.8	0.04306
Dubbs	Phenoxy	High	Slow-phase HS k_2	113	149	1.9	0.00613
Dubbs	Phenoxy	Normal	Slow-phase DFOP k_2	92.4	121	2.8	0.01213
Memphis	Cyano	High	Slow-phase HS k_2	67.2	88.3	5.9	0.05617
Memphis	Cyano	Normal	Slow-phase DFOP k_2	64.3	84.5	0.8	0.00089
Memphis	Phenoxy	High	Slow-phase HS k_2	78.6	103	4.4	0.03393
Memphis	Phenoxy	Normal	Slow-phase HS k_2	85.0	112	6.4	0.08073
Casa Grand	Benzyl	High	FOMC DT_{90}/3.32	25.9	34.0	2.2	-
Casa Grand	Gem	High	HS DT_{90}/3.32	39.0	51.2	6.0	0.01767
				Geometric mean	**54.8***		

* Geometric mean of the Dubbs (56.7 days), Hagerstown (39.7 days), Memphis (96.3 days) and Casa Grand (41.7 days) soils calculated first.

Table 7.1.2.1.1- 12: FOCUS soil temperature and moisture content correction factors

Soil	Temperature (ºC)	Moisture content				FOCUS correction factor
		Measured pF2.5 (% w/w)	Incubation conditions	Incubation (%w/w)	Reference (%w/w)	
[redacted]	25	23.7	75% 1/3 bar	17.8	23.7*	1.313
[redacted]	25	32.6	75% 1/3 bar	24.5	32.6*	1.313
[redacted]	25	37.6	75% 1/3 bar	28.2	37.6*	1.313
[redacted]	25	23.4	75% 1/3 bar	17.5	23.4*	1.313
[redacted]	10	23.7	75% 1/3 bar	17.8	23.7*	0.317
[redacted]	20	-	55% MWHC	31.6	21.8+	1.000
AXXa	20	-	55% MWHC	26.7	15.0+	1.000
[redacted]	20	-	55% MWHC	29.7	37.5+	0.849
[redacted]	20	-	55% MWHC	49.0	36.5+	1.000

* Measured pF2.5 > FOCUS default, so measured pF2.5 used + measured pF2

III. CONCLUSIONS

Deltamethrin is degraded in aerobic soil kept under standardized laboratory conditions with a DT_{50} of 54.8 days. The DT_{50} values and maximum occurences in soil of deltamethrin used as modelling input values for the calculation of predicted environmental concentrations in soil (PEC_{soil}) are summarized in Table 7.1.2- 1, those for predicted environmental concentrations in groundwater (PECgw) in Table 7.1.2- 2.

The following laboratory study on degradation of deltamethrin in soil was found in the literature. It is summarised in the following. The outcome was not included to derive endpoints since non-EU soils were used, and not all EU study requirements for such a study type were fulfilled. The resulting DT_{50} was not worst case and thus covered by the used data.

Report:	**KCA 7.1.2.1.1 /11; Chen, L.; Gu, X.; Dai, R.; Yu, Y.; Zhang, G.; 2008**
Title:	Persistence and dissipation of synthetic pyrethroid pesticides in red soils from the Yangtze River Delta area
Source:	Journal:Environ. Geochem. Health, (2008) 30 (1):67–77
Document No:	M-460924-01-1
Guidelines:	None
GLP:	No, published study (peer-reviewed article)
Literature review classification:	b) supplementary information (EFSA Journal 2011; 9(2):2092)

EXECUTIVE SUMMARY

Laboratory incubation trials were conducted to investigate the effects of several factors on the persistence as well as the dissipation of three synthetic pyrethroid pesticides among them deltamethrin in “red” soils obtained from the Yangtze River Delta region in China.Dissipation half-lives ($T_{1/2}$) tended to correlate with soil pH and soil organic matter contents, but not with soil cation-exchange capacity. The rates of pyrethroid dissipation also tended to increase with increasing initial soil concentration, but were largely unaffected by whether the pesticides were present in the soil separately or as a mixture. Microbial activity appeared to dominate the degradation process.
Dissipation half-lives of 18.4 and 18.1 days were reported for deltamethrin in unsterilized soil when being applied as single compound or as pyrethroid mixture, respectively.

I. MATERIAL AND METHODS

A. Material

1. Test material

Test item:	Deltamethrin
Active substance(s):	Deltamethrin
Chemical state and description:	not reported
Source of test item:	[redacted]. (USA)
Batch number:	not reported
Purity:	98%
Storage conditions:	not reported
Water solubility:	not reported

2. Soil:

Name / classification	not reported
Source, sampling date, storage conditions	Top soil field samples (0-20 cm deep, red), collected from farmland in the three locations in the Yangtze River Delta region: S01, ortho red soil: [redacted]

	Zhejiang province; S02, yellow-red soil [redacted] agriculture and ecology experimental station [redacted]; S03, brown red soil: [redacted] experimental station [redacted].
	Air-dried, sieved 60-mesh, storage in the dark at 20 °C
Soil type:	not reported
Particle size:	S01: Clay (<5 µm): 34%, Silt (5-50 µm): 59%, Sand (>50 µm): 7% S02: Clay (<5 µm): 28%, Silt (5-50 µm): 57%, Sand (>50 µm): 15% S03: Clay (<5 µm): 29%, Silt (5-50 µm): 58%, Sand (>50 µm): 13%
pH:	S01: 6.07, S02: 6.86, S03: 7.13
Organic matter content:	S01: 24.53 mg kg^{-1}, S02: 30.79 mg kg^{-1}, S03: 33.64 mg kg^{-1}

B. Study design and methods

1. Sampling

Sample preparation:	Soil samples were subdivided into 4 batches for treatment with the pyrethroides separately and as a mixture. Product label-specified max. application rate of 2 mg kg^{-1}. Monitoring soil subsamples of 10 g were sampled for quantification of residue contents at intervals of 0, 7, 14, 21, 28, 35, 49, 70, 91, and 112 days following pyrethroid treatment. The following test parameters were investigated: 1) Three pyrethroides among them deltamethrin present in soil separately versus a mixture 2) Sterilized versus unsterilized soil: 3 x autoclavation for 30 min at 121 °C 3) External carbon source: 1 mL of a glucose solution (200 g L^{-1}) was added to each subsample 4) Pesticide concentration: 2, 5, and 20 mg kg^{-1}
Sampling frequency:	0, 7, 14, 28, 35, 49, 70, 91 and 112 days following pyrethroid treatment
Number of samples per site/soil type:	not reported
Storage of samples:	The lab soil samples were kept in an incubation box at 25 °C and a soil moisture content of 25% by weight.

2. Chemical analysis

Method validation:	not reported
Guideline/protocol:	not reported
Method:	Gas chromatograph (GC) equipped with electron capture detector (ECD) and a capillary HP-5 column
Pre-treatment of samples:	The extraction and clean-up procedure is described in detail in literature[2].

[2] Gu, X. Z., Zhang, L., Zhang, G. Y., Fan, C.-X., Chen, L. (2010). Preliminary Evidence that Copper and Zinc Inhibits the Dissipation of Synthetic Pyrethroid in Red Soil. Water Air Soil Pollut, 212: 345-355.

	Briefly, the subsamples were repeatedly (3 x) extracted (extraction step: 50 mL of petroleum ether/acetone (2:1, v/v) at 25 °C for 24 h, 30 min ultrasonic bath, 3,000 rev. min^{-1} centrifugation for 15 min, collect 30 mL of the supernatant into different test tube). The supernatants of the 3 extractions were combined and in total concentrated to ~2 mL (pre-concentration to ~20 mL with rotary evaporator at 40-45 °C, further drying by anhydrous Na_2SO_4 and pre-concentrated in the rotary evaporator to ~ 2mL). The 2 mL extract was cleaned using a florisil column (20×1.5 cm, absorbent cotton, 2 cm anhydrous Na_2SO_4, 3 g florisil) at 4 mL min^{-1}. The analyte was eluted with 60 mL petroleum ether/ethyl acetate (9:1, v/v), followed by a concentration until nearly dry with rotary evaporation. The dried eluate was then re-dissolved in 1 mL petroleum ether and analysed by GC-ECD.
Conduction:	Apparatus: GC equipped with ECD Column: capillary HP-5 column (30 m length, 0.32 mm i.d., 0.25 µm film thickness) Carrier gas: Nitrogen, 40 mL min^{-1} Column head pressure: 50 kPa Column oven temperature: 210 °C (initial time, 1 min) to 285 °C at a rate of 10 °C min^{-1} and held thereupon for 10 min. Injector temperature: 270 °C Detector temperature: 320 °C Injection volume: 1 µL
Compound identification:	Retention time
Reference item:	not reported
Recovery:	89.7 – 93.0%
Limit of detection:	1.0 pg
Limit of quantification:	not reported

II. RESULTS

1. Validity criteria:

None.

2. Analytical findings:

The data from the present study tend to suggest that pyrethroid dissipation in soil is not affected by whether the pesticides are present in soil separately or together as a mixture. Deltamethrin dissipated with half-lives of 18.4 and 18.1 days in unsterilized soil with separate compound application and application as a mixture, respectively.

Increasing concentrations of deltamethrin in soil (2, 5, and 20 mg kg^{-1}) lead to a considerable increase of the half-life of deltamethrin from 18.4 days to 29.2 days in unsterilized soil. Comparing the study data and half-lives between unsterilized and sterilized soils, the results reveal that microbial activity played a dominant role in the pyrethroid degradation in soil, at least up to the first 70 days of cultivation. On the other hand, in the present study, soil pH, soil organic matter contents, and external carbon source were all seen to affect the half-lives of the three pyrethroids in soil somewhat, although to a lesser extent compared to microbial activity.

The results of the study are summarized in the following table.

Table 7.1.2.1.1- 13: Deltamethrin dissipation equations and half-lives (days) in soil resulting from various treatments: sterilized, unsterilized, single compound application, pyrethroid mixture application, pyrethroid soil concentration, external carbon source, soil types

Soil sample	Treatment	Dissipation equation	Correlation coefficient r^2	Half-life [day]	
Single compound or mixture application					
S02	Sterilized - Single	$C_t = 2.35 \cdot e^{-0.0087t}$	−0.9836	79.7	
	Sterilized - Mixture	$C_t = 2.27 \cdot e^{-0.0082t}$	−0.9941	84.5	
	Unsterilized - Single	$C_t = 2.14 \cdot e^{-0.0376t}$	−0.9239	18.4	
	Unsterilized - Mixture	$C_t = 2.05 \cdot e^{-0.0383t}$	−0.9551	18.1	
External carbon source – glucose addition					**Dissipation rate constant (mg kg^{-1} day^{-1})**
S01	None (CK)	$C_t = 2.26 \cdot e^{-0.0341t}$	−0.907	20.3	0.0341
	Glucose added	$C_t = 1.90 \cdot e^{-0.0426t}$	−0.8811	16.2	0.0426
S02	None (CK)	$C_t = 2.14 \cdot e^{-0.0376t}$	−0.9239	18.4	0.0376
	Glucose added	$C_t = 2.40 \cdot e^{-0.0447t}$	−0.9644	15.5	0.0447
S03	None (CK)	$C_t = 2.25 \cdot e^{-0.0440t}$	−0.9072	15.7	0.0440
	Glucose added	$C_t = 2.16 \cdot e^{-0.0501t}$	−0.9225	13.8	0.0501
Deltamethrin concentration (mg kg^{-1})					**Dissipation rate constant (mg kg^{-1} day^{-1})**
S02	2	$C_t = 2.14 \cdot e^{-0.0376t}$	−0.9235	18.4	0.0376
	5	$C_t = 2.03 \cdot e^{-0.0355t}$	−0.9758	19.5	0.0355
	20	$C_t = 2.37 \cdot e^{-0.0237t}$	−0.8789	29.2	0.0237

Regressions of dissipation half-lives on pH, OMC and CEC were performed for deltamethrin. The half-lives appeared to correlate with soil pH (r = -0.9301) and soil OMC (r = -0.9514), but not with soil CEC (r = -0.2987).

III. CONCLUSIONS

Considering single compound application and pyrethroid mixture application in microbial active soil, dissipation half-lives of 18.4 and 18.1 days were reported for deltamethrin, respectively.

Considering the influence of soil type, dissipation half-lives for deltamethrin ranged between 15.1 and 20.3 days in different red soils.

CA 7.1.2.1.2 Aerobic degradation of metabolites, breakdown and reaction products

Maximum formation fractions of Br_2CA (*cis*) and mPBacid, as well as the degradation rate of Br_2CA in soil under aerobic laboratory conditions in the dark were evaluated during the Annex I inclusion using the parent study of **Error! Reference source not found.** (1991) and [redacted] (1978). From the data of 14-90 days samples a DT_{50} of 21 days (r^2 = 0.95) for Br_2CA in one soil was indicated and accepted by the European Commission (SANCO/6504/VI/99-final, 17 October 2002). Not any DT_{50} data were stated for the metabolite mPBacid since it was not regarded as a major metabolite that time. The following still relevant studies needed for both metabolite assessments are included in the Baseline Dossier:

Author(s)	Year	Document No.
[redacted]	1991	M-136659-01-1
[redacted]	1978	M-063775-01-1

In order to fill data gaps new rate of degradation studies (**Error! Reference source not found.**, 2013, report M-455519-01-1, and [redacted] 2011, report M-413119-01-1) have been performed for both major degradation products. They are submitted within this Supplemental Dossier for the deltamethrin renewal of approval, together with an updated kinetics evaluation of their degradation kinetics considering all respective relevant data (see **Error! Reference source not found.** 2013, report M-462053-01-1) in order to derive kinetic parameters suitable for modelling purpose and environmental risk assessment (a summary of the respective final data is given in Table 7.1.2- 2.

Report:	**KCA 7.1.2.1.2/01; [redacted]; [redacted]; 2013**
Title:	[Gemdimethyl-^{14}C]AE F108565 (Br_2CA) - Degradation in four aerobic soils
Report No:	EnSa-13-0193
Document No:	M-455519-01-1
Guidelines:	OECD Test Guideline No. 307 DRAFT SANCO 11802/2010/rev 7 in accordance with Regulation (EC) No 1107/2009 US EPA OCSPP Test Guideline No. 835.4100 / 835.4200
GLP:	Yes

EXECUTIVE SUMMARY

The rate of degradation of [gemdimethyl-^{14}C]AE F108565 (Br_2CA) was studied in four soils under aerobic conditions in the dark in the laboratory for 21 days at 20.1 °C and 54.6% of the maximum water holding capacity. Formation of significant amounts of non-extractable residues and carbon dioxide indicates a participation in the natural carbon cycle of soil and the potential for a complete mineralization of Br_2CA.

The experimental data could be well described by a single first order model for all soils tested. The half-life of Br_2CA under aerobic conditions was less than 6 days in all soils (see Table 7.1.2.1.2- 1).

From this study it is concluded that Br_2CA and its degradation products have no potential for accumulation in the environment.

Table 7.1.2.1.2- 1: Best fit kinetics of Br_2CA degradation in soils under aerobic conditions

Soil (Soil Type)	Best Fit Kinetic Model [1]	DT_{50} [d]	DT_{90} [d]	Chi^2 Error [%]	Visual Assessment [2]
[redacted]	SFO	5.8	19.2	1.4	+
[redacted]AXXa	SFO	3.0	10.2	1.3	+
[redacted]4a	SFO	4.1	13.7	4.2	+
[redacted]II	SFO	3.2	10.6	4.9	+

[1] SFO: Single first order

[2] Visual assessment: + good, o = moderate, - = poor

I. MATERIALS AND METHODS

A. MATERIALS

1. Test Item

Radio-labelled Br_2CA	[Gemdimethyl-^{14}C]AE F108565
Batch Code	KML 9443
Specific radioactivity	7.04 MBq/mg (190.3 µCi/mg)
Radio-chemical Purity:	> 99%
Chemical Purity:	> 99%
Diastereomeric Purity	> 99%

2. Test Soils

Four soils were used (see Table 7.1.2.1.2-2, for more details see Table 1 of report). 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. Microbial biomass determination confirmed that the soils were viable.

Table 7.1.2.1.2- 2: Physico-chemical properties of test soils

Soil	Source	Texture (USDA)	pH *	OC [%]
[redacted]	[redacted] Germany	Sandy loam	5.2	1.8
[redacted]AXXa	[redacted] Germany	Loamy sand	6.5	1.7
[redacted]4a	[redacted] Germany	Silt loam	6.3	1.8
[redacted]II	[redacted] Germany	Loam	7.3	4.7

* pH value derived from suspensions of soil / 0.01 M $CaCl_2$ = 1/2.

B. STUDY DESIGN

1. Experimental Conditions

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

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

The amount of test item for the treatment of test systems was based on the single maximum recommended field application rate (FAR) of the parent active substance Deltamethrin, 12.5 g per hectare, and a maximum formation of approximately 25% of degradation product Br_2CA in a Deltamethrin soil degradation study (see **Error! Reference source not found.** 1991, report M-136665-01-1). Due to analytical reasons, a 40-fold application rate was used, resulting in a nominal study application rate (SAR) of 197 µg per kg soil dry weight following OECD TG No. 307. The FAR was converted to the SAR by assuming a homogeneous distribution of Br_2CA in a soil layer of 2.5 cm depth and a generic soil bulk density of 1.5 g/cm³.

The test item (141896 Bq equal to 20.2 µg, 100% AR) was applied dropwise onto the soil surface of the respective test systems in 400 µL methanol/water 1/1 (*v/v*) using a pipette. After application, the test vessels (except DAT-0 samples) were closed with PU foam plugs.

The test systems were incubated in the dark for 21 days at mean temperature of 20.1 °C (MIN 19.8 °C, MAX 20.3 °C) and soil moisture of 54.6% (MIN 52.3%, MAX 55.4%) of MWHC in a walk-in climatic chamber.

2. Sampling

7 sampling intervals were distributed over the entire incubation period of 21 days. Duplicate samples were processed and analysed 0, 1, 2, 4, 7, 14 and 21 days after treatment (DAT). Microbial soil biomass was determined at the start and after termination of the study (DAT-0, DAT-22).

3. Analytical Procedures

At each sampling interval, the entire soil of each test system was extracted three times at ambient temperature using acetonitrile / water 4/1 (v/v). Furthermore, two microwave-accelerated extraction steps were performed using acetonitrile / water 1/1 (v/v) at 70 °C and methanol / water 1/1 (v/v) at 50 °C. The amount of test item in soil extracts was determined by liquid scintillation counting (LSC) and by HPLC/radiodetection analysis. The amounts of volatiles and non-extractable residues were determined by LSC and combustion/LSC, respectively. The test item was identified by HPLC-MS(/MS) including accurate mass determination. The LOD of the HPLC/radiodetection method was determined as 6.0 Bq absolute on column or 0.4% AR.

The degradation kinetics of the test item was determined according to FOCUS kinetics (2006) using the software KinGUI 2 with three different kinetic models: single first order, first order multi compartment and double first order in parallel. Model input datasets were the residual amounts found in each replicate test system at each sampling interval. The initial recovery at DAT-0 was included in the parameter optimization procedure, but for optimal goodness of fit, the value was allowed to be estimated by the model. The best-fit kinetic model was selected on the basis of the chi^2 scaled-error criterion and on the basis of a visual assessment of the goodness of the fits. DT_{50} and DT_{90} values were calculated from the resulting kinetic parameters.

II. RESULTS AND DISCUSSION

Results indicated that the anticipated standardized aerobic conditions were maintained and that the soils were microbially active over the duration of the laboratory study. Further, the results demonstrated that the sample processing method was well suited to recover high amounts of the applied test item from the soil and that the test item was stable under these conditions.

A. DATA

Table 7.1.2.1.2- 3: Degradation of Br_2CA in soil [redacted] under aerobic conditions (expressed as percentage of applied radioactivity (mean ± SD))

Compound	Mean SD	DAT 0	1	2	4	7	14	21
Br_2CA	Mean	96.3	85.7	78.4	60.9	41.4	18.9	6.6
	SD	± 0.5	± 0.4	± 0.5	± 1.4	± 0.7	± 0.8	± 1.7
Sum of Unid./Diff. Residues [1]	Mean	< LOD	3.9	5.9	8.5	9.5	7.2	5.1
	SD		± 0.2	± 0.5	± 0.7	± 0.5	± 0.1	± 0.0
Total Extractable Residues [2]	Mean	96.3	89.6	84.4	69.4	50.9	26.1	11.7
	SD	± 0.5	± 0.6	± 0.1	± 0.7	± 1.2	± 0.9	± 1.7
Carbon Dioxide [3]	Mean	n.a.	1.5	3.4	7.2	12.4	29.8	37.2
	SD		± 0.1	± 0.1	± 0.1	± 0.0	± 2.6	± 1.2
Volatile Organic Compounds [3]	Mean	n.a.	0.1	0.1	0.3	0.4	0.5	0.5
	SD		± 0.0	± 0.0	± 0.0	± 0.0	± 0.1	± 0.1
Non-Extractable Residues [3]	Mean	0.9	7.3	12.9	23.8	36.3	44.3	48.6
	SD	± 0.2	± 0.2	± 0.6	± 0.7	± 1.0	± 1.1	± 2.4
Total Recovery [2]	Mean	97.1	98.4	100.9	100.6	100.0	100.7	98.1
	SD	± 0.3	± 0.9	± 0.5	± 0.1	± 2.1	± 2.4	± 0.6

Table 7.1.2.1.2- 4: Degradation of Br_2CA in soil [redacted] AXXa under aerobic conditions (expressed as percentage of applied radioactivity (mean ± SD))

Compound	Mean SD	DAT 0	1	2	4	7	14	21
Br_2CA	Mean	98.6	79.8	64.6	41.2	19.7	3.0	1.3
	SD	± 0.2	± 0.1	± 1.5	± 1.0	± 1.3	± 0.6	± 0.0
Sum of Unid./Diff. Residues [1]	Mean	< LOD	5.4	8.8	9.4	8.4	5.5	5.4
	SD		± 0.2	± 0.3	± 0.1	± 0.1	± 0.4	± 0.2
Total Extractable Residues [2]	Mean	99.0	85.2	73.4	50.6	28.1	8.5	6.7
	SD	± 0.6	± 0.3	± 1.2	± 1.1	± 1.1	± 0.2	± 0.2
Carbon Dioxide [3]	Mean	n.a.	2.1	6.3	12.3	19.5	33.3	37.1
	SD		± 0.1	± 0.1	± 0.4	± 0.3	± 0.6	± 0.8
Volatile Organic Compounds [3]	Mean	n.a.	0.1	0.1	0.1	0.3	0.3	0.2
	SD		± 0.0	± 0.0	± 0.0	± 0.1	± 0.0	± 0.0
Non-Extractable Residues [3]	Mean	0.5	10.5	19.5	34.3	47.6	51.7	50.1
	SD	± 0.0	± 0.5	± 0.1	± 0.9	± 0.5	± 0.4	± 0.1
Total Recovery [2]	Mean	99.5	98.0	99.2	97.3	95.6	93.8	94.1
	SD	± 0.6	± 0.9	± 1.2	± 0.2	± 0.3	± 0.8	± 1.2

n.d.: not detected, n.a.: not analyzed, DAT: days after treatment, SD: standard deviation
[1] Minor degradates are summed up to unidentified residues, see Appendix 10 and 11 of report for max. amounts
[2] Difference to material balance values due to rounding errors as well as clean up and chromatographic losses
[3] Values taken from material balance

Table 7.1.2.1.2- 5: Degradation of Br_2CA in soil [redacted] under aerobic conditions (expressed as percentage of applied radioactivity (mean ± SD))

Compound	Mean SD	DAT 0	1	2	4	7	14	21
Br_2CA	Mean	96.9	84.4	75.7	52.5	28.2	5.2	3.8
	SD	± 0.4	± 0.8	± 0.4	± 2.3	± 0.2		± 0.1
Sum of Unid./Diff. Residues [1]	Mean	< LOD	3.6	6.0	8.5	6.6	4.6	4.3
	SD		± 0.3	± 0.1	± 0.3	± 0.1		± 0.3
Total Extractable Residues [2]	Mean	97.2	88.0	81.7	61.0	34.8	9.9	8.1
	SD	± 0.7	± 0.4	± 0.4	± 2.6	± 0.1		± 0.7
Carbon Dioxide [3]	Mean	n.a.	1.4	4.0	8.8	17.0	32.2	36.5
	SD		± 0.1	± 0.1	± 0.5	± 0.3		± 0.7
Volatile Organic Compounds [3]	Mean	n.a.	0.1	0.1	0.1	0.2	0.2	0.3
	SD		± 0.0	± 0.0	± 0.0	± 0.0		± 0.0
Non-Extractable Residues [3]	Mean	0.9	8.8	14.8	28.7	43.0	50.5	47.7
	SD	± 0.0	± 0.3	± 0.4	± 2.4	± 0.3		± 0.4
Total Recovery [2]	Mean	98.1	98.2	100.6	98.7	99.0	92.8	92.6
	SD	± 0.7	± 0.1	± 0.2	± 0.3	± 0.2		± 0.2

*: Material Balance of one sample was < 90% AR, presumably due to a leakage during determination of carbon dioxide. Therefore, the values of this sample were not used for calculations.

Table 7.1.2.1.2- 6: Degradation of Br_2CA in soil [redacted] II under aerobic conditions (expressed as percentage of applied radioactivity (mean ± SD))

Compound	Mean SD	DAT 0	1	2	4	7	14	21
Br_2CA	Mean	93.6	69.9	58.7	41.0	22.0	3.9	1.6
	SD	± 0.5	± 2.6	± 1.3	± 5.3	± 2.6	± 2.5	± 0.9
Sum of Unid./Diff. Residues [1]	Mean	0.5	3.9	5.1	5.6	6.2	5.2	4.9
	SD	± 0.0	± 0.2	± 0.1	± 0.4	± 0.1	± 0.7	± 0.4
Total Extractable Residues [2]	Mean	94.0	73.8	63.8	46.6	28.2	9.1	6.6
	SD	± 1.0	± 2.8	± 1.2	± 4.9	± 2.7	± 1.8	± 0.5
Carbon Dioxide [3]	Mean	n.a.	2.2	5.6	11.5	19.1	34.5	37.7
	SD		± 0.2	± 0.2	± 0.9	± 0.6	± 0.6	± 0.5
Volatile Organic Compounds [3]	Mean	n.a.	< 0.1	0.1	0.1	0.1	0.2	0.1
	SD		± 0.0	± 0.1	± 0.0	± 0.0	± 0.1	± 0.0
Non-Extractable Residues [3]	Mean	2.3	21.4	29.1	39.0	46.1	52.3	50.5
	SD	± 0.2	± 1.5	± 1.0	± 3.3	± 1.1	± 2.0	± 1.7
Total Recovery [2]	Mean	96.3	97.4	98.6	97.3	93.5	96.0	94.8
	SD	± 0.8	± 1.1	± 0.0	± 0.8	± 1.0	± 0.9	± 1.7

n.d.: not detected, n.a.: not analyzed, DAT: days after treatment, SD: standard deviation
[1] Minor degradates are summed up to unidentified residues, see Appendix 10 and 11 of report for max. amounts
[2] Difference to material balance values due to rounding errors as well as clean up and chromatographic losses
[3] Values taken from material balance

B. MASS BALANCE AND DISTRUBUTION OF RADIOACTIVITY

Mean material balance was 99.8% AR (range from 97.5 to 101.6% AR) for soil [redacted] 97.0% AR (range from 94.1 to 99.6% AR) for soil [redacted] AXXa, 96.8% AR (range from 92.8 to 100.8% AR) for soil [redacted] and 96.4% AR (range from 93.9 to 98.6% AR) for soil [redacted] II.

Extractable residues decreased from DAT-0 to DAT-21 from 96.6 to 12.3% AR in soil [redacted] from 99.1 to 7.0% AR in soil [redacted] AXXa, from 97.4 to 8.3% AR in soil [redacted] and from 94.2 to 6.6% AR in soil [redacted] II.

Non-extractable residues (NER) increased from DAT-0 to DAT-21 from 0.9 to 48.6% AR in soil [redacted]. In soil [redacted] AXXa, NER increased from DAT-0 to DAT-14 from 0.5 to 51.7% AR and slightly declined to 50.1% AR until DAT-21. NER increased in soil [redacted] from DAT-0 to DAT-14 from 0.9 to 50.5% AR and declined to 47.7% AR until DAT-21. In soil [redacted] II, NER increased from DAT-0 to DAT-14 from 2.3 to 52.3% AR and slightly declined to 50.5% AR until DAT-21.

The maximum amount of carbon dioxide was 37.2, 37.1, 36.5 and 37.7% AR at study end (DAT-21) in soil [redacted], [redacted] AXXa, [redacted] and [redacted] II, respectively.

Formation of volatile organic compounds (VOC) was insignificant as demonstrated by values of ≤ 0.5% AR at all sampling intervals for all soils.

C. DEGRADATION OF TEST ITEM

The amount of Br_2CA in the soil extracts decreased from DAT-0 to DAT-21 from 96.3 to 6.6% AR in soil [redacted] from 98.6 to 1.3% AR in soil [redacted] AXXa, from 96.9 to 3.8% AR in soil [redacted] and from 93.6 to 1.6% AR in soil [redacted] II.

The experimental data could be well described by a single first order (SFO) kinetic model. The half-life of Br2CA under aerobic conditions was 5.8, 3.0, 4.1 and 3.2 days in soil [redacted], [redacted] AXXa, [redacted] and [redacted] II, respectively. Table 7.1.2.1.2- 1 summarizes the best-fit results of the DT_{50} and DT_{90} calculations.

III. CONCLUSIONS

Br_2CA, a major degradation product of deltamethrin, is fast degraded and mineralized in aerobic soil in the dark. The half-life of Br_2CA under standardized aerobic laboratory conditions was less than 6 days in all soils.

From this study it is concluded that Br_2CA and its degradation products have no potential for accumulation in the environment.

The results are included in the summary of the degradation rates of deltamethrin and its major degradation products in soil in the laboratory given in section CA 7.1.2.

Report:	**KCA 7.1.2.1.2 /02; [redacted]; [redacted]; 2011**
Title:	AE F109036: Aerobic degradation in three European soils
Report No:	S11-01624
Document No:	M-413119-01-1
Guidelines:	OECD Test Guideline No. 307
GLP:	Yes

EXECUTIVE SUMMARY

The rate of degradation of AE F109036 (mPBacid), a degradation product of deltamethrin, was studied in three soils under aerobic conditions in the dark in the laboratory for 48 hours at 20 °C. The average soil moisture content was 55 % of the maximum water holding capacity over the entire period of the

study. The application rate of AE F109036 was 5.72 µg per vessel and 50 g air dried soil, which was equivalent to 0.11 mg AE F109036/kg soil.

The mPBacid was rapidly degraded in all three soils under standardized aerobic laboratory conditions. The experimental data could be well described by a single first order model resulting in a max. DT_{50} and DT_{90} value of 9 and 30 hours for mPBacid (see Table 7.1.2.1.2- 7).

From this study it is concluded that mPBacid has no potential for accumulation in the environment.

Table 7.1.2.1.2- 7: Best fit kinetics of mPBacid degradation in soils under aerobic conditions

Soil (Soil Type)	Best Fit Kinetic Model [1]	DT_{50} [hrs]	DT_{90} [hrs]	Chi^2 Error [%]	Visual Assessment [2]
[redacted]	SFO	7	23	4.6	+
[redacted]4a	SFO	9	30	2.5	+
[redacted] II	SFO	7	23	0.9	+

[1] SFO: Single first order
[2] Visual assessment: + good, o = moderate, - = poor

I. MATERIALS AND METHODS

1. Test Item

Unlabelled mPBacid	AE F109036
Batch No.	AE F109036 00 1B99 0001
Certificate:	AZ 16815
Chemical purity:	98.6 %

2. Test Soils

Three soils were used (see Table 7.1.2.1.2- 8) for more details see Appendix 4 of report). 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. Microbial biomass determination confirmed that the soils were viable.

Table 7.1.2.1.2- 8: Physico-chemical properties of test soils

Soil	Source	Texture (USDA)	pH *	OC [%]
[redacted]	[redacted] Germany	Sandy loam	5.1	1.7
[redacted]4a	[redacted] Germany	Silt loam	6.5	1.6
[redacted] II	[redacted] Germany	Clay loam	7.3	4.8

* pH value derived from suspensions of soil / 0.01 M $CaCl_2$ = 1/2.

B. STUDY DESIGN

1. Experimental Conditions

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

For preparation of the test systems, 50 g dry weight equivalents of the sieved soils were weighed into each flask. Soil moisture was adjusted to 55 ± 5% of the maximum water holding capacity (MWHC) for

the individual test systems by addition of de-ionized water. The flasks were then closed with PU foam plugs and equilibrated to study conditions for 3 days prior to application.

The study application rate (SAR) was based on a single field application rate of deltamethrin of 12.5 g per hectare and a maximum theoretical formation of 100% of mPBacid in soil resulting in a nominal SAR of 118 µg mPBacid per kg soil dry weight.

The test item (actually 5.72 µg / 50 g dry weight of soil) was applied dropwise onto the soil surface of the respective test systems in 200 µL methanol/water 1/1 (*v/v*) using a pipette. After application, the test vessels (except DAT-0 samples) were closed with PU foam plugs.

The test systems were incubated in the dark for 48 hours days at 20 °C and at 55% MWHC soil moisture in a climatic chamber.

2. Sampling

Two treated flasks per soil were taken for analysis at the following sampling dates:

0, 3, 6, 24 and 48 hours after treatment

Note: The selected sampling intervals should guarantee to have at least two data points before the degradation half-life, which is recommended by the referenced OECD TG 307. On the other hand, due to the observed rapid degradation just 5 sampling intervals were investigated within 48 hrs in this study (the test guideline recommendation is at least six, but that during a time period of up to 120 days).

The microbial biomass of the soil was determined by short term respiration immediately after arrival and directly after treatment. It was confirmed that the test soils were viable (see Table 3 of report).

44 untreated flasks containing 50 g (dry weight) soil [redacted] were used for the concurrent recoveries. At every sampling date two samples were fortified with the same amount of test item as the treated flasks and two samples were treated with an amount at the LOQ level.

3. Analytical Procedures

The test item was extracted from the soil with 80 mL acetonitrile/water (1/1, v/v). The suspension was shaken for at least 30 min. The dispersed soil was transferred to a 200 mL glass centrifuge tube. The extract was separated from the sediment by centrifugation at 2600 rpm for 5 minutes. The extraction was repeated for one time.

The additional extraction of the samples was done using a soxhlet extractor. For this the complete soil samples were transferred to soxhlet hull and extracted with 120 mL acetonitrile/water (1/1, v/v) for 3 hours.

After this the ambient and soxhlet extracts were combined for the final analysis. About 1 to 2 mL of the supernatant was filtered over 0.45 µm single-use RC filters and transferred into a glass vial for HPLC-MS/MS analysis.

Concentrations of the test item in extracts and application solutions were determined by HPLC-MS/MS within 3 days after sampling. The test item was also used as analytical standard. The HPLC-MS/MS method was validated with regard to linearity, accuracy and precision (for more details see sections 5.7.4 and 7.2 of report). The fortified samples were processed and analysed 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.

