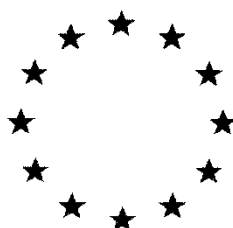# European Commission

Renewal Assessment Report prepared according to the Commission Regulation (EU) N° 1107/2009

Mecoprop-P

Volume 3 – B.8 (AS)

Rapporteur Member State : United Kingdom
Co-Rapporteur Member State : Ireland

Version History

When	What
31/03/2016	Initial Renewal Assessment Report (RAR)

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B.8. <u>ENVIRONMENTAL FATE AND BEHAVIOUR</u>

A summary box outlining the source of the study (eg. existing data or original assessments or new information evaluated or added for the purpose of renewal), the level of UK RMS evaluation and a brief note on how the data have been used has been included at the beginning of every study.

B.8.1. FATE AND BEHAVIOUR IN SOIL

The applicant has requested use of the herbicide mecoprop-P at a maximum rate of one application of 1.2kg a.s/ha on winter cereals at BBCH20-32 and spring cereals at BBCH13-32, to be applied from 1st March for both crops.

B.8.1.1. **Route and rate of degradation in soil**

Aerobic degradation in soil (CA 7.1.1.1)

RMS Comments:	In DAR for original approval (1998) a study on racemic mecoprop in a single soil was assessed. This study is not relied on as an acceptable study on mecoprop-P is available (Schocken, 1997, Addendum 1 to DAR, 2000) No new data has been submitted.

Report:	**Schocken, M (1997)**
Title	MCPP-P Aerobic Soil Metabolism
Guidelines:	FIFRA Pesticide Assessment Guideline N 162-1 and BBA IV-4-1
GLP:	Yes
Deviations	US soil study terminated at 191 days rather than 1 year due to decline in soil microbial activity Temperature deviations: 13.4°C and 27.7°C were reported on one occasion each. Except for those two days, temperature deviations were generally within 1°C of specified 20±°C.

Previous evaluations:	In Addendum 1 to DAR (2000) The original evaluation has been reproduced below. The RMS has briefly reviewed the study and added some additional information. A new analysis of the data has been submitted according to FOCUS guidance (2006) (Hazlerigg 2015), therefore the discussion of kinetics from the original evaluation has been struckthrough. The RMS considers the study acceptable. Mecoprop-P passes directly to non-extractable residues or indirectly via minor degradation products to CO_2. The soil pH's ranged from 6.0 to 7.4 which is insufficient to establish if aerobic degradation is pH dependent.

Methods
The aerobic degradation of ^{14}C-(phenyl)-MCPP-P (ring labelled) at 20°C was investigated in two separate studies: One study with an American sandy loam (Timmerman soil) in accordance with US EPA Guideline 162-1 and one study with the three German standard soils Speyer 2.1, 2.2 and 2.3 in accordance with BBA Guideline IV, 4-1. In both cases ^{14}C-MCPP-P was applied at a dosage of 1.16 µg/g microbial active soil (assuming a soil density of 1.5cm^3 and soil depth of 5cm, this dose rate equates to 870 g a.s/ha). The German soils were run for 100 days. The American soil was planned to run for one year, but as the microbial activity was severely inhibited after 191 days and as the outcome of the study was considered valid at that time, the study was stopped at day 191. The time of sampling is specified in the table of results. The soils are characterised in the table below.

Table B. 8.1. Soil characteristics. *OM: Organic matter. FMC: Field moisture capacity at 1/3bar. CEC: Cation Exchange Capacity, meq/100 g soil*

Soil type	pH (solution not reported)	Sand %	Silt %	Clay %	OM %	FMC %	CEC
Sandy loam (US, Timmerman)	7.4	66	27	7	0.9	12.5	14.4
Sand (Speyer 2.1)	6.9	94	1	5	0.8	7.1	4.1
Loamy sand (Speyer 2.2)	6.0	86	7	7	3.5	13.7	9.0
Sandy loam (Speyer 2.3)	7.4	70	17	13	0.9	19.1	8.9

The moisture level was adjusted to 75% field moisture capacity. The samples were placed in glass chambers which were connected to a series of traps for the collection of volatile components. Duplicate samples were analyzed on the days specified in the tables below. The soil extraction was performed using acetonitrile:acetic acid (99:1) and analysed by LSC and HPLC.

Results

The American sandy loam (Timmerman soil)

The distribution of ^{14}C on different compounds and fractions with time are specified in the table below. All values are averages of two replicas and are expressed in percent of applied ^{14}C. The limit of detection is not clearly specified, but from the precision in the presented data the Danish EPA find it reasonable to suggest a limit of detection in the range of 0.1 % of applied ^{14}C.

Extractable activity decreased to 12 % on day 30 and 4.6 % on day 191, where mecoprop-P accounted for 1.6 %. No metabolites amounted singularly to more than 3 %. The metabolite 4-chloro-2-methylphenol was identified with a maximum of 1.3 % day 128 and 0.1 % day 191. Three metabolites, A, B and C was characterised but not identified. The rapport states that A and B were more polar than mecoprop-P while C was less polar.

Unextractable ^{14}C reached a maximum of 57 % on day 30 and decreased to 44 % on day 191.

Mineralization, expressed as $^{14}CO_2$, amounted to 38 % after 191 days.

Table B. 8.2. Aerobic degradation of MCPP-P in sandy loam. Mass balance and distribution of ^{14}C on extractable, non extractable (NER) and CO_2. Extractable ^{14}C are shown as total (underlined) and as mecoprop-P and the metabolites. 4C-2M is 4-chloro-2-methylphenol. nd: not detected. na: not analysed. All values are averages of two replicas and are expressed in percent of applied ^{14}C.

	Recovery after days in percent of applied ^{14}C, average of two replica									
Day	0	1	3	6	14	30	64	91	128	191
<u>Soil Extract:</u>	<u>103</u>	<u>89.9</u>	<u>70.0</u>	<u>55.6</u>	<u>33.1</u>	<u>11.9</u>	<u>8.64</u>	<u>8.18</u>	<u>9.52</u>	<u>4.58</u>
Mecoprop-P	103	89.9	70.0	54.5	31.7	9.11	5.22	4.89	5.66	1.60
Metabolite 4C-2M	nd	nd	nd	0.77	0.87	0.57	0.70	1.02	1.31	0.08
Metabolite A	nd	nd	nd	nd	0.32	2.38	1.85	1.22	nd	0.25
Metabolite B	nd	nd	nd	nd	nd	0.11	0.09	nd	nd	nd
Metabolite C	nd	nd	nd	nd	nd	0.13	0.52	0.72	2.34	1.99

Day	Recovery after days in percent of applied ^{14}C, average of two replica									
	0	1	3	6	14	30	64	91	128	191
NER	0.62	7.57	20.8	31.7	39.7	56.9	50.2	47.1	52.0	44.4
CO_2	na	1.18	1.78	5.88	15.5	26.4	25.6	25.0	22.1	39.7
Total	104	98.7	92.6	93.1	88.3	95.2	84.4	80.3	83.6	88.7

Table B. 8.3. Degradation profile of mecoprop-P in Timmerman soil

Time	% Applied Radioactivity				
	Mecoprop-P	4C-2M-Phenol	Unknown A	Unknown B	Unknown C
0	102	ND	ND	ND	ND
0	104	ND	ND	ND	ND
1	90.7	ND	ND	ND	ND
1	89.1	ND	ND	ND	ND
3	70.0	ND	ND	ND	ND
3	70.0	ND	ND	ND	ND
6	54.9	0.62	ND	ND	ND
6	54.1	0.93	ND	ND	ND
14	32.0	0.98	0.64	ND	ND
14	31.5	0.76	ND	ND	ND
30	8.62	0.40	2.40	0.23	0.26
30	8.27	0.74	2.37	ND	ND
64	3.65	0.44	2.07	ND	0.35
64	6.78	0.96	1.63	0.18	0.69
91	8.25	0.89	0.38	ND	0.83
91	1.52	1.14	2.05	ND	0.61
128	9.48	1.85	ND	ND	2.27
128	1.83	0.78	ND	ND	2.42
191	2.93	ND	ND	ND	1.42
191	0.27	0.17	0.51	ND	2.56

ND = not detected

The report states that the relatively low recovery of ^{14}C in the last time period of the study compared to the recovery in the German soils (see below) could be explained by loss of volatile ^{14}C ($^{14}CO_2$). In the American part of the study the soils were ventilated 30 minutes pr. day, in the German part there was continuously airflow with trapping of volatiles.

Initial microbial biomass of the soil was determined to be 29 mg C/100g soil by substrate-induced respirometry. Four days after test termination (Day 195), microbial carbon was determined to be 7 mg C/100g soil. Respirometry results were confirmed by fumigation-extraction on day 225. Plate counts demonstrated an increase in total heterotrophic bacteria by day 225. Actinomycetes and fungi counts decreased over the study period, but a viable population remained in the soil by day 225. The RMS notes that mecoprop-P levels in the Timmerman soil were <10%AR by day 30, therefore the decline in microbial activity reported at the end of the study (day 191) is not expected to significantly affect the results.

Table B. 8.4 Microbial biomass measurements in American Sandy Loam

Day	Respirometry (mg C/100g soil)	Fumigation/extraction (mg C/100g soil)	Plate counts (cfu/g)		
			Bacteria (nutrient agar+soil extraction)	Actinomycetes (actinomycete media)	Fungi (peptone dextrose media)
-4	29	-	-	-	-
-1	-	-	1.0×10^2	8.5×10^6	1.1×10^5
195	7	-	-	-	-
225	-	3.7	2.9×10^6	4.7×10^5	7.5×10^4

The three German standard soils (Speyer 2.1, 2.2 and 2.3)

The distribution of ^{14}C on different compounds and fractions with time are specified in the table below. All values are averages of two replica and are expressed in percent of applied ^{14}C. The limit of detection are not clearly specified, but from the precision in the presented data the Danish EPA find it reasonable to suggest a limit of detection in the range of 0.1 % of applied ^{14}C.

Extractable ^{14}C decreased to 3 - 5 % of applied amount on day 100, where mecoprop-P amounted to 1.2 – 2.6 %. No single metabolite amounted to more than 3 %. The metabolite 4-chloro-2-methylphenol was identified; it reached a maximum of 0.9 - 2 % on day 3 or 16 (depending on the soil type) and fall to < 0.1 – 0.3 % day 100. The metabolite A was isolated but not identified. The maximum of A was 2.3 – 2.5 % day 36 in soil 2.1 and 2.2; in soil 2.3 the maximum recorded concentration was reached on the last day of the study.

Non extractable ^{14}C reached a maximum of 50 - 61 % day 36 or 71 and decreased to 43 - 51 % day 100.

Mineralization, expressed as $^{14}CO_2$, amounted to 42 - 51 % after 100 days.

Table B. 8.5. Aerobic degradation of MCPP-P in the three German standard soils. Mass balance and distribution of ^{14}C on extractable, non extractable (NER) and CO_2. Extractable ^{14}C are shown as total (underlined) and as mecoprop-P and the metabolites. 4C-2M is 4-chloro-2-methylphenol. nd: not detected. na: not analysed. All values are averages of two replicas and are expressed in percent of applied ^{14}C.

Day	Recovery after days in percent of applied ^{14}C, average of two replica							
	0	1	3	7	16	36	71	100
Soil extract:								
Speyer 2.1	102	94.5	84.2	56.6	14.4	6.52	4.02	3.68
Speyer 2.2	102	87.9	97.2*	40.8	25.7	12.7	6.27	5.14
Speyer 2.3	103	91.1	76.8	47.8	15.4	6.31	3.62	4.03
Mecoprop-P								
Speyer 2.1	102	94.5	91.4	55.2	12.1	3.45	1.79	1.25
Speyer 2.2	102	87.3	94.5*	38.6	24.7	10.8	3.38	2.58
Speyer 2.3	103	91.1	76.8	46.7	12.8	3.60	1.77	1.16
Metabolite 4C-2M								
Speyer 2.1	nd	nd	0.44	0.98	1.95	0.16	0.20	0.26
Speyer 2.2	nd	0.57	1.74*	0.03	0.91	nd	nd	nd
Speyer 2.3	nd	nd	nd	nd	0.93	0.40	nd	nd
Metabolite A								
Speyer 2.1	nd	nd	nd	nd	nd	2.28	1.30	1.51
Speyer 2.2	nd	nd	nd	1.95	nd	2.48	1.37	2.25
Speyer 2.3	nd	nd	nd	0.67	nd	1.84	1.08	2.17

		Recovery after days in percent of applied ^{14}C, average of two replica						
Day		0	1	3	7	16	36	71	100
NER									
	Speyer 2.1	0.60	6.97	18.0	32.0	50.3	59.8	51.0	43.1
	Speyer 2.2	1.27	10.3	23.6	40.3	48.4	47.5	50.3	44.0
	Speyer 2.3	1.23	7.65	16.8	31.9	47.7	60.6	52.9	51.2
CO_2									
	Speyer 2.1	na	1.18	5.17	13.8	24.6	38.4	47.8	50.5
	Speyer 2.2	na	1.88	7.34	20.2	29.3	39.8	46.4	49.6
	Speyer 2.3	na	1.20	5.93	17.0	37.9	33.8	40.5	42.3
Total									
	Speyer 2.1	102	103	107	102	89.2	105	103	97.3
	Speyer 2.2	103	100	104	101	103	100	103	98.7
	Speyer 2.3	104	100	99.4	96.7	101	101	97.0	97.5

*The RMS notes that there is a discrepancy in the study report data for Speyer 2.2 soil. Day 3 %AR in soil extract is reported in the mass balance table (study report table 12) as 72.2% and 73.5%AR for replicates A and B respectively whilst in the degradate profile table (study report table 16) it is reported as 96.7% and 97.7%AR (mean 97.2%). The values in the degradate profile table (study report table 16) appear to be a typographical error because they are identical to the values in the next column (% of HPLC mecoprop-P) and would result in a mass balance of 128%AR. Using the day 3 extractable %AR values of 72.2% and 73.5% (mean 72.9%), mecoprop-P on day 3 represents 70.8%AR (mean) and metabolite 4C-2M represents 1.31%AR, resulting in a mass balance of 104%AR as given in Table B. 8.5 above. The data listed in B.8.6 to B.8.8 were used by the RMS for the re-evaluation of the kinetics.

Table B. 8.6. Degradation profile of mecoprop-P in Speyer 2.1 soil

Time	% Applied Radioactivity		
	Mecoprop-P	4C-2M-Phenol	Unknown A
0	102	ND	ND
0	101	ND	ND
1	96.2	ND	ND
1	92.8	ND	ND
3	100	ND	ND
3	82.9	0.89	ND
7	58.7	0.38	ND
7	51.7	1.57	ND
16	13.2	1.36	ND
16	11.1	2.54	ND
36	3.55	0.19	2.39
36	3.34	0.14	2.17
71	2.00	0.14	1.34
71	1.57	0.27	1.27
100	0.97	ND	1.60
100	1.53	0.51	1.43

ND = not detected

Table B. 8.7. Degradation profile of mecoprop-P in Speyer 2.2 soil

Time	% Applied Radioactivity		
	Mecoprop-P	4C-2M-Phenol	Unknown A
0	101	ND	ND
0	102	ND	ND

Time	% Applied Radioactivity		
	Mecoprop-P	4C-2M-Phenol	Unknown A
1	89.3	1.13	ND
1	85.3	ND	ND
3	69.8	1.47	ND
3	71.8	1.14	ND
7	38.6	0.06	1.82
7	38.6	ND	2.08
16	24.3	0.62	ND
16	25.2	1.20	ND
36	10.5	ND	2.89
36	11.1	ND	2.07
71	1.47	ND	1.54
71	5.30	ND	1.20
100	3.83	ND	1.54
100	1.33	ND	2.97

ND = not detected

Table B. 8.8. Degradation profile of mecoprop-P in Speyer 2.3 soil

Time	% Applied Radioactivity		
	Mecoprop-P	4C-2M-Phenol	Unknown A
0	105	ND	ND
0	101	ND	ND
1	90.0	ND	ND
1	92.2	ND	ND
3	77.3	ND	ND
3	76.2	ND	ND
7	48.4	ND	ND
7	45.1	ND	1.35
16	12.7	0.87	ND
16	12.8	0.99	ND
36	3.77	0.36	2.04
36	3.44	0.44	1.64
71	1.50	ND	1.29
71	2.05	ND	0.87
100	0.73	ND	1.69
100	1.59	ND	2.65

ND = not detected

The report states that the continuing production of $^{14}CO_2$ together with a falling (NER) indicates a mineralization of the soil bound residues. It states too that the most likely degradation pathway of mecoprop-P in soil is a conversion to 4-chloro-2-methylphenol, over soil bound residues to CO_2.