The disappearance time of the test item was calculated using the software package MATLAB (KINGUI), including information about the dissipation/degradation kinetics according to the recommendations of EC document 9188/VI/97 rev. 8 (2000). The kinetic analysis followed the recommended procedures to derive modeling endpoints outlined by FOCUS (2006) with three different kinetic models: single first order, first order multi compartment and double first order in parallel. Model input datasets were the residual amounts found in each replicate test system at each sampling interval. The initial recovery at DAT-0 was included in the parameter optimization procedure, but for optimal

goodness of fit, the value was allowed to be estimated by the model. The best-fit kinetic model was selected on the basis of the chi^2 scaled-error criterion and on the basis of a visual assessment of the goodness of the fits. DT_{50} and DT_{90} values were calculated from the resulting kinetic parameters.

II. RESULTS AND DISCUSSION

Results indicated that the anticipated standardized aerobic conditions were maintained and that the soils were microbially active over the duration of the laboratory study. No significant differences in biomass of the samples were observed within 7 days.

A. DATA

Table 7.1.2.1.2- 9: Degradation of mPBacid in soils under aerobic conditions (mean values and SD expressed as % AA)

Soil	Sample	Hours after Treatment 0	3	6	24	48
[redacted]	A	102	68	55	12	6
	B	103	74	55	11	4 (<LOQ)
	Mean	102	71	55	12	5 *
[redacted] 4a	A	106	83	61	21	LOQ
	B	105	83	66	15	5
	Mean	106	83	64	18	5 *
[redacted] II	A	98	76	55	10	(<LOQ)
	B	98	69	51	8	(<LOQ)
	Mean	98	73	54	9	2 *

AA: Applied Amount
*: Value taken for kinetics calculation

B. METHOD VALIDATION

Analyses of the samples were performed using a HPLC-MS/MS method, which was validated as required by the SANCO/3029/99 rev.4 working document prior to analysis of the samples. During method validation, recoveries of AE F109036 in soil WW were between 90-100 %, in soil DD between 80-90 % and in soil HH were between 94-104 %. The determined values of the blank samples were less than 20 % of the assigned LOQ of the test item in all soils.
In addition, the extraction efficiency was demonstrated by investigating the concurrent recovery samples at each sampling interval (for data see Table 7 of report). The mean recoveries of all concurrent recoveries were between 100 - 107%.

C. DEGRADATION OF PARENT COMPOUND

The amount of AE F109036 decreased fast during the incubation time from 106 % of the applied amount directly after application to 5 % in soil HH at the end of the study (48 hours). In soil DD the amount of AE F109036 decreased from 98 % to 2 % and in soil WW from 102 % to 5 % during the study. The extraction efficiency during the study was demonstrated by concurrent recovery samples.
The disappearance time (DT_{50} and DT90) of the test item was calculated and is represented in the Table 7.1.2.1.2-7.

III. CONCLUSIONS

AE F109036 (mPBacid), a major degradation product of deltamethrin, is rapidly degraded in aerobic soil in the dark. The half-life of mPBacid under standardized aerobic laboratory conditions was less than 10 hours in all soils.

From this study it is concluded that mPBacid has no potential for accumulation in the environment.
The results are included in the summary of the degradation rates of deltamethrin and its major degradation products in soil in the laboratory given in section CA 7.1.2.

Report:	**KCA 7.1.2.1.2 /03; [redacted]; 2013**
Title:	Deltamethrin: Kinetic Modelling Evaluation of Data from Aerobic Soil Degradation Studies to Derive Trigger and Modelling Endpoints
Report No:	VC/11/026A
Document No:	M-462053-01-1
Guidelines:	- EU Council Directive 91/414/EEC, as amended by Commission Directive 95/36/EC of July 1995, Section 5, Point 7 and Commission Regulation (EC) No 1107/2009 of 21 October 2009; - FOCUS kinetics (2006) [1]
GLP:	No (modelling calculation)

EXECUTIVE SUMMARY

A kinetic evaluation of the relevant aerobic soil degradation studies with the insecticide deltamethrin and its major soil metabolites has been conducted using the computer program KinGUI2 according to FOCUS Kinetics guidance [FOCUS, 2006][1]. The updated kinetics results for the parent compound were summarized earlier, i.e. in the relevant section CA 7.1.2.1.
In the following, the modelling endpoint DT_{50} values derived for the metabolites mPBacid and Br_2CA are summarized, which can be used in environmental exposure assessments.

The resulting DT_{50} values and maximum occurences in soil of deltamethrin's major degradation products used as modelling input values for the calculation of predicted environmental concentrations in soil (PEC_{soil}) are summarized in Table 7.1.2- 1, those for predicted environmental concentrations in groundwater (PEC_{gw}) in Table 7.1.2- 2.

I. METHODS

Laboratory degradation data for the metabolites of deltamethrin (see sections CA 7.1.1 and CA 7.1.2) were evaluated against the FOCUS Kinetics flowcharts [1] for the determination of metabolite modelling endpoints. The chemical structure and names of the metabolites mPBacid and Br_2CA are shown in section 2 of the report. The used data on degradation are shown in the following tables.

Table 7.1.2.1.2- 10: Residue data for the study performed by Error! Reference source not found. **1991, M-136659-01-1**

Time (days)	Benzyl-label Replicate 1 mPBacid (% AR)	Benzyl-label Replicate 2 mPBacid (% AR)	Gem-label Replicate 1 Br_2CA (% AR)	Gem-label Replicate 2 Br_2CA (% AR)
Soil Casa Grand				
0	n.d.	n.d.	0.00	0.00
1	n.d.	n.d.	2.45	2.74
3	n.d.	n.d.	6.83	7.94
7	n.d.	n.d.	10.61	12.20
14	n.d.	n.d.	21.08	25.48
30	n.d.	n.d.	22.91	21.35
59	n.d.	n.d.	8.86	8.35
90	n.d.	n.d.	1.75	2.32
120	n.d.	n.d.	0.00[a)]	0.00[a)]
181	n.d.	n.d.	0.00	0.00

%AR = % applied radioactivity; [a)] lowest tabulated value is 0.17%AR, ½ LOQ is be set as 0.09% for the calculations

Table 7.1.2.1.2- 11: mPBacid residue data for study performed by [redacted] 2011, report M-413119-01-1

Time (hours)	mPBacid (mg/kg)		
	[redacted]	[redacted]	[redacted]
0	0.113	0.121	0.117
0	0.112	0.120	0.117
3	0.087	0.095	0.078
3	0.079	0.095	0.084
6	0.065	0.070	0.063
6	0.058	0.076	0.063
24	0.011	0.024	0.014
24	0.009	0.017	0.012
48	< LOQ	< LOQ	0.007
48	< LOQ	0.006	<LOQ

LOQ level 0.0058 mg/kg

Modelling strategy for data processing, optimisation model and statistics:
See earlier in report summary of **Error! Reference source not found.** 2013, report M-462053-01-1.

II. RESULTS

The mPBacid data (Table 7.1.2.1.2- 11) were entered into the Figure 1 of KinGUI scheme and optimisations conducted in a stepwise procedure according to the FOCUS Kinetics Flowchart 7-2 for the determination of parent modelling endpoints (mPBacid dosed study).

Table 7.1.2.1.2- 12 summarises the optimised model fits for mPBacid for the determination of modelling endpoints. Detailed KinGUI2 output files are shown in the Appendix of report. The three soils from the mPBacid dosed study (**Error! Reference source not found.** et al. 2011, report M-413119-01-1) afforded excellent fits. The resp. study was conducted at 20°C and pF2 and thus the calculated DT_{50} values do not require further normalisation.

The geometric mean DT_{50} of 7.5 hours (Table 7.1.2.1.2- 13) can therefore be used in exposure assessments, along with a conservative formation fraction of 1.0.

Table 7.1.2.1.2- 12: Optimised kinetic model parameters for mPBacid – modelling endpoints

Soil	Label	Info	Parent kinetic	DT_{50} (hours)	DT_{90} (hours)	ffm (-)	Chi^2 error (%)	t-test (-)	Visual fit
[redacted]	N/A	N/A	(SFO)	6.9	23.0	-	1.3	3.41e-09	Excellent
[redacted]	N/A	N/A	(SFO)	9.0	29.9	-	1.9	1.96e-08	Excellent
[redacted]	N/A	N/A	(SFO)	6.9	22.9	-	4.2	2.87e-08	Excellent

Table 7.1.2.1.2- 13: Optimised kinetic model parameters for mPBacid – modelling endpoints (20°C and pF2)

Soil	Label	Info	Parent kinetic	DT_{50} (hours)	Norm. DT_{50} (hours)	ffm (-)	Chi^2 error (%)	t-test (-)	Visual fit
[redacted]	N/A	N/A	(SFO)	6.9	6.9	-	1.3	3.41e-09	Excellent
[redacted]	N/A	N/A	(SFO)	9.0	9.0	-	1.9	1.96e-08	Excellent
[redacted]	N/A	N/A	(SFO)	6.9	6.9	-	4.2	2.87e-08	Excellent
			Geometric mean		**7.5**				

The Br_2CA data (Table 7.1.2.1.2- 11) were entered into the Figure 1 of KinGUI scheme and optimisations conducted in a stepwise procedure according to the FOCUS Kinetics Flowchart 7-2 for the determination of parent modelling endpoints. Detailed KinGUI2 output files are shown in Appendix 8.2.1 and 8.2.2 of the report. The Casa Grand soil (**Error! Reference source not found.** 1991, report M-136659-01-1) is considered to give an acceptable DT_{50} value of 12.8 days (see Table 7.1.2.1.2- 14), 16.8 days when normalised to 20°C and pF2 (see Table 7.1.2.1.2- 15).

Table 7.1.2.1.2- 14: Optimised kinetic model parameters for Br_2CA – modelling endpoints

Soil	Label	Info	Parent kinetic	DT_{50} (days)	DT_{90} (days)	ffm (-)	Chi^2 error (%)	t-test (-)	Visual fit
Casa Grand	Gem	High	HS	12.8	42.5	0.809	12.0	2.3e-10	Very good

Table 7.1.2.1.2- 15 summarises the optimised model fits for Br_2CA for the determination of modelling endpoints, thereby including the further data listed in Table 7.1.2.1.2- 3 to Table 7.1.2.1.2- 6, i.e. of Br_2CA rate of degradation study report [redacted] 2013, report M-455519-01-1 on four soils.

Altogether a geometric mean DT_{50} of 5.0 days can therefore be used in exposure assessments, along with a conservative formation fraction of 1.0.

Table 7.1.2.1.2- 15: Optimised kinetic model parameters for Br_2CA – modelling endpoints (20°C and pF2)

Soil	Label	Info	Parent kinetic	DT_{50} (days)	Norm. DT_{50} (days)	ffm (-)	Chi^2 error (%)	t-test (-)	Visual fit
[redacted]	Gem	N/A	(SFO)	5.8*	5.8	-	1.4	1.82e-15	Very good
AXXa	Gem	N/A	(SFO)	3.0*	3.0	-	1.3	3.10e-16	Very good
[redacted]	Gem	N/A	(SFO)	4.1*	3.5	-	4.2	4.51e-11	Very good
[redacted]	Gem	N/A	(SFO)	3.2*	3.2	-	4.9	1.07e-09	Very good
Casa Grand	Gem	High	HS	12.8	16.8	0.809	12.0	2.3e-10	Very good
				Geometric mean	**5.0**				

* Results taken from [redacted] 2013, report M-455519-01-1

CA 7.1.2.1.3 Anaerobic degradation of the active substance

The degradation rate of deltamethrin in soil under anaerobic conditions in the dark in the laboratory was evaluated during the Annex I inclusion and was accepted by the European Commission (SANCO/6504/VI/99-final, 17 October 2002). The following two studies included in the Baseline Dossier were regareded relevant:

Author(s)	Year	Document No.
[redacted]	1991	M-136665-01-1
[redacted]	1980	M-149538-01-1

Deltamethrin is extensively degraded in soil under anaerobic conditions, DT_{50} ranges from 32 to 105 days (n = 5), however, degradation was somewhat retarded in comparison with the aerobic degradation. The principal degradation pathway under anaerobic conditions was the same as that observed in aerobic conditions.

No additional studies are submitted within this Supplemental Dossier for the deltamethrin renewal of approval. In general, anaerobic conditions are unlikely to occur in soil when deltamethrin is used.

CA 7.1.2.1.4 Anaerobic degradation of metabolites, breakdown and reaction products

During the Annex I inclusion information on degradation of deltamethrin metabolites under anaerobic conditions in the dark in the laboratory was accepted by the European Commission (SANCO/6504/VI/99-final, 17 October 2002), and it was not regarded as a relevant process in soil. Therefore, no additional studies on this topic are submitted within this Supplemental Dossier for the deltamethrin renewal of approval.

In general, anaerobic conditions are unlikely to occur in soil when deltamethrin is used. In the exceptional case that anaerobic conditions occur in soil after deltamethrin was used, it is expected that, temporarily, the major metabolites Br_2CA (*cis*) and mPBacid will be more stable in an anaerobic soil environment, however, will then be rapidly degraded once aerobic conditions are established again (see section CA 7.1.2.1.2 before); subsequently they do not have the potential to reach unaerobic aquifers (see for PECgw calculations in the MCP dossier section 9.2.4).

CA 7.1.2.2 Field studies

The dissipation of deltamethrin in soil under field conditions was evaluated during the Annex I inclusion and was accepted by the European Commission (SANCO/6504/VI/99-final, 17 October 2002).

No additional studies are submitted within this Supplemental Dossier for the deltamethrin renewal of approval. In general, the field studies confirmed the results received by the set of laboratory studies.

CA 7.1.2.2.1 Soil dissipation studies

The following two studies, one from USA and one from Germany, included in the Baseline Dossier were regarded relevant during the Annex I inclusion.

Author(s)	Year	Document No.
[redacted]	1991	M-149730-01-1
[redacted]	1990	M-127756-01-1*

*: German language; the English translation is report M-127756-01-2.

In the terrestrial field soil dissipation studies conducted in Minnesota, US and at four sites in Germany Deltamethrin showed a relatively fast to moderate dissipation from soil under field conditions with field DT_{50} ranging from 14 to 28 days (SFO, n = 5) on bare soil, even after multiple application of exaggerated doses. In the US study soil cores were analysed for deltamethrin and its major soil metabolite Br_2CA down to a depth of 90 cm and 30 cm, respectively. Deltamethrin residues were mainly confined to the upper 15 cm of soil. Br_2CA was not detected above the limit of quantification (LOQ = 0.01 mg/kg soil) under field conditions.

Table 7.1.2.2.1- 1: Agreed EU field DT_{50} values estimated for deltamethrin according to Appendix II of SANCO/6504/VI/99-final, 2002)

Study No.	DT_{50}	Comment
M-149730-01-1	2 – 3 weeks	Both cropped and bare soil (US)
M-127756-01-2	1 – 4 weeks	Four bare soils in GER, overall realistic estimate: 3 weeks

CA 7.1.2.2.2 Soil accumulation studies

Field accumulation and soil residue studies have not been performed and are not required for deltamethrin.

CA 7.1.3 Adsorption and desorption in soil

CA 7.1.3.1 Adsorption and desorption

The adsorption and desorption behaviour of deltamethrin, Br_2CA and mPBacid in soil was evaluated during the Annex I inclusion (compare EU Monograph Annex B7) and was accepted by the European Commission (SANCO/6504/VI/99-final, 17 October 2002). However, not any adsorption and desorption data were stated in the LoEP for the metabolite mPBacid since it was not regarded as a major metabolite that time.

The following table summarizes the adsorption constants $K_{OC(ads)}$ in soils to be used for modelling purposes:

Table 7.1.3.1- 1: Overall summary of adsorption constants $K_{OC(ads)}$ in soils of deltamethrin and its major degradation products

Compound	$K_{OC(ads)}$ [1] [mL/g]	Freundlich exponent 1/n [1]
Deltamethrin	10,240,000	0.93
Br_2CA	25.6	0.89
mPBacid	158.3	0.96

[1] arithmetic mean

CA 7.1.3.1.1 Adsorption and desorption of the active substance

The adsorption and desorption behaviour of deltamethrin in soil in batch equilibrium experiments was evaluated during the Annex I inclusion and was accepted by the European Commission (SANCO/6504/VI/99-final, 17 October 2002). The following study included in the Baseline Dossier was regarded relevant during the Annex I inclusion:

Author(s)	Year	Document No.
[redacted]	1990	M-135594-01-1

The measured Koc values ranged from 460,000 to 16,300,000 mL/g, the arithmetic mean Koc was 10,240,000 mL/g and the arithmetic mean Freundlich exponent 1/n was 0.93 (see table below). No pH depencency was stated.
It was concluded that adsorption and desorption data of deltamethrin indicate that the substance does not have a leaching potential.

Table 7.1.3.1.1- 1 Adsorption data of deltamethrin ([redacted] 1990; M-135594-01-1)

Soil	K_f value [mL/g]	Koc value [mL/g]	Kom value [mL/g]	1/n
Arizona I (sandy loam)	9,600	16,300,000	9,500,000	0.77
Arizona II (sandy loam)	30,000	12,800,000	7,400,000	1.20
Arizona III (clay)	26,700	11,400,000	6,600,000	0.74
Mississippi (silty clay loam)	3,790	460,000	270,000	1.01
Arithmetic mean:	17,520	10,240,000	5,940,000	0.93

Note: In March 2008 the former RMS Sweden (KemI) informed the EU Commission and MS in a letter about the Swedish re-evaluation of the Koc-values stated in Appendix II to the review report on the insecticide deltamethrin (Review report for the active substance deltamethrin (6504/VI/99-final, 17 October 2002). Sweden was RMS for the application of deltamethrin as a biocide (PT 18), in which an adsorption study by [redacted] (1993; M-152148-01-1) was evaluated. This study provides three new Koc-values ranging from 204 000 to 577 000 mL/g in soils with organic carbon contents of 0.46-0.81%. This study was regarded as acceptable by Sweden. A new mean Koc of 408 250 mL/g was proposed by the former RMS which still indicates a very high adsorption to soil and a classification as immobile. The use of this value would not significantly change any predicted environmental concentration calculations. This Koc was also used by KemI in the evaluation of deltamethrin as a biocide. KemI was of the opinion that a harmonised approach for the Draft Assessment Report and the Competent Authority Report is to prefer. However, officially the endpoint was not changed in the list of endpoints under EU directive 91/414 and, therefore, the official value is still used for PEC calculations.

No additional studies are submitted within this Supplemental Dossier for the deltamethrin renewal of approval. A summary of the adsorption and desorption behaviours of deltamethrin and its major degradation products in soil is given in section CA 7.1.3.1.

CA 7.1.3.1.2 Adsorption and desorption of metabolites, breakdown and reaction products

The adsorption and desorption behaviour of Br_2CA and mPBacid in soil in batch equilibrium experiments was evaluated during the Annex I inclusion and was accepted by the European Commission (SANCO/6504/VI/99-final, 17 October 2002). The following studies included in the Baseline Dossier were regarded relevant during the Annex I inclusion:

Author(s)	Year	Document No.
[redacted]	1991	M-150487-01-1
[redacted]	1992	M-149517-01-1

The sorption of Br_2CA was investigated by [Error! Reference source not found.] 1991 (report M-150487-01-1) in a batch equilibrium study with five soils. Sorption values for two of the soils were not included here, following a recommendation in the EU Review Report of Deltamethrin (EU, 2002). The remaining measured Koc values ranged from 10.1 to 43.7 mL/g (see table below). No pH depencency was stated.

Modelling simulations should be conducted with the arithmetic mean Koc = 25.6 mL/g and with the arithmetic mean Freundlich exponent 1/n = 0.89.

Table 7.1.3.1.2- 1: Adsorption data of Br_2CA (Error! Reference source not found. 1991, report M-150487-01-1)

Soil	K_f value [mL/g]	Koc value [mL/g]	Kom value [mL/g]	1/n
Arizona II (sandy loam) a)	0.089	38.2	22.2	1.00
Arizona III (clay) a)	0.109	46.8	27.1	1.00
Mississippi (silty clay loam)	0.355	43.7	25.4	0.96
USA (sandy loam)	0.587	23.0	13.3	0.89
Michigan (clay loam)	0.267	10.1	5.9	0.83
Arithmetic mean:	0.403	25.6	14.9	0.89

a) not included in the average of 26 mL/g, following the recommendation of the EU Review Report (EU, 2002)

The sorption of mPBacid was investigated by **Error! Reference source not found.** 1992 (report M-149517-01-1) in a batch equilibrium study with four soils. The measured Koc values ranged from 50.7 to 287.8 mL/g (see table below). No pH dependency was stated.

Modelling simulations should be conducted with the arithmetic mean Koc (Kom) = 158.3 mL/g (91.8 mg/L) and with the arithmetic mean Freundlich exponent 1/n = 0.96.

Table 7.1.3.1.1- 2 Adsorption data of mPBacid (Error! Reference source not found. 1992, report M-149517-01-1)

Soil	K_f value [mL/g]	Koc value [mL/g]	Kom value [mL/g]	1/n
Arizona (clay)	0.6677	287.76	166.9	0.9898
Mississippi (silty clay loam)	1.5421	189.90	110.2	1.0068
Maryland (sandy loam)	2.6806	105.03	60.9	0.9386
Michigan (clay loam)	1.3397	50.63	29.4	0.9218
Arithmetic mean:	1.558	158.3	91.8	0.96

No additional studies are submitted within this Supplemental Dossier for the deltamethrin renewal of approval. A summary of the adsorption and desorption behaviours in soil of the major degradation products of deltamethrin and is given in section CA 7.1.3.1.

CA 7.1.3.2 Aged sorption

Studies are not required under Commission Regulation (EU) No 283/2013 in accordance with Regulation (EC) No 1107/2009.

CA 7.1.4 Mobility in soil

The mobility of deltamethrin in soil was evaluated during the Annex I inclusion and was accepted by the European Commission (SANCO/6504/VI/99-final, 17 October 2002). Soil column studies and one of the field dissipation studies (see **Error! Reference source not found.** et al 1991, report M-149730-01-1) confirmed the conclusion that deltamethrin has a very low potential to leach through soils and contaminate groundwater or surface water via this route.

Studies on the column leaching of deltamethrin are not required anymore. The leaching behaviour can be assessed from the available adsorption/desorption values combined with other relevant input data by accepted modelling estimations, i.e. PECgw calculations submitted by the respective MCP section 9.2.4.

CA 7.1.4.1 Column leaching studies

CA 7.1.4.1.1 Column leaching of the active substance

The following studies included in the Baseline Dossier were regarded relevant during the Annex I inclusion:

Author(s)	Year	Document No.
[redacted]	1977	M-149491-01-2
[redacted]	1980	M-149493-01-1

No additional studies are submitted within this Supplemental Dossier for the deltamethrin renewal of approval.

CA 7.1.4.1.2 Column leaching of metabolites, breakdown and reaction products

No relevant studies are included in the baseline dossier, and no additional studies are submitted within this Supplemental Dossier for the deltamethrin renewal of approval.

The leaching behaviour can be assessed from the available adsorption/desorption values combined with other relevant input data by accepeted modelling estimations, i.e. PECgw calculations submitted by the respective MCP section 9.2.4.

CA 7.1.4.2 Lysimeter studies

No relevant studies are included in the baseline dossier, since such were not required. No additional studies are submitted within this Supplemental Dossier for the deltamethrin renewal of approval.

CA 7.1.4.3 Field leaching studies

No relevant studies are included in the baseline dossier, since such were not required. No additional studies are submitted within this Supplemental Dossier for the deltamethrin renewal of approval.

CA 7.2 Fate and behaviour in water and sediment

Deltamethrin is hydrolytically stable in water under neutral (pH = 7) and acidic conditions (pH = 5) at 25 °C. The degradation of deltamethrin in water due to hydrolysis is significant only at elevated pH conditions, with a DT_{50} of 31 days at pH = 8 (at 23 °C) and 2.5 days at pH = 9 (at 25 °C). The two major hydrolytic products, mPBaldehyde and Br_2CA, i.e. found at pH 9, result from the ester cleavage of deltamethrin. . If oxygen is present in such aqueous solutions it is expected that the final products of hydrolytic cleavage would have been mPBacid and Br_2CA. Under environmental conditions in the presence of oxygen, mPBaldehyde is rapidly oxidised to mPBacid.

The UV-VIS absorption data in the environmentally relevant pH range showed that deltamethrin in aqueous solutions does only absorb very low amounts of light at wavelengths above 290 nm. Further, the quantum yield of direct photo-transformation in water is rather low ($\Phi = 8.72 \times 10^{-4}$). Therefore, no contribution of the direct photodegradation to the overall elimination of deltamethrin in the aqueous environment is to be expected ($DT_{50} \geq 48$ days). However, the indirect photodegradation of deltamethrin in surface water is faster in the presence of natural photosensitising substances with a DT_{50} of 4 days. There, the main degradation product detected was mPBacid at maximum amounts of 47% of the applied radioactivity in the sensitised system.

The studies evaluated during the last Annex I listing with deltamethrin in two different natural water/sediment systems showed that the compound was thoroughly degraded leading to CO_2 as the end

product of the mineralization process. The adsorption of deltamethrin from water to the sediments accounts for 60 to 88% of the applied radioactivity, and is the most important dissipation route in natural surface water. 50% of the deltamethrin in the water disappeared from the water column within 1 day. The DT_{50} for the entire system (water + sediment) ranged from 40 to 90 days under standard conditions in the dark. Main metabolites in water/sediment systems were: α-R-isomer of deltamethrin (max. 24% of applied radioactivity in sediment,); 4'-OH-deltamethrin (maximum 8% in sediment) and mPBacid (maximum 6% in water). Position of ^{14}C- labelling (benzyl-^{14}C) did not allow measurement of Br_2CA.

The dissipation DT_{50} of deltamethrin in the water column of several micro-/mesocosm and natural pond studies ranged from 1.5 to 24 hours. It was concluded that the substance will rapidly disappear from the water column with an expected half-life of about 1 day. Deltamethrin will mainly be distributed to suspended organic material, biota, and eventually to sediments. Further bioavailability is reduced, which in part may explain the slow biodegradation. In the outdoor microcosm study ([redacted]2001, report M-200619-03-1), with three applications at 7 day intervals, trans-isomer of deltamethrin was observed in the water column at up to 16.6% of TRR (= total radioactive residue) one day after the 1st application.

A conservative DT_{50} of 1000 days for trans-isomer of deltamethrin in water and sediment was used in the FOCUS STEP 1 and 2 calculations.

Despite the low vapour pressure of deltamethrin (1.1×10^{-6} Pa at 20°C), volatilisation from water surface appears to be an additional dissipation route, as deltamethrin may form a microlayer film onto the water surface after spray drift. Volatilisation from this surface microlayer can be explained by the Henry's law constant of deltamethrin of 2.1×10 Pa×m³/mol (referring to distilled water of a final pH 6.8).

The dossier supporting the approval renewal of deltamethrin includes an additional mesocosm study with realistic spray exposure ([redacted], 2005, M-246137-01-1) using 12 test tanks of 6 m³ water and 1 m water depth as representative of a small stagnant water body. It was completed after the Annex I inclusion. Deltamethrin decreased after all applications quickly and steadily with an average half-life in the water column of 22.4 hours, and the DT_{50} for the whole system (water plus sediment) was determined to be 31.6 hours, only.

An additional aerobic water-sediment study for the parent compound ([redacted]2012, M-434820-01-1) is included using a second label position, ^{14}C-gemi-dimethyl label of deltamethrin to allow the investigation of the second half of the deltamethrin molecule. The new study performed with two different water/sediment systems included acidic sediment also. Both topics had been mentioned as a kind of data gap during the earlier EU evaluation.

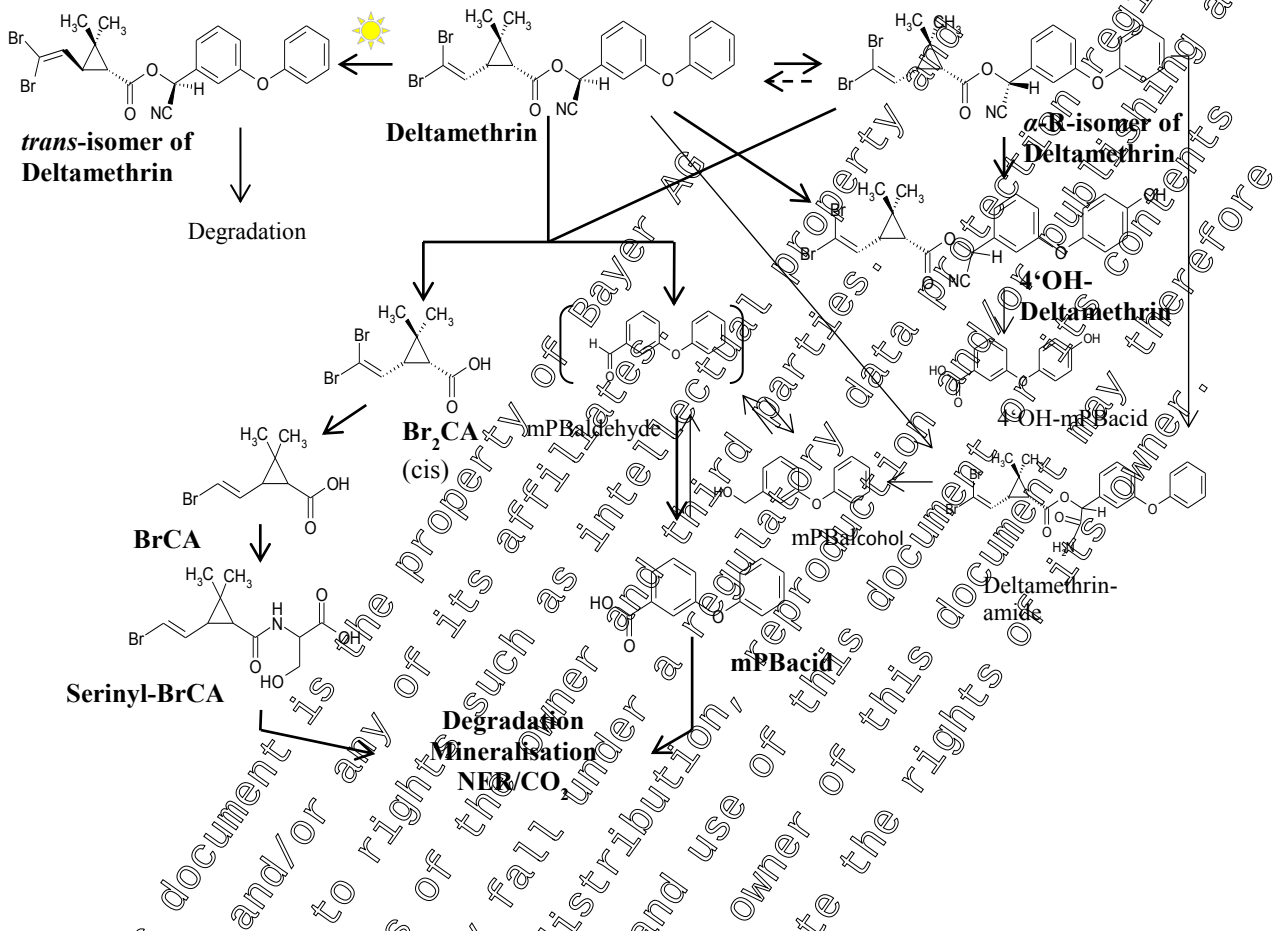
Again it was shown that deltamethrin is thoroughly degraded during the study duration leading to $^{14}CO_2$ as the end product of the mineralization process (max. 39% of AR at 99 days). Further, in total five major metabolites were detected during the study: α-R-isomer of deltamethrin, Br_2CA, Serinyl-BrCA, and BrCA (isomer 1 and 2). The new metabolites resulted from the degradation of Br_2CA which could not be followed by the earlier study performed with the other radiolabel. The proposed updated degradation pathway of deltamethrin in water and sediment is shown in Figure 7.2- 1.

In summary, the major routes of degradation or dissipation of deltamethrin in natural water systems are adsorption to the sediment (as well as to suspended solids and aquatic macrophytes), chemical and photochemical conversion to the trans- and alpha-R-isomer of deltamethrin, and hydrolysis with subsequent oxidation of the transformation products.

In addition, several authors have also stated that volatilisation may be a route of dissipation of deltamethrin from a water surface microlayer.

Altogether deltamethrin has no potential to be present in open waters.

Figure 7.2- 1: Proposed degradation pathway of deltamethrin in water and sediment



In the following a summary of input data, considering the respective new kinetic evaluations of **Error! Reference source not found.** 2013 (report M-461952-01-1) and **Error! Reference source not found.** 2013 (report M-462042-01-1) on degradation in aerobic water/sediment systems according to FOCUS kinetics guidance, is given for deltamethrin and its metabolites in order to be used for surface water and sediment exposure assessments.

Table 7.2.2.3- 14 and Table 7.2.2.3- 15 summarise the resulting optimised modelling and trigger endpoint DT_{50} values for deltamethrin resulting from the new water sediment study.

Table 7.2.2.3- 16 summarises the resulting optimised total system modelling endpoint DT_{50} values for alpha-R isomer of deltamethrin, a primary degradate of the parent compound. The α-R-isomer was observed in the water column at up to 15.6% and in total water sediment system up to 36.5% of the total applied deltamethrin 1 day after the application. In FOCUS STEP 1 and 2 calculations a DT_{50} value of 34.0 days can be used to quantify the degradation in water and sediment.

Table 7.2.2.3- 25 summarises the optimised modelling endpoint DT_{50} values for the sum of deltamethrin and alpha-R isomer of deltamethrin considering the data from the water/sediment studies with both radiolabels, the study with the benzyl-^{14}C-label already evaluated and the new study with the gemi-dimethyl label. In FOCUS$_{sw}$ evaluations, a total system DT_{50} value of 52.2 days can be used as a conservative approach for the water phase degradation along with a default DT_{50} value of 1000 days for the sediment phase degradation.

Table 7.2.2.3- 26 summarises the calculated water phase and total system DT_{50} values for the sum of deltamethrin and alpha-R isomer of deltamethrin considering the data from the water/sediment studies with both labels suitable for use as trigger endpoints.

Table 7.2.2.3- 27 summarises the optimised total system modelling endpoint DT_{50} values for Br_2CA (*cis*). In the new laboratory water/sediment study with deltamethrin, Br_2CA was observed in the water column at up to 32.2% and in total water sediment system up to 43.9% of the total applied deltamethrin 7 days after the application. In FOCUS STEP 1 and 2 a DT_{50} value of 10.7 days can be used to quantify the degradation of Br_2CA in water and sediment.

In the new laboratory water/sediment study with deltamethrin, BrCA isomer 1 was observed in the water column at up to 20.4% and in total water sediment system up to 32.4% of the total applied deltamethrin 30 days after the application. BrCA isomer 2 was observed in the water column at up to 7.7% and in total water sediment system at up to 9.9% of the total applied deltamethrin 50 days after the application. A conservative DT_{50} of 1000 days for BrCA isomer 1 and 2 in water and sediment can be used in the FOCUS STEP 1 and 2 calculations for these metabolites.