Substrate-induced respirometry and plate counts indicate little change in microbial viability in Speyer 2.1 and Speyer 2.3 soils of the 100 day incubation period whilst Speyer 2.2 displayed some decrease in microbial activity.

Table B. 8.9. Microbial biomass measurements in German standards soils

Soil	Day	Respirometry (mg C/100g soil)	Fumigation/ extraction (mg C/100g soil)	Plate counts (cfu/g)		
				Bacteria (nutrient agar+soil extraction)	Actinomycetes (actinomycete media)	Fungi (peptone dextrose media)
Speyer 2.1	-5	-	-	3.9×10^7	1.4×10^7	1.6×10^5
	-1	14	-	-	-	-
	7	14	-	-	-	-
	104	12	-	1.2×10^7	3.6×10^6	5.7×10^4
Speyer 2.2	-5	-	-	4.7×10^7	1.4×10^7	4.6×10^5
	1	42	-	-	-	-
	104	24	-	8.5×10^6	3.0×10^6	4.7×10^4
Speyer 2.3	-4	-	-	2.6×10^7	1.0×10^7	9.4×10^4
	2	20	-	-	-	-
	7	19	-	-	-	-
	104	19	-	2.6×10^7	1.1×10^7	7.8×10^4

2000 Evaluation Comments

The study is acceptable. The degradation of mecoprop-P passed directly to non-extractable residues or indirectly via degradation products to CO_2.

Anaerobic degradation in soil (CA 7.1.1.2)

RMS comments:	In DAR for original approval (1998) an aerobic degradation study on racemic mecoprop in a single soil was assessed and considered acceptable (Saxena, 1988). The applicant has stated that mecoprop-P will be applied early in the season (Spring/Summer) when conditions are not anaerobic. Additionally mecoprop-P is rapidly degraded in aerobic soil therefore significant amounts will not remain in the soil when conditions become anaerobic later in the year. Consequently an anaerobic study on mecoprop-P is not required. The RMS agrees that use under anaerobic conditions is unlikely for the representative use and therefore an anaerobic degradation study on mecoprop-P is not required for this use. Should approval be sought for uses with later timings, then anaerobic degradation data may be necessary. Saxena, 1998, therefore provides supporting data, indicating that degradation and mineralisation are minimal under anaerobic conditions. The study has <u>not</u> been relied on for risk assessment purposes.

Report:	**Saxena AM, 1988**
Title	Aerobic and aerobic/anaerobic soil metabolism of ^{14}C-mecoprop
Guidelines:	EPA 40 CFR 160 N, 162-1
GLP:	
Deviations	

Previous Evaluation:	In DAR for original approval (1998). The original evaluation has been reproduced below.

The aerobic/anaerobic degradation of mecoprop in a sandy loam soil was studied using ^{14}C-mecoprop uniformly labelled in the ring. The radiopurity was 96.3%. The study method was according to EPA 40 CFR 160 N, 162-1.

Methods
The anaerobic degradation was studied on the same soil as in the aerobic study (B.7.1.1.1.1) and also fortified with ^{14}C-MCPP at 9.98 µg/g soil. After 30 days of aerobic degradation, four samples were flooded with water to a height of 3 cm above the soil surface and placed in a glass chamber as the previous and nitrogen was introduced instead of air. The samples were placed in a glass chamber which was connected to a series of traps for the collection of volatile components (ethylene glycol and 2-ethoxyethanol:ethanolamine (1:1)). The temperature was maintained at 24.2^o to 25.6^{o}C. Two samples collected after 30 days aerobic incubation was considered to be day 0 samples in the anaerobic part of the study. Two additional samples were collected after 31 and 61 days of anaerobic incubation. The soil extraction was performed using acetonitrile:acetic acid (99:1) and analysed by LSC and TLC.

Table B. 8.10. *Soil characteristics. OM: Organic matter. FMC: Field moisture capacity. CEC: Cation Exchange Capacity, meq/100 g soil*

Soil	pH	Sand %	Silt %	Clay %	OM %	FMC %	CEC
Sandy loam	5.6	51	36	13	2.4	30.7	5

Results
Under anaerobic conditions, the major component of each organic extracts was MCPP. A minor compound (Peak 1) was observed only in the ACN:HOAc extracts of soil samples. The amount of this degradation product did not exceed 1.1% of applied radioactivity.

Flooding of the soil to introduce the anaerobic part of the study resulted in a distribution of the radioactivity into the water layer. The CO_2 development and the formation of non-extractable residues was inhibited by anaerobic conditions. Because no degradation under anaerobic conditions could be observed the half-life could not be calculated.

Table B. 8.11. *Anaerobic degradation. Mass balance of extractable, non-extractable (NER) and volatile radioactive residues from soil and water phases, and CO_2 development. Included are the results from radio-TLC analysis of extractable residues. NA: not analyzed. ND: Not detected*

Incubation: Aerobic 30 days + anaerobic up to 61 days	Soil		Water		Traps		Total
	Extract	NER	Extract	NER	Volatiles	CO_2	
0 days	22.3	44.0	NA	NA	<0.1	30.8	97.1
MCPP	20.1						
Peak 1	0.9						
31 days	9.1	37.5	15.3	0.9	<0.1	31.6	94.5
MCPP	7.2		14.8				
Peak 1	1.1		ND				
61 days	8.0	40.5	17.1	1.1	<0.1	32.1	98.8
MCPP	6.1		17.6				
Peak 1	1.1		ND				

1998 Evaluation Comments
Racemic mecoprop was used in the study. The anaerobic degradation of MCPP was reduced to an insignificant level. The CO_2 development was inhibited and only increased from 30.8% to 32.1% while the concentration of MCPP increased from 20.1% to 23.7% of applied radioactivity after 61 days under anaerobic conditions. Thus, the degradation and mineralization were reduced to negligible levels or not taking place under anaerobic conditions.

Soil Photolysis (CA 7.1.1.3)

RMS Comments:	In DAR for original approval (1998) a soil photolysis study on racemic mecoprop was assessed (Obrist 1986). Poor mass balances were reported and attributed to loss of volatiles. A supplementary study using similar conditions was submitted to address the poor material balance (Obrist, 1989). Samples were analysed on day 30 only which indicated that mecoprop photodegrades via metabolite 4-chloro-3-methylphenol (max reported 7%). The 1998 RMS considered the studies sufficient to show that photolysis from soil may take place. Obrist 1986 and 1989 are not considered sufficient to meet current guidelines. A new soil photolysis study on mecoprop-P has been submitted (Connor, 1996a). Additionally, the data from Connor 1996a has been re-evaluated according to current guidance (FOCUS 2006) in Hazlerigg & Garratt, 2015.

Report:	CA 7.1.1.3/01, Connor, S.R. (1996a)
Title	MCPP-P – soil photolysis study Report No. 96-1-6346
Guidelines:	FIFRA Subdivision N: § 161-3
GLP:	Yes
Deviations	The temperature exceeded 25°C on several occasions; this deviation was generally corrected within 30 minutes.

Previous evaluations:	None: Submitted for the purpose of renewal under Regulation 844/2012. The RMS considers the study acceptable. Mecoprop-P photodegrades via minor metabolite 4-chloro-2-methylphenol (max 3.23%).

Executive Summary

In a soil photolysis study, the phototransformation of mecoprop-P was studied on a sandy loam soil following 30 days exposure at 25°C to artificial sunlight (xenon arc). Test and control soil samples were treated with radiolabelled mecoprop-P at a rate equivalent to 945 g a.s./ha.

The mass balance ranged from 88.7 to 95.4 % and 93.3 to 101 % of applied radioactivity in the irradiated and control samples respectively. The metabolite 4-chloro-2-methylphenol (PCOC) was detected at up to 3.23 % of the applied radioactivity. PCOC was not found in the dark control samples. There was a steady decrease in extractable residues in the irradiated samples from an average of 92.8 to 74.3% of the applied radioactivity. There was a corresponding increase in non-extractable residues in the irradiated samples reaching a maximum of 14.9 % on Day 30. In the dark controls extractable radioactivity remained constant. After 30 days of incubation volatiles totalled 2.55 and 0.913 % of the applied radioactivity in the irradiated and dark control samples, respectively.

<div align="center">

I.   MATERIALS AND METHODS

</div>

A.   MATERIALS

1.	**Test materials:**	Mecoprop-P / ^{14}C-Mecoprop-P
	Description:	White solid
	Lot/Batch #:	39-170-3 / 515-02
	Purity:	99.3% / 99.2%, 48.2 mCi/mol
	CAS #:	16484-77-8

Stability of test compound:	Stable

2.   Soils:

Location	Timmerman, Washington, USA
Collection Date	5 May 1995
Soil textural class	Sandy loam
Sand	66%
Silt	27%
Clay	7%
Cation exchange capacity	14.4 meq/100g
Bulk density	1.28 g/cc
pH (solution not reported)	7.4
Organic matter	0.9%
Total nitrogen	0.0051%

B.   STUDY DESIGN

1. Dates of experimental work

05 October 1995 – 20 December 1995

2. Experimental conditions

A primary stock solution (0.131 mg/mL) was prepared by dissolving mecoprop-P in acetonitrile. A secondary stock solution was prepared by diluting 1.4 mL of the primary stock to a final volume of 14 mL with acetonitrile (0.0131 mg/mL).

A preliminary study was performed to establish appropriate sampling intervals for the definitive study and to confirm the acceptability of the experimental procedures.

Approximately 5.9 g soil (sieved <2mm) were made into an aqueous slurry, placed in 60 mm diameter petri dishes and allowed to air dry. Based on the soil bulk density of 1.28 g/cm^3 and the area of the petri dish, this amount of soil provided a 1.5 mm layer. A total of 26 soil samples in petri dishes were prepared – 12 designated as irradiated replicates, 12 as dark control replicates and two as soil blanks. Blank samples were used for temperature measurement during the definitive study.

Five hundred microliters of the secondary stock solution (0.0131 mg/mL) was added to each soil replicate (5.43 g on a dry weight basis) to produce a concentration of 1.26 µg/g. Based on standard assumptions of a soil bulk density of 1.5 g/cm^3 and 5 cm soil depth, this equates to a dose rate of 945 g a.s/ha. The organic solvent was allowed to evaporate for 1 hour at room temperature. The soil was mixed to ensure homogeneity and adjusted to 75% field moisture capacity (12.5%).

The treated plates were placed in temperature controlled chambers and exposed to artificial sunlight over a 30 day period at 25°C. The study author notes that on several dates throughout the duration of the testing, the temperature measured within the light exposed test module exceeded 25°C. These incidences generally occurred during the transition from the light cycle to darkness and were corrected within 30 minutes by the recirculating bath (Irradiated samples: min recorded temp 20.1°C, max recorded temp 28.3°C). The RMS does not consider that the short term deviations in temperature will significantly affect the study results.

Sterile, hydrated, CO_2 free air was pulled continually through each module at an approximate flow rate of 10 mL/minute to aerate the soil and trap any volatiles. Test samples were irradiated using a xenon arc lamp, which generates a radiation distribution similar to natural sunlight (filter restricted wavelengths to >300 nm). The light source operated on a 12 h light / 12 h dark cycle. Control samples were subjected to the same conditions, with

the exception that the test module was placed in a separate environmental chamber and covered with a dark cloth to prevent light exposure.

Spectral profiles of the artificial light source were recorded before and after the study. Sunlight measurements were recorded on 1st August 1995 at 12:17pm on a clear, sunny day outside the Wareham, Massachusetts laboratory (42° North latitude). Additionally, spectral measurements to verify complete occlusion of light within the dark control test module were made.

Total light intensities of the artificial light source were made before and after the study and measured on 1st August 1995 for natural sunlight.

3. Sampling

The microbial viability of the test soil was evaluated by means of plate counts prior to initiation. Duplicate samples were taken for analysis at time zero and on five subsequent points (days 5, 11, 15, 22 and 30) for analysis.

4. Description of analytical procedures

Volatile organic compounds were trapped by passing the air flow through a polyurethane foam plug and an ethylene glycol trap. $^{14}CO_2$ was trapped using two potassium hydroxide solutions in succession. $^{14}CO_2$ trapping efficiency of the volatile trapping system was determined using NaH_4CO_3. 104%AR recovery was achieved. A single volatile trapping train was connected to each test module and served as a collective trap for all irradiated soil samples or for the samples incubated in the dark. The polyurethane foam plugs, ethylene glycol and 10% potassium hydroxide solutions were replaced and quantified by radioassay at each sampling interval. LOD is reported as 0.0386%AR for the potassium hydroxide trapping solution.

Soil samples were extracted with 3 x 10 mL acetonitrile : water : acetic acid (8 : 2 : 0.1 v/v/v) using a vortex agitator for three minutes and shaking by hand for 3 minutes after which the samples were centrifuged for 20 minutes and the supernatants combined.

Three 100 µL aliquots were radio-assayed to quantify the overall extractable radioactivity (LOD 0.38%AR). The total radioactivity in the combined extract from each plate was compared to the radioactivity applied to each plate to determine percent recovery. An aliquot of the combined soil extract was profiled by HPLC-RAM to quantify the remaining mecoprop-P and to establish a degradate profile (LOD 1.76%AR). LC-ES/MS and 2D-TLC were used to confirm identity of residual mecoprop-P and photodegradate, 4-chloro-2-methylphenol. Non-extractable residues remaining in the soil were quantified by combustion analysis (LOD 0.127%AR).

Racemic mecoprop was used as the reference standard for HPLC, 2D-TLC and LC-ES/MS. Since the chromatographic and mass spectral properties of the mecoprop isomers are identical under the analytical conditions employed in the study, mecoprop serves as a valid representation of mecoprop-P.

II.   RESULTS AND DISCUSSION

A. DATA

Table B. 8.12. Percentage of applied radioactivity in irradiated soils

Day	Rep	% Applied Radioactivity							
		Mecoprop-P	PCOC	Unknown 1	Unknown 2	Total Extractable	Bound	Volatiles	Mass Balance
0	A	91.4	ND	ND	ND	91.4	0.9	-	92.3
	B	94.2	ND	ND	ND	94.2	1.1	-	95.3
5	A	83.0	1.81	ND	ND	84.8	9.7	0.87	95.4
	B	82.8	2.5	ND	ND	85.3	8.8	0.87	95.0
11	A	71.7	1.75	ND	ND	73.4	16.9	1.43	91.7
	B	77.6	1.93	ND	ND	79.5	13.0	1.43	93.9
15	A	72.1	2.6	ND	ND	74.7	12.2	1.84	88.8
	B	70.1	1.76	ND	ND	71.9	15.0	1.84	88.7
22	A	74.4	1.85	ND	<1	76.9	14.4	2.55	93.8
	B	73.2	2.29	ND	<1	76.1	15.1	2.55	93.7
30	A	65.7	3.23	1.03	ND	70.9	16.8	2.55	90.2
	B	73.3	2.6	<1	ND	77.7	13.0	2.55	93.2

Table B. 8.13. Percentage of applied radioactivity in dark control soils

Day	Rep	% Applied Radioactivity							
		Mecoprop-P	PCOC	Unknown 1	Unknown 2	Total Extractable	Bound	Volatiles	Mass Balance
0	A	-	-	-	-	-	-	-	-
	B	-	-	-	-	-	-	-	-
5	A	92.4	ND	ND	ND	92.4	2.2	0.050	94.7
	B	92.5	ND	ND	ND	92.5	2.0	0.050	94.6
11	A	90.9	ND	ND	ND	90.9	4.1	0.071	95.1
	B	94.3	ND	ND	ND	94.3	3.4	0.071	97.8
15	A	91.6	ND	ND	ND	91.6	3.1	0.081	94.7
	B	90.0	ND	ND	ND	90.0	3.2	0.081	93.3
22	A	95.8	ND	ND	ND	95.8	4.3	0.089	100.0
	B	93.0	ND	ND	ND	93.0	3.8	0.089	96.9
30	A	97.0	ND	ND	ND	97.0	3.1	0.913	101.0
	B	94.7	ND	ND	ND	94.7	3.0	0.913	98.6

B.   MASS BALANCE

The mass balance ranged from 88.7 to 95.4 % and 93.3 to 101 % of applied radioactivity in the irradiated and control samples respectively. Mass balance <90% were for light exposed mecoprop-P on day 15 only (Rep A 88.8%, Rep B 88.7%). Mass balances for all other samples were >90%.