In the new laboratory water/sediment study with deltamethrin serinyl-BrCA was observed in the water column at up to 7.8% and in total water sediment system up to 10.0% of the total applied deltamethrin 73 days after the application. A conservative DT_{50} of 1000 days for serinyl-BrCA in water and sediment can be used in the FOCUS STEP 1 and 2 calculations for this metabolite.

In the laboratory water/sediment study with deltamethrin (**Error! Reference source not found.**, 1993; M-131938-01-1) 4´-OH-deltamethrin was observed in the sediment at up to 8.5% of the total applied deltamethrin 7-14 days after the application. For FOCUS PECsw STEP 1 and 2 calculations the maximum occurrence of 1% in water of study M-131938-01-1 can be used. A conservative DT_{50} of 1000 days for 4´-OH-deltamethrin in water and sediment can be used in the FOCUS STEP 1 and 2 calculations for this metabolite.

In the laboratory aqueous photolysis study of deltamethrin ([redacted] 1991; M-136754-01-1) mPBacid was observed at up to 11%. A conservative DT_{50} of 1000 days for mPBacid in water and sediment can be used in the FOCUS STEP 1 and 2 calculations for this metabolite.

Table 7.2- 1 and Table 7.2- 2 summarise the substance related parameters to be used for deltamethrin and its metabolites in the calculations at FOCUS SW Step1-2 level.

For PECsw calculations the maximum occurrence in the water column is used. For PECsed calculations the maximum occurrence in total water/sediment system is used. For PECsw calculations of metabolites, for which measured Koc values are not available, a Koc of 0 mL/g is used.

For PECsed calculations measured Koc data can be used if available. For the alpha-R isomer and *trans*-isomer of deltamethrin, for which measured Koc values were not available, the Koc of Deltamethrin was used. For metabolites, for which measured Koc values were not available, the default Koc of 1000 mL/g can be used.

Table 7.2- 1: Substance parameters for deltamethrin and its metabolites used in PECsw calculations

Parameter	Unit	Deltamethrin	alpha-R-isomer of deltamethrin	trans-isomer of deltamethrin	Br_2CA	BrCA isomer 1
Molar Mass	g/mol	505.2	505.2	505.2	298.0	219.1
Water Solubility	mg/L	0.00027	0.003	0.0042	9000	10000
Koc	mL/g	10240000	0[A]	0[A]	25.6	0[A]
Degradation						
Soil	days	54.8	1000*	1000*	5.0	1000*
Total System	days	52.2	34.0	1000*	10.7	1000*
Water	days	52.2	34.0	1000*	10.7	1000*
Sediment	days	52.2	34.0	1000*	10.7	1000*
Max Occurrence						
Water / Sediment	%	-	11.6	16.6	32.2	20.4
Soil	%	-	0.001	0.001	23	0.001

Parameter	Unit	BrCA isomer 2	Serinyl-BrCA	4-OH-Deltamethrin	mPBacid
Molar Mass	g/mol	219.1	306.2	521.2	214.2
Water Solubility	mg/L	10000	140000	0.1	9100
Koc	mL/g	0[A]	0[A]	0[A]	158.3
Degradation					
Soil	days	1000*	1000*	1000*	0.31
Total System	days	1000*	1000*	1000*	1000*
Water	days	1000*	1000*	1000*	1000*
Sediment	days	1000*	1000*	1000*	1000*
Max Occurrence					
Water / Sediment	%	7.7	7.8	1	11
Soil	%	0.001	0.001	0.001	5.6

[A] No measured Koc available, in a very conservative approach no adsorption assumed and Koc set to 0
* Default value used

Table 7.2- 2: Substance parameters for deltamethrin and its metabolites used for PECsed calculations

Parameter	Unit	Deltamethrin	alpha-R-isomer of deltamethrin	trans-isomer of deltamethrin	Br_2CA	BrCA isomer 1
Koc	mL/g	10240000	10240000*	10240000[A]	25.6	1000*
Max Occurrence						
Water / Sediment	%	-	36.5	16.6	43.9	32.4

Parameter	Unit	BrCA isomer 2	Serinyl-BrCA	4-OH-Deltamethrin	mPBacid
Koc	mL/g	1000*	1000*	1000*	158.3
Max Occurrence					
Water / Sediment	%	9.9	10	8.5	11

[A] Koc of deltamethrin used
* Default value used

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 deltamethrin in buffers under sterile conditions in the dark in the laboratory were evaluated during the Annex I inclusion using two radiolabel positions, [^{14}C]-benzyl and [^{14}C]-gemdimethyl], and were accepted by the European Commission (SANCO/6504/VI/99-final, 17 October 2002). The following studies included in the Baseline Dossier were regarded relevant during the Annex I inclusion:

Author(s)	Year	Document No.
[redacted]	2002	M-206738-01-1
[redacted]	1990	M-129026-01-1

Deltamethrin is hydrolytically stable in water under neutral (pH = 7) and acidic conditions (pH = 5) at 25 °C. The degradation of deltamethrin in water due to hydrolysis is significant only at elevated pH conditions, with a DT_{50} of 31 days at pH = 8 (at 23 °C) and 2.5 days at pH = 9 (at 25 °C).

The two major hydrolytis products, i.e. found at pH 9, result from the ester cleavage of deltamethrin into mPBaldehyde and Br_2CA. However, under less artificial conditions mPBaldedhyd is rapidly oxidised by oxygen to mPBacid. If oxygen is present in such aqueous solutions it is expected that the final products of hydrolytic cleavage would have been mPBacid and Br_2CA.

Remark: In the LoEP the Br_2CA was listed just to be found in trace during the hydrolysis studies. However, the method used was designed mainly to analyse for parent compound and the mPBaldehyde, which were adequately extracted from the water samples by hexane. The conclusive 2nd hydrolysis product, probably mainly present in the extracted water phase (i.e. Br_2CA) was not adequately quantified. However it is regarded as major degradate as well.

A summary of the route and rate of hydrolytic degradation of deltamethrin in the aquatic systems is given in section CA 7.2. In respective Figure 7.2- 1 the mPBaldehyde is not marked to be major since in all other studies (except in the highly artificial hydrolysis study, where the test solution is lacking of oxidation potential), the respective mPBacid was found as the major terminal degradation product.

No additional studies are submitted within this Supplemental Dossier for the deltamethrin renewal of approval.

CA 7.2.1.2 Direct photochemical degradation

The route and rate of direct photochemical degradation of deltamethrin in buffers under sterile conditions in the dark in the laboratory were evaluated during the Annex I inclusion, e.g. using two radiolabel positions, [^{14}C]-benzyl and [^{14}C]-gemdimethyl], and were accepted by the European Commission (SANCO/6504/VI/99-final, 17 October 2002). The following studies included in the Baseline Dossier were regarded relevant during the Annex I inclusion:

Author(s)	Year	Document No.
[redacted]	1991	M-136754-01-1
[redacted]	1987	M-124981-01-1
[redacted]	1993	M-149258-01-1*
[redacted]	2000	M-197547-01-1 *

*: this information was filed in the pys.-chem section, earlier

Two tests of aqueous photolysis (M-136754-01-1 and and M-124981-01-1) led to the conclusion that transformation by direct photochemical reactions is insignificant in natural environments, as laboratory DT_{50} values of approx. 48 days were obtained. This conclusion is also in agreement with the absorption spectrum of deltamethrin (M-149258-01-1), which shows only a small absorption of wavelengths above 290 nm, and no absorption above 300 nm, and the quantum yield Φ for direct photodegradation of deltamethrin was calculated to be 8.72×10^{-4}, only (M-197547-01-1).
A summary of the route and rate of degradation of deltamethrin in water and sediment is given in section CA 7.2 and Figure 7.2- 1.

No additional studies are submitted within this Supplemental Dossier for the deltamethrin renewal of approval.

CA 7.2.1.3 Indirect photochemical degradation

Route and rate of indirect photochemical degradation of deltamethrin in the laboratory were evaluated during the Annex I inclusion using [^{14}C]-benzyl deltamethrin, and were accepted by the European Commission (SANCO/6504/VI/99-final, 17 October 2002). The following study included in the Baseline Dossier was regarded relevant during the Annex I inclusion:

Author(s)	Year	Document No.
[redacted]	1987	M-124981-01-1

Indirect photochemical reactions are more likely to occur than direct photochemical reactions, since the laboratory DT_{50} in a sensitised system was 4 days. However, due to the fast partitioning of deltamethrin to the sediment within one day, deltamethrin is only expected to remain available for such reactions for a very short period of time, only.
The results are included in the proposed degradation pathway of deltamethrin in aquatic systems shown in Figure 7.2- 1 and in the summary given in section CA 7.2. Not any new main degradation products were found in the sensitised test system.

No additional studies are submitted within this Supplemental Dossier for the deltamethrin renewal of approval.

CA 7.2.2 Route and rate of biological degradation in aquatic systems

CA 7.2.2.1 "Ready biodegradability"

The "ready biodegradability" of deltamethrin was evaluated during the Annex I inclusion using unlabelled deltamethrin, and was accepted by the European Commission (SANCO/6504/VI/99-final, 17 October 2002). The following study included in the Baseline Dossier was regarded relevant during the Annex I inclusion:

Author(s)	Year	Document No.
[redacted]	1994	M-149487-01-1

The parent compound deltamethrin showed less than 2% degradation after 28 days and therefore, is classified as "not readily biodegradable".

No additional studies are submitted within this Supplemental Dossier for the deltamethrin renewal of approval.

CA 7.2.2.2 Aerobic mineralisation in surface water

Since this topic was not yet part and thus not evaluated by the European Commission during the last Annex I inclusion of deltamethrin, no respective study is included in the Baseline Dossier. However, the applicant believes that the circumstances in which the study is required are not fulfilled for deltamethrin, considering its intrinsic properties (i.e. available information on the fate and behaviour in the environment) and realistic exposure conditions.

"Studies on aerobic mineralisation in surface water shall be provided unless the applicant shows that contamination of open water (freshwater, estuarine and marine) will not occur" (Commission Regulation (EU) No 283/2013, L 93, Section 7.2.2.2, page 52).

Deltamethrin is used as spray application in various crops, and the main exposure of surface water is spray-drift. However, in order to reach an acceptable risk for aquatic organisms, it is necessary to implement mitigation measures such as drift reduction nozzles or buffer zones to limit the amount of deltamethrin that will reach the water bodies at the edge of the field. It is thus very unlikely that contamination of open water (i.e. surface water far away from the edge of the field) will occur. Moreover, deltamethrin is immobile in soil (see below and section CA 7.1.3.1); accordingly, drainage entires to water bodies are very unlikely.

Deltamethrin is very low soluble in water. Cs at 20°C in distilled water of pH 6.8 is 0.27 µg/L (ref. [redacted], 2012: M-439336-01-1, KCA 2.5/03 and please refer also MCA 2.5). In addition, deltamethrin shows a very strong adsorption on particles and surfaces thus the substance must be classified as immobile in soil (compare SANCO/6504/VI/99-final, 17 October 2002).

Due to both before mentioned properties any presence in a water phase should be minimal whenever some particles and solid surfaces are present. In particular due to the quick and strong adsorption and portioning to the sediment, the very low quantities of deltamethrin present in water do not have enough time to reach any open water after its use on a cropped field. This fact was confirmed by the evaluation of monitoring studies published in the literature (see section CA 7.5).

Deltamethrin is stable to hydrolysis at a pH up to 7, but hydrolyses under alkaline conditions (see section CA 7.2). It should be noted that the majority of surface waters in agricultural areas tend to be slightly alkaline (around pH 8) and are thus in a pH range where hydrolysis of deltamethrin starts. This further reduces the small quantities of deltamethrin that might occur in open water bodies.

The most important situations of exposure and degradation of deltamethrin at the edge of a treated field are described by all the laboratory studies summarized in the following section. The applicant therefore

believes that no further testing is required to meet the current section 7.2.2.2 of Commission Regulation (EU) No 283/2013.

Further, the following article was found in the literature well supporting above mentioned position that deltamethrin can hardly be present in open waters.

Report:	**KCA 7.2.2.2 /01; Wang, Q.; Liu, Q.; Li, J.; Chi, H.; Wang, J; 2011**
Title:	Residual elimination and kinetics of low concentration of deltamethrin in water.
Source:	Nongye Huanjing Kexue Xuebao 2007, 26 (5):1725-1728
Document No:	M-461213-01-2 (English translation)
GLP:	No, published study
Literature review classification:	b) supplementary information (EFSA Journal 2011; 9(2):2092)

EXECUTIVE SUMMARY

The degradation of deltamethrin in different water environments was studied to assess aquaculture ecology and environments of freshwater and seawater systems in China. The test was performed in eight separate groups: sterilised freshwater, sterilised freshwater bottom mud, natural freshwater, natural freshwater bottom mud, sterilised seawater, sterilised seawater bottom mud, natural seawater and natural seawater bottom mud; with an initial concentration of deltamethrin of 5 µg/L in the water. Deltamethrin detection was performed by using HPLC.

Deltamethrin degraded quickly after pesticide application. As time went on, its degradation rate gradually slowed and became undetectable by day 21 in each group. Half-lives (DT_{50}) of deltamethrin ranged from 1.34 (water + mud) to 4.45 (water) days in the seawater system, and from 1.32 (water + mud) to 5.99 (water) days in the freshwater system.

MATERIAL AND METHODS

A. Material

1. Test material

Test item and source:	2.5% deltamethrin miscible oil prepared agent, manufactured by the Sichuan Huaqiang Fishery and Animal Husbandry and Pharmaceutical Company.
Active substance(s):	Deltamethrin standard (chromatographically pure, Agro-Environmental Protection Institute of the Ministry of Agriculture)
Chemical state and description:	2.5% miscible oil prepared agent
Batch number and Purity:	Not given
Storage conditions:	Not given

2. Water and bottom mud samples

Sampling area:	Freshwater and bottom mud were obtained from the [redacted] China. Seawater and bottom mud were obtained from [redacted], China.

B. Study design and methods

1. Sampling

Sampling interval:	Not reported

Sampling method:	Not reported
Test design:	The test was performed in eight separate groups: - sterilised freshwater, - sterilised freshwater bottom mud, - natural freshwater, - natural freshwater bottom mud, - sterilised seawater, - sterilised seawater bottom mud, - natural seawater - natural seawater bottom mud. The tests were performed in PP household boxes (44 cm x 31.5 cm x 28.5 cm). Test with bottom mud included a bottom mud thickness of 4.6 ±0.3 cm with a water volume of 25 L. Water temperature was 18-20 °C, pH value was 8.2 – 8.3 (seawater) and 7.0 – 7.2 (freshwater).
Sample processing:	Sterilized water was natural water boiled for 20 minutes; the sterilised bottom mud was wet heat sterilised at 120°C for 15 minutes. The properties of bottom mud are summarized in Table 7.2.2.2- 1
Test item concentration:	5 µg/L in the water phase
Sampling point:	2 hours after pesticide application
Replicates:	3
2. Chemical analysis	
Guideline/protocol:	Not given
Extraction:	250 mL of water was added to a 500 mL liquid separation funnel, 10 mL normal hexane was added. The sample was shaken vigorously for 5 minutes and was set aside for 15 minutes. The liquid was separated and the upper layer of liquid (normal hexane) transferred into a 10 mL glass centrifuge tube, blown dry with the nitrogen blower. Then 0.5 mL mobile phase added, mixed thoroughly for 1 minute on a vortex mixer and a 0.22 µm filter membrane used to filter it into a 1 mL centrifuge tube, to await testing.
Analytical method:	The ultraviolet detection wavelength was 230 nm; for the solid phase a Hypersilo ODS column (250 mm × 4.6 mm, 5 µm) was used with a mobile phase methanol: water (85:15); flow rate 1 mL/min; column temperature was room temperature; sampling quantity was 30 µL. The external standard method was used for quantification.
Recovery:	For the amount of 0.05, 0.1, 1, and 5 µg deltamethrin/L added: Freshwater: 94.33 – 98.87% Seawater: 95.22 – 99.52%
Limit of detection:	LOD: 0.02 µg/L

Table 7.2.2.2- 1: Summary of the bottom mud properties

Property	Freshwater	Seawater
pH	7.6	8.2
Quantities of bottom mud of different grain diameters (1-0.05mm) [%]	32.42	43.24
Quantities of bottom mud of different grain diameters (<0.05mm) [%]	67.58	56.76
Quantity of organic material [g/kg]	52.97	46.32
Total quantity of positive ion exchange [cmol/kg]	59.21	53.48

RESULTS

1. Validity criteria:

No validity criteria defined.

2. Analytical findings:

Deltamethrin degraded quickly after pesticide application. As time went on its degradation rate gradually slowed and became undetectable by day 21 in each group (see Figure 1 of article for the deltamethrin degradation curve in seawater, and see Figure 2 of article for the degradation curve in freshwater.

The half-lives of deltamethrin ranged between 4.98 – 5.99 days for freshwater and 1.32 – 1.60 days for freshwater mud, and between 4.28 – 4.45 days for seawater and 1.34 – 2.10 days for seawater mud (for summary of results see Table 7.2.2.2- 2). The role of microorganisms in freshwater was significant while their role in seawater was not significant.

Table 7.2.2.2- 2: Elimination Equation of Each Deltamethrin Sample in Water

Kind of Sample	Equation	Correlation coefficient (r^2)	Half-life [day]
Natural seawater bottom mud	$C_t = 4.920\ 3e^{-0.5168t}$	0.9347	1.34
Sterilised seawater	$C_t = 4.944\ 5e^{-0.1620t}$	0.9779	4.28
Natural seawater	$C_t = 4.640\ 5e^{-0.1556t}$	0.9769	4.45
Sterilised seawater bottom mud	$C_t = 5.145\ 0e^{-0.3307t}$	0.9571	2.10
Natural freshwater bottom mud	$C_t = 4.843\ 1e^{-0.5276t}$	0.9379	1.32
Sterilised freshwater	$C_t = 4.742\ 6e^{-0.1156t}$	0.9815	5.99
Natural freshwater	$C_t = 4.505\ 7e^{-0.1411t}$	0.9774	4.98
Sterilised freshwater bottom mud	$C_t = 4.801\ 1e^{-0.4319t}$	0.9791	1.60

$C_t = C_0 e^{-kt}$

In the formula: C_0 is the first sediment quantity after pesticide application, k is the elimination rate constant, t is the number of days after pesticide application and C_t is the deltamethrin concentration at interval t after pesticide application.

III. CONCLUSION

Comparatively short half-lives of deltamethrin in different Chineese water environments were determined in order to assess aquaculture ecology and environments of freshwater and seawater systems. The outcome indicates that any longer presence of deltamethrin in open waters should be minimal.

CA 7.2.2.3 Water/sediment study

Route and rate of degradation of deltamethrin in water/sediment systems under aerobic conditions were evaluated during the Annex I inclusion using [^{14}C]-benzyl labelled deltamethrin, as well as unlabelled deltamethrin, and were accepted by the European Commission (SANCO/6504/VI/99-final, 17 October 2002). During the evaluation the summary of micro/mesocosm/pond studies on the fate of deltamethrin in water were listed under this section, too. Nowadays, however, those studies should be better grouped into the new section where influence of natural sunlight is included (see next section).
The following studies included in the Baseline Dossier were regarded relevant during the Annex I inclusion:

Author(s)	Year	Document No.
[redacted]	1985	M-124982-01-1
[redacted]	1993	M-131938-01-1

The studies with deltamethrin in two different natural water/sediment systems showed that the compound was thoroughly degraded leading to CO_2 as the end product of the mineralization process. The adsorption of deltamethrin from water to the sediments accounts for 60 to 88% of the applied radioactivity, and is the most important dissipation route in natural surface water. 50% of the deltamethrin in the water disappeared from the water column within 1 day. The DT$_{50}$ for the entire system (water + sediment) ranged from 40 to 90 days under standard conditions in the dark. Main metabolites in water/sediment systems were: α-R-isomer of deltamethrin (max. 24% of applied radioactivity in sediment, lacks insecticidal activity), 4'-OH-deltamethrin (maximum 8% in sediment) and mPBacid (maximum 6% in water). Position of ^{14}C- labelling (benzyl-^{14}C) did not allow measurement of Br_2CA.

The dossier supporting the approval renewal of deltamethrin includes the following new aerobic water-sediment study for the parent compound using a second label position, ^{14}C-gemi-dimethyl label of deltamethrin, to allow the investigation of the second half of the deltamethrin molecule. The new study performed with two different water/sediment systems included acidic sediment, also. Both topics had been discussed to be clarified better during the earlier EU evaluation.

Report:	**KCA 7.2.2.3 /04; [redacted]; [redacted]; [redacted]; 2012**
Title:	[gem-dimethyl-^{14}C]Deltamethrin: Aerobic Aquatic Metabolism
Report No:	EnSa-12-0181
Document No:	M-434820-01-1
Guidelines:	OECD Guideline for the Testing of Chemicals No. 308, Commission Directive 95/36/EC amending Council Directive 91/414/EEC (AnnexesII and III, Fate and Behaviour in the Environment), 1995 US EPA Fate, Transport and Transformation Test Guidelines, OPPTS 835.4300 and OPPTS 835.4400, Aerobic and Anaerobic Aquatic Metabolism, 2008
GLP:	Yes

EXECUTIVE SUMMARY

The aerobic transformation of [gem-dimethyl-^{14}C]deltamethrin was studied in two types of water/sediment systems for a maximum of 99 days in the dark at 20 ± 2 °C. The water/sediment systems were taken from [redacted] [water: pH 7.6, TOC = 4 mg/L; sediment: loam, pH 6.1 ($CaCl_2$), TOC = 4.6%)] and [redacted] [water: pH 7.7, TOC < 2 mg/L; sediment: sand, pH 7.2 ($CaCl_2$), TOC = 0.34%].
The nominal application rate of 7.8 µg deltamethrin per test system was the 12-fold overdose of an application rate calculated according to a single maximum field use rate of 12.5 g/ha. Laboratory

microcosm flasks, filled with a volume ratio of water to sediment: 3:1 were treated with ^{14}C-deltamethrin. During incubation the supernatant water was in smooth motion.
Samples were taken after 0, 0.125, 0.5, 1, 2, 3, 7, 14, 30, 50, 73 and 99 days of incubation. Water phase and sediment extracts were analyzed by LSC and HPLC. The evolved $^{14}CO_2$ as well as the non-extractable residues were determined. At the last sampling date, sediment aliquots were also used to determine the amount of $^{14}CO_2$ in the sediment.
The test conditions outlined in the study protocol were maintained throughout the study. The overview of material balance and distribution of radioactivity in the two test series is summarized by Table 7.2.2.3- 3, for more detailed data see Table 7.2.2.3- 8 and Table 7.2.2.3- 9. Shortly after treatment the radioactivity in the water phase of both test systems decreased rapidly, then it increased until DAT-30 and declined to less than 6% of AR towards the end of the study. Extractable ^{14}C residues in the sediment increased to a maximum of 80.0% at DAT-0.5 and declined then to towards the end of the study.

Table 7.2.2.3- 3: Results synopsis on material balance and distribution of applied ^{14}C

Water/Sediment System	[redacted]	[redacted]
Material Balance [% AR] *	85.8 – 99.7	88.4 – 101.0
Water Phase [% AR]	4.2 – 56.7	5.6 – 62.7
Sediment Extract [% AR]	24.6 – 80.0	7.2 – 77.8
Max. $^{14}CO_2$ [% AR]	21.3	39.1
Max. NER [% AR]	36.8	33.4

*: minimum values at the last samplings, always NER = non extractable residues

In the water phase of [redacted] and [redacted] respectively, the amounts of deltamethrin decreased to amounts < LOD from DAT-30 onwards. In the sediment phase of [redacted], the amounts of deltamethrin increased from 36.0% of AR at day 0 to a maximum of 57.3% at DAT-0.5 and declined then to 4.0% of AR towards the end of the study. In the [redacted] sediments the amounts of Deltamethrin accounted for 36.5% of AR at day 0, increased to 54.6% of AR at DAT-0.5 and declined to 1.0% of AR towards the end of the study.

The dissipation of Deltamethrin from the supernatant water phase was characterized by translocation into the sediment as well as by degradation. This was best described using the DFOP kinetic model with DT_{50} and DT_{90} values of 0.03 and 0.64 days for [redacted] and using the HS kinetic model with DT_{50} and DT_{90} values of 0.06 and 0.84 days for [redacted], respectively. The corresponding modeling endpoints were either determined using the DFOP kinetic model ([redacted]), resulting in a DT_{50} value of 0.2 days, or the HS kinetic model ([redacted]) with a DT_{50} value of 0.3 days.

In both entire water/sediment systems, deltamethrin was degraded well which was best described using the FOMC kinetic model. The estimated DT_{50} and DT_{90} values were 1.0 and 28.8 days for [redacted] and 0.9 and 20.6 days for [redacted], respectively. The corresponding modeling endpoints were determined with DT_{50} values of 8.7 days for [redacted] and 6.2 days for [redacted] respectively.

Table 7.2.2.3- 4: Results synopsis on "best fit" dissipation kinetics for deltamethrin in the supernatant water layers (persistence endpoints)

Test System	Kinetic Model	DT_{50} [days]	DT_{90} [days]	Chi^2 Error [%]
[redacted]	DFOP	0.03	0.64	8.35
[redacted]	HS	0.06	0.84	7.97

DFOP = Double First Order in Parallel Model; HS = Hockey stick model

Table 7.2.2.3- 5: Results synopsis on "best fit" dissipation kinetics for deltamethrin in the entire test systems (persistence endpoints)

Test System	Kinetic Model	DT_{50} [days]	DT_{90} [days]	Chi^2 Error [%]
[redacted]	FOMC	1.02	28.8	11.34
[redacted]	FOMC	0.88	20.6	12.21

FOMC = First Order Multi Compartment Model

In the water/sediment systems from [redacted], three major transformation products were detected. They were identified as α-R-isomer of deltamethrin, Br_2CA (AE F108565, *cis*), and an isomer of BrCA (BrCA-isomer 1). In the water/sediment systems from [redacted], α-R-isomer of deltamethrin, Br_2CA, Serinyl-BrCA, BrCA-isomer 1 and 2 were found as major degradation products.

Table 7.2.2.3- 6: Results synopsis on metabolism of deltamethrin in the entire test systems

Sediment Type	[redacted] Loam	[redacted] Sand
Major transformation products	CO_2 NER α-R-Isomer of Deltamethrin Br_2CA BrCA-isomer 1	CO_2 NER α-R-Isomer of Deltamethrin Br_2CA Serinyl-BrCA BrCA-isomer 1 and BrCA-isomer 2
Minor transformation products	Serinyl-BrCA BrCA-isomer 2	-

* Criteria for "major":
> 10% of AR in total system,
> 5% of AR at two successive DAT's per compartment
> 5% and increasing at the end of the study per compartment
NER = non extractable residues

From this study it is concluded that deltamethrin and its degradation products have no potential for accumulation in the aqueous environment.

I. MATERIALS AND METHODS

1. Test Item

[Gem-dimethyl-^{14}C]deltamethrin:	Batch KATH 6385
Specific Radioactivity:	3.96 MBq (106.9 µCi) / mg
Radiochemical Purity:	99% (HPLC, radioactivity-detector) 99% (TLC, scan)
Chemical purity:	98.6 %
Diastereomeric purity:	> 99% (HPLC, radioactivity-detector)

2. Test Systems

The study was carried out with natural water/sediment systems from two locations:

- [redacted] Germany): This is an artificially dammed pond in the course of the "[redacted]". On account of it's in- and outlet the pond (approx. 1000 m^2 in surface area) has strong water current.

- [redacted] Germany): in the raw data it was named [redacted], always. However, since it is a small lake, i.e. a reclaimed gravel-pit which is used for fishing only, it was re-named within the current report. The lake is entirely enclosed by a fence.

Fresh water and sediment samples were taken separately and poured into plastic containers prior to the start of the study. A description of water and sediment collection and storage is given in Appendix 2 of report. The results of the on-site measurements as well as the other system characteristics are given in following Table 7.2.2.3- 7.

Table 7.2.2.3- 7: Physico-chemical properties of water and sediment

Properties of Waters		
Parameter	[redacted]	[redacted]
Temperature [°C][1]	17.8	21.0
pH[1]	7.6	7.7
Hardness [mmole/L]*	0.60	1.7
Oxygen Concentration (saturation) [mg/L][1]	8.8	10.0
Total Organic Carbon (TOC) [mg/L]*,5	4.5	< 2.9
Dissolved Organic Carbon (DOC) [mg/L]*	2	2
Redox Potential E_h [mV][1,4]	433.9	414.6
Properties of Sediments		
Geographic Location	[redacted] Germany	[redacted] Germany
Soil Taxonomic Classification (USDA)#	Loam	Sand
Sand (2000 – 50 µm) [%]#	45	97
Silt (< 50 – 2 µm) [%]#	42	0
Clay (< µm) [%]#	13	3
pH[1]	6.5	7.1
pH#	6.1 ($CaCl_2$); 6.6 (H_2O)	7.2 ($CaCl_2$); 7.8 (H_2O)
Temperature [°C][1]	17.6	21.6
Organic Carbon [%]*,5	4.6 / 4.3	0.34 / 0.29
Organic Matter [%]*,3	7.9 / 7.4	0.6 / 0.5
Sediment Microbial Activity [mg CO_2-C/kg sediment (dry wt)][2,6]	30.82 / 20.42 / 19.58	1.25 / 2.50 / 1.25
Cation Exchange Capacity [meq/100 g]#	8.1	2.9
Total Nitrogen [mg/kg]	4400	< 1000
Total Phosphorus [ppm]*	1000	150
Redox Potential E_h [mV][1,4]	197.6	201.3

* Analyzing laboratory: [redacted], Germany
# Analyzing laboratory: [redacted], USA, start of acclimatization
[1] Measurement at day of sampling
[2] Measurement at DAT-0 and at the end of the study
[3] %organic matter =%organic carbon x 1.724
[4] Potential difference between used electrode and H_2-electrode at 20°C: 210 [mV]
Theoretical potential of used buffer solution for Pt-Ag/AgCl electrode at 25°C: 220 [mV]
[5] start of pre-equilibration and at the end of the study
[6] Measurement at the start of pre-equilibration
n.a. = not analyzed

B. STUDY DESIGN

1. Experimental Conditions

The collected sediment samples were sieved with 2 mm mesh-size to remove parts of e.g. plants and stones. The collected water phases were filtered through a 0.06 mm sieve. Water and sediment phases were stored in the laboratory until the assembling of the water/sediment test systems (1 day). Static test flasks, laboratory microcosm flasks, for degradation in aquatic systems under aerobic conditions were used. For the assembling of the water/sediment systems, sediment aliquots, either 74 g ([redacted]) or 250 g ([redacted]) dry weight sediment corresponding to a volume of 175 mL (height approx. 2.5 cm) were poured into the vessels and 520 mL (height approx. 6 cm) of the corresponding natural water were added. Then, the systems were closed with a solid trap attachment for absorbing volatile compounds. The water to sediment ratio was about 3/1 (v/v). The microbial biomass of the sediment was determined by short term respiration measurements.

For technical reasons the study application rate (SAR) of of 7.8 µg [^{14}C]deltamethrin dissolved in approx. 1 mL of acetone per test system was the 12-fold overdose of the application rate calculated based on the intended single maximum field use rate of 12.5 g/ha. Since deltamethrin is very low soluble in water a co-solvent was inevitable. During incubation the supernatant water was in smooth motion.

2. Sampling

Two treated flasks per test system were taken and processed completely for analyses at the following sampling dates:

0, 0.125, 0.5, 1, 2, 3, 7, 14, 30, 50, 73 and 99 days after treatment and respective aerobic incubation

3. Analytical Procedures

Aliquots of the water phase were taken to determine the dissolved amount of $^{14}CO_2$. Then, the water layer was decanted and centrifuged with 5 mL acetone to avoid adsorption on the walls. After centrifugation, the volume of the supernatant water was determined and doubled by the addition of acetone. One half of the mixture was deep frozen while the other half was treated with formic acid (20 µL / 10 mL) to stabilize the ratio of the test item and the α-R-isomer of deltamethrin.

The moist sediment was extracted with 2 x 80 mL acetone containing 1% formic acid and subsequently with 3 x 80 mL pure acetone (ambient organic extracts). Afterwards, the sediment was extracted once more with 80 mL acetone using a microwave-accelerated solvent extraction (10 min. at 50 °C, aggressive organic extract). The acidified water phase, the combined extract of the ambient extraction steps as well as the aggressive extract were concentrated and analyzed by LSC and HPLC in order to determine the amounts of the test item and its transformation products. Identification of the test item was achieved by NMR and GC-MS/MS or co-chromatography (HPLC).

The transformation products were identified by HPLC or TLC co-chromatography and / or HPLC-MS and HPLC-MS/MS with accurate mass determination (for more details see section 4.5 of report).

The extracted sediment phase was air-dried, homogenized and combusted in an oxidizer. The evolved $^{14}CO_2$ was trapped in a scintillation cocktail and measured by LSC to determine the non-extractable residues. At the last sampling date, sediment aliquots were also used to determine the amount of $^{14}CO_2$ in the sediment.

The data of dissipation/degradation kinetics according to the recommendations of EC document 9188/VI/97 rev. 8 (2000) were directly taken from **Error! Reference source not found.** 2013, report M-461952-01-1, which is summarized later. Respective print-outs of modelling calculations were filed in the raw data.

II. RESULTS AND DISCUSSION

Results indicated that the anticipated standardized aerobic conditions were maintained and that the supernatant water was aerobic (approx. 4.7 – 8.7 mg O_2/L) during the entire incubation period in the dark. The mean incubation temperatures were 20.4 ± 0.1 °C for [redacted] and 19.6 ± 0.04 °C for [redacted] test systems.

The pH value in the water phase of the water/sediment systems varied throughout the study period and showed a slight decrease during the course of the study, ranging from pH 5.8 - 8.4 for [redacted] and from pH 7.3 - 8.7 for [redacted]. The redox potential E_h in the supernatant water of test systems ranged from 278 – 503 mV for [redacted] and from 325 – 455 mV for [redacted].

The pH value in the sediment of the test systems slightly decreased in [redacted]. Overall it varied between pH 6.2 - 7.2 for [redacted] and from pH 6.5 – 7.9 for [redacted]. The redox potential E_h in the sediment ranged from 47 – -175 mV for [redacted] and from 70 – 386 mV for [redacted].

The microbial activity in the sediments indicated that the systems were biologically active during the entire period of the test (see Table 7.2.2.3- 7). In the [redacted] systems, a reduction of the microbial activity in the course of the experiment was observed. This is characteristic for a laboratory experiment due to the gradual depletion of nutrients in the sediment and lacking supply of organic matter as a source of energy.

A. DATA

All calculations for radioactivity (as % of applied radioactivity) in water and sediment extract, in the solid materials and in the trap attachments are listed in Table 7.2.2.3- 8 and Table 7.2.2.3- 9, the overview was presented in Table 7.2.2.3- 3, already.

Complete material balances were found for all sampling dates except for the last sampling interval for [redacted] and for the last two sampling intervals for [redacted] where the material balance was below 90% of AR. The losses were obvious in those flasks where higher amounts of $^{14}CO_2$ radioactivity were measured, probably the large formed gaseous portions have not entirely been trapped and were thus lost from the test flasks, or some parts were lost during processing of the matrices.

Significant formation of $^{14}CO_2$ was observed in both water/sediment systems. At termination of the study, the $^{14}CO_2$ recovery (mean values of duplicates) was 21.3% and 39.1% of the applied radioactivity in systems from [redacted] and [redacted] respectively. From these data it can be concluded that deltamethrin is mineralized in water/sediment systems. The majority of total $^{14}CO_2$ accounted for the volatile $^{14}CO_2$ trapped by soda lime. Just a minor portion included in those values was found to be ^{14}Carbonate dissolved in the water phases or contained in the sediments. No significant amounts of organic volatiles were found (≤ 0.2% of AR).

The mean radioactivity in the water phase of [redacted] test systems decreased rapidly from 56.7% of the applied radioactivity at day 0 to 14.6% at DAT-0.5. Afterwards, the radioactivity increased to 32.0% of AR until DAT-30 and declined then to 5.4% of AR towards the end of the study. The radioactivity in the water phase of [redacted] test systems showed a similar pattern. It decreased from 62.7% of the applied radioactivity at day 0 to 19.2% of AR at DAT-0.5. Then, it increased to 39.7% until DAT-30 and declined to 5.6% of AR towards the end of the study.

Table 7.2.2.3- 8: Distribution of radioactivity during aerobic aquatic metabolism in [redacted], expressed as percent of applied radioactivity (% AR)

		Replicate	DAT										
		No.	0	0.125	0.5	1	2	3	7	14	30	50	73	99
Volatiles														
	$^{14}CO_2$	1	n.a.	<0.1	0.1	0.1	0.2	0.2	0.6	2.1	3.8	16.9	14.8	21.3
		2	n.a.	<0.1	<0.1	0.1	0.3	0.3	0.6	2.0	0.9	12.5	20.0	21.3*
		Mean		**<0.1**	**0.0**	**0.1**	**0.2**	**0.3**	**0.6**	**2.0**	**2.4**	**14.7**	**17.4**	**21.3**
	Volatile organics	1	n.a.	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	0.1	0.1	0.1	0.2
		2	n.a.	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	0.1	0.1	0.1	0.1
		Mean		**<0.1**	**<0.1**	**<0.1**	**<0.1**	**<0.1**	**<0.1**	**<0.1**	**0.1**	**0.1**	**0.1**	**0.1**
	Total	1	n.a.	<0.1	0.06	0.1	0.2	0.2	0.6	2.1	3.9	17.1	15.0	21.4
		2	n.a.	<0.1	<0.1	0.1	0.3	0.3	0.6	2.0	1.0	12.6	20.1	21.4
		Mean		**<0.1**	**0.0**	**0.1**	**0.2**	**0.3**	**0.6**	**2.0**	**2.4**	**14.8**	**17.6**	**21.4**
Extractable Radioactivity														
	Water (W)	1	66.1	14.6	13.8	31.1	25.2	26.4	24.5	35.0	33.8	15.8	4.4	4.8
		2	47.3	25.1	16.4	23.0	23.6	22.2	22.2	27.6	30.2	13.8	4.0	5.9
		Mean	**56.7**	**19.9**	**14.6**	**27.1**	**24.4**	**24.3**	**23.3**	**31.3**	**32.0**	**14.8**	**4.2**	**5.4**
	Ambient Extract (SO)	1	29.5	75.5	79.9	64.0	71.1	67.2	60.8	44.4	43.4	25.5	33.0	22.7
		2	47.1	67.2	75.9	72.2	66.1	67.0	65.3	55.5	48.4	35.5	29.5	25.2
		Mean	**38.3**	**71.3**	**77.9**	**68.1**	**68.6**	**67.1**	**63.1**	**50.0**	**45.9**	**30.5**	**31.3**	**24.0**
	Aggressive Extract (SH)	1	0.8	2.1	2.1	2.0	1.8	1.7	1.5	1.1	1.1	0.8	0.9	0.6
		2	1.4	1.7	2.1	2.3	1.8	1.9	1.7	1.3	1.2	1.0	0.8	0.7
		Mean	**1.1**	**1.9**	**2.1**	**2.2**	**1.8**	**1.8**	**1.6**	**1.2**	**1.1**	**0.9**	**0.9**	**0.6**
	Total	1	96.4	92.2	95.7	97.1	98.1	95.3	86.8	80.5	78.3	42.1	38.4	28.2
		2	95.7	94.0	93.4	97.5	91.5	91.2	89.2	84.5	79.7	50.2	34.3	31.8
		Mean	**96.1**	**93.1**	**94.6**	**97.3**	**94.8**	**93.3**	**88.0**	**82.5**	**79.0**	**46.1**	**36.3**	**30.0**
Bound Residues		1	0.8	1.9	2.6	2.1	2.1	2.8	8.0	11.8	12.0	27.5	37.0	34.4
		2	1.1	1.6	2.3	2.5	2.5	2.8	7.5	11.5	12.5	30.9	36.6	34.5
		Mean	**1.0**	**1.7**	**2.4**	**2.3**	**2.3**	**2.8**	**7.7**	**11.6**	**12.3**	**29.2**	**36.8**	**34.5**
Material Balance		1	97.2	94.0	98.4	99.3	100.4	98.3	95.4	94.3	94.2	86.6	90.3	84.0
		2	96.9	95.6	95.7	100.1	94.3	94.2	97.3	97.9	93.3	93.7	91.1	87.7
		Mean	**97.0**	**94.8**	**97.0**	**99.7**	**97.3**	**96.3**	**96.4**	**96.1**	**93.7**	**90.1**	**90.7**	**85.8**

n.a.: not analyzed, DAT: day after treatment
* Due to a leak during the determination of volatile CO_2, the results of the first replicate were taken

Table 7.2.2.3- 9: Distribution of radioactivity during aerobic aquatic metabolism in [redacted] expressed as percent of applied radioactivity (% AR)

		Replicate	DAT											
		No.	0	0.125	0.5	1	2	3	7	14	30	50	73	99
Volatiles														
	$^{14}CO_2$	1	n.a.	0.1	0.1	0.2	0.9	1.2	2.6	6.4	12.0	14.7	15.4	37.7*
		2	n.a.	<0.1	0.1	0.1	1.0	0.5	2.3	7.1	11.1	17.0	20.2	40.5
		Mean		**0.0**	**0.1**	**0.1**	**1.0**	**0.8**	**2.4**	**6.7**	**11.6**	**15.8**	**17.8**	**39.1**
	Volatile organics	1	n.a.	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	0.1	0.2	0.1	0.2	0.2
		2	n.a.	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	0.1	0.1	0.2	0.3	0.2
		Mean		**<0.1**	**<0.1**	**<0.1**	**<0.1**	**<0.1**	**<0.1**	**0.0**	**0.1**	**0.2**	**0.2**	**0.2**
	Total	1	n.a.	0.1	0.14	0.2	0.9	1.2	2.6	6.4	12.2	14.8	15.6	37.9
		2	n.a.	<0.1	0.12	0.1	1.0	0.5	2.3	7.1	11.2	17.2	20.5	40.7
		Mean		**0.0**	**0.1**	**0.1**	**1.0**	**0.8**	**2.4**	**6.7**	**11.7**	**16.0**	**18.1**	**39.3**
Extractable Radioactivity														
	Water (W)	1	70.2	32.3	22.6	31.5	28.5	27.5	39.0	33.8	38.4	36.8	24.8	8.4
		2	55.2	37.8	15.8	34.0	25.1	37.9	39.0	41.6	41.0	36.4	20.8	2.8
		Mean	**62.7**	**35.0**	**19.2**	**32.8**	**26.8**	**32.7**	**39.0**	**37.7**	**39.7**	**36.6**	**22.8**	**5.6**
	Ambient Extract (SO)	1	30.2	59.5	67.2	59.6	62.1	61.1	46.1	39.4	25.7	22.5	16.5	7.8
		2	44.4	55.5	82.5	59.2	65.3	52.6	49.2	30.1	22.1	19.6	14.1	6.0
		Mean	**37.3**	**57.5**	**74.9**	**59.4**	**63.7**	**56.8**	**47.6**	**34.8**	**23.9**	**21.0**	**15.3**	**6.9**
	Aggressive Extract (SH)	1	0.4	1.0	5.3	0.9	1.0	0.8	0.6	0.7	0.4	0.4	0.3	0.3
		2	0.7	0.7	0.5	0.9	1.0	1.0	0.8	0.5	0.5	0.5	0.4	0.3
		Mean	**0.5**	**0.9**	**2.9**	**0.9**	**1.0**	**0.9**	**0.7**	**0.6**	**0.5**	**0.5**	**0.3**	**0.3**
	Total	1	100.8	92.8	95.2	92.1	91.6	89.4	85.7	73.9	64.6	59.6	41.6	16.5
		2	100.2	94.0	98.8	94.1	91.4	91.5	88.9	72.2	63.5	56.5	35.3	9.2
		Mean	**100.5**	**93.4**	**97.0**	**93.1**	**91.5**	**90.5**	**87.3**	**73.0**	**64.1**	**58.1**	**38.5**	**12.8**
Bound Residues		1	0.5	1.0	4.9	1.2	3.4	3.5	8.9	16.0	18.1	20.2	29.3	35.3
		2	0.6	0.8	1.5	1.8	3.5	3.1	9.2	16.1	17.8	23.9	28.4	31.5
		Mean	**0.5**	**0.9**	**3.2**	**1.5**	**3.5**	**4.3**	**9.0**	**16.1**	**18.0**	**22.1**	**28.8**	**33.4**
Material Balance		1	101.3	93.6	100.2	93.5	95.9	96.1	97.1	96.3	94.9	94.6	86.5	89.7
		2	100.8	94.8	100.4	96.0	95.9	95.0	100.4	95.4	92.6	97.6	84.2	81.5
		Mean	**101.0**	**94.3**	**100.3**	**94.8**	**95.9**	**95.6**	**98.8**	**95.8**	**93.7**	**96.1**	**85.4**	**85.6**

n.a.: not analyzed, DAT: day after treatment
* Due to a leak during the determination of volatile CO_2, the results of the second replicate were taken

Table 7.2.2.3- 10: Biotransformation of deltamethrin in [redacted] under aerobic conditions, expressed as percent of applied radioactivity (mean ± SD)

Compound	Source	Mean SD	DAT 0	0.125	0.5	1	2	3	7	14	30	50	73	99
Deltamethrin	Water	Mean	54.1	14.3	7.5	12.0	7.1	4.0	0.7	0.7	0.0	0.0	0.0	0.0
		SD	±9.4	±4.5	±1.1	±2.5	±0.5	±0.9	±0.3	±0.7	±0.0	±0.0	±0.0	±0.0
	Sediment	Mean	36.0	54.3	57.3	33.1	32.7	23.9	15.0	12.1	10.1	3.0	8.6	4.0
		SD	±8.8	±3.2	±1.1	±4.0	±1.7	±1.3	±1.3	±2.2	±1.5	±0.2	±0.3	±0.1
α-R-Isomer of Deltamethrin	Water	Mean	1.5	3.1	2.6	9.3	5.9	3.5	0.0	0.3	0.0	0.0	0.0	0.0
		SD	±0.8	±0.2	±0.3	±1.7	±0.3	±1.0	±0.0	±0.3	±0.0	±0.0	±0.0	±0.0
	Sediment	Mean	0.0	5.9	11.5	14.6	20.5	18.6	9.4	8.5	7.9	3.2	9.9	3.8
		SD	±0.0	±2.0	±2.8	±0.3	±3.7	±2.0	±0.6	±1.7	±1.7	±0.7	±1.8	±0.2
Br_2CA (ROI 3)	Water	Mean	0.0	1.0	3.8	4.6	9.7	13.8	16.8	13.2	2.8	0.5	0.0	0.0
		SD	±0.0	±0.1	±0.5	±0.0	±2.0	±0.0	±0.7	±2.0	±0.9	±0.1	±0.0	±0.0
	Sediment	Mean	1.9	8.6	7.8	18.0	10.2	13.3	27.0	10.8	6.6	11.4	0.0	10.7
		SD	±0.3	±0.3	±0.5	±0.4	±2.1	±0.2	±0.9	±0.3	±1.4	±3.7	±0.0	±1.3
ROI 4	Water	Mean	0.0	0.0	0.0	0.0	0.0	0.4	0.0	0.0	0.0	0.0	0.0	0.0
		SD	±0.0	±0.0	±0.0	±0.0	±0.0	±0.4	±0.0	±0.0	±0.0	±0.0	±0.0	±0.0
	Sediment	Mean	0.0	0.2	1.2	0.7	2.9	3.1	3.1	3.4	1.6	1.1	2.0	0.8
		SD	±0.0	±0.2	±0.6	±0.0	±0.6	±0.5	±0.7	±0.6	±0.4	±0.1	±0.0	±0.3
ROI 5	Water	Mean	0.0	0.0	0.0	0.0	0.3	0.6	0.0	0.0	0.0	0.0	0.0	0.0
		SD	±0.0	±0.0	±0.0	±0.0	±0.3	±0.1	±0.0	±0.0	±0.0	±0.0	±0.0	±0.0
	Sediment	Mean	0.0	0.6	0.9	0.6	2.3	2.5	3.5	3.7	1.4	1.7	1.9	1.1
		SD	±0.0	±0.2	±0.2	±0.2	±0.0	±0.2	±0.3	±0.4	±0.1	±0.1	±0.1	±0.5
BrCA-isomer 1 (ROI 9)	Water	Mean	0.0	0.0	0.0	0.0	0.2	0.4	3.5	11.4	20.4	4.2	0.0	0.0
		SD	±0.0	±0.0	±0.0	±0.0	±0.2	±0.4	±0.5	±0.0	±1.0	±1.2	±0.0	±0.0
	Sediment	Mean	0.0	0.0	0.0	0.0	0.0	0.6	2.2	6.8	12.0	4.3	1.7	0.6
		SD	±0.0	±0.0	±0.0	±0.0	±0.0	±0.1	±0.1	±0.2	±0.3	±0.2	±0.5	±0.0
Serinyl-BrCA (ROI 10)	Water	Mean	0.0	0.0	0.0	0.0	0.0	0.0	0.7	1.8	2.3	7.0	4.0	5.2
		SD	±0.0	±0.0	±0.0	±0.0	±0.0	±0.0	±0.1	±0.0	±0.3	±1.2	±0.2	±0.6
	Sediment	Mean	0.0	0.0	0.0	0.0	0.0	0.7	0.2	0.7	0.9	2.3	4.8	2.4
		SD	±0.0	±0.0	±0.0	±0.0	±0.0	±0.7	±0.2	±0.1	±0.0	±0.4	±1.0	±0.3

ROI = region of interest in chromatogram

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Table 7.2.2.3- 8 cont.: Biotransformation of deltamethrin in [redacted] under aerobic conditions, expressed as percent of applied radioactivity (mean ± SD)

Compound	Source	Mean SD	DAT 0	0.125	0.5	1	2	3	7	14	30	50	73	99
BrCA-isomer 2 (ROI 11)	Water	Mean	0.0	0.0	0.0	0.0	0.0	0.0	0.7	1.7	2.3	2.6	0.0	0.0
		SD	±0.0	±0.0	±0.0	±0.0	±0.0	±0.0	±0.3	±0.3	±1.4	±1.0	±0.0	±0.0
	Sediment	Mean	0.0	0.0	0.0	0.0	0.0	0.3	0.0	1.0	1.8	1.4	0.0	0.0
		SD	±0.0	±0.0	±0.0	±0.0	±0.0	±0.1	±0.0	±0.1	±0.1	±0.4	±0.0	±0.0
Non-char. RA	Water	Mean	1.0	1.5	0.7	1.2	1.1	1.7	1.0	2.2	4.2	0.5	0.3	0.2
		SD	±0.4	±0.5	±0.3	±0.4	±0.4	±0.5	±0.3	±0.7	±1.7	±0.2	±0.1	±0.1
	Sediment	Mean	1.6	3.6	1.4	3.3	1.7	5.8	4.1	4.2	4.8	3.2	3.2	1.2
		SD	±0.5	±1.0	±0.5	±0.9	±0.7	±1.6	±1.1	±1.1	±1.3	±1.0	±0.9	±0.4
TER	Water	Mean	56.7	19.9	14.6	27.1	24.4	24.3	23.3	31.3	32.0	14.8	4.2	5.4
		SD	±9.4	±5.2	±0.8	±4.1	±0.8	±2.1	±1.1	±3.7	±1.8	±1.0	±0.2	±0.5
	Sediment	Mean	39.4	73.2	80.6	70.3	70.4	68.9	64.7	57.2	47.1	31.3	32.1	24.6
		SD	±9.1	±4.3	±3.0	±4.3	±0.0	±0.0	±2.3	±5.7	±2.5	±5.1	±1.8	±1.3
Total $^{14}CO_2$	Entire System	Mean	n.a.	0.0	0.0	0.1	0.2	0.3	0.6	2.8	2.4	14.7	17.4	21.3
		SD		±0.0	±0.0	±0.0	±0.0	±0.0	±0.0	±0.0	±1.4	±1.6	±2.6	±0.0
Total organic volatiles	Entire System	Mean	n.a.	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.1	0.1	0.1	0.1
		SD		±0.0	±0.0	±0.0	±0.0	±0.0	±0.0	±0.0	±0.0	±0.0	±0.0	±0.0
NER	Sediment	Mean	1.0	1.7	2.4	2.3	2.3	2.8	7.7	11.6	12.3	29.2	36.8	34.5
		SD	±0.2	±0.1	±0.2	±0.2	±0.2	±0.0	±0.2	±0.1	±0.3	±1.7	±0.2	±0.0
Total recovery	Water	Mean	56.7	19.9	14.6	27.1	24.4	24.3	23.3	31.3	32.0	14.8	4.2	5.4
		SD	±9.4	±5.2	±0.8	±4.1	±3.0	±2.1	±1.1	±3.7	±1.8	±1.0	±0.2	±0.5
	Sediment	Mean	40.4	75.0	82.4	72.6	72.7	74.7	72.4	62.8	59.3	60.5	68.9	59.1
		SD	±9.1	±4.3	±3.0	±4.3	±2.5	±0.0	±2.3	±5.7	±2.5	±5.1	±1.8	±1.3
	Entire System	Mean	97.0	94.8	97.0	99.7	97.3	96.3	96.4	96.1	93.7	90.1	90.7	85.8
		SD	±0.2	±0.8	±1.3	±0.4	±3.0	±2.0	±0.9	±1.8	±0.5	±2.9	±0.5	±1.8

n.a.: not analyzed, DAT: day after treatment, SD: standard deviation
Non-char. RA: Non characterized radioactivity (including minor peaks and diffuse radioactivity)
ROI = region of interest in chromatogram

Table 7.2.2.3- 11: Biotransformation of deltamethrin in [redacted] under aerobic conditions, expressed as percent of applied radioactivity (mean ± SD)

Compound	Source	Mean SD	DAT 0	0.125	0.5	1	2	3	7	14	30	50	73	99
Deltamethrin	Water	Mean	57.3	22.5	9.3	13.1	4.6	4.6	1.1	0.8	0.0	0.0	0.0	0.0
		SD	±6.1	±2.7	±1.3	±0.4	±1.2	±1.2	±0.5	±0.3	±0.0	±0.0	±0.0	±0.0
	Sediment	Mean	36.5	45.7	54.6	31.4	30.7	24.9	17.2	9.2	5.0	4.3	2.7	1.0
		SD	±7.1	±2.4	±6.2	±1.2	±1.4	±2.8	±2.0	±2.8	±0.4	±0.3	±0.5	±1.0
α-R-Isomer of Deltamethrin	Water	Mean	3.2	9.3	6.2	11.6	5.9	4.8	0.8	0.2	0.0	0.0	0.0	0.0
		SD	±1.1	±0.4	±2.3	±0.9	±0.8	±1.4	±0.2	±0.2	±0.0	±0.0	±0.0	±0.0
	Sediment	Mean	0.0	11.9	20.0	24.8	23.2	21.1	12.6	7.5	5.2	4.5	4.6	1.4
		SD	±0.0	±0.2	±1.2	±0.8	±0.2	±0.4	±1.3	±1.4	±0.9	±0.8	±0.8	±1.4
Br_2CA (ROI 3)	Water	Mean	0.0	1.5	3.3	7.7	14.7	20.4	32.2	24.4	13.5	3.0	0.0	0.0
		SD	±0.0	±0.1	±0.6	±0.2	±0.9	±1.6	±1.1	±4.3	±2.3	±0.3	±0.0	±0.0
	Sediment	Mean	0.0	0.0	0.4	0.3	1.4	1.9	3.9	4.4	2.1	0.5	0.3	0.0
		SD	±0.0	±0.0	±0.0	±0.3	±0.0	±0.1	±0.5	±0.2	±0.2	±0.0	±0.3	±0.0
ROI 4	Water	Mean	0.0	0.0	0.0	0.0	0.0	0.2	0.0	0.0	0.0	0.0	0.0	0.0
		SD	±0.0	±0.0	±0.0	±0.0	±0.0	±0.2	±0.0	±0.0	±0.0	±0.0	±0.0	±0.0
	Sediment	Mean	0.0	0.4	1.9	1.0	4.6	3.9	5.2	3.1	1.3	1.1	0.3	0.0
		SD	±0.0	±0.0	±0.5	±0.2	±0.1	±0.3	±0.2	±0.4	±0.2	±0.1	±0.3	±0.0
ROI 5	Water	Mean	0.0	0.0	0.0	0.0	0.4	0.8	0.0	0.0	0.3	0.0	0.0	0.0
		SD	±0.0	±0.0	±0.0	±0.0	±0.4	±0.3	±0.0	±0.0	±0.3	±0.0	±0.0	±0.0
	Sediment	Mean	0.0	0.0	0.5	0.8	3.2	3.1	5.8	3.8	2.2	1.5	0.0	0.0
		SD	±0.0	±0.0	±0.1	±0.0	±0.3	±1.0	±0.1	±0.5	±0.2	±0.6	±0.0	±0.0
BrCA-isomer 1 (ROI 9)	Water	Mean	0.0	0.0	0.0	0.0	0.0	0.4	1.1	6.2	14.4	17.3	6.5	0.0
		SD	±0.0	±0.0	±0.0	±0.0	±0.0	±0.4	±0.7	±1.2	±0.1	±1.2	±0.3	±0.0
	Sediment	Mean	0.0	0.0	0.0	0.0	0.0	0.0	1.4	3.9	4.6	4.3	2.1	0.0
		SD	±0.0	±0.0	±0.0	±0.0	±0.0	±0.0	±0.1	±0.3	±0.0	±0.8	±0.2	±0.0
Serinyl-BrCA (ROI 10)	Water	Mean	0.0	0.0	0.0	0.0	0.0	0.0	1.2	2.1	4.1	7.4	7.8	5.5
		SD	±0.0	±0.0	±0.0	±0.0	±0.0	±0.0	±0.5	±0.2	±0.4	±0.4	±1.7	±2.7
	Sediment	Mean	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.4	1.0	1.5	2.2	1.5
		SD	±0.0	±0.0	±0.0	±0.0	±0.0	±0.0	±0.0	±0.4	±0.0	±0.1	±0.5	±1.5

ROI = region of interest in chromatogram

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Table 7.2.2.3- 9 cont.: Biotransformation of deltamethrin in [redacted] under aerobic conditions, expressed as percent of applied radioactivity (mean ± SD)

Compound	Source	Mean SD	DAT 0	0.125	0.5	1	2	3	7	14	30	50	73	99
BrCA-isomer 2 (ROI 11)	Water	Mean	0.0	0.0	0.0	0.0	0.0	0.0	1.1	1.5	4.3	7.7	7.2	0.0
		SD	±0.0	±0.0	±0.0	±0.0	±0.0	±0.0	±0.6	±0.9	±1.9	±0.1	±0.9	±0.0
	Sediment	Mean	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.8	1.4	2.2	2.2	0.0
		SD	±0.0	±0.0	±0.0	±0.0	±0.0	±0.0	±0.0	±0.0	±0.0	±0.1	±0.1	±0.0
Non-char. RA	Water	Mean	2.1	1.9	0.4	0.3	1.2	1.4	1.5	2.5	3.2	1.2	1.2	0.1
		SD	±0.6	±0.6	±0.2	±0.1	±0.4	±0.5	±0.6	±0.9	±1.1	±0.5	±0.5	±0.1
	Sediment	Mean	1.4	0.4	0.3	1.9	1.6	2.7	2.1	2.6	1.4	1.9	1.8	3.4
		SD	±0.5	±0.1	±0.1	±0.6	±0.5	±1.0	±0.6	±0.8	±0.4	±0.6	±0.5	±1.6
TER	Water	Mean	62.7	35.0	19.2	32.8	26.8	32.7	39.0	37.7	39.7	36.6	22.8	5.6
		SD	±7.5	±2.7	±3.4	±1.2	±1.7	±5.2	±0.0	±3.9	±1.3	±0.2	±2.0	±2.8
	Sediment	Mean	37.8	58.3	77.8	60.3	64.7	57.7	48.3	35.4	24.4	21.5	15.7	7.2
		SD	±7.2	±2.1	±5.2	±0.2	±0.0	±4.2	±1.6	±4.8	±1.8	±1.3	±1.2	±0.8
Total $^{14}CO_2$	Entire System	Mean	n.a.	0.0	0.1	0.1	1.0	0.8	2.4	6.7	11.6	15.8	17.8	39.1
		SD		±0.0	±0.0	±0.0	±0.0	±0.0	±0.1	±0.0	±0.5	±1.2	±1.7	±0.0
Volatile organics	Entire System	Mean	n.a.	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.2	0.2	0.2	0.2
		SD		±0.0	±0.0	±0.0	±0.0	±0.0	±0.0	±0.0	±0.0	±0.1	±0.1	±0.0
NER	Sediment	Mean	0.5	0.9	3.2	1.7	3.5	4.3	9.0	16.1	18.0	22.1	28.8	33.4
		SD	±0.1	±0.1	±1.7	±0.3	±0.1	±1.2	±0.2	±0.1	±0.1	±1.8	±0.4	±0.0
Total recovery	Water	Mean	62.7	35.0	19.2	32.8	26.8	32.7	39.0	37.7	39.7	36.6	22.8	5.6
		SD	±7.5	±2.7	±3.4	±1.2	±0.6	±5.2	±0.0	±3.9	±1.3	±0.2	±2.0	±2.8
	Sediment	Mean	38.4	59.2	81.0	61.9	68.2	62.0	57.4	51.4	42.3	43.6	44.5	40.6
		SD	±7.2	±2.1	±5.2	±0.2	±1.6	±4.2	±1.6	±4.8	±1.8	±1.3	±1.2	±0.8
	Entire System	Mean	101.0	94.3	100.3	94.8	95.9	95.6	98.8	95.8	93.7	96.1	85.4	85.6
		SD	±0.2	±0.4	±0.1	±1.2	±0.0	±0.8	±1.4	±0.1	±1.1	±1.5	±0.4	±2.5

n.a.: not analyzed, DAT: day after treatment, SD: standard deviation
Non-char. RA: Non characterized radioactivity (including minor peaks and diffuse radioactivity)
ROI = region of interest in chromatogram

Table 7.2.2.3- 12: Biotransformation of deltamethrin in total water sediment system [redacted] under aerobic conditions, expressed as percent of applied radioactivity

Compound	Replicate	Sampling Times [days]											
		0	0.125	0.50	1	2	3	7	14	30	50	73	99
Deltamethrin	1	90.7	67.2	62.6	43.5	41.0	27.5	14.7	11.2	8.6	2.8	9.0	4.1
	2	89.5	69.9	67.1	46.5	38.6	28.3	16.7	14.2	11.5	3.2	8.5	3.9
	Mean	**90.1**	**68.6**	**64.9**	**45.0**	**39.8**	**27.9**	**15.7**	**12.7**	**10.1**	**3.0**	**8.6**	**4.0**
α-R-Isomer of Deltamethrin	1	2.3	10.7	17.3	26.0	29.8	25.1	8.5	7.5	6.2	2.6	11.7	4.0
	2	0.7	7.2	10.8	23.0	23.1	19.0	9.7	10.2	9.7	3.9	8.2	3.5
	Mean	**1.5**	**8.9**	**14.0**	**24.0**	**26.5**	**22.0**	**9.1**	**8.9**	**7.9**	**3.2**	**9.9**	**3.8**
Br_2CA (ROI 3)	1	1.6	9.8	12.6	23.0	19.8	26.9	45.4	25.7	11.7	8.0	0.0	9.3
	2	2.1	9.5	10.6	22.2	20.0	27.4	42.3	22.3	7.0	15.3	0.0	12.0
	Mean	**1.9**	**9.7**	**11.6**	**22.6**	**19.9**	**27.1**	**43.9**	**24.0**	**9.4**	**11.6**	**0.0**	**10.7**
ROI 4	1	0.0	0.6	1.8	0.7	3.6	2.7	3.0	2.8	1.2	1.3	1.9	0.5
	2	0.0	0.5	0.5	0.6	2.3	4.6	4.3	4.0	2.0	1.0	2.0	1.1
	Mean	**0.0**	**0.2**	**1.2**	**0.7**	**2.9**	**3.7**	**3.7**	**3.4**	**1.6**	**1.1**	**2.0**	**0.8**
ROI 5	1	0.0	0.4	0.7	0.4	2.3	3.3	3.2	3.4	1.2	1.8	1.9	1.6
	2	0.0	0.8	1.0	0.8	3.1	2.9	3.8	4.1	1.5	1.8	1.8	0.7
	Mean	**0.0**	**0.6**	**0.9**	**0.6**	**2.7**	**3.1**	**3.5**	**3.7**	**1.4**	**1.7**	**1.9**	**1.1**
BrCA-isomer 1 (ROI 9)	1	0.0	0.0	0.0	0.0	0.0	1.6	5.2	18.0	31.1	7.2	2.3	0.6
	2	0.0	0.0	0.0	0.0	0.5	0.5	6.0	18.4	33.7	9.9	1.2	0.6
	Mean	**0.0**	**0.0**	**0.0**	**0.0**	**0.2**	**1.0**	**5.6**	**18.2**	**32.4**	**8.6**	**1.7**	**0.6**
Serinyl-BrCA (ROI 10)	1	0.0	0.0	0.0	0.0	0.0	1.3	1.1	1.8	2.9	10.8	8.0	6.8
	2	0.0	0.0	0.0	0.0	0.0	0.0	0.5	2.6	3.4	7.7	9.6	8.5
	Mean	**0.0**	**0.0**	**0.0**	**0.0**	**0.0**	**0.7**	**0.8**	**2.5**	**3.2**	**9.3**	**8.8**	**7.6**
BrCA-isomer 2 (ROI 11)	1	0.0	0.0	0.0	0.0	0.0	0.3	1.0	2.4	2.8	5.3	0.0	0.0
	2	0.0	0.0	0.0	0.0	0.0	0.2	0.3	3.0	5.4	2.6	0.0	0.0
	Mean	**0.0**	**0.0**	**0.0**	**0.0**	**0.0**	**0.3**	**0.7**	**2.7**	**4.1**	**4.0**	**0.0**	**0.0**

ROI = region of interest in chromatogram

Table 7.2.2.3- 13: Biotransformation of deltamethrin in total water sediment system [redacted] under aerobic conditions, expressed as percent of applied radioactivity

Compound	Replicate	Sampling Times [days]											
		0	0.125	0.50	1	2	3	7	14	30	50	73	99
Deltamethrin	1	92.8	67.9	59.1	42.9	35.1	31.2	16.7	13.1	5.4	4.6	3.0	1.9
	2	94.8	68.4	68.8	46.1	35.6	28.0	19.8	7.0	4.6	4.0	2.4	n.d.
	Mean	**93.8**	**68.1**	**63.9**	**44.5**	**35.3**	**29.6**	**18.2**	**10.0**	**5.0**	**4.3**	**2.7**	**1.0**
α-R-Isomer of Deltamethrin	1	4.3	20.6	29.8	36.3	29.7	25.0	15.0	9.2	6.0	5.3	4.8	2.1
	2	2.1	21.7	22.7	36.7	28.5	27.0	11.9	6.1	4.3	3.7	3.2	n.d.
	Mean	**3.2**	**21.1**	**26.3**	**36.5**	**29.1**	**26.0**	**13.4**	**7.7**	**5.2**	**4.5**	**4.0**	**1.4**
Br_2CA (ROI 3)	1	0.0	1.6	3.1	7.9	15.2	20.9	34.5	24.4	13.5	3.9	0.7	0.0
	2	0.0	1.3	4.3	8.1	16.9	23.8	37.7	32.6	17.6	3.2	0.0	0.0
	Mean	**0.0**	**1.5**	**3.7**	**8.0**	**16.1**	**22.3**	**36.1**	**28.5**	**15.5**	**3.5**	**0.3**	**0.0**
ROI 4	1	0.0	0.4	1.4	1.2	4.5	4.3	5.0	3.5	1.8	1.0	0.5	0.0
	2	0.0	0.4	2.4	0.9	4.8	4.0	5.5	2.7	1.3	1.2	0.0	0.0
	Mean	**0.0**	**0.4**	**1.9**	**1.0**	**4.6**	**4.1**	**5.2**	**3.1**	**1.5**	**1.1**	**0.3**	**0.0**
ROI 5	1	0.0	0.0	0.6	0.8	4.2	2.6	5.7	4.4	2.9	2.0	0.0	0.0
	2	0.0	0.0	0.4	0.9	2.8	5.2	5.9	3.3	2.0	0.9	0.0	0.0
	Mean	**0.0**	**0.0**	**0.5**	**0.8**	**3.5**	**3.9**	**5.8**	**3.8**	**2.4**	**1.5**	**0.0**	**0.0**
BrCA-isomer 1 (ROI 9)	1	0.0	0.0	0.0	0.0	0.0	0.8	3.1	8.6	19.2	19.6	8.7	0.0
	2	0.0	0.0	0.0	0.0	0.0	0.0	2.0	11.7	18.8	23.5	8.7	0.0
	Mean	**0.0**	**0.0**	**0.0**	**0.0**	**0.0**	**0.4**	**2.6**	**10.1**	**19.0**	**21.5**	**8.7**	**0.0**
Serinyl-BrCA (ROI 10)	1	0.0	0.0	0.0	0.0	0.0	0.0	0.6	3.0	4.7	9.5	11.2	11.2
	2	0.0	0.0	0.0	0.0	0.0	0.0	1.7	1.8	5.5	8.3	8.9	2.8
	Mean	**0.0**	**0.0**	**0.0**	**0.0**	**0.0**	**0.0**	**1.2**	**2.4**	**5.1**	**8.9**	**10.0**	**7.0**
BrCA-isomer 2 (ROI 11)	1	0.0	0.0	0.0	0.0	0.0	0.0	0.4	1.4	7.6	9.7	10.1	0.0
	2	0.0	0.0	0.0	0.0	0.0	0.0	1.7	3.2	3.9	10.1	8.6	0.0
	Mean	**0.0**	**0.0**	**0.0**	**0.0**	**0.0**	**0.0**	**1.1**	**2.3**	**5.7**	**9.9**	**9.4**	**0.0**

ROI = region of interest in chromatogram

B. METHOD VALIDATION

In pre-tests it was shown that α-R-isomer of deltamethrin was stable in acetone over a period of 96 hrs. It was also shown that deltamethrin and α-R-isomer of deltamethrin were not stable in mixtures of deionized water and acetonitrile (80/20, v/v) under neutral conditions (pH 7) but in mixtures of deionized water and acetonitrile (80/20, v/v) adjusted to acidic pH of 3 over a period of 92 hrs. Therefore, the water phase was acidified with formic acid prior to processing within this study.