C.   BOUND AND EXTRACTABLE RESIDUES

There was a steady decrease in extractable residues in the irradiated samples from an average of 92.8 to 74.3% of the applied radioactivity. There was a corresponding increase in non-extractable residues in the irradiated samples reaching a maximum of 14.9% on Day 30. In the dark controls extractable radioactivity remained essentially constant between 90 and 97%AR with no more than 4.3%AR associated with the soil after extraction. The study author notes that the lack of degradation in the dark controls was most likely due to minimal retention of soil moisture in both irradiated and dark control samples in spite of initially providing moisture at 75% field

capacity and continuously aerating with hydrated air. Since both irradiated and dark control samples were kept under essentially identical conditions, the difference in degradation between the irradiated and dark samples can be ascribed to the effect of the irradiation.

D.   VOLATILIZATION

After 30 days of incubation volatiles totalled 2.55 and 0.913 % of the applied radioactivity in the irradiated and dark control samples, respectively.

E.   TRANSFORMATION OF PARENT COMPOUND

The minor metabolite 4-chloro-2-methylphenol (PCOC) was detected at up to 3.23 % of the applied radioactivity in irradiated soils by HPLC. The identity of PCOC was confirmed by 2D-TLC. It was not found in the dark control samples.

4-chloro-2-methylanisole was detected as a minor metabolite in the TLC profiling of day 30 irradiated soil extracts (0.8% of the radioactivity on the plate), but was not detected in the HPLC analysis. 5.6% of the detected radioactivity remained at the origin of the TLC plate. Since this radioactivity was not apparent in the HPLC profile, it was ascribed to air oxidation at the silica gel surface after application and prior to development.

F.   MICROBIAL VIABILITY IN SOIL

Soil microbial plate counts confirmed that the soil remained viable throughout the study.

Table B. 8.14. Soil microbial plate counts

		cfu/g
Study initiation		9.0×10^6
Study termination	Light exposed	4.2×10^6
	Dark control	2.9×10^6

G.   COMPARISON OF ARTIFICIAL LIGHT SOURCE TO NATURAL SUNLIGHT

Total intensity measurements were 3.40×10^{-3} and 1.67×10^{-2} W/cm^2 for the artificial light source and natural sunlight respectively. The total intensity of the artificial light source was approximately 20.4% that of natural sunlight. Following termination of the study, total light intensity of the artificial light source was 3.69×10^{-3} W/cm^2 representing 22.1% the intensity of natural sunlight. Spectral profiles of artificial light and natural sunlight indicate that the artificial light source was a reasonable model for sunlight and that the light intensity and spectral profile of the artificial light remained stable during the time of the study.

The data from this study were assessed according to FOCUS kinetics in a separate study. Results are summarised in Table B. 8.15 below. For full details of the kinetic analysis, see the evaluation of Hazlerigg & Garratt, 2015.

Table B. 8.15. Summary of kinetic endpoints for soil photolysis of mecoprop-P

Fit		Artificial light	Natural sunlight (42°N)	
			Hazlerigg calcualtion	RMS calculation
SFO	DT$_{50}$ (days)	73.8	14.8	20.66
	DT$_{90}$ (days)	245	49.0	68.6

Rate of degradation in soil (CA 7.1.2.1.1)

RMS comments:	For the original Annex I approval of mecoprop-P, endpoints for the rate of degradation in aerobic soil were taken from Schocken, 1997. A new study has been submitted to update the kinetics from Schocken, 1997, to modern guidance – Hazlerigg & Garratt, 2015. One study was identified as potentially relevant by the applicant during the literature review.

Report:	**Hazlerigg, C & Garratt, J (2015)**
Title	A kinetic analysis of the degradation of mecoprop-P and its metabolites in aerobic soils as well as via photolysis in soil and water Report No E2015-11
Guidelines:	FOCUS Kinetics 2006, 2014
GLP:	No
Deviations	None

Previous evaluations:	None: Submitted for the purpose of renewal under Regulation 844/2012

Hazlerigg, 2015 analyses data from three studies:
1. Degradation of mecoprop-P in four aerobic soils (Schocken, 1997)
2. Degradation of mecoprop-P due to photolysis in soil (Connor 1996a)
3. Degradation of mecoprop-P due to photolysis in water (Connor 1996b)

Kinetic analysis was performed using CAKE v3.1 with OLS optimisation. The report states that IRLS optimiser was used where confidence limits with the initial OLS fit were unreliable.

1. Schocken (1997) – aerobic soils

Two separate studies were performed and reported in Shocken, 1997: the first using a sandy loam soil collected from agricultural land in the United States (FIFRA study - Timmerman soil), the second using three soils obtained from Germany (BBA study - Speyer 2.1, 2.2 and 2.3 soils). Both studies were performed at 20°C and 75% field moisture capacity at 1/3bar. A clear decline in the concentration of the parent substance was observed in all four soils, with final concentrations of mecoprop-P reaching less than 10 % applied radioactivity in all soils studied. No relevant metabolites were identified in any of the soils. Hazlerigg, 2015, contains a kinetic analysis of minor metabolite 2-methyl-4-chlorophenol. As this was not identified as a relevant aerobic soil metabolite, the RMS has not evaluated the metabolite kinetics. As the LOD is not clearly reported in Shocken 1997, the LOD was assumed to be 0.06%AR based on the lowest recorded %AR in the entire study.

    1.1. Timmerman soil (FIFRA study)

Hazlerigg modelling:

As an initial step, the kinetics models were fitted to the entire data-set. SFO and FOMC passed the statistical requirements to be considered a good fit including t-test, confidence limits not including zero and χ^2-error (Table B. 8.16). The FOMC was shown to have a slightly lower χ^2-error and the visual fit is reported as better as the SFO fit under-estimated later time-points, however fits and residuals plots including all the data points are not presented in the study report.
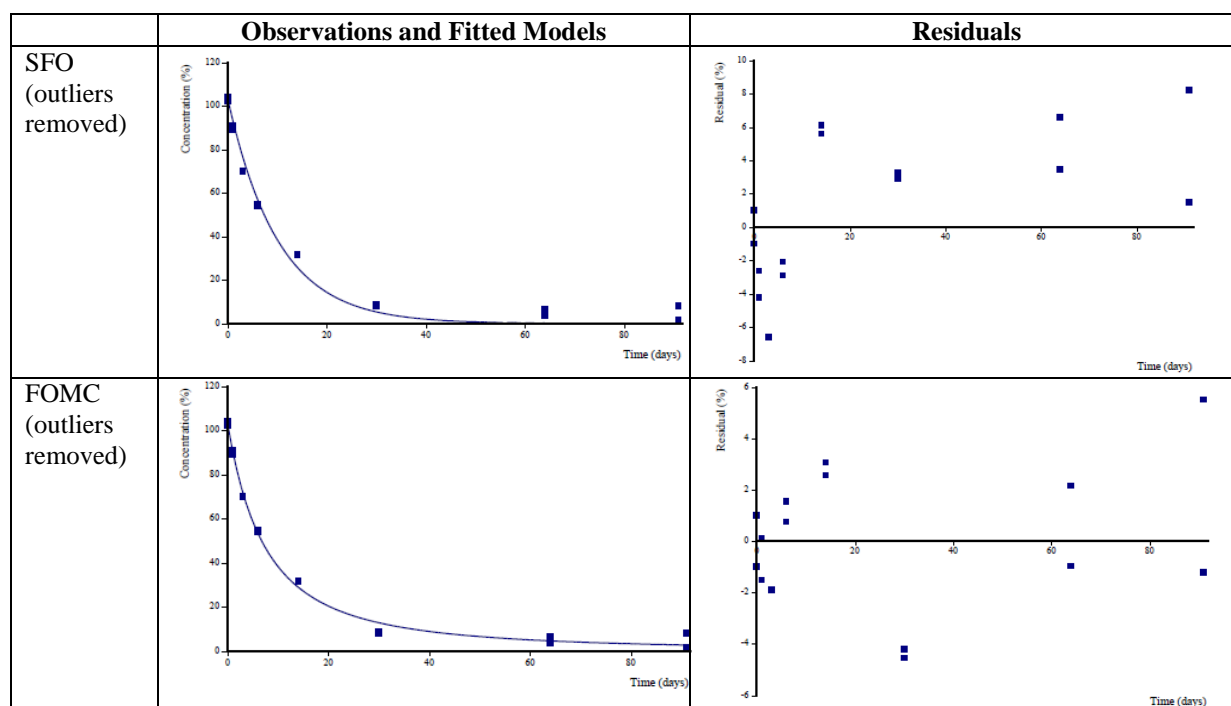
A decline in the microbial activity was described in the Timmerman (FIFRA) soil in the Schocken (1997) study. Four days prior to the start of the study microbial biomass accounted for 5.5 % of the organic carbon in the system. By the end of the study microbial biomass accounted for only 1.3 % of the organic carbon in the system. Both values are higher than the minimum of 1 % recommended by the guideline OECD 307, however, the decrease in microbial biomass was significant and therefore, the last two time-points were removed from the data-set as outliers. Additionally the data was weighted (log-transformed) to assess the applicability of bi-phasic

degradation kinetics. FOMC gave a better visual fit. DFOP kinetics were fitted to compare with FOMC, however the confidence limits for k2 included zero and so FOMC was considered to be the best fit for the data-set.

Table B. 8.16. Fitting parameters for decline of mecoprop-P for the Timmerman (FIFRA) soil data-set Kinetic model reported in Hazlerigg 2015

	Fitted parameters	**Comments**
SFO (OLS)	$M0 = 98.68\ \%$ $k1 = 0.091\ d\text{-}1$	Visual fit is good, under-estimation of later time-point residuals T-test passing for k (p < 0.1 %) χ^2-error = 8.45 %
SFO (OLS, outliers removed, log transformed)	$M0 = 1.95\ \%\ *$ $k1 = 0.018\ d\text{-}1\ *$	Visual fit is good, slight under-estimation of later time-point residuals T-test passing for k (p < 0.1 %) χ^2-error = 5.8 %
FOMC (OLS)	$M0 = 102.6\ \%$ $\alpha = 1.6$ $\beta = 11.82$	Visual fit is good Confidence limits do not include 0 for α (1.1-2.1) or β (6.6-17.1). χ^2-error = 5.16 %
DFOP (OLS)	$M0 = 100.2\ \%$ $k1 = 0.11$ $k2 = <0.01$ $g = 0.91$	Visual fit is good Confidence limits do include 0 for $k2$ (-0.002-0.016). Confidence limits do not include 0 for $k1$ (0.09-0.13) or g (0.83-0.98). χ^2-error = 5.54 %

* The values presented are those for a log transformation which when back-calculated provide values of $M_0 = 88.72$, k1 = 0.43

	Observations and Fitted Models	**Residuals**
SFO (outliers removed)		
FOMC (outliers removed)		

RMS modelling:

The RMS has repeated the kinetic modelling for the Timmerman soil including data from all time-points using CAKE v2.0 with OLS optimisation and SFO, FOMC and DFOP models.   Data were unweighted and M_0 was not fixed.   Input data are listed in

Table B. 8.17. Plots of fitted models and residuals are given in Table B. 8.18 and parameters are listed in Table B. 8.19.

Table B. 8.17. Degradation of mecoprop-P in Timmerman soil

Time (days)	Parent (%)
0	102
0	104
1	90.7
1	89.1
3	70
3	70
6	54.9
6	54.1
14	32
14	31.5
30	8.96
30	9.39
64	3.65
64	6.78
91	8.25
91	1.52
128	9.48
128	1.83
191	2.93
191	0.27

Table B. 8.18. Fitted models and residual plots for Timmerman soil

	Observations and Fitted Model	**Residuals**
SFO		
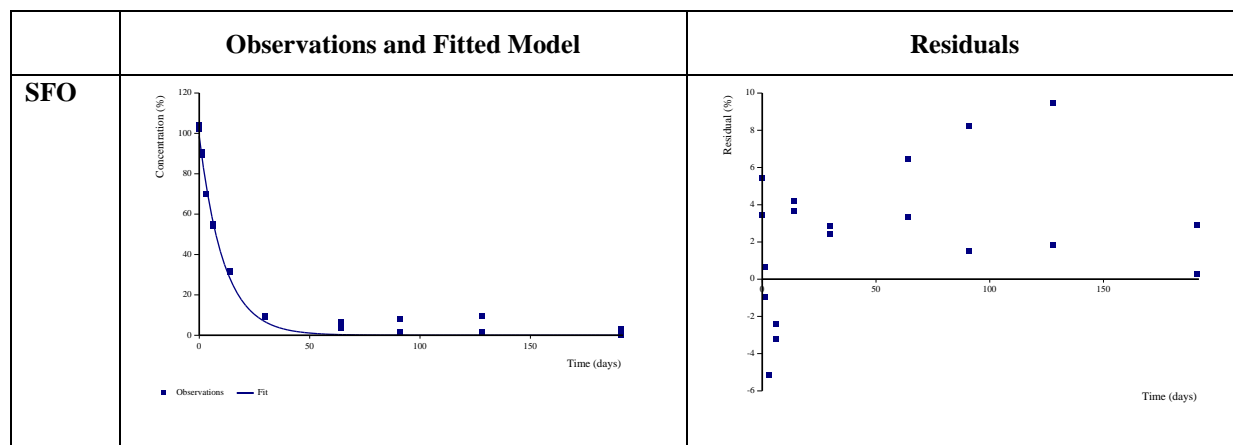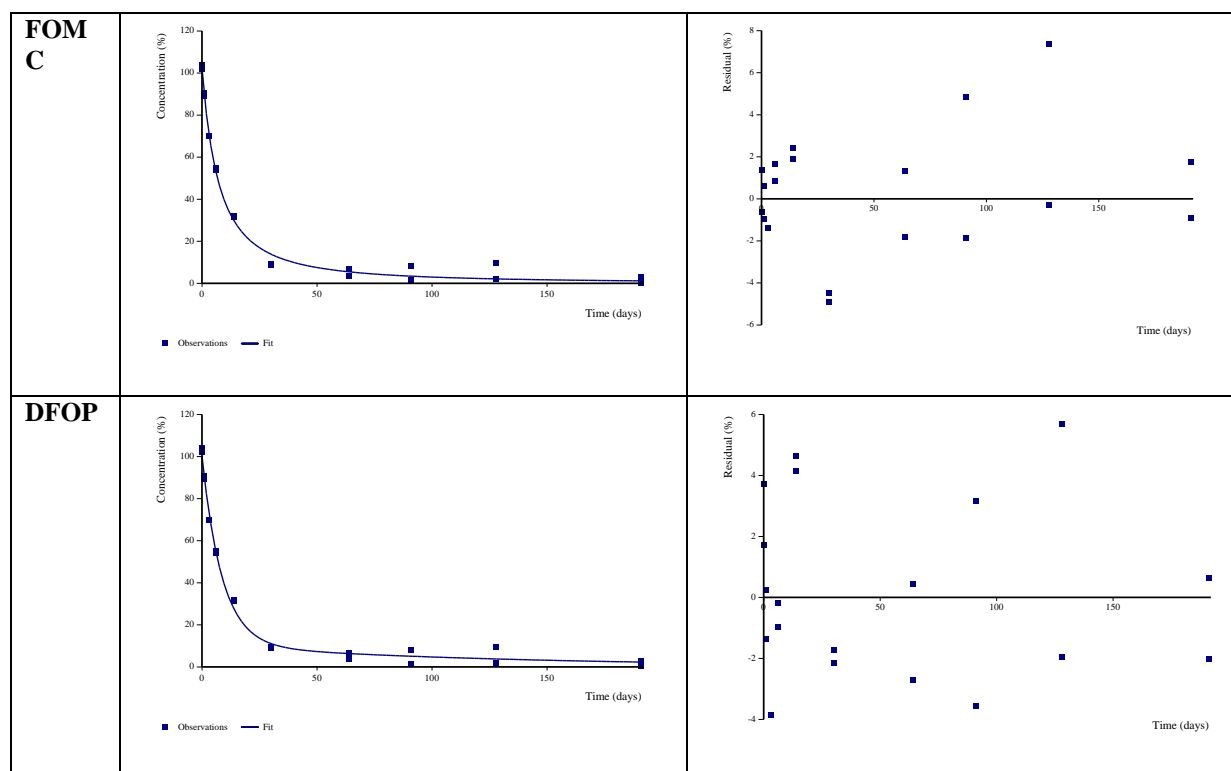
FOM C		
DFOP		