In order to investigate if the metabolites are stable under acidic conditions, acidified water phase of Anglersee (DAT-50, replicate 1 and 2) was re-analyzed with the primary chromatographic method after 55 days of freezer storage. The results were compared with those obtained by first analyses, as well as with the results obtained for samples that were deep frozen without acidification. The corresponding fractions for Br_2CA, Serinyl-BrCA and the 2 isomers of BrCA were well comparable, showing that the mentioned metabolites were stable under the prevailing experimental conditions.

In addition, various tests (see Section 3.6.5.1 of report) demonstrated that Br_2CA (AE F108565; *cis*) is stable under acidic, neutral and alkaline conditions in deionized water as well as in the water phase of [redacted] and [redacted].

The extraction procedure of sediment was established in pre-tests prior to the start of this study. In order to stabilize the ratio of deltamethrin and α-R-isomer of deltamethrin, the extraction solvent acetone was acidified for the first and second extraction step. Throughout the entire study, the portions extractable with the aggressive extraction method were low (≤ 2.9%). At the last sampling date, the amount of radioactivity extracted with the aggressive extraction method was remarkably lower than the amount of radioactivity determined in the ambient extracts. This indicates that the extraction was exhaustive.

The test item was stable under the conditions of the extraction procedure and sample processing. The DAT-0 recoveries for deltamethrin were 90.1 and 93.8% of AR for the entire systems from [redacted] and [redacted] respectively. This shows that the extraction method was well suited to extract Deltamethrin from the sediment matrix.

The recovery of radioactivity after the concentration procedure was checked for samples taken at DAT-0.5 and DAT-50 and ranged from 94.0 – 108.4%.

A reversed-phase HPLC method was used for data evaluation. A good reproducibility demonstrated the suitability of the separation and quantitation. A retention time of approximately 53.2 min was determined for the test item deltamethrin. The HPLC limit of quantification (LOQ) for a single peak in the water phases and sediment extracts was ≤ 1% of AR. The recovery of radioactivity after HPLC analysis for a representative aged sample was 98.6% indicating that no radioactivity was lost on the HPLC column. Representative samples were analyzed with a confirmation method (normal-phase HPLC). The analysis was not performed immediately after sampling, but after a storage period of about three month, in which the water phases and sediment extracts were deep-frozen. For storage stability testing samples were re-analyzed with the primary chromatographic method, and the results of these analyses were used for comparison.
With the normal-phase HPLC method it was only possible to confirm the results for deltamethrin and α-R-isomer of deltamethrin; the metabolites could not be detected with this method. Since the radioactivity bound in metabolites would be added to deltamethrin or α-R-isomer of deltamethrin, the ratio "α-R-isomer of deltamethrin/deltamethrin" was used to compare the results with the primary chromatographic method (see Appendix 12 of report). For most samples the ratios were in a similar range.
In order to confirm the results for the polar metabolites, several HPLC-runs were performed from which all peaks were collected and applied separately onto a TLC plate. For Br_2CA and the two BrCA-isomers one radioactive spot besides the origin was visible on the TLC plates, respectively, and the results of both methods were comparable. This confirms that no major hidden peaks were present. However, the radioactivity eluted with the retention time of Semiyl-BrCA was distributed into several peaks, especially in the water phase.

C. DEGRADATION OF PARENT COMPOUND

A synopsis on biotransformation of deltamethrin in aerobic water/sediment test system is shown by Table 7.2.2.3- 6, and the results were included in the proposed pathway of degradation in water and sediment (see Figure 7.2- 1). More detailed data (expressed as percent of applied radioactivity, mean ± SD) are summarized for the [redacted] and [redacted] in Table 7.2.2.3- 10 and Table 7.2.2.3- 11.

Water phase:

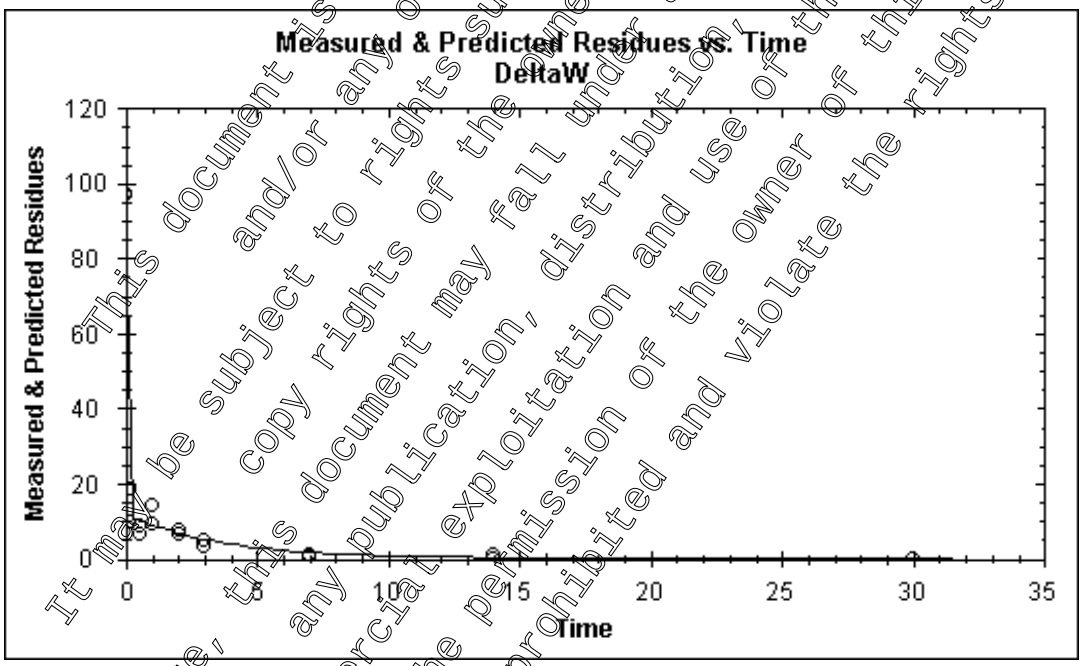
In the water phase of [redacted] and [redacted] respectively, the amounts of deltamethrin decreased from 54.1% and 57.3% of AR at day 0 to amounts < LOD from DAT-30 onwards.
Three major transformation products accounting for 2 x > 5% of AR or increasing towards the end of the study were detected and identified in the [redacted] water: α-R-isomer of deltamethrin, Br_2CA and one isomer of BrCA (BrCA-isomer 1). The α-R-isomer of deltamethrin accounted for up to 9.3% of AR (DAT-1), Br_2CA for up to 16.8% of AR (DAT-7) and BrCA-isomer 1 for up to 20.4% of AR (DAT-30).

In addition, four minor transformation products were characterized according to their retention times in HPLC-analysis. Two of them were identified as Serinyl-BrCA and BrCA-isomer 2 and accounted for up to 7.0 and 2.6% of AR (DAT-50), respectively. Two minor transformation products were characterized according to their retention times (ROI 4 and ROI 5) and accounted for maximum amounts of 0.4 (DAT-3) and 0.6% of AR (DAT-3), respectively.

In the [redacted] water, five major transformation products were detected and identified: α-R-isomer of deltamethrin, Br_2CA, Serinyl-BrCA and two isomers of BrCA (BrCA-isomer 1 and BrCA-isomer 2). α-R-isomer of deltamethrin accounted for up to 11.6% of AR (DAT-1), Br_2CA for up to 32.2% of AR (DAT-7), Serinyl-BrCA for up to 7.8% of AR (DAT-73), BrCA-isomer 1 for up to 17.3% of AR (DAT-50) and BrCA-isomer 2 was found with a maximum amount of 7.7% of AR (DAT-50). The minor unidentified transformation products ROI 4 and ROI 5 accounted for maximum amounts of 0.2% and 0.8% of AR (DAT-3), respectively.
The maximum amount of the non-characterized radioactivity in the water phases was 4.2% of AR (DAT-30, [redacted]). It contains various minor transformation products as well as the diffuse radioactivity which was not assigned to individual peaks.

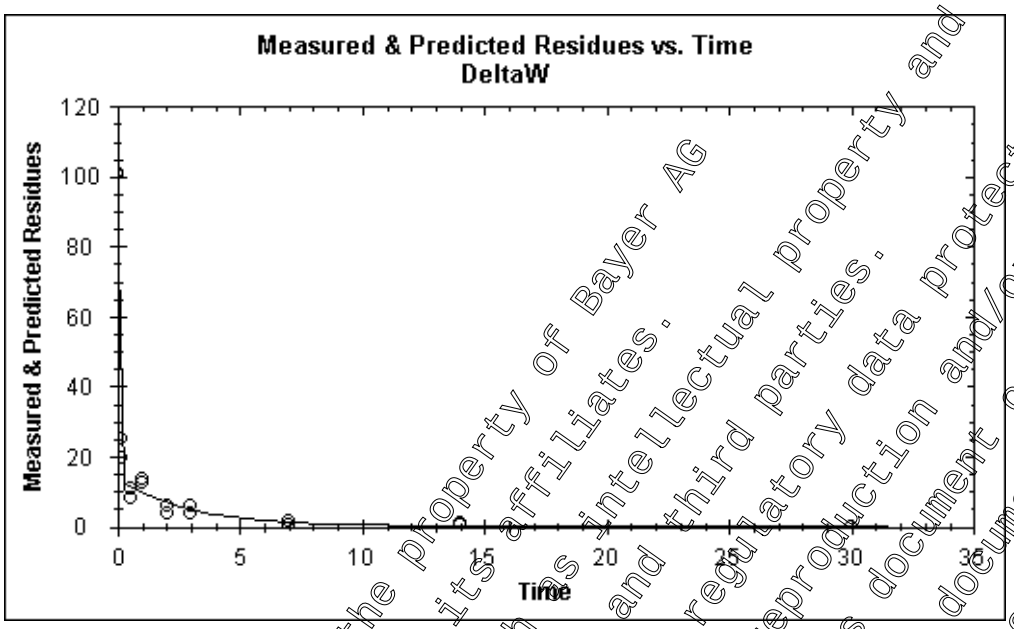
Deltamethrin was eliminated from the supernatant water via translocation into the sediment as well as via degradation (for a summary of DT_{50} and DT_{90} values of deltamethrin in the supernatant water see Table 7.2.2.3- 4. In the following just the best fit dissipation kinetics graphs and their outcome were shown.

In case of [redacted] FOMC was better than SFO, so DFOP and HS were additionally evaluated. DFOP was overall best-fit (time expressed as days after treatment):



Persistence endpoint:	Modelling endpoint:
DFOP DegT_{50} = 0.03 days DFOP DegT_{90} = 0.64 days	within measured DT_{90}, so DT_{50} = DFOP DT_{90}/3.32 = 0.2 days

In case of [redacted] FOMC was better than SFO, so DFOP and HS were additionally evaluated. HS was overall best-fit (time expressed as days after treatment):



Persistence endpoint:	Modelling endpoint:
HS $DegT_{50}$ = 0.06 days	within measured DT_{90}
HS $DegT_{90}$ = 0.84 days	so DT_{50} = HS DT_{90}/3.32 = 0.3 days

Sediment phase:

In the sediment phase of [redacted], the amounts of deltamethrin increased from 36.0% of AR at day 0 to a maximum of 57.3% at DAT-0.5 and declined then to 4.0% of AR towards the end of the study. In the [redacted] sediments the amounts of deltamethrin accounted for 36.5% of AR at day 0, increased to 54.6% of AR at DAT-0.5 and declined to 1.0% of AR towards the end of the study.

In the sediment extracts of [redacted] α-R-isomer of deltamethrin, Br_2CA and BrCA-isomer 1 were found as major transformation products and accounted for up to 20.5 (DAT-2), 27.0 (DAT-7) and 12.0% of AR (DAT-30), respectively. Serinyl-BrCA and BrCA-isomer 2 which were identified in the water phases of samples applied with the ten-fold application rate were detected with maximum amounts of 4.8 (DAT-73) and 1.8% of AR (DAT-30), respectively. Furthermore, two unidentified transformation products were characterized according to their retention times (ROI 4 and ROI 5). Both of them accounted for up to 3.7% of AR.

In the sediment extracts of [redacted] α-R-isomer of deltamethrin was detected as a major transformation product and accounted for up to 24.8% of AR (DAT-1). Furthermore, several minor transformation products were detected. Br_2CA accounted for up to 4.1% of AR (DAT-14), Serinyl-BrCA for up to 2.2% of AR (DAT-73), BrCA-isomer 1 for up to 4.6% of AR (DAT-30) and BrCA-isomer 2 was found with maximum amounts of 2.2% of AR (DAT-50, DAT-73). The unidentified minor transformation products ROI 4 and ROI 5 were characterized according to their retention times and accounted for maximum amounts of 5.2% of AR (DAT-7) and 5.8% of AR (DAT-7), respectively.

The maximum amount of the non-characterized radioactivity in the sediment extracts was 5.8% of AR (DAT-3[redacted]). It contains various minor transformation products as well as the diffuse radioactivity which was not assigned to individual peaks.

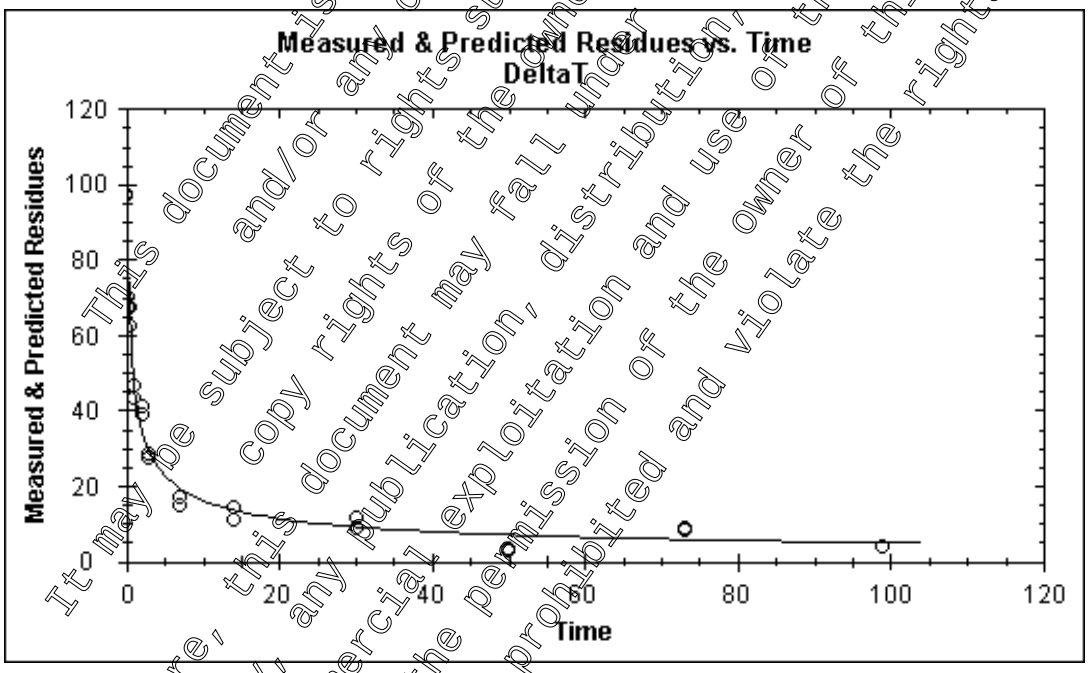
The bound and thus non-extractable residues (NER) in test systems from [redacted] accounted for 1.0% of the applied radioactivity at day 0 and increased to 36.8% of AR until DAT-73 (before slightly decreasing to 34.5% of AR at DAT-99). The maximum amount of bound residues (36.8% of AR) was detected on DAT-73. For [redacted] water/sediment system, the amount of bound residues was 0.5% of the applied radioactivity at day 0 and increased to 33.4% towards the end of the study (DAT-99).

The bound residues were further characterized into humic acids, fulvic acids and insoluble humins for representative samples. For the test system from [redacted] most of the radioactivity was found in the humic acid fraction (17.4% of AR) while similar amounts were associated with the fulvic acids (9.6% of AR) and the insoluble humins (7.9% of AR). For the [redacted] test system, a different pattern was observed. The major part of radioactivity (17.4% of AR) was detected in the fulvic acid fraction whereas only 4.7% of AR where observed in the humic acid fraction. In the humin fraction, 12.0% of AR was found.

Total test system:

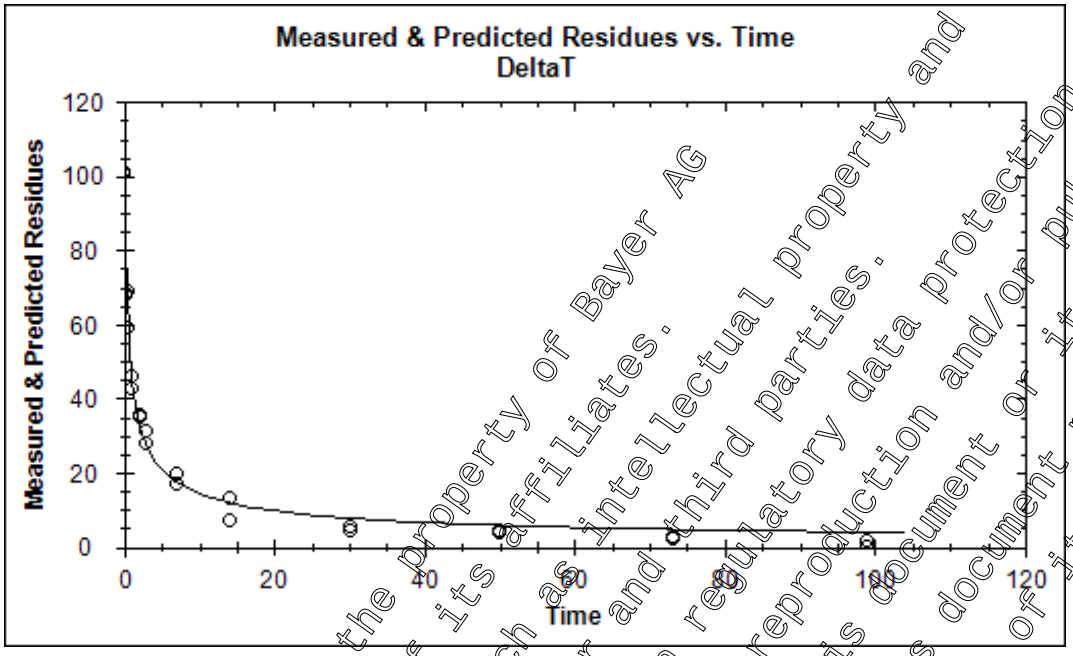
Table 7.2.2.3- 12 and Table 7.2.2.3- 13 show the content of deltamethrin and its transformation products in the total water/sediment test systems. The elimination of deltamethrin from total water/sediment body occurred via degradation (for respective DT_{50} and DT_{90} values of deltamethrin see Table 7.2.2.3- 5). In the following just the best fit dissipation kinetics graphs and their outcome were shown.

In case of [redacted] FOMC was better than SFO, so DFOP and HS were additionally evaluated. FOMC was overall best-fit (time expressed as days after treatment):



Persistence endpoint:	Modelling endpoint:
FOMC $DegT_{50}$ = 1.0 days FOMC $DegT_{90}$ = 28.8 days	within measured DT_{90}, so DT_{50} = FOMC DT_{90}/3.32 = 8.7 days

In case of [redacted] FOMC was better than SFO, so DFOP and HS were additionally evaluated. FOMC was overall best-fit (time expressed as days after treatment):



Persistence endpoint:	Modelling endpoint:
FOMC DegT$_{50}$ = 0.9 days FOMC DegT$_{90}$ = 20.6 days	within measured DT$_{90}$, so DT$_{50}$ = FOMC DT$_{90}$/3.32 = 6.2 days

III. CONCLUSIONS

The dissipation of deltamethrin from the supernatant water phase was characterized by translocation into the sediment as well as by degradation. This was best described using the DFOP kinetic model with DT$_{50}$ and DT$_{90}$ values of 0.03 and 0.64 days for [redacted] and using the HS kinetic model with DT$_{50}$ and DT$_{90}$ values of 0.06 and 0.84 days for [redacted] respectively. The corresponding modeling endpoints were either determined using the DFOP kinetic model [redacted] resulting in a DT$_{50}$ value of 0.2 days, or the HS kinetic model, [redacted] with a DT$_{50}$ value of 0.3 days.

In both entire water/sediment systems, deltamethrin was degraded well which was best described using the FOMC kinetic model. The estimated DT$_{50}$ and DT$_{90}$ values were 1.0 and 28.8 days for [redacted] and 0.9 and 20.6 days for [redacted] respectively. The corresponding modeling endpoints were determined with DT$_{50}$ values of 8.7 days for [redacted] and 6.2 days for [redacted], respectively.

Altogether in the water/sediment systems tested five “major” transformation products were detected. They were identified as cis-isomer of deltamethrin, Br$_2$CA (AE F108565; *cis*), Serinyl-BrCA, BrCA-isomer 1 and BrCA-isomer 2.
Along with degradation significant mineralization of deltamethrin to $^{14}CO_2$ (max. 39.1 %) and formation of bound residues (NER, max. 36.8 %) occurred in the viable aerobic water/sediment systems.

From this study it is concluded that deltamethrin and its residues have no potential for accumulation in the environment. The outcome is included in the summary of the degradation rates of deltamethrin and its major degradation products in soil in the laboratory given in section CA 7.2.

Report:	**KCA 7.2.2.3 /05; [redacted]; 2013**
Title:	Kinetic Modelling Analysis of Deltamethrin from a Water/ Sediment Study
Report No:	VC/11/015A
Document No:	M-461952-01-1
Guidelines:	- EU Council Directive 91/414/EEC, as amended by Commission Directive 95/36/EC of July 1995, Section 5, Point 7 and Commission Regulation (EC) No 1107/2009 of 21 October 2009 - FOCUS kinetics (2006) [1]
GLP:	No (modelling calculation)

EXECUTIVE SUMMARY

The aim of this evaluation was to conduct a kinetic modelling analysis of the data from a water/ sediment degradation study with deltamethrin ([redacted] 2012; report M-434820-01-1) in order to derive DT_{50} values for use as trigger and modelling endpoints.

For the determination of DT_{50} values for deltamethrin, all datasets were evaluated according to FOCUS Kinetics guidance (2006)[1] using the water/sediment Level P-I flowcharts for trigger or modelling endpoints. The alpha-R isomer of deltamethrin in the total system was evaluated using the Level M-I flowchart.

Table 7.2.2.3- 14 summarises the resulting optimised modelling endpoint DT_{50} values, Table 7.2.2.3-15 summarises the resulting optimised trigger endpoints DT_{50} values for deltamethrin.

Table 7.2.2.3- 16 summarises the resulting optimised total system modelling endpoint DT_{50} values for alpha-R isomer of deltamethrin, a primary degradate of the parent compound.

Table 7.2.2.3- 14: SFO DT_{50} values for deltamethrin for use as modelling endpoints

Water/ sediment system	SFO DT_{50} (days)	Comment (kinetic determination of DT_{50})
[redacted] – water phase	0.19	DFOP, DT_{90} 0.64/3.32
[redacted] – water phase	0.25	HS, DT_{90} 0.84/3.32
Geomean	**0.22**	
[redacted] – total system	8.7	FOMC, DT_{90} 28.8/3.32
[redacted] – total system	6.2	FOMC, DT_{90} 20.6/3.32
Geomean	**7.3**	

Table 7.2.2.3- 15: DT_{50} values for deltamethrin for use as trigger endpoints

Water/ sediment system	DT_{50} (days)	DT_{90} (days)	Best-fit kinetic
[redacted] – water phase	0.03	0.64	DFOP
[redacted] – water phase	0.06	0.84	HS
Geomean	**0.04**		
[redacted] – total system	1.0	28.8	FOMC
[redacted] – total system	0.88	20.6	FOMC
Geomean	**0.95**		

Table 7.2.2.3- 16: DT_{50} values for alpha-R-deltamethrin for use as modelling endpoints

Water/ sediment system	SFO DT_{50} (days)	Comment (kinetic, determination of DT_{50})
[redacted] – total system	63.1	HS, DT_{90} 210/3.32
[redacted] – total system	18.3	DFOP, DT_{90} 60.8/3.32
Geomean	**34.0**	

I. METHODS

Laboratory degradation data for deltamethrin and its alpha-R isomer (Error! Reference source not found. et al. 2012, report M-434820-01-1) were evaluated against the FOCUS Kinetics flowcharts[1] for the determination of trigger and modelling endpoints.

The chemical structure and names of test items are shown in section 2.1 of report; Table 7.2.2.3- 7 shows all the physico-chemical properties of the test systems. The used data on degradation used for the modelling calculations are shown in the following tables.

Table 7.2.2.3- 17: Biotransformation of deltamethrin in [redacted] under aerobic conditions at 20 °C in the dark, expressed as % of applied radioactivity

Compound / Source	Rep	DAT (days)											
		0	0.125	0.50	1	2	3	7	14	30	50	73	99
Deltamethrin	1	63.5	9.8	6.4	14.4	6.7	4.9	0.9	1.3	n.d.	n.d.	n.d.	n.d.
Water	2	44.7	18.8	8.6	9.5	7.6	3.1	0.4	n.d.	n.d.	n.d.	n.d.	n.d.
	Mean	**54.1**	**14.3**	**7.5**	**12.0**	**7.1**	**4.0**	**0.7**	**0.7**	**0.0**	**0.0**	**0.0**	**0.0**
Deltamethrin	1	27.2	57.5	56.2	29.1	34.4	22.6	13.7	9.9	8.6	2.8	9.0	4.1
Sediment	2	44.7	51.0	58.5	37.1	31.0	25.3	16.3	14.2	11.5	3.2	8.3	3.9
	Mean	**36.0**	**54.3**	**57.3**	**33.1**	**32.7**	**23.9**	**15.0**	**12.1**	**10.1**	**3.0**	**8.6**	**4.0**
Deltamethrin	1	90.7	67.2	62.6	43.5	41.0	27.5	14.7	11.2	8.6	2.8	9.0	4.1
Total system	2	89.5	69.9	67.1	46.5	38.6	28.3	16.7	14.2	11.5	3.2	8.3	3.9
	Mean	**90.1**	**68.6**	**64.9**	**45.0**	**39.8**	**27.9**	**15.7**	**12.7**	**10.1**	**3.0**	**8.6**	**4.0**
α-R-isomer of Deltamethrin	1	2.3	2.9	2.9	11.0	5.6	4.5	n.d.	0.7	n.d.	n.d.	n.d.	n.d.
Water	2	0.7	3.3	2.2	7.6	6.2	2.5	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	Mean	**1.5**	**3.1**	**2.6**	**9.3**	**5.9**	**3.5**	**0.0**	**0.3**	**0.0**	**0.0**	**0.0**	**0.0**
α-R-isomer of Deltamethrin	1	n.d.	7.9	14.4	14.9	24.2	20.6	8.5	6.8	6.2	2.6	11.7	4.0
Sediment	2	n.d.	3.9	8.6	14.4	16.9	16.5	9.7	10.2	9.7	3.9	8.2	3.5
	Mean	**0.0**	**5.9**	**11.5**	**14.6**	**20.5**	**18.6**	**9.1**	**8.5**	**7.9**	**3.2**	**9.9**	**3.8**
Deltamethrin		2.3	10.7	17.3	26.0	29.8	25.1	8.5	7.5	6.2	2.6	n.d	n.d.
Total system	2	0.7	7.2	10.8	22.0	23.1	19.0	9.7	10.2	9.7	3.9	n.d.	n.d.
	Mean	**1.5**	**8.9**	**14.0**	**24.0**	**26.5**	**22.0**	**9.1**	**8.9**	**7.9**	**3.2**	**0.0**	**0.0**

n.d. non-detect, LOQ of 0.1%

Table 7.2.2.3- 18: Biotransformation of deltamethrin in [redacted] under aerobic conditions at 20 °C in the dark, expressed as % of applied radioactivity

Compound Source	Rep	DAT (days)											
		0	**0.125**	**0.50**	**1**	**2**	**3**	**7**	**14**	**30**	**50**	**73**	**99**
Deltamethrin	1	63.4	19.8	10.6	12.8	5.8	3.5	1.5	1.1	n.d.	n.d.	n.d.	n.d.
Water	2	51.2	25.1	8.0	13.5	3.4	5.8	0.6	0.5	n.d.	n.d.	n.d.	n.d.
	Mean	**29.4**	**48.1**	**48.4**	**30.2**	**29.3**	**27.7**	**15.1**	**12.0**	**5.4**	**4.6**	**3.0**	**1.9**
Deltamethrin	1	43.6	43.3	60.8	32.6	32.1	22.1	19.2	6.4	4.6	4.0	2.4	n.d.
Sediment	2	4.3	8.9	8.6	10.7	6.7	4.5	1.0	0.4	n.d.	n.d.	n.d.	n.d.
	Mean	**2.1**	**9.6**	**3.9**	**12.6**	**5.1**	**6.2**	**0.6**	**n.d.**	**n.d.**	**n.d.**	**n.d.**	**n.d.**
Deltamethrin	1	92.8	67.9	59.1	42.9	35.1	31.2	16.7	13.1	5.4	4.6	3.0	1.9
Total system	2	94.8	68.4	68.8	46.1	35.6	28.0	19.8	7.0	4.6	4.0	2.4	n.d.
	Mean	**93.8**	**68.1**	**63.9**	**44.5**	**35.3**	**29.6**	**18.2**	**10.0**	**5.0**	**4.3**	**2.7**	**1.0**
α-R-isomer of Deltamethrin	1	n.d.	11.7	21.2	25.6	23.0	21.5	14.0	8.8	6.0	5.3	4.8	2.7
Water	2	n.d.	12.0	18.8	24.1	23.4	20.8	11.3	6.1	4.3	3.7	3.2	n.d.
	Mean	**63.4**	**19.8**	**10.6**	**12.8**	**5.8**	**3.5**	**1.5**	**1.1**	**n.d.**	**n.d.**	**n.d.**	**n.d.**
α-R-isomer of Deltamethrin	1	51.2	25.1	8.0	13.5	3.4	5.8	0.6	0.5	n.d.	n.d.	n.d.	n.d.
Sediment	2	29.4	48.1	48.4	30.2	29.3	27.7	15.1	12.0	5.4	4.6	3.0	1.9
	Mean	**43.6**	**43.3**	**60.8**	**32.6**	**32.1**	**22.1**	**19.2**	**6.4**	**4.6**	**4.0**	**2.4**	**n.d.**
Deltamethrin	1	4.3	20.6	29.8	36.3	29.7	25.0	15.0	9.2	6.0	5.3	4.8	2.7
Total system	2	2.1	21.7	23.1	36.7	28.5	27.0	11.9	6.1	4.3	3.7	3.2	n.d.
	Mean	**3.2**	**21.1**	**26.3**	**36.5**	**29.1**	**26.0**	**13.4**	**7.7**	**5.2**	**4.5**	**4.0**	**1.4**

n.d. non-detect, <LOQ of 0.1%

Modelling strategy for data processing, optimisation model and statistics:

The residue data summarised before was used in the evaluations without further processing. For the kinetic evaluations to derive DT_{50} values for use as trigger or modelling endpoints, the recovered time zero values were used for deltamethrin in the water phase and total system. During the kinetic evaluations, residue data for the first timepoint <LOQ (n.d., non-detect) were set to ½ LOQ of 0.05%. Subsequent <LOQ data were not used in the kinetic evaluations.

Following the recommended procedure for determining modelling endpoints acc. to FOCUS 2006, all datasets were initially evaluated using SFO kinetics with free optimisation of parameters. Where datasets were statistically and/or visually unacceptable, further evaluation with FOMC, DFOP and HS kinetics were applied. A comparison between the models was made and the best-fit kinetic model was selected.

Following the recommended procedure for determining persistence endpoints acc. to FOCUS 2006, all datasets were initially evaluated using SFO and FOMC kinetics with free optimisation of parameters. Where datasets were statistically and/or visually unacceptable, further evaluation DFOP and HS kinetics were applied. A comparison between the models was made and the best-fit kinetic model was selected. The kinetic evaluations were performed according to the respective decision flowchart for the determination of level P-I parent endpoints for use in modelling (FOCUS, 2006; Figure 10-2, p. 198) and as trigger endpoints (FOCUS, 2006; Figure 10-1, p. 197). The sampling times and residue data (see tables above) were entered into KinGUI (Figure 1 of report) and optimisations carried out for SFO (Figure 3 of report), FOMC (Figure 4 of report), DFOP (Figure 5 of report) or HS (Figure 6 of report) kinetics.

The alpha-R isomer of deltamethrin in the total system was evaluated using the Level M-I flowchart (FOCUS, 2006; Figure 10-9, p. 227) and the KinGUI scheme in Figure 2 of report.

II. RESULTS

Deltamethrin:

Optimisations using SFO kinetics showed both visually and statistically unacceptable fits to the data with Table 7.2.2.3- 19 summarising the calculated DT_{50} values for deltamethrin.

Table 7.2.2.3- 19: Deltamethrin parameter optimisation results (SFO) all datasets – free optimisation

Water/ sediment system	DT_{50} (days)	DT_{90} (days)	Min Chi^2 error (%)	t-test (-)	Visual assessment
[redacted] – water phase	0.05	0.15	27.4	1.03E-05	Poor
[redacted] – total system	1.8	6.0	21.3	1.04E-05	Poor
[redacted] – water phase	0.06	0.19	26.6	0.64E-05	Poor
[redacted] – total system	1.7	5.6	22.2	1.61E-05	Poor

Optimisations using FOMC kinetics showed both visually and statistically acceptable fits to the data with Table 7.2.2.3- 20 summarising the calculated DT_{50} values for deltamethrin.

Table 7.2.2.3- 20: Deltamethrin parameter optimisation results (FOMC) all datasets – free optimisation

Water/ sediment system	DT_{50} (days)	DT_{90} (days)	Min Chi^2 error (%)	t-test (-)	Visual assessment
[redacted] – water phase	0.01	0.41	12.1		Acceptable
[redacted] – total system	1.0	28.8	11.3	-	Very good
[redacted] – water phase	0.02	0.63	10.0	-	Acceptable
[redacted] – total system	0.88	20.6	12.2	-	Acceptable

Optimisations using DFOP kinetics showed both visually and statistically acceptable fits to the data with Table 7.2.2.3- 21 summarising the calculated DT_{50} values for deltamethrin.

Table 7.2.2.3- 21: Deltamethrin parameter optimisation results (DFOP) all datasets – free optimisation

Water/ sediment system	DT_{50} (days)	DT_{90} (days)	Min Chi^2 error (%)	t-test * (-)	Visual assessment
[redacted] – water phase	0.03	0.64	8.3	0.0100	Very good
[redacted] – total system	1.3	38.2	14.8	0.0582	Very good
[redacted] – water phase	0.05	0.84	8.0	0.00147	Excellent
[redacted] – total system	0.90	8.8	12.5	0.0127	Poor

* worst-case of k_1 and k_2 results

Optimisations using HS kinetics showed both visually and statistically acceptable fits to the data with Table 7.2.2.3- 22 summarising the calculated DT_{50} values for deltamethrin.

Table 7.2.2.3- 22: Deltamethrin parameter optimisation results (HS) all datasets – free optimisation

Water/ sediment system	DT_{50} (days)	DT_{90} (days)	Min Chi^2 error (%)	t-test * (-)	Visual assessment
[redacted] – water phase	0.05	0.64	8.3	0.00995	Very good
[redacted] – total system	1.6	42.1	16.6	0.0794	Very good
[redacted] – water phase	0.06	0.84	8.0	0.00219	Poor
[redacted] – total system	0.92	15.0	15.1	0.00604	Good

* worst-case of k_1 and k_2 results

Table 7.2.2.3- 14 summarises the resulting optimised modelling endpoint DT_{50} values, Table 7.2.2.3-15 summarises the resulting optimised trigger endpoints DT_{50} values for deltamethrin.

Alpha-R isomer of Deltamethrin:

According to the respective flowchart, FOMC was chosen as the best-fit kinetic for deltamethrin along with SFO kinetics for the alpha-R isomer of deltamethrin. Optimisations using FOMC/SFO kinetics showed both visually and statistically unacceptable fits to the data with Table 7.2.2.3- 23 summarising the results.

Table 7.2.2.3- 23: Deltamethrin parameter optimisation results (HS) all datasets – free optimisation

Water/ sediment system	DT_{50} (days)	DT_{90} (days)	Min Chi^2 error (%)	t-test (-)	Visual assessment
[redacted] – total system	3.3	10.9	22.9	0.000926	Poor
[redacted] – total system	2.6	8.8	18.3	8.55E-06	Poor

Metabolite dissipation fits (decline from maximum) were therefore evaluated according to the Level M-I flowchart. HS and DFOP kinetics were determined to be the best-fit for the two datasets, with the optimisation results summarised in Table 7.2.2.3- 24.

Table 7.2.2.3- 24: Level M-I total system metabolite decline DT_{50} parameter optimisation results for the alpha-R isomer of deltamethrin

Water/ sediment system	Best-fit kinetic	DT_{50} (days)	DT_{90} (days)	Min Chi^2 error (%)	t-test (-)	Visual assessment
[redacted] – total system	HS	3.3	210	15.9	0.1505	Acceptable
[redacted] – total system	DFOP	4.0	60.8	4.0	0.00773	Excellent

SFO modelling endpoint DT_{50} values were derived for the two systems. Table 7.2.2.3- 16 summarises the resulting optimised total system modelling endpoint DT_{50} values for alpha-R isomer of deltamethrin.

III. CONCLUSIONS

Kinetic modelling analysis of datasets from a water/ sediment degradation study for deltamethrin showed good model fits when determining trigger and modelling endpoints. The calculated SFO DT_{50} values can be used for environmental exposure assessments.

Report:	**KCA 7.2.2.3 /06; [redacted]; 2013**
Title:	Kinetic modelling analysis of deltamethrin from two water/sediment studies
Report No:	VC/11/015B
Document No:	M-462042-01-1
Guidelines:	- EU Council Directive 91/414/EEC, as amended by Commission Directive 95/36/EC of July 1995, Section 5, Point 7 and Commission Regulation (EC) No 1107/2009 of 21 October 2009 - FOCUS kinetics (2006) [1]
GLP:	No (modelling calculation)

EXECUTIVE SUMMARY

The aim of this evaluation was to conduct a kinetic modelling analysis of the data from two water/ sediment degradation studies with deltamethrin (**Error! Reference source not found.** 1993, report M-131938-01-1 and **Error! Reference source not found.** et al. 2012, report M-434820-01-1) in order to derive DT_{50} values for use as trigger and modelling endpoints. In the first study separate analysis of deltamethrin and the alpha-R isomer of deltamethrin was conducted for some sediment samples, only. Therefore a separate kinetic analysis of both compounds was not possible with the data of this study. As a consequence, all kinetic evaluations were performed using the sum of deltamethrin and the alpha-R isomer of deltamethrin in each phase (water and total system).

For the determination of DT_{50} values for the sum of deltamethrin and the alpha-R isomer of deltamethrin all datasets were evaluated according to FOCUS Kinetics guidance (2006)[1] using the water/sediment Level P-I flowcharts for trigger or modelling endpoints. The metabolite Br_2CA in the total system was evaluated using the Level M-I flowchart.

Table 7.2.2.3- 25 summarises the optimised modelling endpoint DT_{50} values for the sum of deltamethrin and the alpha-R isomer of deltamethrin. In FOCUS$_{sw}$ evaluations a total system DT_{50} value of 52.2 days can be used as a conservative approach for the water phase degradation along with a default DT_{50} value of 1000 days for the sediment phase degradation.

Table 7.2.2.3- 26 summarises the calculated water phase and total system DT_{50} values for the sum of deltamethrin and the alpha-R isomer of deltamethrin suitable for use as trigger endpoints.

Table 7.2.2.3- 27 summarises the optimised total system modelling endpoint DT_{50} values for Br_2CA.

Table 7.2.2.3- 25: SFO DT_{50} values for the sum of deltamethrin and the alpha-R isomer of deltamethrin for use as modelling endpoints

Water/ sediment system	SFO DT_{50} (days)	Comment (kinetics, determination of DT_{50})
[redacted] – water phase	0.78	HS, DT_{90} 2.6/3.32
[redacted] – water phase	0.85	HS, DT_{90} 2.8/3.32
[redacted] – water phase	0.86	HS, DT_{90} 2.8/3.32
[redacted] – water phase	0.09	HS, DT_{90} 0.29/3.32
Geomean	**0.48**	
[redacted] – total system	72.9	HS, slow-phase k_2 (0.009503)
[redacted] – total system	11.9	DFOP, DT_{90} 39.5/3.32
[redacted] – total system	61.2	HS, slow-phase k_2 (0.011322)
[redacted] – total system	140	HS, slow-phase k_2 (0.004968)
Geomean	**52.2**	

Table 7.2.2.3- 26: SFO DT_{50} values for the sum of deltamethrin and the alpha-R isomer of deltamethrin for use as trigger endpoints

Water/ sediment system	DT_{50} (days)	DT_{90} (days)	Best-fit kinetics
[redacted] – water phase	0.05	2.6	HS
[redacted] – water phase	0.07	2.9	HS
[redacted] – water phase	0.09	2.8	HS
[redacted] – water phase	0.09	0.29	HS
Geomean	**0.07**		
[redacted] – total system	3.9	101	HS
[redacted] – total system	3.8	39.5	DFOP
[redacted] – total system	18.9	181	HS
[redacted] – total system	109	433	HS
Geomean	**15.8**		

Table 7.2.2.3- 27: Total system SFO DT_{50} values for Br_2CA for use as modelling endpoints

Water/ sediment system	SFO DT_{50} (days)	ffm (-)	Comment (kinetics, determination of DT_{50})
[redacted] – total system	9.3	0.92	SFO
[redacted] – total system	12.2	0.64	SFO
Geomean	**10.7**		
Average	-	**0.78**	

I. METHODS

Laboratory degradation data of two water/sediment studies (Error! Reference source not found. 1993, report M-131938-01-1 and [redacted] 2012, report M-434820-01-1) were evaluated in order to derive DT_{50} values for use in subsequent exposure assessments. All kinetic evaluations were performed using the sum of deltamethrin and the alpha-R isomer of deltamethrin in each phase (water and total system). The respective residue data were evaluated against the FOCUS Kinetics flowcharts [1] for the determination of trigger and modelling endpoints.

The chemical structure and names of test items are shown in section 2.1 of report; Table 1 of report summarizes the physico-chemical properties of the test systems evaluated.

The data on degradation used for the modelling calculations are shown in the following tables (Table 7.2.2.3- 28 to Table 7.2.2.3- 31).

Table 7.2.2.3- 28: Biotransformation of deltamethrin in the [redacted] system under aerobic conditions (values in % of applied radioactivity)

Compound Source	Rep	DAT (days)											
		0	0.125	0.50	1	2	3	7	14	30	50	73	99
Deltamethrin Water	1	63.5	9.8	6.4	14.4	6.7	4.9	0.9	1.3	n.d.	n.d.	n.d.	n.d.
	2	44.7	18.8	8.6	9.5	7.6	3.1	0.4	n.d.	n.d.	n.d.	n.d.	n.d.
	Mean	**54.1**	**14.3**	**7.5**	**12.0**	**7.1**	**4.0**	**0.7**	**0.7**	**0.0**	**0.0**	**0.0**	**0.0**
Deltamethrin Sediment	1	27.2	57.5	56.2	29.1	34.4	22.6	13.7	9.9	8.6	2.8	9.0	4.1
	2	44.7	51.1	58.5	37.1	31.0	25.3	16.3	14.2	11.5	3.2	8.3	3.9
	Mean	**36.0**	**54.3**	**57.3**	**33.1**	**32.7**	**23.9**	**15.0**	**12.1**	**10.1**	**3.0**	**8.6**	**4.0**
Deltamethrin Total system	1	90.7	67.2	62.6	43.5	41.0	27.5	14.7	14.2	8.6	2.8	9.0	4.1
	2	89.5	69.9	67.1	46.5	38.6	28.3	16.7	14.2	11.5	3.2	8.3	3.9
	Mean	**90.1**	**68.6**	**64.9**	**45.0**	**39.8**	**27.9**	**15.7**	**12.7**	**10.1**	**3.0**	**8.6**	**4.0**
α-R-isomer of Deltamethrin Water	1	2.3	2.9	2.9	11.0	5.6	4.5	n.d.	0.7	n.d.	n.d.	n.d.	n.d.
	2	0.7	3.3	2.2	7.6	6.2	2.5	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	Mean	**1.5**	**3.1**	**2.6**	**9.3**	**5.9**	**3.5**	**0.0**	**0.3**	**0.0**	**0.0**	**0.0**	**0.0**
α-R-isomer of Deltamethrin Sediment	1	n.d.	7.9	14.4	14.9	24.2	20.6	8.5	6.8	6.2	2.6	11.7	4.0
	2	n.d.	3.9	8.6	14.4	16.9	16.5	9.7	10.2	9.7	3.9	8.2	3.5
	Mean	**0.0**	**5.9**	**11.5**	**14.6**	**20.5**	**18.6**	**9.1**	**8.5**	**7.9**	**3.2**	**9.9**	**3.8**
Deltamethrin Total system	1	2.3	10.7	17.3	26.0	29.8	25.1	8.5	7.5	6.2	2.6	n.d	n.d.
	2	0.7	7.2	10.8	22.0	23.1	19.0	9.7	10.2	9.7	3.9	n.d.	n.d.
	Mean	**1.5**	**8.9**	**14.0**	**24.0**	**26.5**	**22.0**	**9.1**	**8.9**	**7.9**	**3.2**	**0.0**	**0.0**
Br_2CA Water	1	n.d.	0.9	4.3	4.6	11.7	13.8	17.5	15.2	3.7	0.6	n.d.	n.d.
	2	n.d.	1.1	3.3	4.6	7.8	13.8	16.2	11.2	1.8	0.4	n.d.	n.d.
	Mean	**0.0**	**1.0**	**3.8**	**4.6**	**9.7**	**13.8**	**16.8**	**13.2**	**2.8**	**0.5**	**0.0**	**0.0**
Br_2CA Sediment	1	1.6	8.9	8.2	18.4	8.1	13.1	27.9	10.5	8.0	7.5	n.d.	9.3
	2	2.1	8.4	7.3	17.6	12.2	13.5	26.1	11.1	5.2	14.8	n.d.	12.0
	Mean	**1.9**	**8.6**	**7.8**	**18.0**	**10.2**	**13.3**	**27.0**	**10.8**	**6.6**	**11.1**	**0.0**	**10.7**
Br_2CA Total system	1	1.6	9.8	12.6	23.0	19.8	26.9	46.4	25.7	11.7	8.0	0.0	9.3
	2	2.1	9.5	10.6	22.2	20.0	27.4	42.3	22.3	7.0	15.3	0.0	12.0
	Mean	**1.9**	**9.7**	**11.6**	**22.6**	**19.9**	**27.1**	**43.9**	**24.0**	**9.4**	**11.6**	**0.0**	**10.7**

n.d. non-detect <LOQ of 0.1%
Time zero recovered amount: Rep 1 = 97.2%, Rep 2 = 96.9%

Values in % of applied radioactivity, sum of deltamethrin + alpha-R isomer of deltamethrin

Compound Source	Rep	DAT (days)											
		0	0.125	0.50	1	2	3	7	14	30	50	73	99
Deltamethrin+ alpha-R isomer of deltamethrin Water	1	65.9	12.7	9.3	25.4	12.2	9.4	0.9	2.0	n.d.	n.d.	n.d.	n.d.
	2	45.4	22.1	10.9	17.1	13.8	5.6	0.4	n.d.	n.d.	n.d.	n.d.	n.d.
	Mean	**55.7**	**17.4**	**10.1**	**21.3**	**13.0**	**7.5**	**0.7**	**1.0**	**n.d.**	**n.d.**	**n.d.**	**n.d.**
Deltamethrin+ alpha-R isomer of deltamethrin Sediment	1	27.2	65.3	70.6	44.0	58.6	43.2	22.2	16.7	14.8	5.4	20.7	8.1
	2	44.7	54.9	67.1	51.4	47.9	41.8	25.9	24.5	21.2	7.1	16.5	7.4
	Mean	**36.0**	**60.1**	**68.8**	**47.7**	**53.2**	**42.5**	**24.1**	**20.6**	**18.0**	**6.3**	**18.6**	**7.8**
Deltamethrin+ alpha-R isomer of deltamethrin Total system	1	93.1	78.0	79.9	69.5	70.8	52.6	23.1	18.7	14.8	5.4	9.0	4.1
	2	90.2	77.0	77.9	68.5	61.7	47.3	26.3	24.5	21.2	7.1	8.3	3.9
	Mean	**91.6**	**77.5**	**78.9**	**69.0**	**66.3**	**50.0**	**24.7**	**21.6**	**18.0**	**6.3**	**8.6**	**4.0**

Table 7.2.2.3- 29: Biotransformation of deltamethrin in the [redacted] system under aerobic conditions (values in % of applied radioactivity)

Compound Source	Rep	DAT (days)											
		0	0.125	0.50	1	2	3	7	14	30	50	73	99
Deltamethrin Water	1	63.4	19.8	10.6	12.8	5.8	3.5	1.5	1.1	n.d.	n.d.	n.d.	n.d.
	2	51.2	25.1	8.0	13.5	3.4	5.8	0.6	0.5	n.d.	n.d.	n.d.	n.d.
	Mean	**29.4**	**48.1**	**48.4**	**30.2**	**29.3**	**27.7**	**15.1**	**12.0**	**5.4**	**4.6**	**3.0**	**1.9**
Deltamethrin Sediment	1	43.6	43.3	60.8	32.6	32.1	22.1	19.2	6.4	4.6	4.0	2.4	n.d.
	2	4.3	8.9	8.6	10.7	6.7	3.5	1.0	0.4	n.d.	n.d.	n.d.	n.d.
	Mean	**2.1**	**9.6**	**3.9**	**12.6**	**5.1**	**6.2**	**0.6**	**n.d.**	**n.d.**	**n.d.**	**n.d.**	**n.d.**
Deltamethrin Total system	1	92.8	67.9	59.1	42.9	35.1	31.2	16.7	13.1	5.4	4.6	3.0	1.9
	2	94.8	68.4	68.8	46.1	35.6	28.0	19.8	7.0	4.6	4.0	2.4	n.d.
	Mean	**93.8**	**68.1**	**63.9**	**44.5**	**35.3**	**29.6**	**18.2**	**10.0**	**5.0**	**4.3**	**2.7**	**1.0**
α-R-Deltamethrin Water	1	n.d.	11.7	21.2	23.6	23.0	21.5	14.0	8.8	6.0	5.3	4.8	2.7
	2	n.d.	12.0	18.8	24.1	23.4	20.8	11.3	6.1	4.3	3.7	3.2	n.d.
	Mean	**63.4**	**19.8**	**10.6**	**12.8**	**5.8**	**3.5**	**1.5**	**1.1**	**n.d.**	**n.d.**	**n.d.**	**n.d.**
α-R-isomer of Deltamethrin Sediment	1	51.2	25.1	8.0	13.5	3.4	5.8	0.6	0.5	n.d.	n.d.	n.d.	n.d.
	2	29.4	48.1	48.4	30.2	29.3	27.7	15.1	12.0	5.4	4.6	3.0	1.9
	Mean	**43.6**	**43.3**	**60.8**	**32.6**	**32.1**	**22.1**	**19.2**	**6.4**	**4.6**	**4.0**	**2.4**	**n.d.**
Deltamethrin Total system	1	4.3	20.0	29.8	36.3	29.7	25.0	15.0	9.2	6.0	5.3	4.8	2.7
	2	2.1	21.7	22.7	30.7	28.5	27.0	11.9	6.1	4.3	3.7	3.2	n.d.
	Mean	**3.2**	**21.1**	**26.3**	**36.5**	**29.1**	**26.0**	**13.4**	**7.7**	**5.2**	**4.5**	**4.0**	**1.4**
Br_2CA Water	1	n.d.	1.6	2.7	7.9	13.8	18.8	31.1	20.1	11.2	3.4	n.d.	n.d.
	2	n.d.	1.3	3.8	7.5	15.5	22.0	33.3	28.7	15.8	2.7	n.d.	n.d.
	Mean	n.d.	n.d.	0.4	n.d.	1.4	2.0	2.4	4.3	2.3	0.5	0.7	n.d.
Br_2CA Sediment	1	n.d.	n.d.	0.4	0.7	1.4	1.8	4.4	3.9	1.8	0.5	n.d.	n.d.
	2	n.d.	1.6	2.7	7.9	13.8	18.8	31.1	20.1	11.2	3.4	n.d.	n.d.
	Mean	n.d.	1.3	3.8	7.5	15.5	22.0	33.3	28.7	15.8	2.7	n.d.	n.d.
Br_2CA Total system	1	0.0	1.6	3.1	7.9	13.2	20.9	34.5	24.4	13.5	3.9	0.7	0.0
	2	0.0	1.3	4.3	8.1	16.9	23.8	37.7	32.6	17.6	3.2	0.0	0.0
	Mean	**0.0**	**1.5**	**3.7**	**8.0**	**16.1**	**22.3**	**36.1**	**28.5**	**15.5**	**3.5**	**0.3**	**0.0**

n.d. non-detect, <LOQ of 0.1%
Time zero recovered amount: Rep 1 = 101.2% ; Rep 2 = 100.8%

Values in % of applied radioactivity, sum of deltamethrin + alpha-R isomer of deltamethrin

Compound Source	Rep	DAT (days)											
		0	0.125	0.50	1	2	3	7	14	30	50	73	99
Deltamethrin+ alpha-R isomer of deltamethrin Water	1	67.7	28.7	19.2	23.5	12.5	6.9	2.5	1.5	n.d.	n.d.	n.d.	n.d.
	2	53.3	34.7	11.9	26.1	8.6	12.0	1.2	0.5	n.d.	n.d.	n.d.	n.d.
	Mean	60.5	31.7	15.6	24.8	10.6	9.5	1.9	1.0	n.d.	n.d.	n.d.	n.d.
Deltamethrin+ alpha-R isomer of deltamethrin Sediment	1	99.4	59.8	69.6	55.7	52.2	49.2	29.1	20.8	11.4	9.9	7.9	4.7
	2	43.6	55.3	79.7	56.7	55.5	42.9	30.5	12.5	8.9	7.7	5.6	n.d.
	Mean	36.5	57.6	74.6	56.2	53.9	46.1	29.8	16.7	10.2	8.8	6.7	2.3
Deltamethrin+ alpha-R isomer of deltamethrin Total system	1	97.1	88.5	88.8	79.2	64.8	56.2	31.6	22.3	11.4	9.9	7.9	4.7
	2	96.9	90.1	91.6	82.8	64.1	54.9	31.8	13.1	8.9	7.7	5.6	n.d.
	Mean	97.0	89.3	90.2	81.0	64.4	55.6	31.7	17.7	10.2	8.8	6.7	2.3

Table 7.2.2.3- 30: Biotransformation of Deltamethrin + alpha-R isomer in [redacted] system under aerobic conditions (values in % of applied radioactivity)

Compound Source	Rep	DAT (days)									
		0	0.25	1	2	4	7	14	28	56	84
Deltamethrin+ alpha-R isomer of deltamethrin Water	1	13	12	13	9	11	6	4	na	na	na
	2	31	13	15	11	8	5	3	na	na	na
	Mean	22	12.5	14	10	9.5	5.5	3.5	na	na	na
Deltamethrin+ alpha-R isomer of deltamethrin Sediment	1	78	59	59	71	62	60	65	41	34	29
	2	46	54	78	74	73	64	54	37	40	27
	Mean	62	56.5	68.5	72.5	67.5	62	59.5	39	37	28
Deltamethrin+ alpha-R isomer of deltamethrin Total system	1	91	71	72	80	73	66	69	41	34	29
	2	77	67	93	85	81	69	57	37	40	27
	Mean	84	69	82.5	82.5	77	67.5	63	39	37	28

na not analysed, <LOQ of 1%
Time zero recovered amount: Rep 1 = 103%, Rep 2 = 98%

Table 7.2.2.3- 31: Biotransformation of Deltamethrin + alpha-R isomer in the [redacted] system under aerobic conditions (values in % of applied radioactivity)

Compound Source	Rep	DAT (days)									
		0	0.25	1	2	4	7	14	28	56	84
Deltamethrin+ alpha-R isomer of deltamethrin Water	1	24	16	5	6	3	1	5	na	na	na
	2	22	10	4	4	5	6	1	na	na	na
	Mean	23	13	4.5	5	4	3.5	3	na	na	na
Deltamethrin+ alpha-R isomer of deltamethrin Sediment	1	61	47	85	75	88	85	80	68	68	54
	2	58	58	84	84	83	78	80	72	64	52
	Mean	59.5	52.5	84.5	79.5	85.5	81.5	80	70	66	53
Deltamethrin+ alpha-R isomer of deltamethrin Total system	1	85	63	90	81	91	86	85	68	68	54
	2	80	68	88	88	88	84	81	72	64	52
	Mean	82.5	65.5	89	84.5	89.5	85	83	70	66	53

na not analysed, <LOQ of 1%
Time zero recovered amount: Rep 1 = 99%, Rep 2 = 97%

Modelling strategy for data processing, optimisation model and statistics:

For the kinetic evaluations to derive DT_{50} values for use as trigger or modelling endpoints, the recovered time zero values were used for deltamethrin in the water phase and total system. During the kinetic evaluations, residue data for the first timepoint <LOQ (n.d., non-detect) were set to ½ LOQ of 0.05%. Subsequent <LOQ data were not used in the kinetic evaluations.

Following the recommended procedure for determining modelling endpoints, (FOCUS, 2006), all datasets were initially evaluated using SFO kinetics with free optimisation of parameters. Where datasets were statistically and/or visually unacceptable, further evaluation with FOMC, DFOP and HS kinetics were applied. A comparison between the models was made and the best-fit kinetic model was selected.

Following the recommended procedure for determining persistence endpoints all datasets were initially evaluated using SFO and FOMC kinetics with free optimisation of parameters. Where datasets were statistically and/or visually unacceptable, further evaluation DFOP and HS kinetics were applied. A comparison between the models was made and the best-fit kinetic model was selected.

DT_{50} and DT_{90} values were determined for the degradation of deltamethrin. The determinations of the kinetic values followed the recommendations of FOCUS rules. These were aimed at deriving DT_{50} values for use as trigger endpoints and model input according to the FOCUS guidance document on degradation kinetics. The kinetic evaluations were performed according to the respective decision flowchart for the determination of level P-I parent endpoints for use in modelling (FOCUS, 2006; Figure 10-2, p. 198) and as trigger endpoints (FOCUS, 2006; Figure 10-1, p. 197).

The sampling times and residue data were entered into KinGUI (Figure 1 of report) and optimisations carried out for SFO, FOMC, DFOP or HS kinetics (Figures 3, 4, 5 or 6 of report).

The Br_2CA metabolite in the total system was evaluated using the Level M-I flowchart (FOCUS, 2006; Figure 10-9, p. 227) and the KinGUI scheme in Figure 2 of report.

The kinetic evaluations and the statistical calculations were conducted with KinGUI (v2.0) using iteratively re-weighted least-squares (IRLS) optimisation.

Optimisation statistics was described in section 3.4.1 of report. The model fits were evaluated using a chi-square (χ^2) error statistic and visual inspection of residual plots. The kinetic analyses and optimisations were carried out using the replicate data, however for the χ^2 analysis the predicted concentration is compared to the mean measured value.

II. RESULTS

Optimisations using SFO kinetics showed both visually and statistically unacceptable fits to the majority of data sets with Table 7.2.2.3- 32 summarising the calculated DT_{50} values for deltamethrin + alpha-R.

Table 7.2.2.3- 32: Deltamethrin + alpha-R isomer of deltamethrin parameter optimisation results (SFO) all datasets – free optimisation

Water/ sediment system	DT_{50} (days)	DT_{90} (days)	Min Chi² error (%)	t-test (-)	Visual assessment
[redacted] – water phase	0.05	0.17	39.8	0.000627	Poor
[redacted] – total system	4.8	15.8	17.5	4.36E-05	Poor
[redacted] – water phase	0.08	0.27	39.3	0.000785	Poor
[redacted] – total system	4.4	14.8	9.5	5.61E-10	Poor
[redacted] – water phase	0.08	0.28	29.9	0.000178	Poor
[redacted] – total system	41.6	138	11.0	9.59E-06	Acceptable
[redacted] – water phase	0.09	0.29	15.9	9.30E-08	Poor
[redacted] – total system	126	418	8.2	6.51E-05	Acceptable

Optimisations using FOMC kinetics showed both visually and statistically improved fits to the data with Table 7.2.2.3- 33 summarising the calculated DT_{50} values for the sum of deltamethrin and the alpha-R isomer of deltamethrin.

As FOMC showed improvement over SFO the datasets were also evaluated using DFOP and HS kinetics.

Table 7.2.2.3- 33: Deltamethrin + alpha-R isomer of deltamethrin parameter optimisation results (FOMC) all datasets – free optimisation

Water/ sediment system	DT_{50} (days)	DT_{90} (days)	Min Chi^2 error (%)	t-test (-)	Visual assessment
[redacted] – water phase	0.005	1.4	21.5	-	Poor
[redacted] – total system	3.8	70.1	11.3	-	Very good
[redacted] – water phase	0.04	2.2	16.9	-	Poor
[redacted] – total system	3.8	30.1	4.8	-	Excellent
[redacted] – water phase	0.003	1.1	10.2	-	Poor
[redacted] – total system	32.8	689.1	9.8	-	Good
[redacted] – water phase	0.01	0.42	5.3	-	Very good
[redacted] – total system	119	395.2	8.6	-	Acceptable

Optimisations using DFOP kinetics showed both visually and statistically acceptable fits to the data with Table 7.2.2.3- 34 summarising the calculated DT_{50} values for the sum of deltamethrin and the alpha-R isomer of deltamethrin. Optimisations using HS kinetics showed both visually and statistically acceptable fits to the data with Table 7.2.2.3- 35 summarising the calculated DT_{50} values for the sum of deltamethrin and the alpha-R isomer of deltamethrin.

Table 7.2.2.3- 34: Deltamethrin + alpha-R isomer of deltamethrin parameter optimisation results (DFOP) all datasets – free optimisation

Water/ sediment system	DT_{50} (days)	DT_{90} (days)	Min Chi^2 error (%)	t-test* (-)	Visual assessment
[redacted] – water phase	0.01	3.6	15.8	0.47877	Very good
[redacted] – total system	3.7	116	10.5	0.12	Very good
[redacted] – water phase	0.06	2.8	12.6	0.00128	Very good
[redacted] – total system	3.8	39.5	4.2	0.00294	Excellent
[redacted] – water phase	0.01	2.8	4.1	0.474	Excellent
[redacted] – total system	30.4	473	10.3	0.409	Good
[redacted] – water phase	0.08	0.30	2.3	0.0498	Excellent
[redacted] – total system	126	418	9.1	0.4731	Acceptable

* worst-case of k_1 and k_2 results

Table 7.2.2.3- 35: Deltamethrin + alpha-R isomer of deltamethrin parameter optimisation results (HS) all datasets – free optimisation

Water/ sediment system	DT_{50} (days)	DT_{90} (days)	Min Chi^2 error (%)	t-test* (-)	Visual assessment
[redacted] – water phase	0.05	2.6	15.8	0.00705	Very good
[redacted] – total system	3.9	101	10.2	0.043	Very good
[redacted] – water phase	0.08	2.8	12.6	0.00243	Very good
[redacted] – total system	3.6	38.5	5.8	0.00013	Very good
[redacted] – water phase	0.09	2.8	4.1	8.88E-05	Excellent
[redacted] – total system	38.9	181	10.9	0.02716	Good
[redacted] – water phase	0.09	0.29	2.3	0.0466	Excellent
[redacted] – total system	109	433	7.9	0.012273	Very good

* worst-case of k_1 and k_2 results

SFO kinetics was applied to all datasets and verified according to FOCUS acceptability criteria (minimum Chi^2 error <15%, t-test parameter significance >95% and visually acceptable). For the water phase dissipation, SFO evaluations showed poor model fits to the data. DT_{90} values were within the experimental period for all datasets and therefore conservative modelling endpoint SFO DT50 values were calculated from the best-fit (FOMC, DFOP or HS) kinetic DT90/3.32.
For the total system degradation, SFO evaluations showed poor model fits to the data. DT_{90} values were within the experimental period for the Anglersee dataset and therefore a conservative modelling endpoint SFO DT50 value was calculated from the best-fit (DFOP) kinetic DT90/3.32. For the remaining three datasets, DT_{90} values were outside of the experimental period with conservative modelling endpoint SFO DT50 values thus being derived from the HS k_2 'slow-phase' degradation rate.
Table 7.2.2.3- 25 summarises the calculated SFO DT_{50} values for the sum of deltamethrin and the alpha-R isomer of deltamethrin, suitable for use as modelling endpoints in FOCUSsw evaluations, the geometric mean total system DT_{50} value of 52.2 days can be used as a conservative approach for the water phase degradation along with a default DT50 value of 1000 days for the sediment phase degradation.

Table 7.2.2.3- 26 summarises the calculated water phase and total system DT_{50} values for the sum of deltamethrin and the alpha-R isomer of deltamethrin suitable for use as trigger endpoints.

Br_2CA metabolite of deltamethrin:

According to the flowchart, HS [redacted] and DFOP [redacted] were chosen as the best-fit kinetic for the sum of deltamethrin and the alpha-R isomer of deltamethrin along with SFO kinetics for the Br_2CA metabolite.

Optimisations using FOMC/SFO kinetics showed both visually and statistically acceptable fits to the data with Table 7.2.2.3- 36 summarising the results.

Table 7.2.2.3- 36: Level M-I total system $DegT_{50}$ parameter optimisation results for the Br_2CA metabolite of deltamethrin

Water/ sediment system	DT_{50} (days)	DT_{90} (days)	ffm (-)	Min Chi^2 error (%)	t-test (-)	Visual assessment
[redacted] – total system	9.3	30.8	0.92	26.2	0.000134	Acceptable
[redacted] – total system	12.2	40.4	0.64	11.2	3.43E-14	Excellent

Table 7.2.2.3- 27 summarises the optimised total system modelling endpoint DT_{50} values for Br_2CA.

III. CONCLUSIONS

Kinetic modelling analysis of datasets from two water/ sediment degradation studies for deltamethrin showed good model fits when determining trigger and modelling endpoints. The calculated SFO DT_{50} values can be used for environmental exposure assessments.

The results are included in the summary of the route and rate of degradation of deltamethrin and its major degradation products in water and sediment given in section CA 7.2.

Further information on the behaviour of deltamethrin in the water/sediment system was published in the literature by Meyer, et al, 2013 (for respective summary see below).

Report:	**KCA 7.2.2.3 / 07; Meyer, B.; Jones, R.; Moore, S.; Lam, C.; 2013**
Title:	Laboratory Degradation Rates of 11 Pyrethroids under Aerobic and Anaerobic Conditions
Source:	J. Agric. Food Chem. 2013, 61, 4702−4708
Document No:	M-462374-01-1
Guidelines:	None
GLP:	No, published study
Literature review classification:	b) supplementary information (EFSA Journal 2011; 9(2):2092)

EXECUTIVE SUMMARY

Degradation of 11 pyrethroids was measured over approximately 100 days in three sediment/water systems under aerobic and anaerobic conditions at 25 °C in the dark. The three California sediments represented a range of textures and organic matter. Deltamethrin was analyzed by liquid chromatography/tandem mass spectrometry using deltamethrin-phenoxy-$^{13}C_6$ as an internal standard. First-order half-lives under aerobic conditions ranged from 11.7 to 44.6 days. Under anaerobic conditions, the range was from 59.9 to 100 days.