Table B. 8.19. Kinetic fit parameters for Timmerman soil

Fit (Optimisation)	SFO (OLS)	FOMC (OLS)	DFOP (OLS)
M_0	98.57	102.6	100.3
k	0.09034		k1 0.1148 k2 0.007932
alpha		1.553	
beta		11.4	
g			0.8959
tb			
Visual fit	Fits early time points well, underestimate later time points	Good	Good
χ^2 % error	8.52	4.78	5.37
Prob. > t	2.32E-011		k1 1.19E-008 k2 0.07682
Lower (90%) CI		α 1.114 β 6.66	
Upper (90%) CI		α 1.991 β 16.14	
DT_{50} (days)	7.67	6.42	6.99*
DT_{90} (days)	25.5	38.8	33.1*
k1 DT_{50} (days)			6.04
k2 DT_{50} (days)			87.4

*Overall

SFO; visually fits the early time points well but underestimate the later time points. χ^2 % error is acceptable (8.52%) and the t-test is passed. FOMC; visually fits the data well and is better than SFO. χ^2 % error (4.78%) is lower than that for SFO and the confidence intervals for α and β do not contain zero. DFOP; visually fits the

data well and is better than SFO. χ^2 % error (5.37%) is lower than for SFO, but higher than FOMC. The t-test is passed for k1 but failed for k2. The RMS considers the best fit model for persistence endpoints to be FOMC. SFO fits the early part of the data well in which <10% of the applied dose is reached, χ^2 % error is <15%, therefore SFO is the acceptable for modeling endpoints.

Table B. 8.20. Summary of kinetic endpoints for Timmerman soil

	Fit	20°C / 75% FMC (1/3bar)	
		DT$_{50}$ (days)	DT$_{90}$ (days)
Persistence endpoints	FOMC	6.42	38.8
Modelling endpoints	SFO	7.67	25.5

1.2. Speyer 2.1 (BBA soil 1)

Hazlerigg modelling:

Kinetics models were fitted to the entire data-set. SFO and FOMC kinetics produced a good visual fit to the data-points from Speyer 2.1 soil (Table B. 8.22). SFO kinetics passed all statistical requirements, with a χ^2-error of 10.5 % (Table B. 8.21). FOMC kinetics passed with a χ^2-error of 11.2 %, however the confidence limits of α and β both included zero. Therefore, SFO kinetics provides a reliable estimation of the degradation of mecoprop-P in this soil and DFOP was not performed as it was unnecessary. The RMS verified the modelling for Speyer 2.1 soil using Cake v2.0 with OLS optimisation and agrees with the kinetic analysis. SFO is the appropriate model for persistence and modelling endpoints for the Speyer 2.1 soil.

Table B. 8.21. Fitting parameters for decline of mecoprop-P for the Speyer 2.1 soil data-set as reported in Hazlerigg 2015

Kinetic model	Fitted parameters	Comments
SFO (OLS)	*M0 = 107.1 %* *k1 = 0.100 d-1*	Visual fit is good T-test passing for *k* (p < 0.1 %) χ^2-error = 10.5 %
FOMC (OLS)	*M0 = 107.1 %* α = 8.2 x 105 β = 8.2 x 106	Visual fit is good Confidence limits do include 0 for α (-2.7 x 107 - 2.9 x 107) and β (-2.7 x 108 – 2.9 x 108). χ^2-error = 11.2 %
DFOP	Not performed, unnecessary	

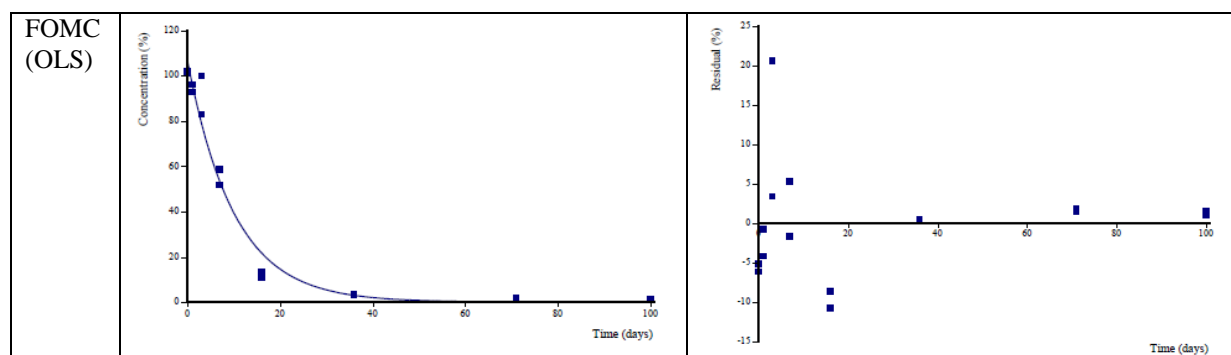Table B. 8.22. Fitted models and residual plots for Speyer 2.1 soil as reported in Hazlerigg 2015
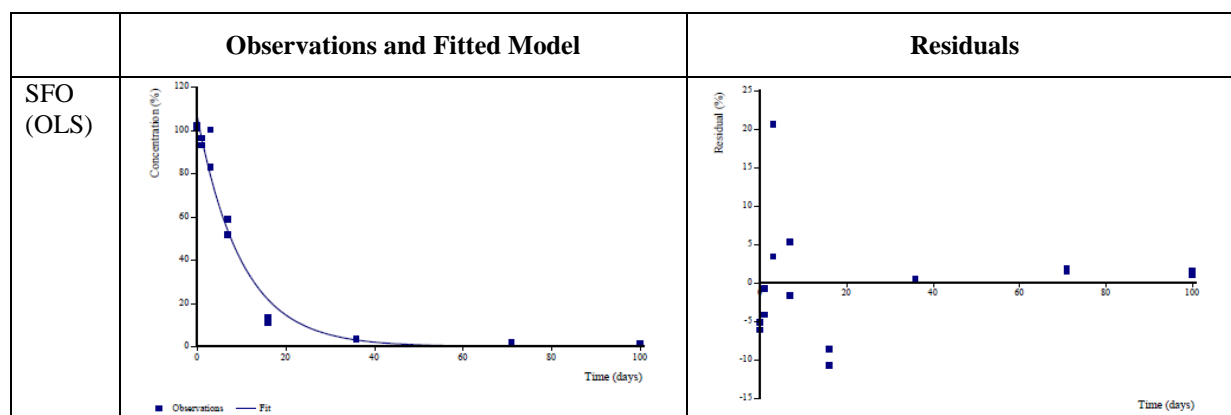
Table B. 8.23. Summary of kinetic endpoints for Speyer 2.1 soil

|	Fit	20°C / 75% FMC (1/3bar)	
		DT_{50} (days)	DT_{90} (days)
Trigger endpoints	SFO	7.0	23.1
Modelling endpoints	SFO	7.0	23.1

1.3. Speyer 2.2 (BBA soil 2)

Hazlerigg modelling:

Microbial biomass decreased by around half in the Speyer 2.2 soil (BBA soil 2). Initially all data-points were used in the fit, but the final data-point (time 100 days) was removed in the final kinetics fitting procedure due to reduced microbial biomass. SFO and FOMC kinetics produced a good visual fit to the data-points (with outlier removed) from Speyer 2.2 soil (Table B. 8.25). SFO kinetics passed the t-test for the degradation constant k and was below the guidance threshold of 15 % for the χ^2-error value, with an χ^2-error of 14.4 % (Table B. 8.24). FOMC kinetics failed both statistical tests, with an χ^2-error or 15.2 % and the confidence limits of α and β both included zero. FOCUS guidance states that the use of the 15 % χ^2-error is a guideline and in fact a fit may still be considered acceptable if the visual fit is good. SFO kinetics provide a reliable estimation of the degradation of mecoprop-P in this soil and DFOP was not performed as it was unnecessary.

Table B. 8.24. Fitting parameters for decline of mecoprop-P for the Speyer 2.2 (BBA soil 2) data-set as reported in Hazlerigg 2015

Kinetic model	Fitted parameters	Comments
SFO (OLS, outlier removed)	$M0 = 102.6\ \%$ $k1 = 0.095\ d-1$	Visual fit is good T-test passing for k (p < 0.1 %) χ^2-error = 14.4 %
FOMC (OLS, outlier removed)	$M0 = 103.8\ \%$ $\alpha = 3.54$ $\beta = 32.08$	Visual fit is good Confidence limits do include 0 for α (-5.33 – 12.4) and β (-63.21 – 127.4). χ^2-error = 15.2 %
DFOP (OLS)	Not performed, unnecessary	

Table B. 8.25. Fitted models and residual plots for Speyer 2.2 soil as reported in Hazlerigg 2015

	Observations and Fitted Model	Residuals

SFO (OLS)		
FOMC (OLS)		
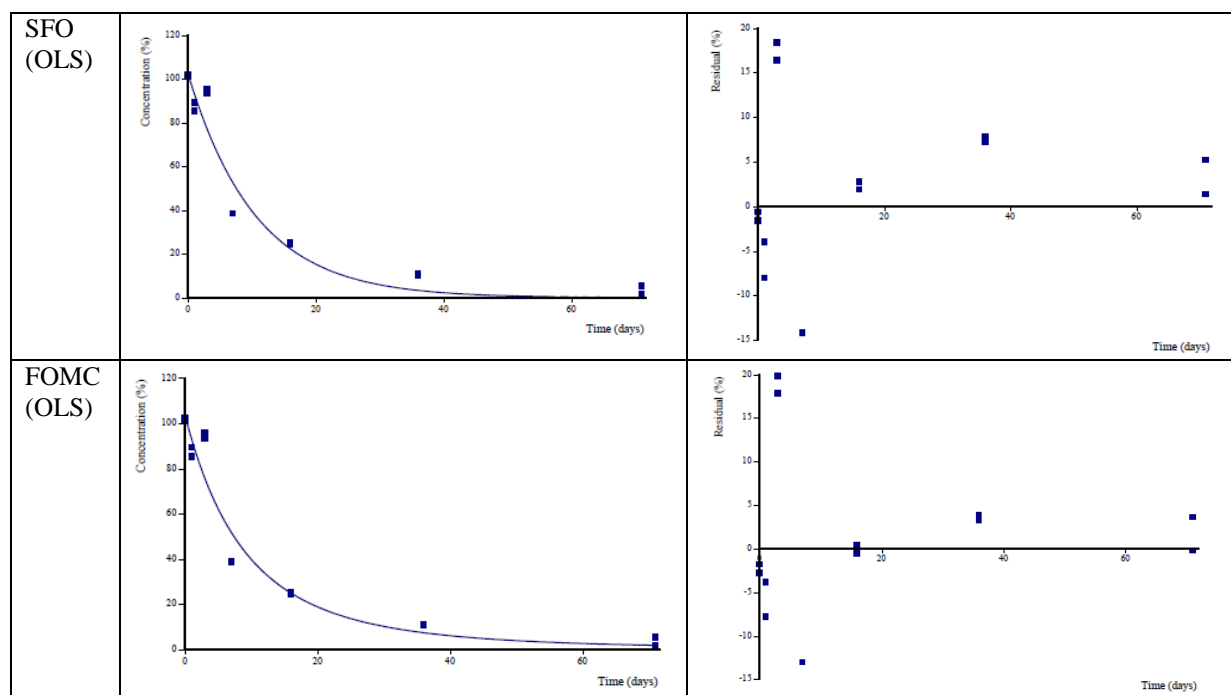
RMS modelling:

The RMS has repeated the kinetic modelling for the Speyer 2.2 soil including data from all time-points using CAKE v2.0 with OLS optimisation and SFO, FOMC and DFOP models. Data were unweighted and M_0 was not fixed. Input data are listed in Table B. 8.26. Plots of fitted models and residuals are given in Table B. 8.27 and parameters are listed in Table B. 8.28.

Table B. 8.26. Degradation of mecoprop-P in Speyer 2.2 soil

Time (days)	Parent (%)
0	101
0	102
1	89.3
1	85.3
3	69.8
3	71.8
7	38.6
7	38.6
16	24.3
16	25.2
36	10.5
36	9.8
71	1.47
71	5.3
100	3.83
100	1.33

Table B. 8.27. Fitted models and residual plots for Speyer 2.2 soil

	Observations and Fitted Model	Residuals
SFO		
FOMC		
DFOP		
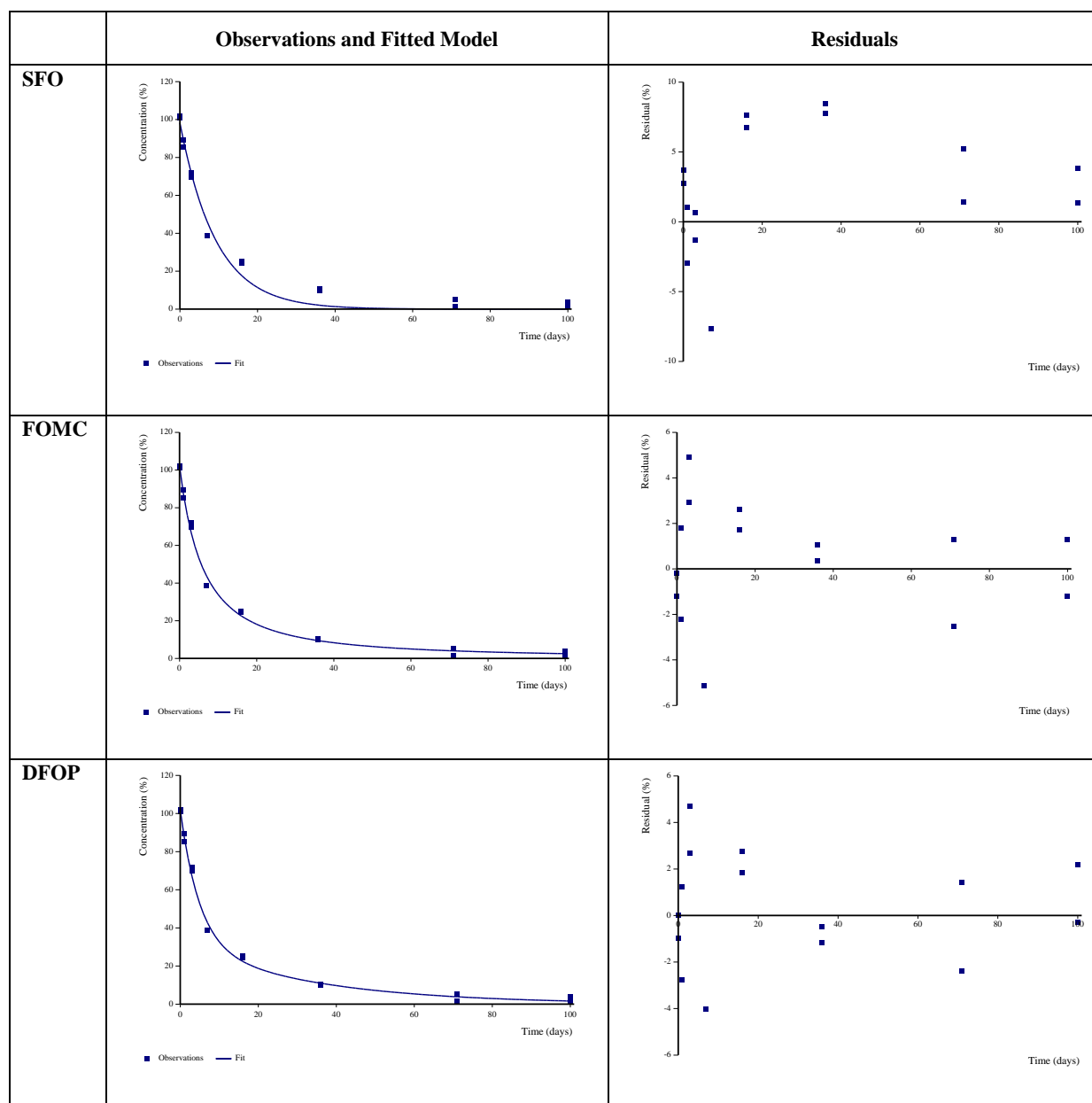
Table B. 8.28. Kinetic fit parameters for Speyer 2.2 soil