I. MATERIAL AND METHODS

A. Material

1. Test material

Test item:	Deltamethrin
Active substance(s):	Deltamethrin; CAS 52918-63-5
Chemical state and description:	(S)-cyano(3-phenoxyphenyl)methyl (1R,3R)-3-(2,2-dibromoethenyl)-2,2-dimethylcyclopropanecarboxylate
Source of test item:	Not reported
Batch number:	Not reported
Purity:	99.4 %
Storage conditions:	Refrigerated and stored in the dark
Water solubility	Not reported

2. Soil: See Table 7.2.2.3- 37.

B. Study design and methods

1. Sampling

Sampling technique:	All sediments were sieved (2 mm) and thoroughly mixed; The time between sediment collection and dosing ranged between 2 and 8 weeks. Test systems were sampled in duplicate at seven intervals (approximately 0, 3, 7, 14, 28, 60, and 100 days post-treatment).
Sampling frequency:	5 replications

2. Measurements

pH, redox:	On day 0, DO concentrations, pH, and redox were measured: pH was between 5.6 and 8.4
Bioactivity:	Bioactivity was determined at Agvise Laboratories, Northwood, ND, by aerobic or anaerobic plate counts in representative untreated flasks at day 0 and approximately

	day 100
3. Chemical analysis	
Guideline/protocol:	None
Method:	LC-MS
Pre-treatment of samples:	For analysis of deltamethrin, a 10 mL aliquot of the filtrate was applied to a conditioned 1 g ENVI-Carb cartridge (Sigma-Aldrich, St. Louis, MO), rinsed with acetonitrile/water (3:2) and methanol, and eluted with dichloromethane (DCM). The internal standard (deltamethrin-phenoxy-$^{13}C_6$) was added to the eluate, which was concentrated to dryness and redissolved in methanol/water (9:1).
Conduction:	Prior to treatment of the test systems, a pre-incubation period (ranging from 12 to 32 days) was used to acclimate and establish the appropriate conditions (aerobic or anaerobic) as judged by dissolved oxygen (DO) and redox. Also during this period, the analytical method was validated for the specific batch of sediment.
Reference item:	Deltamethrin-phenoxy-$^{13}C_6$
Recovery:	71 – 114%; the overall mean of concurrent recoveries was 95.8% (standard deviation of 6.2%)
Limit of detection:	Ranged from 0.2-1.4 ppb
Limit of quantification:	1-8% for 50ppb

Table 7.2.2.3- 37: Description of the three California sediments

parameter	sediment 1	sediment 2	sediment 3
location			
description	sandy creek, east of San Diego	white slough (King Island)	Franks Tract State Recreation Area
county	San Diego	Contra Costa	Contra Costa
latitude	33° 01′ 54.22″ N	38° 04′ 31′ N	38° 02.885′ N
longitude	116° 37′ 49.51 W	121° 36.250′ W	121° 36.850′ W
texture[a]			
class	sand	clay	sandy clay loam
sand (%)	90.3	20.4	49.5
silt (%)	1.8	30.1	25.9
clay (%)	7.9	49.5	24.6
pH[a]			
1:1 soil/water	6.8	6.0	6.9
saturated paste	7.1	6.0	6.8
0.01 M $CaCl_2$	6.4	5.8	6.6
organic matter[a] (%)	1.0	13.7	4.7
organic carbon[a] (%)	0.6	7.4	2.7
cation-exchange capacity[a] (meq/100 g)	6.0	19.0	14.8
moisture capacity[a]			
at 0.33 bar (%)	8.4	80.4	37.2
at 15 bar (%)	3.6	53.7	19.0
bulk density[a] (g/cm^3)	1.19	0.60	0.79

[a]Determined by Agvise Laboratories, Northwood, ND.

II. RESULTS

1. Validity criteria

Recovery was within the range of 70-120 % (usual acceptance criteria).

2. Analytical findings:

The data showed a decline in residues in all of the total water/sediment systems, and the rate of decline varied among the three sediments. Degradation rates appear to follow first-order kinetics until about 50−75% of the compound has degraded, and then degradation rates slow. To provide an indication of the degradation curve, Table 7.2.2.3- 38 provides the times required for 50 and 90% of the material to degrade (in cases where this occurs within the study period) and the amount remaining at the end of the study period. Single first-order degradation rates are provided in Table 7.2.2.3- 39 along with confidence intervals for deltamethrin.

Table 7.2.2.3- 38: Characterization of the degradation curves in the aerobic and anaerobic studies

	DT_{50}[a]	DT_{90}[a]	End amount [b]	DT_{50}[a]	DT_{90}[a]	End amount [b]	DT_{50}[a]	DT_{90}[a]	End amount [b]
Aerobic									
Deltamethrin	9.8	88	8[f], 4[f]	36	d	27, 26	12	64	8[f], 14
Anaerobic									
Deltamethrin	106	d	53, 46	54	d	46, 43	60	d	28, 31

a The time to 50 and 90% degradation of the starting material was determined by the best fitting kinetic model if these points were reached during the study period.

b The duplicate values from the last time interval are reported. The last time interval was 100 days for the aerobic studies with sediments 1 and 3 and the anaerobic study with sediment 3, 103 days for the aerobic study with sediment 2, 101 days for the anaerobic study with sediment 1 (except for deltamethrin, which was 108 days), and 104 days for the anaerobic study with sediment 2.

c Test mixture 1.

d Not reached during the study period.

e Test mixture 2.

f The concentration in the sample was below the LOQ.

g The amount remaining in the samples at the end of the study at 100 days corresponded to 90% or greater degraded. The model prediction was slightly longer than the study length.

Table 7.2.2.3- 39: Summary of the degradation rates (expressed as half-lives) obtained with nonlinear regression using single first-order kinetics

	First order half-life (days)					
	Sediment 1		Sediment 2		Sediment 3	
	aerobic	anaerobic	aerobic	anaerobic	aerobic	anaerobic
Deltamethrin	11.7 (6-18)	100 (81-131)	44.6 (37-56)	68.4 (51-103)	14.4 (11-22)	59.9 (55-66)

III. CONCLUSIONS

First-order half-lives for deltamethrin under aerobic conditions ranged from 11.7 to 44.6 days. Under anaerobic conditions, the range was from 59.9 to 100 days.

These published DT_{50} results on aerobic US test systems were in good agreement with the before-mentioned data for the EU, but not worst case. Therefore, they were not included in the set of data used as input parameter for EU exposure assessments (compare section CA 7.2).

Data for anaerobic aquatics are a special US requirement but not needed for the EU.

CA 7.2.2.4 Irradiated water/sediment study

Degradation of deltamethrin in water/sediment systems under outdoor conditions were evaluated during the Annex I inclusion, and were accepted by the European Commission (SANCO/6504/VI/99-final, 17 October 2002). The following studies included in the Baseline Dossier were regarded relevant during the Annex I inclusion:

Author(s)	Year	Document No.
[redacted]	1991	M-136641-01-1
[redacted]	1989	M-124144-01-1 See KCP 9.2.4/03*
[redacted]	1985	M-113322-01-1
[redacted]	1991	M-150693-01-1 See KCP 9.2.5/03*
[redacted]	2001	M-200619-03-1

* Please refer to the baseline dossier for Deltamethrin EC 25g/L.

The dissipation DT_{50} of deltamethrin in the water column of several micro-/mesocosm and natural pond studies ranged from 1.5 to 24 hours. It was concluded that the substance will rapidly disappear from the water column with an expected half-life of about 1 day. Deltamethrin will mainly be distributed to suspended organic material, biota, and sediments. Further bioavailability is reduced.

Despite the low vapour pressure of deltamethrin (1.1×10^{-6} Pa at 20°C) volatilisation from the water surface appears to be an additional dissipation route as deltamethrin may form a microlayer film onto the water surface after spray drift (M-124144-01-1). Volatilisation from this surface microlayer can be explained by the Henry's law constant of deltamethrin of 2.1 Pa × m^3/mol at 20°C.

The dossier supporting the approval renewal of deltamethrin includes an additional mesocosm study with realistic spray exposure (**Error! Reference source not found.** et al 2005, report M-246137-01-1, see nex page) using 12 test tanks of 6 m^3 water and 1 m water depth, as representative of a small stagnant water body. It was completed after the Annex I inclusion.
Test mesocosms were treated with deltamethrin, formulated as Deltamethrin EW 015, at five different treatment levels.

In conclusion deltamethrin present in a mesocosm pond was subject to fast dissipation by biotic and/or abiotic processes. Deltamethrin decreased after all applications quickly and steadily with an average half-life in the water column of 22.4 hours, and the DT_{50} for the whole system (water plus sediment) was determined to be 31.6 hours, only. A slight increase in sediment residues was detected approximately seven weeks after application at higher test concentrations, and thereafter steadily decreased.

Report:	**KCA 7.2.2.4 /01; [redacted]; [redacted]; [redacted]; 2005**
Title:	Biological Effects and Fate of Deltamethrin EW 015 in Outdoor Mesocosm Ponds
Report No:	HBF/BT 07
Document No:	M-246137-01-1
Guidelines:	- OECD Guidance Document "Simulated Freshwater Lentic Field Tests (Outdoor Microcosms and Mesocosms)", July 2004 (Draft) - Guidance Document on Testing Procedures for Pesticides in Freshwater Microcosms (SETAC-Europe Workshop, Monks Wood, UK, July 1991) - Community-Level Aquatic System Studies – Interpretation Criteria (2002) (Proceeding from the CLASSIC Workshop)
GLP:	Yes

EXECUTIVE SUMMARY

Only the part of the study relevant to the environmental fate of deltamethrin is summarised in section 7 Fate and behaviour in the environment. The data relevant to the ecotoxicological assessment is summarised in the MCP section 10.

The distribution and degradation of deltamethrin was studied in mesocosm ponds containing natural sediment and water in Gemany for 105 days. Test mesocosms were treated with deltamethrin, formulated as Deltamethrin EW 015, at five different treatment levels. The nominal test concentrations ranged from 4.8 to 111 ng deltamethrin/L. The formulation was applied on three occasions with an interval of 7 days between each application.

Deltamethrin dissipated very rapidly from water by degradation and partitioning to sediment, with a mean DT_{50} value of 24 hours. Only two thirds of the total deltamethrin detected in pond water was dissolved in water, with the remaining third adsorbed to algae or particulate matter. The mean DT_{50} for the whole system (water plus sediment) was 32 hours.

Deltamethrin present in sediment was also subject to dissipation by biotic and/or abiotic processes. A slight increase in sediment residues was detected approximately seven weeks after application at higher test concentrations, and thereafter steadily decreased. From this study it is concluded that deltamethrin has no potential for accumulation in the aqueous environment.

I. MATERIALS AND METHODS

1. Test Item

Deltamethrin EW 015, an oil/water emulsion containing 1.64% w/w of deltamethrin

2. Test Systems

The study was carried in mesocosm ponds:
Natural water and sediment from the Nespen water reservoir in Oberbergisches Land, 80 km from the test facility were used to fill artificial ponds to a sediment level of about 15 cm. Additional local ground water and water from an uncontaminated pond near Monheim, Germany was added up to 1 m depth. The ponds were filled 7 months before application of the test item.

3. Experimental Conditions

The distribution of deltamethrin, formulated as Deltamethrin EW 015, was investigated in aquatic mesocosm containing natural sediment and water under realistic outdoor conditions. The mesocosms were installed at the Bayer CropScience [redacted] Germany. The twelve test tanks used in this study are part of system designed to establish virtually identical conditions in each tank. The tanks were covered with a layer of natural sediment. The water was composed of local

ground water and water from a nearby uncontaminated pond. Natural biological communities developed during the months before the start of the study. Each pond was 2.75 m in diameter, with a water layer of ca. 1 m in depth, a sediment layer of ca. 15 cm and contained 5940 L of water.

The test substance was applied three times during the early growing season in May 2004 at an interval of 7 days onto the water surface of nine test ponds. Each application was made with a commercial compressed air sprayer. The treatment levels were 4.8, 10.5, 23, 51 and 111 ng a.s./L per application (two replicates of 4.8 to 51 ng a.s./L, one replicate for 111 ng a.s./L). Three further tanks were used as untreated controls.

The mesocosms were investigated for a period of 14 days before and 105 days after the first treatment. Water and sediment samples were taken for biological and chemical analysis at time points up to 105 days. Further biological parameters were investigated but are not directly relevant for the evaluation of the fate and behaviour of deltamethrin in aquatic systems, and therefore are not addressed in this dossier chapter. The data relevant to the ecotoxicological assessment is summarised in the MCP section 10. The water temperature of the mesocosms ranged from 12 to 16°C in the pre-treatment phase, increasing during the summer to 23 °C. Dissolved oxygen values ranged between 8 and 26 mg/L. The pH ranged between 8 and 10.1 before and during the three treatments. Thereafter, the pH was between 9.8 and 10.3.

Table 7.2.2.4- 1: Physicochemical and biological characteristics of water and sediment of the mesocosm ponds

Origin	[redacted] **Germany**
Sediment	
Texture class (USDA)	silt loam
Sand Silt Clay	31.5 % 54.5 % 14.0 %
Organic carbon	4.2 %
Nitrogen	0.4 %
Phosphorous	820 mg/kg
Cation Exchange Capacity	11.8 Meq/100 g
Water	
pH (during experimental period)	9.9 (mean, range 8.3 - 10.4)
Hardness (mean values)	4 – 8 mg/L
Alkalinity (mean values)	3 – 7 mg/L
Conductivity (mean values)	384 – 521 µS/cm
Oxygen content	6.5 - 26.1 mg/L

4. Sampling

Water samples for residues analysis (approx. 500 - 800 mL) were collected at 0 (1 hour before and 4 hours after 1st application), 1, 2, 4, 7 (1 hour before and 4 hours after 2nd application), 8, 9, 11, 14 (1 hour before and 4 hours after 3rd application), 15, 16, 18 and 21 days after the initial application. Later timepoints were taken but not analysed as the levels of deltamethrin in water rapidly dropped below the limit of detection. On selected occasions, water samples were obtained from four depths (approx. 10 – 30, 30 – 50, 50 - 70 and 70 – 90 cm beneath water surface), to reveal the distribution of the test substance in the water column during the first 48 hours after each application. Sediment samples were collected at 0 (1 hour before 1st application), 2, 4, 7 (1 hour before 2nd application), 9, 11, 14 (1 hour before 3rd application), 16, 18, 21, 29, 35, 42, 49, 56, 63, 70, 84, 91 and 105 days after the initial application. Sediment samples were taken at two positions in each pond by means of a grab sampler. The upper 2 cm of both samples were mixed and used for analysis.

Samples were frozen and stored at < 18 °C until analysed. Analytical samples in the control mesocosms were taken before the first application and one day after each application for water samples or two days after for sediment samples.

5. Analytical Procedures

Water samples (ca. 500 and 800 mL) were diluted with 150 mL of acetonitrile + 10 mmol/L ammonium acetate, and analysed by HPLC-MS/MS using an internal standard. The limit of quantification (LOQ) was 5.0 ng a.s./L and the limit of detection (LOD) was 2.0 ng a.s./L.

The percentage of adsorbed deltamethrin in selected water samples was determined by filtering the sample and extracting the filter with acetonitrile. Acetonitrile was evaporated to dryness and the sample reconstituted in test water / acetonitrile (4/1, v/v) + 10 mmol/L ammonium acetate. The reconstituted sample and the filtered water were analysed by HPLC-MS/MS as described above.

Deltamethrin was extracted from sediment with acetonitrile / 10 mmol/L ammonium acetate (9/1, v/v) using a microwave extractor. The extract was centrifuged to remove any fine particles of sediment and analysed by HPLC-MS/MS using an internal standard. The LOQ was 0.1 µg a.s./kg dry weight sediment and the LOD was 0.03 µg a.s./kg dry weight sediment.

No deltamethrin was detected in control water or sediment above the limits of quantification.

II. RESULTS AND DISCUSSION

1. Data

For all tested concentrations the distribution of the active substance in <u>water</u> (given as ng deltamethrin equivalents/L) is shown by Table 7.2.2.4- 2, that in the <u>sediment</u> (given as µg deltamethrin equivalents/kg dry weight) by Table 7.2.2.4- 3.

The water sample results taken four hours after each application indicate that the test systems were correctly dosed, with measured concentrations on average 94.1% of nominal.

The distribution of the active substance in <u>water and sediment</u> given as % of applied amount is shown by Table 7.2.2.4- 4 for the three highest test concentrations. The residues in sediment were too low to calculate mass balances for lower test concentrations.

During the first 48 hours after each application the distribution of deltamethrin in the water column was investigated by sampling water from four different depths, on the other sampling occasions mixed samples of the whole water column were analysed. Clear stratification of deltamethrin concentrations was detected four hours after each application, when the major part of the test amount was found in the uppermost water layer. 24 hours after application deltamethrin was distributed homogeneously throughout the entire water column. Deltamethrin residues declined rapidly in the water phase after all applications, with no residues > LOQ (5 ng a.s./L) remaining by the following application days at 7 and 14 days. At selected sampling dates, the percentage of adsorbed deltamethrin in water was determined. Approximately two third of the total deltamethrin in pond water was dissolved in water, with the remaining third adsorbed to algae or particulate matter.

The test substance was detected only once, shortly after the first application, in sediment from the two lowest test concentrations (4.8 and 10.5 ng/L, LOD = 0.03 µg/kg dry weight). The results of the higher test levels (23 - 111 ng/L) show a slight increase in sediment concentrations for about 7 weeks after application resulting in up to 20% of the total applied amount in sediment, followed by a steady decline to less than 6% of the total applied amount by the end of the study at 105 days.

As the study was conducted under outdoor conditions, the influence of volatilisation into the air was not possible to evaluate.

2. Dissipation of parent compound

The mean DT_{50} value for dissipation of deltamethrin from the water phase was 22.4 hours and 31.6 hours for the entire system (water plus sediment) assuming FOMC kinetics, reported as providing the best fits. Simple first order fits of the water phase and whole systems gave DT_{50} values of 23.6 hours and 32.1 hours, respectively.

Table 7.2.2.4- 2: Distribution of the active substance in water after spray application of Deltamethrin EW 15 to mesocosm ponds and incubation under German outdoor conditions (given as ng deltamethrin equivalents/L)

Time after application (days)	Application Rate								
	4.8 ng a.s/L		10.5 ng a.s/L		23 ng a.s/L		51 ng a.s/L		111 ng a.s/L
	A	B	A	B	A	B	A	B	
0/+4h [a]	6.6		10.6	10.8	26.9	26.6	78.0	(67.1) [b]	87.4
1 [a]	< LOQ	< LOD	6.6	< LOQ	14.9	16.0	33.9	16.8	36.7
2 [a]	< LOD	< LOD	< LOQ	< LOQ	10.4	[b]	24.9	< LOQ	12.0
4	< LOD	< LOD	< LOD	< LOD	< LOQ	< LOQ	10.3	< LOQ	7.1
7/-1h	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	< LOQ	< LOD	< LOQ
7/+4h [a]	7.1	< LOQ	15.8	7.2	34.6	(35.9) [b]	77.8	44.2	126.1
8 [a]	6.3	< LOQ	7.7	7.6	9.1	10.0	19.8	13.4	24.6
9 [a]	< LOQ	< 9.2	7.3	< LOQ	9.3	(9.4) [b]	17.1	11.0	18.3
11	n.d.	< LOD	< LOQ	< LOD	< LOQ	< LOQ	8.0	< LOD	7.7
14/-1h	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOQ	< LOD	< LOQ
14/+4h [a]	< LOD	< LOQ	< LOQ	< LOQ	10.0	15.4	35.8	14.4	26.3
15 [a]	< LOD	< LOD	< LOQ	< LOQ	7.3	12.2	29.2	7.9	17.4
16 [a]	< LOD	< LOD	< LOQ	< LOD	< LOQ	5.0	15.6	< LOQ	15.7
18	n.d.	n.d.	n.d.	n.d.	n.d.	< LOD	< LOQ	< LOQ	< LOD
21	n.d.	n.d.	n.d.	n.d.	n.d.	< LOD	< LOQ	< LOD	< LOD

n.d.: not determined
a) average value for four depths
b) sample broken
LOQ: Limit of quantification = 5 ng a.s./L
LOD: Limit of detection = 2 ng a.s./L

Table 7.2.2.4- 3: Distribution of the active substance in sediment after spray application of Deltamethrin EW 15 to mesocosm ponds and incubation under German outdoor conditions (given as µg deltamethrin equivalents/kg dry weight)

Time after application (days)	Application Rate								
	4.8 ng a.s/L		10.5 ng a.s/L		23 ng a.s/L		51 ng a.s/L		111 ng a.s/L
	A	B	A	B	A	B	A	B	
0 (-1h)	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
2	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
4	0.18	0.52	< LOQ	< LOD	< LOQ	< LOD	0.16	0.18	0.16
7 (-1h)	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	0.38	< LOQ	0.28
9	< LOD	< LOD	< LOD	0.24	< LOQ	< LOQ	0.31	< LOQ	0.79
11	< LOD	< LOD	< LOD	< LOD	0.16	< LOQ	0.70	< LOQ	0.42
14 (-1h)	< LOD	< LOD	< LOD	< LOD	0.40	0.29	0.44	< LOD	< LOD
16	< LOD	< LOD	< LOD	< LOD	0.26	0.51	0.47	0.17	0.30
18	< LOD	< LOD	< LOD	< LOD	0.31	0.55	0.36	0.37	0.29
21	n.a.	n.a.	n.a.	n.a.	0.14	< LOQ	0.71	0.29	0.23
29	n.a.	n.a.	n.a.	n.a.	0.23	0.14	0.35	0.32	0.28
35	n.a.	n.a.	n.a.	n.a.	0.46	0.13	0.69	0.19	0.29
42	< LOD	< LOD	< LOD	< LOD	0.31	< LOQ	0.32	< LOQ	0.73
49	< LOD	< LOD	< LOD	< LOD	0.31	0.56	0.29	0.39	0.59
56	< LOD	< LOD	< LOD	< LOD	0.39	0.18	0.60	0.27	0.70
63	< LOD	< LOD	< LOD	< LOD	0.35	0.32	0.51	0.15	0.22
70	< LOD	< LOD	< LOD	< LOD	0.39	0.15	0.37	0.33	0.34
84	< LOD	< LOD	< LOD	< LOD	< LOQ	0.25	0.33	< LOQ	0.24
91	< LOD	< LOD	< LOD	< LOD	< LOQ	0.22	0.31	0.15	0.31
105	< LOD	< LOD	< LOD	< LOD	< LOQ	0.19	0.26	0.24	0.14

LOQ: Limit of quantification = 1.0 µg a.s./kg dry weight
LOD: Limit of detection = 0.3 µg a.s./kg dry weight
n.a. = not analysed

Table 7.2.2.4- 4: Distribution of the active substance in water and sediment after spray application of Deltamethrin EW 15 to mesocosm ponds and incubation under German outdoor conditions (given as as % of applied amount)

Time after application (days)	Application Rate								
	23 ng a.s/L			51 ng a.s/L			111 ng a.s/L		
	water	sediment	sum [a)]	water	sediment	sum [a)]	water	sediment	sum [a)]
0 (+4h)	116.55	n.a.	116.55	144.04	n.a.	144.04	79.17	n.a.	79.17
1	67.59	n.a.	67.59	50.57	n.a.	50.57	33.22	n.a.	33.22
2	38.77	0	38.77	29.37	0	29.37	10.84	0	10.84
4	10.99	1.33	12.32	12.93	4.05	16.97	6.45	1.76	8.21
7	n.a.	0	0	2.56	5.15	7.71	2.28	3.11	5.39
7 (+4h)	155.86	n.a.	155.86	123.85	n.a.	123.85	114.77	n.a.	114.77
8	42.16	n.a.	42.16	33.52	n.a.	33.52	22.36	n.a.	22.36
9	41.18	2.66	43.83	28.26	4.02	32.28	16.63	8.41	25.05
11	10.92	5.54	16.46	8.04	8.26	16.30	6.97	4.47	11.44
14	0	18.34	18.34	2.47	4.88	7.36	2.25	0	2.25
14 (+4h)	54.78	n.a.	54.78	49.53	n.a.	49.53	23.66	n.a.	23.66
15	41.67	n.a.	41.67	36.51	n.a.	36.51	15.59	n.a.	15.59
16	17.49	17.47	34.96	18.66	7.10	25.77	14.05	3.35	17.4
18	n.a.	19.34	19.34	4.86	8.27	13.13	0	3.24	3.24
21	n.a.	4.11	4.11	2.44	11.17	13.60	0	2.57	2.57
29	n.a.	8.35	8.35	n.a.	7.57	7.57	n.a.	3.06	3.06
35	n.a.	13.23	13.23	n.a.	9.74	9.74	n.a.	3.22	3.22
42	n.a.	7.95	7.95	n.a.	4.07	4.07	n.a.	8.04	8.04
49	n.a.	19.72	19.72	n.a.	7.88	7.88	n.a.	6.46	6.46
56	n.a.	12.57	12.57	n.a.	9.80	9.80	n.a.	7.72	7.72
63	n.a.	15.14	15.14	n.a.	7.32	7.32	n.a.	2.45	2.45
70	n.a.	11.88	11.88	n.a.	8.03	8.03	n.a.	3.70	3.70
84	n.a.	6.93	6.93	n.a.	4.16	4.16	n.a.	2.60	2.60
91	n.a.	6.11	6.11	n.a.	5.16	5.16	n.a.	3.41	3.41
105	n.a.	5.41	5.41	n.a.	5.68	5.68	n.a.	1.55	1.55

n.a. = not analysed

a) Assuming that only a negligible part of the applied amount reached the sediment during the first 24 hours after application

III. CONCLUSION

Deltamethrin disappeared very rapidly from water by degradation and partitioning to sediment, suspended organic matter and to biota (e.g. macrophytes). The mean DT_{50} for dissipation of deltamethrin in the water column of mesocosms was 24 hours. The mean DT_{50} for the whole system (water plus sediment) was 32 hours.

Deltamethrin present in sediment is also subject to dissipation by biotic and/or abiotic processes, albeit more slowly than in the water phase.

CA 7.2.3 Degradation in the saturated zone

The degradation of deltamethrin in the saturated zone was not studied since deltamethrin is not expected to reach the saturated zone after its use according to good agricultural practices.
A summary of the route and rate of degradation of deltamethrin in water and sediment is given in section CA 7.2 and Figure 7.2- 1.

No additional studies are submitted within this Supplemental Dossier for the deltamethrin renewal of approval.

CA 7.3 Fate and behaviour in air

Deltamethrin has a low vapour pressure of 1.1×10^{-6} Pa (at 20°C), indicating a low volatility of the active substance. In wind tunnel experiments, deltamethrin showed a negligible volatilisation from bean leaves and soil with 0.6 – 1.1% and 0.2% of the applied radioactivity over 24 hours, respectively.
Volatilisation of deltamethrin from a water surface microlayer was observed in laboratory and pond studies. This is in agreement with the calculated Henry's Law Constant of 2.1 Pa m^3/mol at 20°C, which indicated some volatilisation of deltamethrin from the water surface.
The indirect photolytic degradation after reaction with OH-radicals is rapid, with a calculated atmospheric DT_{50} of 16 hours, assuming the 24 hours average OH radical concentration for calculation.

According to these results, an accumulation or long-range transport of deltamethrin in the air and a subsequent contamination by wet or dry deposition are not to be expected. This fact was confirmed by the evaluation of monitoring studies published in the literature (see section CA 7.5).

Despite the new pys.-chem data on vapour pressure, Henry's Law Constant (see section MCA 2) no additional studies are submitted within this Supplemental Dossier for the deltamethrin renewal of approval.

CA 7.3.1 Route and rate of degradation in air

Route and rate of degradation of deltamethrin in air was evaluated during the Annex I inclusion and was accepted by the European Commission (SANCO/6504/VI/99-final, 17 October 2002). The following study included in the Baseline Dossier was regarded relevant during the Annex I inclusion:

Author(s)	Year	Document No.
[redacted]	1999	M-184105-01-1

The potential persistence of the compound in air has been estimated according to the models developed by Atkinson. Half-life for reaction with OH-radicals was calculated to be 16 hours and the half-life for reaction with ozone was calculated to be 51.4 days (M-184105-01-1).

It can be concluded from its degradability in air that deltamethrin will not accumulate in the atmosphere, or be transported in gaseous phase over large distances.

CA 7.3.2 Transport via air

In the Baseline Dossier this section includes one laboratory study on volatilisation from water, one study on volatilisation from dwarf bean plants in a wind-tunnel, one field study on volatilisation from soil and field beans, and finally, one field study on volatilisation from soil, glass beads and various plants (letuce, kohlrabi, green beans and wheat). All studies were evaluated during the Annex I inclusion and were accepted by the European Commission (SANCO/6504/VI/99-final, 17 October 2002). The following studies included in the Baseline Dossier were regarded relevant during the Annex I inclusion:

Author(s)	Year	Document No.
[redacted]	1991	M-136601-01-1 See KCP 9.2.4/02*
[redacted]	1993	M-132365-02-2 See also KCP 9.3/02*
[redacted]	1993	M-131700-01-2
[redacted]	1993	M-132706-01-2
[redacted]	1993	M-132707-01-2
Boehnecke, A., Siebers, J., Nolting, H. G. (Publication)	1990	M-151719-01-1 See KCP 9.3/01*

* Please refer to the baseline dossier for Deltamethrin EC 25g/L.

As overall conclusion, small amounts of deltamethrin may be lost by volatilisation from plants and soil in the field. Indirect measurements in the field most probably overestimated the volatilisation rate. Tunnel results were considered more reliable by the former RMS Sweden. From water, a significant volatilisation may occur.

Since the substance is not likely to be susceptible to direct phototransformation, the rate of reaction with OH-radicals is the most important dissipation route (see section CA 7.3.1 before). Model calculation indicates that deltamethrin reacts with photochemically produced hydroxyl radicals in air, with a half-life of 16.4 hours. From its degradability in air it can be concluded that deltamethrin will not accumulate in the atmosphere, or be transported in gaseous phase over large distances.

CA 7.3.3 Local and global effects

Local and global effects of deltamethrin are not to be considered since its half-life in air is ≤ 2 days (**Error! Reference source not found.** 1999, M-184105-01-1, see section CA 7.3.1).

CA 7.4 Definition of the residue

CA 7.4.1 Definition of the residue for risk assessment

The proposed residue definitions relevant for exposure assessments, which can be used as basis for risk assessments in each compartment, are the following:

Compartment	Residue Definition
Soil	Deltamethrin (AE F032640) Br_2CA (AE F108565, *cis*) mPBacid (AE F109036)
Groundwater	Deltamethrin (AE F032640) Br_2CA (AE F108565, *cis*) mPBacid (AE F109036)
Surface water and sediment	Deltamethrin (AE F032640) Alpha-R-isomer of deltamethrin (AE F108569) *Trans*-isomer of deltamethrin (AE 0035073) 4´-OH-Deltamethrin (AE 0035082) Br_2CA (AE F108565, *cis*) BrCA isomer 1 (code not given) BrCA isomer 2 (code not given) Serinyl-BrCA (BCS-CW57835) mPBacid (AE F109036)
Air	Deltamethrin (AE F032640)

CA 7.4.2 Definition of the residue for monitoring

For the compartments soil, groundwater, surface water, sediment and air the proposed residue definition for monitoring is deltamethrin.

CA 7.5 Monitoring data

Monitoring data of deltamethrin were evaluated during the Annex I inclusion, and were accepted by the European Commission (SANCO/6504/VI/99-final, 17 October 2002). The following study regarded relevant for the current section is included in the Baseline Dossier:

Author(s)	Year	Document No.
[redacted]	1991	M-136600-01-1

More recent monitoring data received from literature review have been evaluated and are submitted within this Supplemental Dossier for the deltamethrin renewal of approval. Data were available for deltamethrin in soil, surface water, ground/drinking water, sediment and air.

The results from monitorings published in literature, which were regarded relevant for the EU, are summarized in the following. Generally they well confirmed the knowledge about fate and behaviour of deltamethrin in the environment and the used endpoints for exposure modellings.

If detected at all, the observed concentrations of deltamethrin in all mentioned compartments are very low.

Soil Compartment:

Report:	**KCA 7.5 /02; Goncalves, C.; Alpendurada, M. F.; 2005**
Title:	Assessment of pesticide contamination in soil samples from an intensive horticulture area, using ultrasonic extraction and gas chromatography-mass spectrometry
Source:	Talanta, 65, 5, p. 1179-1189
Document No:	M-460866-01-1
Guidelines:	None
GLP:	No, published study
	Literature review
Literature review classification:	b) supplementary information (EFSA Journal 2011; 9(2):2092)

EXECUTIVE SUMMARY

This paper describes the development and application of an ultrasonic extraction (USE) technique combined with gas chromatography and mass spectrometric detection for the analysis of OCPs, OPPs, triazines, pyrethroids, acetanilides and other miscellaneous pesticides in soil samples from an intensive horticulture area in North Portugal.
The implemented monitoring program is expected to allow observing temporal trends on pesticide contamination as well as variations according to depth in five sampling points, during two years.
Material and methods as well as results are summarized for validation of the method and the monitoring study of deltamethrin.
An uncontaminated bulk soil sample was selected to use in the validation experiments and spiked with 10 µg/kg deltamethrin (Pestanal® grade; [redacted] Germany). Real soil samples from five sampling points at three depths (surface, 10 and 20 cm) were collected in four sampling dates and analysed with the USE method. This monitoring program was scheduled to include a sampling event approximately every 3 months. After collection and transport to the laboratory in aluminium foil packets, the samples were dried in an oven at 40°C during 48 h, sieved at 500 µm, perfectly well homogenized and kept refrigerated at 4 °C before analysis.
For extraction, 5 g of soil samples was placed in small Erlenmyer flasks and 5ml of a suitable organic solvent added. The soil samples were firstly manually agitated and then exposed to USE in a Bandelin RK 100H (80/160 W) ultrasonic bath (Sonorex, Germany) for 15 min, three times. After each extraction period, extracts were collected by pouring the extractant through a funnel plugged with a small piece of cotton wool overlaid by a portion of anhydrous sodium sulfate, which had been previously washed with the same solvent. In order to achieve the adequate concentration factor, 5 g aliquot of sample was submitted to extraction and the final extract (ca. 15 ml) evaporated to dryness under a gentle stream of nitrogen without need of any clean-up procedure and redissolved in 200 µl of ethyl acetate. The following chromatographic analyses were carried out in a gas chromatograph Agilent 6890 (Palo Alto, CA, USA) interfaced to an Agilent 5973N mass selective detector.
Limit of detection and recovery was 4.0 µg/kg and 111% (n=6), respectively. No deltamethrin was found in the soil samples.

I. MATERIAL AND METHODS

A. Material

1. Test material

Test item:	Deltamethrin
Source of test item:	[redacted], Germany)
Batch number:	-
Purity:	Pestanal® grade;
Storage conditions:	-

2. Site description

Location/country:	North Portugal [redacted] 2001/2002)
Amount of sampling areas:	5 soil sampling points at 3 depths (Surface, 10 and 20 cm)

3. Soil:

Soil type:	Soil 1: Sand, Soil 5: Sandy-loam, Soil 18: Sand, Soil 22: Sandy; Soil 25: Sandy-loam (Reference soil: Bulk soil: sandy-loam)
Particle size:	-
pH:	-
Organic carbon content (% w/w):	Soil 1: 1.69, Soil 5: 7.82, Soil 18: 4.08, Soil 22: 8.62, Soil 25: 8.01 (Reference soil: Bulk soil: 7.44)
Humidity:	Soil 1: 0.12, Soil 5: 0.73, Soil 18: 0.33, Soil 22: 0.75; Soil 25: 0.89 (Reference soil: Bulk soil: 7.44)

B. Study design and methods

1. Test procedure

Test system	Monitoring and validation test
Test concentration(s):	10 µg/kg
Application method:	-
Number of replicates:	-
Application interval:	-

2. Sampling

Sampling technique:	-
Sampling frequency:	Every 3 months
Number of samples per site/soil type:	3
Sampling depth:	Surface, 10 and 20 cm
Transport/storage of samples:	Aluminium foil packets

4. Chemical analysis

Guideline/protocol:	-
Method:	Ultrasonic extraction procedure and gas chromatography with mass selective detector
Extraction:	Ultrasonic extraction (three repetitions), evaporation to dryness under a N_2 stream and redissolved with 200 µl ethyl acetate
Analysis:	Gas chromatograph Agilent 6890 (Palo Alto, CA, USA) interfaced to an Agilent 5973N mass selective detector
Reference item:	Deltamethrin
Recovery:	111±9.7% (n=6)
Limit of detection:	4.00 µg/kg
Limit of quantification:	-

II. RESULTS

1. Validity criteria:

No validity criteria were mentioned.

2. Analytical findings:

Limit of detection and recovery was 4.0 µg/kg and 111% (n=6), respectively. No deltamethrin was found in the soil samples.

III. CONCLUSION

No deltamethrin was found in the soil samples from an intensive horticulture area. Therefore, it is not regarded as a persistent compound in soil.

Report:	**KCA 7.5 /03; Fernandez-Alvarez, M.; Llompart, M.; Lamas, J. P.; Lores, M.; Garcia-Jares, C.; Cela, R.; Dagnac, T.; 2008**
Title:	Simultaneous determination of traces of pyrethroids, organochlorines and other main plant protection agents in agricultural soils by headspace solid-phase microextraction-gas chromatography
Source:	J. Chromatogr., A, 1188, 2, p. 154-163
Document No:	M-455938-01-1
Guidelines:	None
GLP:	No, published study
Literature review classification:	b) supplementary information (EFSA Journal 2011; 9(2):2092)

EXECUTIVE SUMMARY

A solvent-free and simple method based on headspace solid-phase microextraction (HS-SPME) was developed in order to determine simultaneously 36 common pesticides and breakdown products (mostly pyrethroids and organochlorine compounds) in soil. The analysis was carried out by gas chromatography with micro-electron-capture detection (GC-μECD). As far as we know, this is the first study about the SPME of pyrethroid insecticides from soil. However, material and methods as well as results are summarized only for the monitoring of deltamethrin.

Different soil samples (A–G) were collected from several gardens (A, B) and agricultural locations (C–G) of NW Spain. The soil samples (0.5 g) were placed in 10mL vials. Sodium chloride was added in proportion of 20% (w/v) in the required experiments. The vials were then sealed with aluminium caps and PTFE-faced septa. Samples were let to equilibrate in a water bath at the working temperature for 5 min and the SPME fiber was then exposed to the headspace over the sample for 30min under stirring. Once finished the exposition period, the fiber was thermally desorbed for 5 min into the GC injector port and the chromatographic analysis was carried using GC-μECD.

In order to assess the performance of the HS-SPME procedure, analytical quality parameters were measured using spiked soil samples with known concentrations of the target compounds. Therefore, garden soil A (7.4% of organic matter –OM- content) was spiked at levels raning from 0.5 to 200 ng/g. Fortification of the sample was carried out by weighing 30 g of soil in a big beaker and adding 15 ml of the corresponding working solution so that the entire sample got covered with organic solvent. The slurry was allowed to stand and stirred occasionally until the acetone completely evaporated (9–12 h). Afterward, 0.5 g fractions were collected and kept in a freezer at −20 ◦C until 5–10min before the analysis. For the analytical performance assessment, aliquots of the same soil sample (A) spiked at different concentration levels ranging from 0.5 to 200 ng/g were analysed as described before.

The calculated LOD and LOQ for deltamethrin were 1.2 and 4.0 ng/g, respectively. Recovery efficiency of optimized method was 81%. No deltamethrin was found in non-spiked real soil samples.

I MATERIAL AND METHODS

A. Material

1. Test material

Test item:	Deltamethrin
Adjuvant / Surfactant:	-
Source of test item:	[redacted] USA)
Lot/Batch number:	-
Purity:	-

Storage conditions:	-
2. Soil:	
Name / Classification	-
Source, sampling date and storage conditions	Different soil samples (A–G) were collected from several gardens (A, B) and agricultural locations (C–G) of NW Spain.
Soil type:	-
Particle size:	Sieved to 2 mm
pH:	-
Organic carbon content:	A: 7.4%; B: 13.7%, C: 8.3%, G:11.2%

B. Study design and methods

1. Test procedure	
Test system (study type):	Monitoring and analytical quality test
Treatments:	Analytical quality test: Deltamethrin
Application rate:	Analytical quality test: 0.5 to 200 ng/g
Number of replicates	-
Application:	Analytical quality test: 15 ml working solution was added to 30 g of soil in a big beaker. The slurry was allowed to stand and stirred occasionally until the acetone completely evaporated (9-12 h).
Sampling technique:	-
Sampling frequency:	Analytical quality test: Only once
Storage of samples:	Analytical quality test: -20°C
3. Chemical analysis	
Guideline/protocol:	-
Method:	HS-SPME and GC-µECD
Extraction:	Headspace solid-phase microextraction using sodium chloride (20% w/v) and SPME Fiber
Analysis:	Hewlett-Packard 6890 GC system equipped with 63Ni - ECD system,
Reference item:	Deltamethrin
Recovery:	81%
Limit of detection:	1.2
Limit of quantification:	4.0

II. RESULTS

1. Validity criteria:

No validity criteria were mentioned.

2. Analytical findings:

No deltamethrin was found in non-spiked real soil samples.

III. CONCLUSION

Deltamethrin was not found in real soil samples from agricultural areas. Therefore, it is not regarded as a persistent compound.

Aquatic Compartment:

Report:	**KCA 7.5 /04; Figueiredo, F.; Ribeiro, M.; Rocha, M.; Cruzeiro, C.; Rocha, E.; 2012**
Title:	Development and validation of a GC-MS method for determination of 39 common pesticides in estuarine water – targeting hazardous amounts in the Douro River estuary
Source:	Intern. J. Environ. Anal. Chem. Vol. 92, No. 14, 10 December 2012, 1587–1608
Document No:	M-457780-01-1
Guidelines:	None
GLP:	No, published study
Literature review classification:	b) supplementary information (EFSA Journal 2011; 9(2):2092)

EXECUTIVE SUMMARY

An analytical method based on solid-phase extraction followed by gas chromatography mass spectrometry (GC-MS) was developed and validated for the quantification of 39 pesticides with distinct physico-chemical characteristics (including some degradates) in estuarine water samples. Method detection limits were between 3.6 and 61.2 ng/L. The obtained sensitivity and accuracy, associated with the inherent confirmatory potential of GC-MS, validate the method as a tool in environmental monitoring. Analyses of water samples (n=84) taken from the Douro River estuary, from March to May 2009, showed the presence of deltamethrin.
The measured concentrations ranged from 151.2 ng/L in March to 276.6 ng/L in April, however, the methodology used was not adequate to rule out that detects were caused by particles trapped on the filters.

I. MATERIALS AND METHODS

A. MATERIALS

Test item:	Deltamethrin (chemical state and description: not reported)
Source of test item:	[redacted], Germany)
Batch number:	Not reported
Purity:	Analytical grade
Storage conditions:	prepared in methanol to produce a final stock solution of 1000 mg/L and kept in the dark, at -20°C
Water samples:	Surface water samples were collected from the [redacted] estuary. After sampling, all water was kept refrigerated (-4°C), transported in the dark to the laboratory

B. STUDY DESIGN AND METHODS

Sampling:	Water samples were collected into 2.5-L amber glass bottles, which were rinsed in the laboratory with ultrapure water and later, on site, with water sample.
Sampling frequency:	Twice a day according to both high and low tides, from late March to late May 2009 (n=84).
No. of samples/site:	N=84 in total
Storage of samples:	All samples were maintained at 4° C in dark until extraction
Sampling depth:	Sampled from a depth of approximately 1m using a peristaltic pump (Global Water, model: WS 3000, California, USA).

Measurement of temperature and pH:	Temperature and pH were measured immediately after collection using a Consort C868 electrochemical apparatus
Statistics:	After checking assumptions of normality and homogeneity of variances (Kolmogorov-Smirnov and the Bartlett tests), data sets were analyzed by one-way analysis of variance (ANOVA) (Holm-Sidak test or post-hoc Tukey test with ranked sums).
Chemical analysis of samples	
Guideline/protocol:	none
Method:	GC-MS
Pre-treatment:	After sampling all water was kept refrigerated and then immediately vacuum filtered through 0.45 mm glass fibre filter to remove suspended particles. Thereafter, each filter was washed with approximately 2mL of methanol and this volume was added to the filtrate. Solid-phase extraction followed.
Conduction:	After extraction 1 g of anhydrous sodium sulfate was added to the sample bottle to remove any residual water and the bottle was rinsed three times with approximately 4 mL of dichloromethane. This volume, reduced to 1mL under a gentle nitrogen stream, was added to the ethyl acetate fraction which was concentrated to 200 mL.
Reference item:	Standard solutions of pesticide standards purchased from Sigma-Aldrich
Recovery:	107.2% (RSD 8.6%)
Limit of detection:	4.8 ng/L
Limit of quant.:	15.8 mg/L

II. RESULTS AND DISCUSSION

1. Validity criteria (IUPAC validation guidelines)**:**
- evaluation of linearity: blank matrices (free of all target pesticides)
- accuracy: percentage of agreement between the method results and the nominal amount of added compound (three replicates of each QC samples)
- precision: relative standard deviation (%RSD) of the replicate measurements (three replicates of each QC samples)
- limit of detection and quantification: was determined evaluating the signal/noise ratio (S/N 3 for LODs and S/N 10 for LOQs)

2. Analytical findings:

Deltamethrin was detected in 94% of all measured water samples. In April its amounts were higher than in March and May (Table 7.5-1). Deltamethrin values reported for water include the extraction of particles on filters.

Table 7.5- 1: Environmental levels of deltamethrin in the [redacted] estuary (n = 84). Deviation to the mean is represented by +/- SE [ng/L]

Frequency	March (n=2)	April n (=8)				May (n=4)	
[%]	4th week	1st week	2nd week	3rd week	4th week	2nd week	4th week
94.0	151.2 +/-8.1	228.0 +/-18.5	179.5 +/- 13.8	184.6 +/-13.7	276.6 +/-24.5	133.9 +/-7.5	132.5 +/-4.7

III. CONCLUSION

Deltamethrin was found in 94% of analysed samples (n = 84) taken from the [redacted] estuary, from March to May 2009 in concentrations up to 276.6 ng/L. However, the methodology was not adequate to

rule out that detects were caused by particles been trapped on the 0.45 mm glass fibre filters.
Since the amount of trapped particles is not given, but the filter wash solution was added to the filtrate, the interpretation of results is quite difficult. It is reasonable for a very well adsorbing compound like deltamethrin that the major portion of deltamethrin reported for the water phase in fact was bound to particles of samples, which were not specified in detail.

Report:	**KCA 7.5 /05; Menkissoglu-Spiroudi, U.; Tsochatzis, E.; Papageorgiou, M.; Tzimou-Tsitouridou, R.; Karpouzas, D.; 2012**
Title:	Development and validation of an HPLC-DAD method for the simultaneous determination of most common rice pesticides in paddy water systems
Source:	Intern. J. Environ. Anal. Chem. Vol. 92, No. 5, 548–560
Document No:	M-457791-01-1
Guidelines:	None
GLP:	No, published study
Literature review classification:	b) supplementary information (EFSA Journal 2011; 9(2):2092)

EXECUTIVE SUMMARY

Rice crop is mainly cultivated in large river basins which constitute unique ecosystems and their ecological quality is invaluable. However, the high loads of pesticides used in rice cultivation contribute to the contamination of the water resources in such rice-cultivated regions. To regularly monitor the quality of such water resources there is a need for a rapid and sensitive multi-residue analytical method. This study presents the development and validation of a new analytical method for the simultaneous determination of most rice pesticides including deltamethrin.

A solid-phase extraction (SPE) procedure followed by high performance liquid chromatography (HPLC) with diode array detection (DAD) was used. A C18 RP column operated at 30 °C was utilised and the analytes were separated with a mobile phase of acetonitrile/water mixture in a linear gradient. Clean-up of water samples and isolation of pesticides was performed on SPE Bakerbond octadecyl cartridges and an ethyl acetate-dichlomethane mixture (9:1 v/v, 2 mL) was used for elution.

Method validation was performed by means of intra-day (n=5) and inter-day accuracy and precision (n=8), sensitivity and linearity. The relative recovery of the deltamethrin in paddy water samples was acceptable (99.2 %) and the relative standard deviation (RSD%) ranged from 3.0 to 4.2 %. Limits of detection (LOD) and limits of quantification (LOQ) were 0.2 ng/mL and 0.6 ng/mL respectively.
Deltamethrin was not detected at the 10 sampling sites.

I. MATERIAL AND METHODS

A. Material

1. Test material

Test item:	Deltamethrin
Chemical state and description:	Not reported
Source of test item:	Not reported
Batch number:	Not reported
Purity:	Not reported
Storage conditions:	Not reported

2. Soil:

Ten water samples were collected from rice paddies and receiving canals located in the [redacted] river basin. These paddies (organic and conventional fields) were experimental field facilities [redacted] of Greece [redacted] Five samples were collected at mid-June 2008, while five more samples were collected during the period

from end of July to mid August 2008.
Soil parameters like soil type, particle size, pH, OC content were not reported.

B. Study design and methods

1. Sampling

Sampling technique:	Not reported
Sampling frequency:	Not reported
Number of samples per site/soil type:	Not reported
Storage of samples:	In refrigeration for safe preservation between +2°C and -2°C until analysis.

2. Measurements

Temp., soil moisture, pH, OC :	Not reported

3. Chemical analysis

Guideline/protocol:	Not reported
Method:	HPLC-DAD
Pre-treatment of samples:	The paddy water samples analysed were first filtered Through a Glass Fibre filter (GF/A) and then transferred to J.T. Baker BAKERBOND octadecyl SPE cartridges.
Conduction:	Not reported
Reference item:	Not reported
Recovery:	99.2 %
Limit of detection:	0.2 ng/mL
Limit of quantification:	0.6 ng/mL

II. RESULTS

1. Validity criteria: No validity criteria defined.

2. Analytical findings:

Table 7.5.2: Pesticide concentrations (ng/mL) detected in the water samples collected from rice paddies and receiving drainage canals located in the [redacted] river basin (Northern Greece) and processed using the analytical method developed.

Sample 1	Sample 2	Sample 3	Sample 4	Sample 5	Sample 6	Sample 7	Sample 8	Sample 9	Sample1 0
< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD

Samples 1–5 were collected in mid-June while samples 6–10 were collected during a period from end of July to mid-August.

III. CONCLUSION

Deltamethrin was not detected at all 10 sampling sites (common paddy rice water system).

Report:	**KCA 7.5 /06; Laubel, A.; Friberg, N.; Kronvang, B.; Larsen, S.; 2003**
Title:	Pesticides and heavy metals in Danish streambed sediment
Source:	Hydrobiologia, 494, p. 93-101
Document No:	M-460841-01-1
Guidelines:	None
GLP:	No, published study
Literature review classification:	b) supplementary information (EFSA Journal 2011; 9(2):2092)

EXECUTIVE SUMMARY

The role of streambed sediment as a sink for pesticides and heavy metals was investigated in 30 Danish lowland streams. For heavy metals, material and methods as well as results were not summarized. The investigated streams drain catchments varying in hydrology, topography, soil type and land use. The <250 µm newly accumulated fraction of the uppermost 1–2 cm layer of streambed sediment was analysed for 19 old and modern pesticides and 9 heavy metals by using GC-EC and GC-MS (using both EI-ionisation and NCI-ionisation).

DDE was present in the sediment of all the streams. Of the herbicides, fungicides and insecticides currently in use, the most frequently detected was diuron (50.0%), fenpropimorph (66.7%) and lambda-cyhalothrin (6.7%), respectively.

The pesticides detected in the highest concentration were fenpropimorph (1700 ng/g), propiconazole (130 ng/g) and isoproturon (110 ng/g).

Deltamethrin was found in Danish lowland stream sediment samples at concentrations up to 50 ng per g DW; detection frequency was comparatively low (≤5%).

The average number of pesticides detected in the 27 streams draining predominantly agricultural catchments was (3.7±2.0) being higher ($p = 0.077$) than in the three streams draining non-agricultural catchments (1.7±0.6). Pesticides were significantly related to catchment size, soil type and hydrological regime.

I. MATERIAL AND METHODS

A. Material

1. Site description

Location/country:	Small headwater streams / Denmark
Nr. of catchments:	30

B. Study design and methods

2. Sampling

Sampling technique:	Kajak corer
Sampling date:	Autumn 1998
Number of samples per site:	30-50 core-samples
Sampling depth:	1–2 cm of newly accumulated fine sediment and detritus
Transport/storage of samples:	Samples were pooled and to one composite sample for each stream and transported in 2 l glass bottles. The <250 µm portion was stored frozen in an aluminium foil tray.

3. Measurements

Grain size distribution:	Laser diffraction spectrometer
Organic matter content:	The content of organic matter was measured as the loss on ignition in a subsample by combusting the sediment samples at 500 ◦C for 4 h.

4. Chemical analysis

Guideline/protocol:	-
Method:	GC-EC and GC-MS (using both EI-ionisation and NCI-ionisation)
Pre-treatment of samples:	Samples were extracted with acetone/dichlormethane 1:1 in a Soxtec Avanti 2050 Auto system
Conduction:	Half of the extract was analysed with GC-EC. The other half of the extract was analysed with GC-MS using both EI-inonisation and NCI-ionisation.
Recovery:	Deltamethrin: 106%
Limit of detection:	10 ng/g DW
Limit of quantification:	-

II. RESULTS

1. Validity criteria: No validity criteria were mentioned.

2. Analytical findings:

DDE was present in the sediment of all the streams. Of the herbicides, fungicides and insecticides currently in use, the most frequently detected was diuron (50.0%), fenpropimorph (66.7%) and lambda-cyhalothrin (6.7%), respectively.

Deltamethrin was found in sediment samples in concentrations up to 50 ng/g DW; detection frequency was comparatively low (< 5%). The average number of pesticides detected in the 27 streams draining predominantly agricultural catchments was (3.7±2.0) being higher ($p = 0.077$) than in the three streams draining non-agricultural catchments (1.7±0.6). Pesticides were significantly related to catchment size, soil type and hydrological regime.

3. Other measurements

Median grain size was 17.7 μm, median clay content 16.3% and median organic matter content 15.4%.

III. CONCLUSION

Deltamethrin was found in Danish lowland stream sediment samples up to 50 ng/g DW, detection frequency was comparatively low (< 5%).

Drinking Water:

Report:	**KCA 7.5 /07; Nazimek, T.; Badach, H.; Kaminska, I.; 2007**
Title:	Pesticide content in drinking water samples collected from orchard areas in central Poland
Source:	Ann. Agric. Environ. Med.,14, 1, p. 109-114
Document No:	M-458077-01-1
Guidelines:	None
GLP:	No, published study
Literature review classification:	b) supplementary information (EFSA Journal 2011; 9(2):2092)

EXECUTIVE SUMMARY

Samples of drinking water collected in [redacted] of central Poland were tested for the presence of pesticides. Data obtained from analysis of water samples will be used for future epidemiological and environmental studies in the region. Samples were collected during spring and autumn of 2002-2003 from dug wells, deep wells and water mains in 81 randomly selected rural households scattered throughout this region of extensive agriculture. The concentration of pesticides from four main chemical groups was determined by gas chromatography: organochlorines (lindane, DDT, methoxychlor), triazines (atrazine, simazine), organophosphates (acephate, diazinon, fenitrothion) and pyrethroids (alpha-cypermethrin, deltamethrin). Two-year monitoring of drinking water samples indicated the presence of DDT and methoxychlor contamination. Pyrethroids e.g. deltamethrin, were generally not detected, with the exception of alpha-cypermethrin found in only a few samples. Triazines were also found in water samples collected in the course of the study with higher incidence during spring period. Organophosphates were by far the most common contaminants of drinking water in this region. Almost all samples were contaminated by significant amounts of fenitrothion.

I. MATERIAL AND METHODS

A. Material

1. Site description

Location/country: Water mains (20%), Water dug (40%) and Water deep weels (40%); Poland [redacted]

Amount of sample sites:
Cultivated crops: Study area in the immediate vicinity of large orchards

B. Study design and methods

1. Sampling

Sampling technique:
Sampling frequency: Single samples
Sampling date: Spring and autumn of 2002-2003
Number of samples: 81 water intakes
Sampling depth: -
Transport/storage of samples: -

2. Chemical analysis

Guideline/protocol:	Badach et al. 2000[3]; Juhler 1997[4]; LeBel et al. 1979[5]
Method:	Gas Chromatography
Pre-treatment of samples:	Solid Phase Extraction with Octadecyl C18 columns
Conduction:	A Hewlett-Packard 5890 Series II (Hewlett-Packard, Germany) gas chromatograph equipped with an electron capture detector and a capillary RTX column was used. (Duplicates were tested)
Reference item:	-
Recovery:	89% for pyrethroide
Limit of detection:	Deltamethrin: 0.10 µg/L
Limit of quantification:	-

II. RESULTS

1. Validity criteria: No validity criteria were mentioned.

2. Analytical findings:

Two-year monitoring of drinking water samples indicated the presence of DDT and methoxychlor contamination. Pyrethroids were generally not detected, with the exception of alpha-cypermethrin found in only a few samples. Organophosphates were by far the most common contaminants of drinking water in this region. Almost all samples were contaminated by significant amounts of fenitrothion. In the following tables just the results for deltamethrin are shown.

Table 7.5- 3: Concentration and prevalence of pesticide-contaminated samples collected from water mains in the [redacted] region during spring and autumn of 2002/2003

Compound	Total number of samples	Number of contaminated samples				Range of concentrations	
		Spring		Autumn		Spring	Autumn
	N	n	%	n	%	µg/L	µg/L
2002							
Deltamethrin	17	0	0.0	0	0.0	not detected	not detected
2003							
Deltamethrin	13	0	0.0	0	0.0	not detected	not detected

Table 7.5- 4: Concentration and prevalence of pesticide-contaminated samples collected from deep wells in the [redacted] region during spring and autumn of 2002/2003

Compound	Total no. of samples	Number of contaminated samples		Range of concentrations	
		Spring	Autumn	Spring	Autumn

[3] Badach H, Nazimek T, Kamiński R, Turski AW: Organochlorine pesticides concentration in the drinking water from regions of extensive agriculture in Poland. Ann Agric Environ Med 2000, 7, 25-28.
[4] Juhler RK: Optimized method for the determination of organophosphorus pesticides in meat and fatty matrices. J Chromatogr A 1997, 786, 145-153.
[5] LeBel GL, Williams DT, Griffith G, Benoit FM: Isolation and concentration of organophosphorus pesticides from drinking water at the ng/L level, using macroreticular resin. J Assoc Off Anal Chem 1979, 62, 241-249.

	N	n.	%	n.	%	µg/L	µg/L
2002							
Deltamethrin	32	0	0.0	0	0.0	not detected	not detected
2003							
Deltamethrin	31	0	0.0	0	0.0	not detected	not detected

Table 7.5- 5: Concentration and prevalence of pesticide-contaminated samples collected from dug wells in [redacted] region during spring and autumn of 2002/2003

Compound	Total no. of samples	Number of contaminated samples				Range of concentrations	
		Spring		Autumn		Spring	Autumn
	N	n.	%	n.	%	µg/l	µg/l
2002							
Deltamethrin	32	0	0.0	0	0.0	Not detected	Not detected
2003							
Deltamethrin	32	0	0.0	0	0.0	Not detected	Not detected

III. CONCLUSION

During two year monitoring of drinking water samples in Polish orchard areas no deltamethrin residues were detected.

Air Compartment:

Report:	**KCA 7.5 /08; Hart, E.; Pastor, A.; Yusa, V.; Coscolla, C.; 2013**
Title:	GC-MS characterization of contemporary pesticides in PM10 of Valencia Region, Spain
Source:	Atmospheric Environment 62; 118-129
Document No:	M-462167-01-1
Guidelines:	None
GLP:	No, published study
Literature review classification:	b) supplementary information (EFSA Journal 2011; 9(2):2092)

EXECUTIVE SUMMARY

Better knowledge of the occurrence of pesticides in the inhalable fraction of particulate matter (PM10) could be very useful for future exposure assessment in individuals of the general public. The present work studies the spatial and temporal distribution of the occurrence of currently used pesticides (CUPs) in PM10. Ambient air samples were collected from January through December 2010 at one remote, one urban and three rural sites in Valencia Region (Spain) and analyzed for 42 CUPs using a gas chromatography coupled to mass spectrometry in tandem (GC-MS/MS) approach.
Deltamethrin was not detected in any sample.

I. MATERIAL AND METHODS

A. Material

1. Test material	
Test item:	deltamethrin
Chemical state and description:	Not reported
Source of test item:	Not reported – monitoring study
Batch number:	Not reported – monitoring study
Purity:	Not reported – monitoring study
Storage conditions:	Not reported – monitoring study
Water solubility:	Not reported
2. Site description:	
Location/country:	Valencia Region, Spain
Sampling sites (air samples):	one remote ([redacted]), one urban ([redacted]) and three rural ([redacted]) sampling sites
Cultivated crops:	Citrus fruits, irrigated herbaceous crops, wooded forest and unirrigated fruit trees and olive grooves
Pesticides used on fields:	Not reported

B. Study design and methods

1. Sampling	
Sampling technique:	Collected using a high volume sampler from Digitel (Madrid, Spain) and quartz fiber filters of 150 mm in diameter were supplied by Munktell filter AB (Falun, Sweden). The sampling flow was 30 m3 h1 for 24 h, giving a total volume of filtered air around 720 m3. In order to determine the possibility of background pollution, blank filters were routinely deployed in the field to determine any contamination during sample handling.
Sampling frequency:	Not reprted (between January and December)
Number of samples per site/soil type:	A total of 217 samples were collected from January to December 2010
Transport/storage of samples:	Samples were either analyzed immediately or were stored at 18 °C until ready for analysis. To check for loss and degradation during retrieval, transportation and storage, spiked blank filters were used. In general, no loss or degradation was detected.
2. Chemical analysis	
Guideline/protocol:	Following a previously published method (Coscollà et al., 2011)
Method:	GC-MS/MS
Pre-treatment of samples:	Extraction of PM10-bound pesticides by microwave-assisted extraction (MAE) followed by gel-permeation chromatogr. (GPC) clean-up
Reference item:	Not reported
Recovery:	Not reported
Limit of detection:	Not reported
Limit of quantification:	13.16 pg m^{-3}

II. RESULTS

1. Analytical findings:

Deltamethrin was not detected by analytical method of microwave-assisted extraction (MAE) followed by gel-permeation chromatography (GPC) clean-up and determination by GC-MS/MS.

III. CONCLUSION

Deltamethrin was not detected in any sample sampled from January through December 2010 at one remote ([redacted]), one urban ([redacted]) and three rural ([redacted]) sampling sites located across Valencia Region, Spain.

Report:	**KCA 7.5 /09; Gonzalez, F.; Granero, A.; Glass, C.; Frenich, A.; Vidal, J., 2004**
Title:	Screening method for pesticides in air by gas chromatography/tandem mass spectrometry
Source:	Rapid Commun. Mass Spectrom., 18, 5, p. 537-543
Document No:	M-455826-01-1
Guidelines:	None
GLP:	No, published study
Literature review classification:	b) supplementary information (EFSA Journal 2011; 9(2):2092)

EXECUTIVE SUMMARY

A multiresidue method for determining more than 70 pesticides in air has been validated using a single injection with gas chromatography/tandem mass spectrometry (GC/MS/MS). However, material and methods are summarized for recovery and monitoring of deltamethrin only.
The efficiency of the extraction method was studied by spiking sampling cartridges containing the granular sorbents (Tenax TA or Chromsorb 106) with standard solutions, and applying the extraction method. Three analyte levels were assessed (30, 60 and 100 ng Deltamethrin (purity: > 99%, [redacted], Germany)). Cartridges were extracted by eluting with ethyl acetate at a flow of 1 ml/min for 10 min. The eluents were concentrated close to dryness with a nitrogen flow, the internal standard (caffeine) was added, and the final volume adjusted to 2 mL with ethyl acetate. Another extraction method was tested, in which the sorbents were treated with three sequential portions of 20mL of ethyl acetate, and sonicating each for 15 min. The solution was transferred to a round-bottomed flask and concentrated to dryness under vacuum; the internal standard was then added, and the volume made up to 2 mL with ethyl acetate. The two extraction methods yielded similar results, but the first is more amenable to automation, allowing savings of solvent and time. The gained extracts were used for GC/MS analysis using a Varian 3800 gas chromatograph, equipped with electronic flow control (EFC) and a Saturn 2000 ion trap mass spectrometer (Varian Instruments, Sunnyvale CA, USA). Six replicates were performed.
For the monitoring study, 30 samples were analysed. 20 of these were collected close to urban areas surrounded by greenhouses with intensive agricultural activities (therefrom 15 during afternoon and evening and 5 in the morning), and 10 others were collected in areas close to open fields (southern Spain). Ambient temperature and relative humidity were recorded during the sampling periods. Sampling duration was in general 6 h. Extraction and analysis procedure was conducted as described for the efficiency test.
Efficiency test with 30 ng deltamethrin indicated a LOQ of 4.0 ng and a recovery of 85%. However, no deltamethrin was found in the air samples.

I. MATERIAL AND METHODS

A. Material

1. Test material

Test item:	Deltamethrin
Chemical state and description:	-
Source of test item:	[redacted], Germany)
Batch number:	-
Purity:	> 99%,
Storage conditions:	-
Water solubility:	-

2. Site description (for soil)	
Location/country:	Southern Spain
Amount of sampling sites:	30 (15: close to urban areas surrounded by greenhouses with intensive agricultural activities (afternoon to evening); 5 close to urban areas surrounded by greenhouses with intensive agricultural activities (morning); 10: areas close to open fields)
Temperature/Humidity:	15 afternoon to evening samples (25-28°C and 85% humidity); 5 morning samples (19-25°C and 60% humidity)
Other specifications:	Delete if not stated

B. Study design and methods

1. Test procedure	
Test system	Monitoring study and Efficiency study
Test concentration	30, 60 and 100 ng (Efficiency study)
Sampling technique:	Cartridge container with granular sorbents (Tenax TA or Chromsorb 106)
Sampling frequency:	Once over approx. 6 h (Monitoring study)
Number of samples per site/soil type:	-
Storage of samples:	-
3. Chemical analysis	
Guideline/protocol:	-
Method:	Elution or sonication of the cartridges containing sorbents with following analysis with gas chromatography with electronic flow control and ion trap mass spectrometer.
Extraction:	Elution with ethyl acetate at a flow of 1 ml/in for 10 min or three sequential extractions using a ultrasonic homogenizer with 20ml of ethyl acetate for 15 min
Analysis:	The gained extracts were used for GC/MS analysis using a Varian 3800 gas chromatograph, equipped with electronic flow control (EFC) and a Staturn 2000 ion trap mass spectrometer (Varian Instruments, Sunnyvale CA, USA)
Reference item:	Deltamethrin
Recovery:	85% (30 ng initial concentration)
Limit of detection:	
Limit of quantification:	4.0 ng

II. RESULTS

1. Validity criteria: No validity criteria were stated.

2. Analytical findings:
Efficiency test with 30 ng deltamethrin indicated a LOQ of 4.0 ng and a recovery of 85%. However, no deltamethrin was found in the air samples.

III. CONCLUSION

No deltamethrin was found in the air samples from Southern Spain taken close to urban areas surrounded by greenhouses with intensive agricultural activities and close to open fields.

Report:	**KCA 7.5 /10; Schummer, C.; Mothiron, E.; Appenzeller, B.; Rizet, A.; Wennig, R.; Millet, M.; 2010**
Title:	Temporal variations of concentrations of currently used pesticides in the atmosphere of Strasbourg, France
Source:	Environ. Pollut. Volume 158, Issue 2, p. 576-584
Document No:	M-457521-01-1
Guidelines:	None
GLP:	No, published study
Literature review classification:	b) supplementary information (EFSA Journal 2011;9(2):2092)

EXECUTIVE SUMMARY

Deltamethrin was determined in atmospheric samples collected in [redacted] France, between April 17th and May 29th, 2007, by a multimethod comprising 71 pesticides in total.

The number of pesticides detected in atmospheric samples is very low given the total number of molecules that were monitored. This may be due to a non-application of them during the sampling period or to applications at very low amounts, to too high limits of detection, for example for Deltamethrin (LOD = 230 pg m^{-3}) that give very weak analytical responses in mass spectrometry when it is operated in electron impact mode, or to the physic-chemical properties of the molecules. In fact, the detection of atmospheric pesticides requires good stability of the compounds for them to remain in atmosphere. Many of the pesticides that were not detected are not persistent in the atmosphere.

The detected concentrations of deltamethrin ranged from 5.8 - 79 ng/m^3 with an average of 27 ng/m^3. Deltamethrin was mostly present in the solid phase with a gas-particle distribution of less than 5:95. This indicates that the deltamethrin present such samples is strongly bound to particles which are transported in the air.

I. MATERIALS AND METHODS

A. MATERIALS

1. Standards

Deltamethrin and tecnazen, which was used as internal standard, were of certified quality (purity > 98%).

2. Test Site

Air samples were collected in [redacted] with a high volume sampler, which was placed in the botanic garden [redacted], approximately 0.5 km from the town centre, 2 km from industrial zones and about 5 km from the first exploitation of high maize and cereal crops. Trifloxystrobin was not used in the botanical garden.

B. STUDY DESIGN

1. Experimental Conditions

A high volume sampler collected simultaneously particulate and gaseous samples on 30 cm (diameter) glass fibre filters and 20g XAD-2 resin, a copolymer of styrene/divinylbenzene and macroporous acrylic ester, at a flow rate of 9.96 L/min.

2. Sampling

Air samples were collected at 10 sampling intervals for 48 hour periods on average between April 17th and May 29th, 2007. After sampling, filters and resins were stored in the dark at -20 °C for a maximum of 4 days until extraction.

3. Analytical Procedures

Prior to sampling, the glass fibre filters and the XAD-2 resin were Soxhlet-cleaned for 24 hours with n-hexane/CH_2Cl_2 1/1 and dried. After drying, they were individually wrapped in clean plastic bags or aluminium foil, and stored in the dark at -20 °C.

The extraction of the pesticides from the filters and the resin was done separately by Soxhlet extraction for 20 hours with n-hexane/CH_2Cl_2 1/1. After extraction, the solvents were concentrated to approximately 1 mL in a rotary evaporator at 40 °C, and spiked with tecnazen, which was used as internal standard.

A multimethod was developed for the determination of 71 pesticides in air by GC-MS/MS or GC-ECD, including deltamethrin. Intraday and interday accuracies and variabilities were determined by spiking blank filters and resin samples with two different concentrations. The analysis has been performed on samples of particulate and gaseous phases, respectively. The results of both phases were combined to obtain the concentration found in the total atmosphere. The limit of detection in air was approximately 230 pg m^{-3} for deltamethrin.

II. RESULTS

Table 7.5- 6: Summary of concentration data obtained in 10 air samples (expressed as ng/m^3)

Compound	No of Detections	Range	Average ± 95% CI [1]
Deltamethrin	8	5.8 – 79.0	27.41 ± 28.03

CI: confidence interval

[1] Average and CI were calculated from the arithmetic mean and standard deviation of samples with concentration superior to the LOQ.

III. CONCLUSIONS

The detected concentrations of deltamethrin in air were low and therefore of no toxicological or ecotoxicological relevance, even during the period of main use. The detected concentrations of deltamethrin ranged from 5.8 – 79.0 ng/m^3 with an average of 27 ng/m^3.

Deltamethrin was mostly present in the solid phase with a gas-particle distribution of less than 5:95. This indicates that the deltamethrin present in such samples is strongly bound to particles.