Fit (Optimisation)	SFO (OLS)	FOMC (OLS)	DFOP (OLS)
M_0	98.27	102.2	102
k	0.1077		k1 0.2045 k2 0.02972
alpha		1.49	
beta		9.112	
g			0.6878
tb			
Visual fit	Poor	Good	Good
χ^2 % error	9.53	4.9	4.71
Prob. > t	1.08E-008		k1 2.05E-005 k2 0.001639
Lower (90%) CI		α 1.04 β 5.028	

		α 1.939 β 13.2	
Upper (90%) CI			
DT_{50} (days)	6.44	5.4	5.29*
DT_{90} (days)	21.4	33.6	38.4*
k1 DT_{50} (days)			3.39
k2 DT_{50} (days)			23.3

*Overall

SFO; visually is a poor fit to the data and underestimates the later time points. χ^2 % error (9.53%) is acceptable and the t-test is passed. FOMC; visually fits the data well, χ^2 % error (4.9%) is lower than SFO and the confidence intervals for α and β do not contain zero. DFOP; visually fits the data well, χ^2 % error (4.71%) is lower than SFO and slightly lower than FOMC. The t-test is passed for k1 and k2. The RMS considers the best fit model for persistence endpoints to be DFOP. Less than 10% of the applied dose was reached within the study period therefore for modeling endpoints, DT_{50} is calculated from FOMC $DT_{90}/3.32$ (33.6/3.32 = 10.12 days).

Table B. 8.29. Summary of kinetic endpoints for Speyer 2.2 soil

	Fit	20°C / 75%FMC(1/3bar)	
		DT_{50} (days)	DT_{90} (days)
Trigger endpoints	DFOP	5.29	38.4
Modelling endpoints	FOMC	10.12*	33.6

*calculated from FOMC $DT_{90}/3.32$

1.4. Speyer 2.3 (BBA soil 3)

Hazlerigg modelling:

Kinetics models were fitted to the entire data-set. SFO and FOMC kinetics produced a reasonable visual fit to the data-points from Speyer 2.3 (BBA soil 3), though both slightly under-estimated concentrations at later time-points (Table B. 8.31). Both SFO and FOMC kinetics pass the statistical tests, including t-tests, confidence limits of parameters not including zero and χ^2-error values under 15 % (Table B. 8.30). SFO had a marginally lower χ^2-error of 3.98 %, compared with that of FOMC of 4.24 %. The SFO model provides a better fit to the data and given that the DT90 value produced (19.9 days) is covered by the fit well (in the earlier time-points where the visual fit is good) supports the use of this SFO fit in determining the degradation kinetics of mecoprop-P in this soil. The RMS verified the modelling for Speyer 2.3 soil using Cake v2.0 with OLS optimisation and agrees with the kinetic analysis.

Table B. 8.30. Fitting parameters for decline of mecoprop-P for the Speyer 2.3 soil (BBA soil 3) data-set as reported in Hazlerigg 2015

Kinetic model	Fitted parameters	Comments
SFO (OLS)	*M0 = 103.9 %* *k1 = 0.116 d-1*	Visual fit is good, slight under-estimation of later time-point residuals T-test passing for *k* (p < 0.1 %) χ^2-error = 3.98 %
FOMC (OLS)	*M0 = 103.9 %* α = 5.53 x 107 β = 4.78 x 108	Visual fit is good, slight under-estimation of later time-point residuals Confidence limits do not include 0 for α (4.69 x 107 – 6.38 x 107) or β (3.93 x 108 – 5.62 x 108). χ^2-error = 4.24 %
DFOP (OLS)	Not performed, unnecessary.	

Table B. 8.31. Fitted models and residual plots for Speyer 2.3 soil as reported in Hazlerigg 2015

	Observations and Fitted Model	Residuals

SFO (OLS)	
FOMC (OLS)	
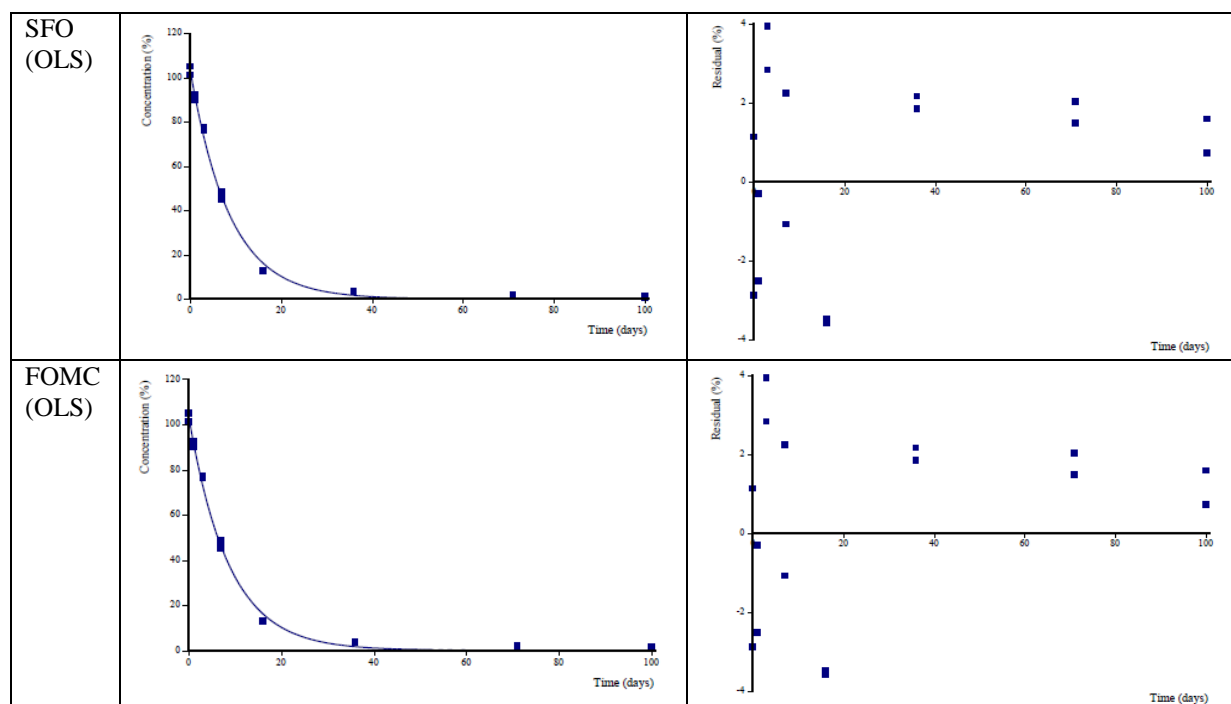
Table B. 8.32. Summary of kinetic endpoints for Speyer 2.3 soil

	Fit	20°C / 75%FMC (1/3bar)	
		DT_{50} (days)	DT_{90} (days)
Persistence endpoints	SFO	6.0	19.9
Modelling endpoints	SFO	6.0	19.9

Summary of rate of degradation of mecoprop-P aerobic laboratory soil studies

Laboratory aerobic soil study persistence endpoints are summarised in Table B. 8.33. Studies were carried out at 0.75% FMC at 1/3bar and 20°C, therefore the RMS corrected modelling endpoints to pF2 following FOCUS groundwater guidance 2000 (Table B. 8.34 and Table B. 8.35).

Table B. 8.33. Persistence endpoints (best-fit)

Soil	Fit	20°C / 75% FMC (1/3bar)	
		DT_{50} (days)	DT_{90} (days)
Timmerman	FOMC	6.42	38.8
Speyer 2.1	SFO	7.0	23.1
Speyer 2.2	DFOP	5.29	38.4
Speyer 2.3	SFO	6.0	19.9

Table B. 8.34. Calculated moisture correction factors

Soil	Soil Type	FMC at 1/3bar (%)[1]	θ_{EXP} Experimental moisture content (%) (0.75%FMC)	θ_{REF} Gravimetric water content at pF2 (FOCUS)[2]	Moisture correction factor $(\theta_{EXP}/\theta_{REF})^{0.7}$
Timmerman	Sandy Loam	12.5	9.38	19	0.61
Speyer 2.1	Sand	7.1	5.33	12	0.57
Speyer 2.2	Loamy Sand	13.7	10.28	14	0.81
Speyer 2.3	Sandy Loam	19.1	14.33	19	0.82

[1]Schocken 1997

[2]FOCUS groundwater 2000

Table B. 8.35. Modelling endpoints

Soil	Soil Type	Fit	20°C / 75% FMC (1/3bar)		20°C / pF2	
			DT_{50} (days)	DT_{90} (days)	DT_{50} (days)	DT_{90} (days)
Timmerman	Sandy Loam	SFO	7.67	25.5	4.7	15.6
Speyer 2.1	Sand	SFO	7.0	23.1	4.0	13.2
Speyer 2.2	Loamy Sand	FOMC	10.12*	33.6	8.2	27.2
Speyer 2.3	Sandy Loam	SFO	6.0	19.9	4.9	16.3

*calculated from FOMC DT_{90}/3.32

2. Connor (1996a) – soil photolysis

A 30 days soil photolysis was conducted using Timmerman soil at 25°C under artificial light. In irradiated samples, mecoprop-P declined steadily to approximately 70%AR at the end of the study. Degradation of mecoprop-P was not evident in dark control samples. No relevant metabolites were identified.

Hazlerigg modelling:

SFO provided a reasonable visual fit to the data, though there was a slight 'wave' to the residuals (Table B. 8.37), whilst the statistical tests were passed for both the degradation constant and the χ^2-error value (Table B. 8.36). FOMC provided a good visual fit to the data, however the confidence interval for β did include zero. The SFO fit is accepted as providing a reliable fit to the degradation of mecoprop-P in this soil via photolysis and DFOP kinetics were not performed as this was unnecessary. The RMS verified the soil photolysis modelling using Cake v2.0 with OLS optimisation and agrees with the kinetic analysis.

Table B. 8.36. Fitting parameters for decline of mecoprop-P for the soil photolysis data-set as reported in Hazlerigg 2015

Kinetic model	Fitted parameters	Comments
SFO (OLS)	M0 = 87.8 % k1 = 0.009 d-1	Visual fit is reasonable, though slight 'wave' in time-point residuals T-test passing for k (p < 0.1 %) χ-error = 3.96 %
FOMC (OLS)	M0 = 92.96 % α = 0.102 β = 1.786	Visual fit is good Confidence limits do include 0 for β (-1.58 - 5.15) χ-error = 2.03 %
DFOP (OLS)	Not performed, unnecessary.	

Table B. 8.37. Fitted models and residual plots for the soil photolysis data set as reported in Hazlerigg 2015

| FOMC (OLS) | | |
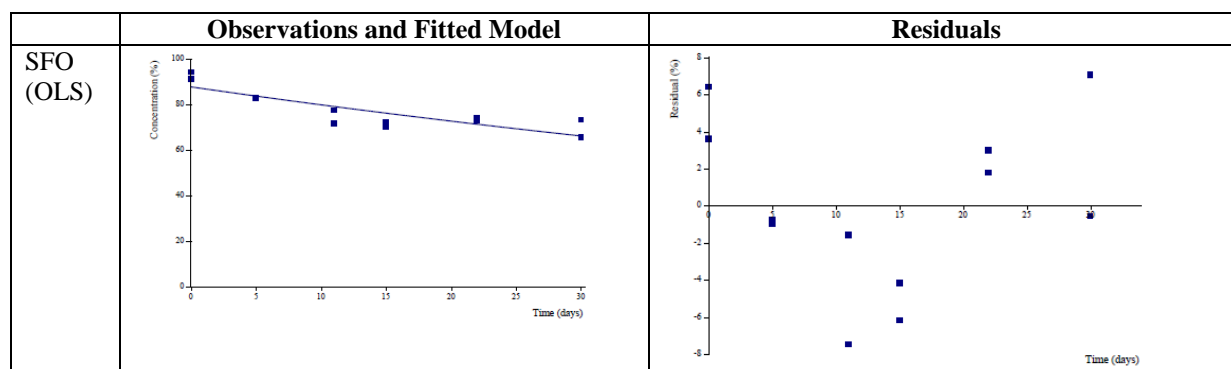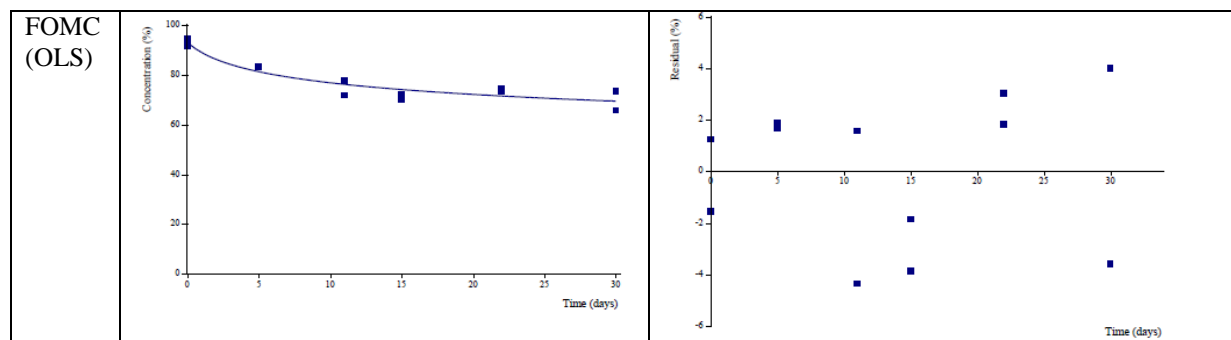
The study author corrected the experimental results under artificial sunlight to field values using a correction factor of 0.2 based on the approximate ratio of intensities of the artificial light to natural summer sunlight at 42°N. This results in a DT$_{50}$ of 14.8 days and a DT$_{90}$ of 49.0 days at 42°N.

The RMS has corrected the experimental artificial light values to natural sunlight at 42°N using the formula outlined in the draft OECD guideline on photo-transformation of chemicals on soil surfaces (2002); this assumes that the equivalent days of natural sunlight can be calculated assuming that the average daily sun radiation is approximately 75% of the maximum intensity over a 12 hour period whereas the xenon lamp is constant over time. Total light intensities of the artificial light source were made before and after the study. Sunlight measurements were recorded on 1st August 1995 at 12:17pm at 42°N latitude. The light intensity of the artificial light source was determined to be 20.4% of natural sunlight at the start of the study and 22.1% at the end of the study (mean 21.25%). The artificial light source operated on a 12h light/12 dark cycle. One day of the study (12 hours artificial light, 21.25% intensity of natural light at 42°N) is therefore equivalent to 0.28 days of natural sunlight at 42°N. This results in a DT$_{50}$ of 20.66 days and a DT$_{90}$ of 68.6 days.

Table B. 8.38. Summary of kinetic endpoints for soil photolysis of mecoprop-P

Fit		Artificial light	Natural sunlight (42°N)	
			Hazlerigg calculation	RMS calculation
SFO	DT$_{50}$ (days)	73.8	14.8	20.66
	DT$_{90}$ (days)	245	49.0	68.6

3.   Connor (1996b) – aqueous photolysis

A 30 day aqueous photolysis study was performed at 25°C under artificial light at pH 5, 7 and 9. A decline in the concentration of mecoprop-P to less than 10% AR was observed for all pH tested by the end of the study. The photodegradate profile is reported for pH 7 only in which *o*-cresol was observed at a maximum of 30.4% AR on day 30. No decline phase was observed before the end of the study, but a plateau in concentration was evident. Photodegradation in dark control systems was not observed.

    3.1. Hazlerigg modelling:

Kinetic modelling is presented for pH 7 data only.
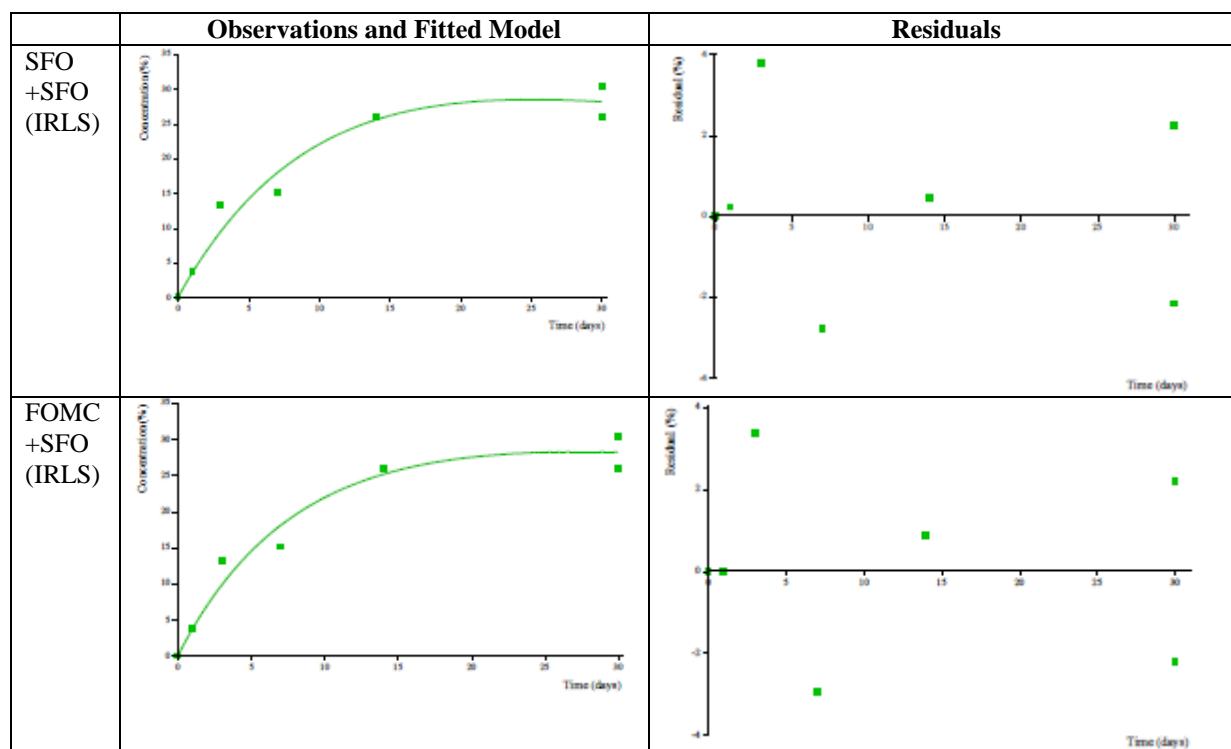
Mecoprop-P

SFO provided a good visual fit to the data (

Table B. 8.40) and the statistical tests were passed for both the degradation constant and the χ-error value (Table B. 8.39). FOMC provided a good visual fit to the data, however the confidence interval for α and β did include zero. The SFO fit is accepted as providing a reliable fit to the degradation of mecoprop-P in this study via photolysis and DFOP kinetics were not performed as this was unnecessary.

Table B. 8.39. Fitting parameters for decline of mecoprop-P for the pH 7 aqueous photolysis data-set as reported in Hazlerigg 2015

Kinetic model	Fitted parameters	Comments
SFO (OLS)	*M0 = 99.63 %* *k1 = 0.098 d-1*	Visual fit is good T-test passing for *k* (p < 0.1 %) χ-error = 3.4 %
FOMC (OLS)	*M0 = 100.7 %* α = 5.71 β = 51.98	Visual fit is good Confidence limits do include 0 for α and β (- 6.96 – 18.39 and -76.03 - 180) χ-error = 3.23 %
DFOP (OLS)	Not performed, unnecessary.	

Table B. 8.40. Fitted models and residual plots for the pH 7 aqueous photolysis dataset as reported in Hazlerigg 2015
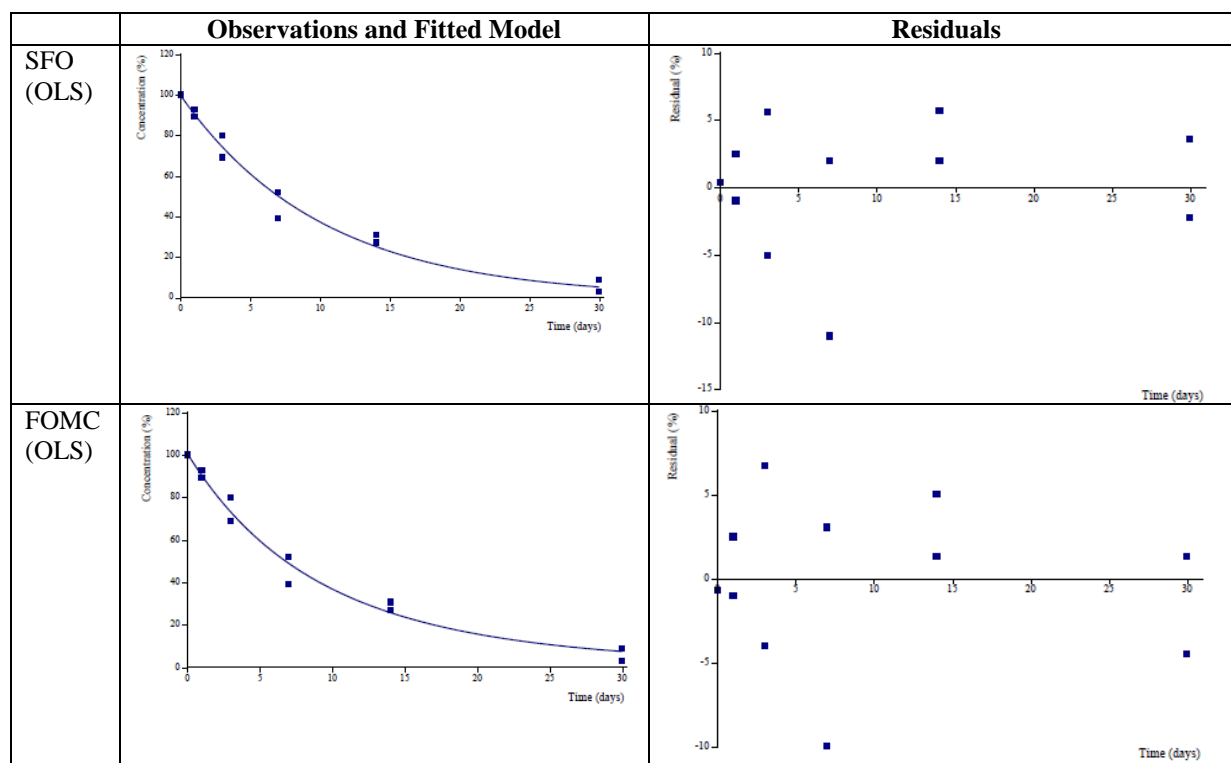
o-Cresol

The OLS had difficulty in securing confidence limits for kinetics fitting to this soil data-set and therefore the IRLS optimiser was used as a refinement. SFO + SFO kinetics for both parent and metabolite provided good visual fits for the metabolite (Table B. 8.42). All statistical tests passed, including the t-test which passed for the metabolite degradation constant and the confidence limits of *ffM* did not include zero (Table B. 8.41). The χ-error for the metabolite was 9.81%. FOMC + SFO kinetics for the parent and metabolite respectively once again provided a good visual fit for the metabolite. However, the t-test failed for the metabolite degradation constant and confidence limits for *α* and *β* both included zero. Therefore, the SFO + SFO kinetics fit can be considered to provide reliable values for the formation and degradation of the *o*-cresol metabolite via aqueous photolysis.

Table B. 8.41. Fitting parameters for *o*-cresol for the pH 7 aqueous photolysis data-set as reported in Hazlerigg 2015

Parent	Metabolite	Fitted parameters	Comments

model	model		
SFO (IRLS)	SFO	*M0 = 99.52 %* *k1 = 0.098 d-1* *km = 0.011* *ffM = 0.378*	Visual fit of metabolite is good and residuals randomly distributed. The t-test on *km* passes (p = 8 %) The confidence limits on *ffM* do not include zero (0.282 – 0.475) χ-error = 7.42 % (Parent = 3.4 %, metabolite = 9.81 %)
FOMC (IRLS)	SFO	*M0 = 100.7 %* *α = 5.48* β = 49.82 *km = 0.008* *ffM = 0.361*	Visual fit of metabolite is good and residuals randomly distributed. The t-test on *km* fails (p = 17 %) The confidence limits on *ffM* do not include zero (0.263 – 0.458) The confidence limits on *α* and β do include zero (-6.45 – 17.41 and -70.95 – 170.6) χ-error = 7.47 % (Parent = 3.24 %, metabolite = 9.48 %)
FOMC	DFOP	Not performed, unnecessary.	

Table B. 8.42. Fitted models and residual plots for *o*-cresol for the pH 7 aqueous photolysis dataset as reported in Hazlerigg 2015

	Observations and Fitted Model	Residuals
SFO +SFO (IRLS)		
FOMC +SFO (IRLS)		

3.2. RMS modelling:

The RMS has repeated the modelling for the pH 7 data using CAKE v2.0 with OLS optimisation. The RMS has also fitted the pH 5 and 9 data for mecoprop-P (photodegradate data at pH 5 and 9 were not reported). All data were included in the analysis and used unweighted. M_0 was not fixed for mecoprop-P, M_0 for *o*-cresol was set to zero.

3.2.1.   pH 7

Input   data   are   listed   in

Table B. 8.43. Plots of fitted models and residuals are given in Table B. 8.44and parameters are listed in

Table B. 8.45.

Table B. 8.43. Input data for pH 7 aqueous photolysis of mecoprop-P and photodegradate *o*-cresol

Time	%AR	
	Mecoprop-P	*o*-Cresol
0	100	0
0	100	-
1	89.3	3.71
1	92.8	-
3	69.1	13.2
3	79.8	-
7	52	15.1
7	39	-
14	30.8	26
14	27.1	-
30	2.98	26
30	8.79	30.4

-     data not reported

Table B. 8.44. Final fitted models and residual plots for pH 7 aqueous photolysis of mecoprop-P and photodegradate *o*-cresol
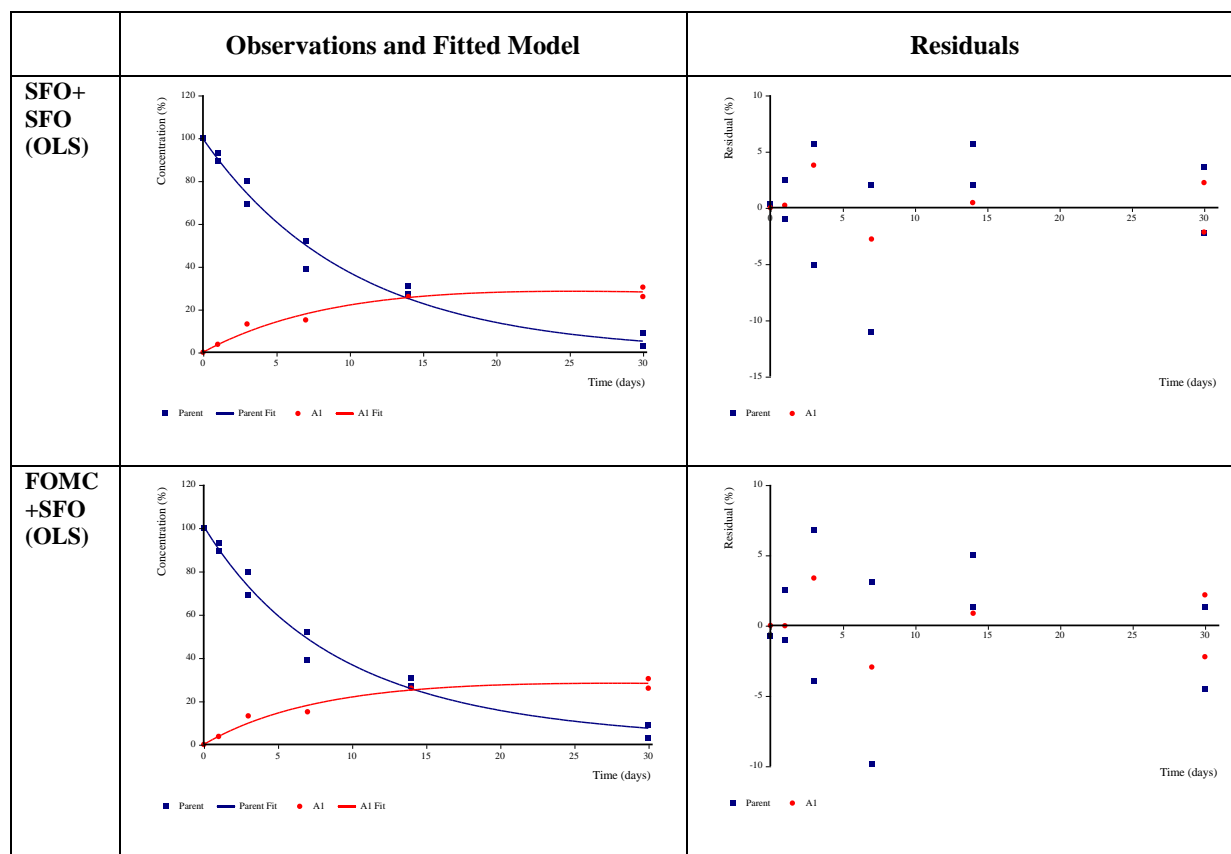
Table B. 8.45. Final kinetic fit parameters for pH 7 aqueous photolysis of mecoprop-P and photodegradate *o*-cresol

	Fit (Optimisation)	**SFO+SFO (OLS)**	**FOMC+SFO (OLS)**
Mecoprop-P	M_0	99.64	100.7
	k	0.09846	
	alpha		5.555
	beta		50.35
	Visual fit	Good	Good
	χ^2 % error	3.4	3.24
	Prob. > t	6.18E-011	
	Lower (90%) CI		α -4.19 β -47.94
	Upper (90%) CI		α 15.3 β 148.6
	DT_{50} (days)	7.04	6.69
	DT_{90} (days)	23.4	25.9
o-Cresol	k	0.01092	0.0079
	Visual fit	Good	Good
	χ^2 % error	10.7	10.3
	Prob. > t	0.1801	0.2518
	DT_{50} (days)	63.5	87.7
	DT_{90} (days)	211	291
All data	χ^2 % error	5.41	5.13
	Formation fraction (ff)	0.376	0.3593
	Lower (90%) CI	ff 0.2433	ff 0.2301
	Upper (90%) CI	ff 0.5087	ff 0.4886

SFO+SFO: For mecoprop-P SFO visually fits the data well. χ^2 % error is low (3.4%) and the t-test is passed.
   For *o*-cresol, SFO also fits the data well, χ^2 % error is acceptable (10.7%) but the t-test is failed.
   The overall χ^2 % error is low (5.41%) and the confidence interval for the formation fraction does not contain zero.

FOMC+SFO: For mecoprop-P FOMC visually fits the data well. χ^2 % error is marginally lower than for SFO (3.24%) but the confidence intervals for α and β contain zero.
   For *o*-cresol, SFO visually fits the data well, χ^2 % error is low (10.3%) but the t-test is failed.
   The overall χ^2 % error is low (5.13%) and the confidence interval for the formation fraction does not contain zero.

The RMS agrees with Hazlerigg's assessment that SFO+SFO provide the best fit for mecoprop-P and *o*.cresol in the pH 7 systems:
   Mecoprop-P DT_{50} 7.04 days, DT_{90} 23.4 days
   o-Cresol DT_{50} 63.5 days, DT_{90} 211 days, formation fraction 0.38

   3.2.2.   pH 5

Input   data   are   listed   in

Table B. 8.46. Plots of fitted models and residuals are given in Table B. 8.47 and parameters are listed in table

Table B. 8.48.

Table B. 8.46. Input data for pH 5 aqueous photolysis of mecoprop-P

Time	%AR Mecoprop-P
0	100
0	100
1	85.4
1	76.5
3	49.8
3	49.9
7	37.5
7	47.5
14	13.9
14	23.8
30	1.69
30	0.871

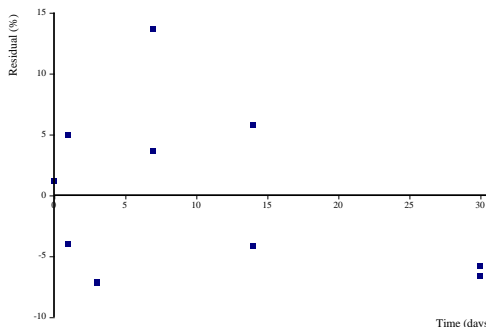Table B. 8.47. Fitted models and residual plots for pH 5 aqueous photolysis of mecoprop-P
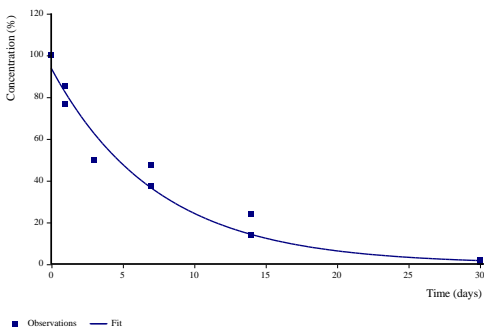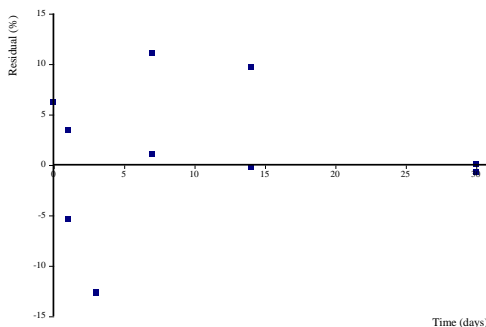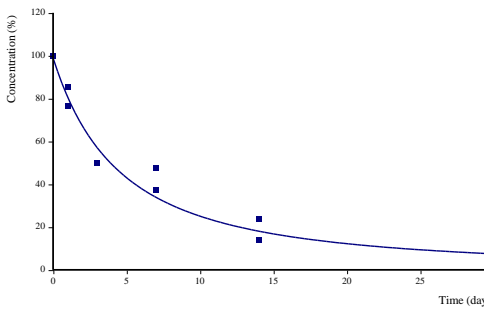
	Observations and Fitted Model	Residuals
SFO		
FOMC		

Table B. 8.48. Kinetic fit parameters for pH 5 aqueous photolysis of mecoprop-P

Fit (Optimisation)	SFO (OLS)	FOMC (OLS)
M_0	93.76	98.86
k	0.135	
alpha		1.564
beta		7.116
Visual fit	good	good
χ^2 % error	10.7	9.44
Prob. > t	9.35E-006	
Lower (90%) CI		α 0.07319 β -2.665
Upper (90%) CI		α 3.054 β 16.9
DT_{50} (days)	5.13	3.97
DT_{90} (days)	17.1	23.9

SFO: Visually fits the data reasonably well. χ^2 % error is acceptable (10.7%) and the t-test is passed.
FOMC: Visually fits the data reasonably well. χ^2 % error is marginally lower than for SFO (9.44%) but the confidence interval for α includes zero.

The RMS considers SFO is the most appropriate fit for the aqueous photolysis of mecoprop-P at pH 5; DT_{50} 5.13 days, DT_{90} 17.1 days.

3.2.3.   pH 9

Input data are listed in Table B. 8.49.   Plots of fitted models and residuals are given in

Table B. 8.50 and parameters are listed in Table B. 8.51.

Table B. 8.49. Input data for pH 9 aqueous photolysis of mecoprop-P

Time	%AR Mecoprop-P
0	100
0	100
1	90.5
1	93.5
3	72.1
3	79.0
7	29.2
7	48.7
14	20.1
14	35.3
30	2.43
30	9.04

Table B. 8.50. Fitted models and residual plots for pH 9 aqueous photolysis of mecoprop-P

	Observations and Fitted Model	**Residuals**
SFO		
FOMC		
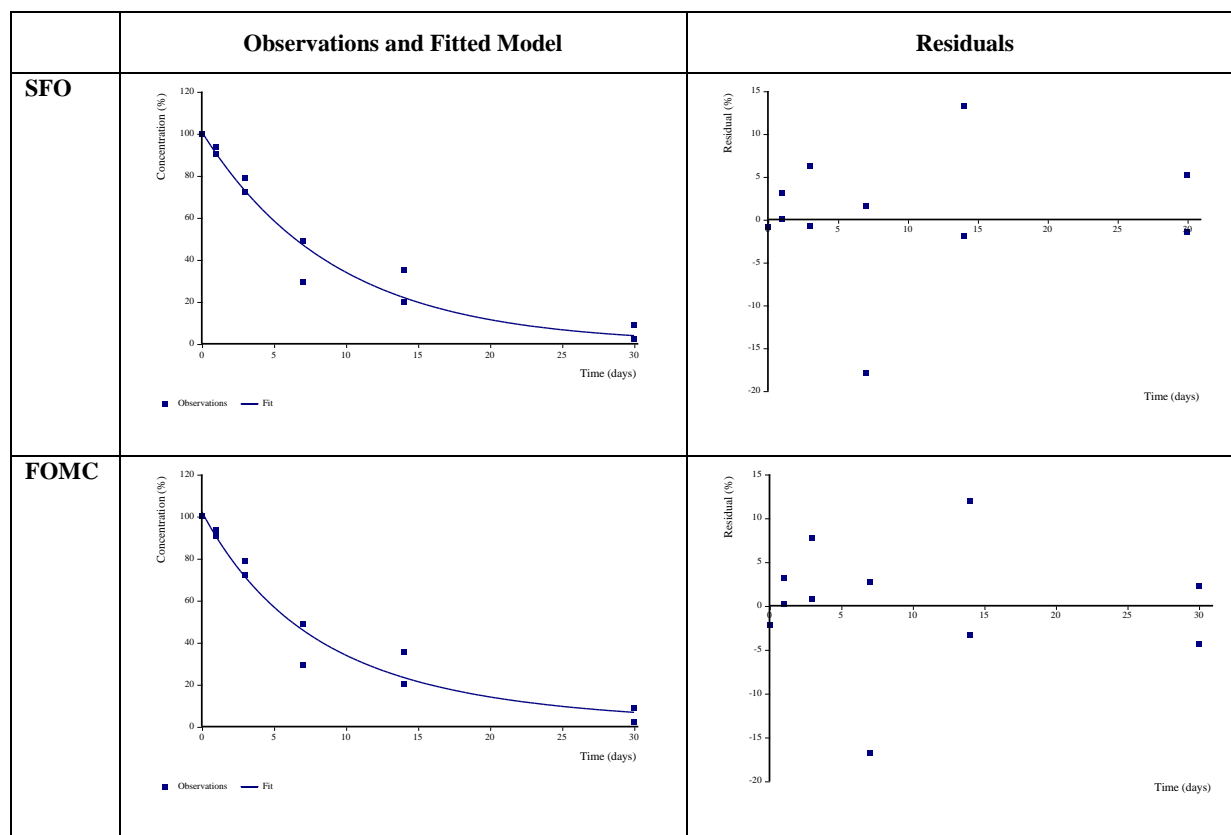
Table B. 8.51. Kinetic fit parameters for pH 9 aqueous photolysis of mecoprop-P

Fit (Optimisation)	SFO (OLS)	FOMC (OLS)
M_0	100.8	102.2
k	0.1086	
alpha		4.366
beta		34.85
Visual fit	good	good
χ^2 % error	6.1	6.15
Prob. > t	2.59E-006	
Lower (90%) CI		α -6.962 β -68.84
Upper (90%) CI		α 15.69 β 138.5
DT_{50} (days)	6.38	6
DT_{90} (days)	21.2	24.2

SFO: Visually fits the data reasonably well. χ^2 % error is acceptable (6.1%) and the t-test is passed.
FOMC: Visually fits the data reasonably well. χ^2 % error is marginally higher than for SFO (6.15%) and the confidence intervals for α and β include zero.

The RMS considers SFO is the most appropriate fit for the aqueous photolysis of mecoprop-P at pH 9; DT_{50} 6.38 days, DT_{90} 21.2 days.

The kinetics endpoints for the aqueous photolysis of mecoprop-P are summarised in Table B. 8.52. The RMS has calculated the experimental artificial light values using the formula outlined in the draft OECD guideline on

photo-transformation of chemicals on soil surfaces (2002); this assumes that the equivalent days of natural sunlight can be calculated assuming that the average daily sun radiation is approximately 75% of the maximum intensity over a 12 hour period whereas the xenon lamp is constant over time. Total light intensities of the artificial light source were made before and after the study at 6 and 10.5 inches from the xenon lamp. Sunlight measurements were recorded on 1st August 1995 at 12:17pm at 42°N latitude. The light intensity of the artificial light source was determined to be 47% (mean) of natural sunlight. The artificial light source operated on a 12h light/12 dark cycle. One day of the study (12 hours artificial light, 47% intensity of natural light at 42°N) is therefore equivalent to 0.66 days of natural sunlight at 42°N. Results corrected for light intensity are given in Table B. 8.52.

Table B. 8.52. Summary of kinetic endpoints for aqueous photolysis of mecoprop-P

	pH	Fit	Artificial light		Sunlight 42°N	
			DT_{50} (days)	DT_{90} (days)	DT_{50} (days)	DT_{90} (days)
Mecoprop-P	7	SFO	7.04	23.4	4.65	15.44
	5	SFO	5.13	17.1	3.39	11.29
	9	SFO	6.38	21.2	4.21	14.0
o-Cresol (formation fraction 0.38)	7	SFO	63.5	211	41.91	139.26

Report	**Rodríguez-Cruz *et al* (2006)**
Title	Field-scale study of the variability in pesticide biodegradation with soil depth and its relationship with soil characteristics.
Guidelines	None
GLP	No, literature data

Previous evaluations;	None: Submitted for the purpose of renewal under Regulation 844/2012.
	This paper was identified by the applicant as relevant during the literature review.
	The paper investigates field scale variability in the degradation of 3 pesticides (including mecoprop) with soil depth and soil characteristics. The RMS notes that the paper refers to both mecoprop and mecoprop-P interchangeably so it is not clear whether the racemic mix or resolved isomer is under investigation. The experimental conditions are not fully reported. Generally the results show faster degradation in topsoil than in subsoil.
	The study does not provide new endpoints and has not been relied on for the risk assessment.

Executive summary

The extent of within-field spatial variability of pesticide degradation was characterised in topsoil and subsoil, using the compounds isoproturon, bentazone and mecoprop, which are major contaminants of groundwater and surface freshwater in Europe. However only the information concerning mecoprop is relevant to this submission and therefore only those have been reported in this summary.

Twenty topsoil samples from 0 to 15 cm depth and twenty subsoil samples from 50 to 60 cm depth were collected from a single agricultural field within a 160x90 grid. It was shown that degradation rates of all compounds declined with soil depth.

Variability of mecoprop degradation rates, sorption and formation of non-extractable residues was higher in subsoil relative to topsoil. Furthermore, in the subsoil, there was variation in large scale soil physicochemical composition, which did not occur in topsoil.

The greater variability in mecoprop degradation rates in subsoil relative to topsoil could be the result of a greater range of degradation kinetics, which could reflect greater spatial variability in the distribution and/or activities of pesticide metabolising communities.

I.   MATERIALS AND METHODS

The aims of this study were:
1. To compare the extent of variability in pesticide biodegradation rate and sorption within and between, top soil and subsoil.
2. To determine whether variability in pesticide degradation and sorption were related to variability in gross soil microbial, chemical and physical properties.

1.   Pesticides

Three pesticides were used in this study; the moderately mobile compound, isoproturon, and the more mobile compounds; bentazone and mecoprop, along with a ^{14}C labelled analogue of each pesticide (> 95% purity). Only information on mecoprop will be summarised here.

2.   Soil

Soil samples were collected from different sites in Long Close field, Warwick HRI, Wellesbourne, UK in April 2003. In general, soil taken from this field is a sandy clay loam. A previous study had shown a gradient of pH and organic matter in the field. For the current study the sampling regime was designed to encompass the range of variability in pH and organic matter in the field. Twenty holes were excavated using a mechanical digger to 1m depth. The holes were located within a 160x90m grid at intervals of 40m (North/South) and 30m (East/West). From every hole, 2 kg of soil were collected from 0 to 15 cm depth (topsoil) and 50-60cm depth (subsoil). Soil was sieved (<3mm) with the sieve sterilised with ethanol between samples. There had been no application of mecoprop to the soil samples over at least the previous 10 years.

3.   Laboratory incubation experiments

Suspensions of a commercial formulation of mecoprop-p were prepared in distilled water and the ^{14}C labelled analogue were added to 300g fresh weight of soil from each sampling location to give a concentration of 5 mgkg^{-1} and an activity of 200 Bq g^{-1} with soil water potential at -33kPa. A CO_2 trap, consisting of a scintillation vial containing 1M NaOH (1ml) was attached to the lid via a stainless steel clip. Soil moisture was maintained by addition of sterile distilled water as necessary. Incubation conditions such as temperature, light exposure and study period are not reported in the study. Sampling time points are not reported in the study.

4.   Pesticide extraction and analysis

After pesticide addition, duplicate samples were taken from each bottle in order to check variability associated with pesticide extraction and analysis. Thereafter, soils were repeatedly sampled at regular intervals depending on the pesticide.
The HPLC mobile phase used to elute pesticides was acetonitrile/water/orthophosphoric acid (75:25:0.25 for mecoprop-p) at a flow rate of 1ml min^{-1}. Detection was by UV absorbance at 230 nm.
Pesticide recoveries from the soil in the range from 1.0 to 5.0 mg/kg^{-1} varied from 98.2% to 98.8% for mecoprop.
Duplicate samples at each concentration were used to assess recovery values. After the incubation period the soil samples were analysed for residual ^{14}C-pesticide residues.

5.   Chemical and biological analysis of soils

pH, total organic carbon and dehydrogenase activity were determined according to Bending *et al* (2006).

6.   Pesticide adsorption

Adsorption of mecoprop in soils was determined by treating 5g of dried soil (sieved <3mm) with 10 ml of a 5 μg ml^{-1} solution of the commercial pesticide formulation in 0.01M $CaCl_2$. Suspensions were shaken for 24h at 25ºC. After shaking, suspensions were centrifuged at 6000 rpm for 5 min and the concentration of pesticide was determined in the equilibrium solution. The amount of herbicide adsorbed (C_s) was calculated by determining the difference between the initial and the equilibrium concentrations (C_e). Adsorption coefficients (K_d)

calculated from the relationship between C_s and C_e were considered as a measure of pesticide adsorption capacity by the soil. All determinations were carried out in duplicate.

7. Statistical analysis of the data

GenStat software was used to produce DT_{50} values (best fit model) and also a multivariate analysis of the data to obtain correlations between variables. Linear, exponential and Gompertz kinetic models were fitted to the data. Best fit models were chosen based on visual fit and standard error (SE).

To compare variability of different parameters between top soil and sub soil, the coefficients of variation (%CV) was determined. The percentage of total variability attributable to within sample variability was determined using a first-order Taylor series approximation.

II. RESULTS AND DISCUSSION

A. Chemical and biological analysis of soils

Dehydrogenase activity was tenfold higher in topsoil compared with subsoil.
Soil organic matter content significantly decreased with depth.
There was no significant difference in average soil textural characteristics between topsoil and subsoil. However there was considerably greater variability in sand, silt and clay content in subsoil compared to topsoil.

Table B. 8.53 Chemical, physicochemical and biological properties (mean value) and coefficient of variation (CV) of topsoil and subsoil samples

	Dehydrogenase (μg TPF g^{-1})[a]	pH	Organic matter (%)	Sand (%)	Silt (%)	Clay (%)
Topsoil	44.3	6.69	2.88	68.7	8.09	23.4
CV(%)	36.3	6.80	26.9	5.69	18.8	13.5
Subsoil	4.59	7.42	1.59	65.3	8.30	26.5
CV(%)	32.3	7.24	36.5	26.4	69.7	48.5
P[b]	<0.001	<0.001	<0.001	NS	NS	NS

[a]Triphenyl formazan
[b]indicates significance of difference in soil properties between topsoil and subsoil at level indicated. NS; not significantly different

B. Degradation

DT_{50} of all pesticides was significantly higher in subsoil than topsoil.
For mecoprop, 16 topsoil samples showed a lag phase of between 7.2 and 18.4 days, which was followed by a rapid phase of degradation, with kinetics fitted to the Gompertz model ($SE_{DT50} < 1.62$). In the remaining 4 topsoil samples, degradation showed a progressive linear decline in residue concentration over time. DT_{50} values in topsoil ranged between 7.4 and 19.7 days ($SE_{DT50} < 1.24$).

In 15 subsoil samples degradation of mecoprop had a lag period of between 22.4 and 59.7 days before a period of rapid degradation, with kinetics fitted to the Gompertz model ($SE_{DT50} < 3.54$). Two sites showed no degradation and the remaining 3 sites showed progressive linear decrease in concentration over time and DT_{50} values ranged from 27.9 to 114 days (SE < 11.3).

The coefficient of variation of DT_{50} was higher in subsoil than in topsoil for the three pesticides.

Table B. 8.54 Average values of mecoprop DT_{50}. ^{14}C-ring mineralised and non-extractable residue amounts, distribution coefficients (K_d) and coefficients of variation (CV) in topsoil and suboil.

DT_{50} (days)		
Topsoil	Average	15.0
	CV (%)	22.1
Subsoil	Average	42.3[b]
	CV (%)	50.6[b]
P[c]		<0.001

% Pesticide ^{14}C-ring mineralised		
Topsoil	Average	19.3
	CV (%)	40.4
Subsoil	Average	13.1
	CV (%)	41.6
P[c]		<0.01

% Non-extractable pesticide residue		
Topsoil	Average	52.7
	CV (%)	12.8
Subsoil	Average	38.9
	CV (%)	53.7
P[c]		<0.01

K_d (ml/g)		
Topsoil	Average	0.26
	CV (%)	25.9
Subsoil	Average	0.07
	CV (%)	24.3
P[c]		<0.001

[b]subsoil DT_{50} excludes 2 samples in which degradation was too slow to allow calculation of DT_{50} values
[c]indicates significance of difference in soil properties between topsoil and subsoil at level indicated. NS; not significantly different

C. Mineralisation of pesticide to CO_2 and non-extractable residues

Mineralisation was significantly lower in subsoil relative to topsoil. 6.8 to 39.9% of mecoprop was mineralised to [14]CO_2 after 153 days in top soil samples. In subsoil, mineralisation after 153 days ranged from 1.10% to 21.5%.

For mecoprop a significantly greater proportion of pesticide was converted to non-extractable forms in topsoil relative to subsoil. After 153 days 42.8 to 68.7% remained as non-extractable residues in topsoil and between 0% and 63.2% in subsoil.

D. Adsorption

Sorption of mecoprop was significantly higher in topsoil than subsoil. Kd values in the top soil ranged from 0.12 to 0.39 ml/g and in the sub soil ranged from 0.04 to 0.09 ml/g.

III. CONCLUSIONS

It was shown that degradation rate of mecoprop declined with soil depth.

Variability of degradation rates, sorption and formation of non-extractable residues was higher in subsoil relative to topsoil. Furthermore, in the subsoil, there was variation in large scale soil physicochemical composition, which did not occur in topsoil.

Aerobic degradation of metabolites, breakdown and reaction products (CA 7.1.2.1.2)

No data required – there are no relevant metabolites to consider.

Anaerobic degradation of active substance (CA 7.1.2.1.3)

No data required – anaerobic conditions considered unlikely for the representative use.

Anaerobic degradation of metabolites, breakdown and reaction products (CA 7.1.2.1.4)

No data required – anaerobic conditions considered unlikely for the representative use.

Field studies (CA 7.1.2.2)

Soil dissipation studies (CA 7.1.2.2.1)

RMS comments:	Soil dissipation studies are not required. For mecoprop-P, $DT_{50,lab}$ are all less than 60 days, and $DT_{90,lab}$ are all less than 200 days.
	No soil dissipation studies were assessed for the original Annex I approval of mecoprop-P.
	Two studies were identified as potentially relevant by the applicant from the literature review.

Article:	**CA 7/01, Buss, S.R. *et al*. (2006)** Quarterly Journal Of Engineering Geology And Hydrogeology, 39, pp283-292
Title	A review of mecoprop attenuation in the subsurface
Guidelines:	review article, no specific guideline
GLP:	Not applicable
Deviations	Not applicable

Previous evaluations	None: Submitted for the purpose of renewal under Regulation 844/2012.
	This paper was identified by the applicant as potentially relevant during the literature review.
	The paper summary and relevance/reliability assessment provided by the applicant have been reproduced below. The RMS agrees with the applicant's assessment. The paper is a literature review that provides a qualitative assessment of the behaviour of mecoprop in the subsurface. The study does not provide new endpoints and has not been relied on for the risk assessment.

Executive summary

This review paper refers to studies linked with the leaching to groundwater and underground degradation of mecoprop in the UK and other countries.

The review begins by looking at the extent of contamination of groundwater and surface water by mecoprop. A UK survey comprising 980 boreholes between 1998 and 2003 was examined. Mecoprop was detected in 105 (10.7%) of boreholes of which 1.6 % were contaminated above 0.1 µg L^{-1}, with a maximum concentration of 62µg L^{-1}. Sample points containing mecoprop were not specific to any aquifer type. Large-scale or ubiquitous surface water contamination was reported in the UK (2003) and in North America (2004).

The sources of mecoprop in soil and groundwater were investigated in the literature. The identified sources were agricultural uses of mecoprop, agricultural machinery depots, landfill/waste disposal sites, sewage treatment works, and non-crop herbicide use including hard surfaces and recreational grass areas. Landfill leachates included the highest measured concentration of mecoprop (up to 0.432 g L^{-1}) with up to 3000µg L^{-1} in groundwater immediately down gradient of the site. One study reported the contribution of the mecoprop load to surface waters from non-agricultural uses (flat roof treatments in Switzerland) was of the same order of magnitude as the load from agricultural applications. However, conclusions on the relative significance of each source for groundwater contamination are not reported.

The degradation pathway of mecoprop in soil and aquifers is mainly aerobic biodegradation. Anaerobic degradation may occur but mecoprop may be persistent in these conditions. Under aerobic conditions 4-chloro-2-methylphenol (4-CMP or PCOC) is a metabolite and highly toxic to aquatic organisms, but degrades quickly into benign end-products in aerobic conditions, while its degradation is less predictable in anaerobic conditions.

The degradation rates of the R- and S-isomers may be significantly different, however the available literature shows no consistency for which of the isomers is more rapidly degraded. The possible cause of the differences in literature data was suggested to be the redox conditions.

A number of studies show that biodegradation of mecoprop in soil has dependence on the concentration, temperature, moisture content, redox conditions and depth. The biodegradation in top-soils is likely to occur at significant rates if soil conditions are amenable to microbial activity (typically less than 25 days), while in sub-soils there is likely to be little or no degradation.

The biodegradation in aerobic aquifers is highly unpredictable. A lag phase may precede the degradation. Durations of 20 to 120 days were reported in the literature, and for some unpolluted aquifers in UK and Denmark no degradation at all was reported after 200 and 371 days, respectively. The lag phase depended on several factors but the most commonly cited was the previous exposure of the aquifer to mecoprop, which reduces the duration of the lag and also the concentration of mecoprop within the aquifer, with which a higher concentration of exposure resulted in more rapid degradation. After the initial lag phase observed around 50% degradation was observed in most samples, followed by degradation of the remaining mecoprop after a second lag phase.

Very little evidence of biodegradation in anaerobic aquifers was found. Nitrate-reducing conditions can sometimes support degradation, manganese- and iron-reducing conditions rarely, but under sulphate-reducing and methanogenic conditions, degradation has not been observed.

The sorption of mecoprop to mineral surfaces is reported as often more important than on organic carbon in aquifers. Sorption of mecoprop has been found to be largely dependent upon soil pH. Most sorption studies report a value of Kd (range 0 - 2.8) rather than a value of Koc (range 5.3 - 25). The generally made assumption that K_d is proportional to f_{oc} does not appear to have been tested.

I. MATERIALS AND METHODS

A. MATERIALS

The materials of a review paper are the reference sources. Please refer to the reference list of the original paper.

B. STUDY DESIGN

The methodology used to gather the relevant papers is not described.

II. RESULTS AND DISCUSSION

Refer to the reference list in the full-text paper for reference details. The type of study (field or laboratory) is specified only when explicitly indicated in the review paper.

III. CONCLUSION

Mecoprop is a widely used herbicide that can enter the subsurface environment as a result of normal use, waste disposal and other operations. It enters surface waters, subsoil and groundwater as a result of surface application and leaching, leakage from landfills and from other operations. The rate and extent of biodegradation of mecoprop in the subsurface is highly variable. Biodegradation can be significant, principally under aerobic conditions, which will be particularly prevalent in well-drained topsoil, which is also biologically active. If there is little rainfall in the period after agricultural application then mecoprop is likely to be completely removed by biodegradation in the topsoil. Heavy precipitation immediately following application is likely to cause mecoprop to be leached in runoff to surface water or to subsoil and groundwater where biodegradation is slower, or, frequently, negligible. Biodegradation of mecoprop has been reported in some aerobic aquifers, but data are insufficiently consistent to predict when, and at what rate, degradation will occur. Biodegradation is particularly unreliable in anaerobic groundwater and has not been observed under sulphate-reducing or methanogenic conditions, which means that where mecoprop has been disposed of to landfill it is frequently among the most persistent organic compounds in the landfill plume. The degree of mecoprop attenuation by sorption to sediment is related to the sediment mineralogy and geochemistry. Proportions of organic matter, clay mineralogy and iron oxyhydroxides may all have a role in determining the amount of sorption, particularly because mecoprop

sorption is pH controlled. It is suggested that the generally applied model that uses Koc for predicting sorption of organic solutes may not be appropriate for use with mecoprop, and a better approach would be to obtain site-specific Kd values at solute concentrations that are representative of field conditions. However, the use of a Koc value in contaminant transport modelling may be conservative, as it does not take account of sorption to mineral phases.

Assessment of methodological quality

	Relevance	Reliability	Transparency & repeatability
Material (experiments)	Mecoprop. The racemic mixture was considered, not specifically Mecoprop-P	Materials of experiments reported in the review could not be assessed	Various sources, cannot be assessed
Material (bibliographic)	Suitable bibliographic material, mainly UK and DK studies, a few from North America. Taking into account the strong emphasis on two particular countries (UK and DK), the review may not be complete at the European level.	Bibliographic sources are mostly reliable and consist in peer-reviewed papers and UK Environment agency reports; Reported studies may not be GLP-compliant	References are detailed and can be retrieved
Method (experiments)	Analytical methods and experimental designs of individual studies could not be assessed		
Method (bibliographic)	Method for literature review is not cited	The choice of references may be biased, however the paper was written by scientists attached to a government agency and there should be no motivation for bias	The recent relevant papers not cited in the review of SR Buss should appear in the actual literature review.
Results & interpretation	Qualitative information, no new usable endpoints	Various sources, cannot be assessed	Various sources, cannot be assessed

Report:	**CA 7/02 Rodriguez-Cruz, S. *et al.* (2010)**
	Soil biology & biochemistry, 42, pp32-39
Title	Biodegradation of the herbicide mecoprop-P with soil depth and its relationship with class III *tfdA* genes
Guidelines:	None stated
GLP:	Not stated, but assumed not GLP
Deviations	Not applicable

Previous evaluations	None: Submitted for the purpose of renewal under Regulation 844/2012.
	This paper was identified by the applicant as potentially relevant during the literature review.
	The paper summary and relevance/reliability assessment provided by the applicant have been reproduced below. The RMS agrees with the applicant's assessment. The paper investigated the degradation of mecoprop-P with soil depth and the genes associated with it. The study does not provide new endpoints and has not been relied on for the risk assessment.

Executive Summary

The authors investigated the effect of soil depth on mecoprop-P biodegradation and its relationship with the number and diversity of *tfdA* related genes, which are the most widely known genes involved in degradation of the phenoxyalkanoic acid group of herbicides by bacteria. Mecoprop-P half-life (DT_{50}) was approximately 12 days in soil sampled from <30 cm depth, and increased progressively with soil depth, reaching over 84 days at 70–80 cm. In sub-soil there was a lag period of between 23 and 34 days prior to a phase of rapid degradation. No lag phase occurred in top-soil samples prior to the onset of degradation. The maximum degradation rate was the same in top-soil and sub-soil samples. Although diverse *tfdAα* and *tfdA* genes were present prior to mecoprop-P degradation, real time PCR revealed that degradation was associated with proliferation of *tfdA* genes. The number of *tfdA* genes and the most probable number of mecoprop-P degrading organisms in soil prior to mecoprop-P addition were below the limit of quantification and detection respectively. Melting curves from the real time PCR analysis showed that prior to mecoprop-P degradation both class I and class III *tfdA* genes were present in top- and sub-soil samples. However at all soil depths only *tfdA* class III genes proliferated during degradation. Denaturing gradient gel electrophoresis confirmed that class III *tfdA* genes were associated with mecoprop-P degradation. Degradation was not associated with the induction of novel *tfdA* genes in top- or sub-soil samples, and there were no apparent differences in *tfdA* gene diversity with soil depth prior to or following degradation.

I.   MATERIALS AND METHODS

A.   MATERIALS

1.	**Test materials:**	Commercial Mecoprop-P formulation (Duplosan, Mirfield Sales Services Ltd., Doncaster, UK; 48% w/w)
2.	**Soils:**	Sampling occurred in Long Close field on the farm at Warwick HRI,Wellesbourne,Warwickshire, UK. The soil is a sandy loam of the Wick series.

Mecoprop-P and a related herbicide (Fenoxaprop-P-ethyl) had been applied3 and 5 years prior to sampling, respectively.

Soil was collected from five depths (0 to 10, 20 to 30, 40 to 50, 60 to 70 and 70 to 80 cm depth) at three sampling locations separated by 60 m.

Soil samples were left on the bench overnight to reduce moisture content, before being passed through surface sterilised 3 mm sieves. In the sieved soil, total organic matter and microbial biomass-C were measured (see Table B. 8.55).

B.   STUDY DESIGN

1. Experimental conditions

Commercial Mecoprop-P formulation (Duplosan, Mirfield Sales Services Ltd., Doncaster, UK; 48% w/w) was dissolved in distilled water and added to single 300 g fresh weight portions of soil from each location to provide 5 mg pesticide kg^{-1} soil, and further water was added to bring the water holding capacity to 40%. Each soil was mixed thoroughly by hand, and then further mixed by passing through a <3 mm sieve five times. Soil was transferred to a sterile polypropylene container which was loosely capped and incubated at 15°C. Moisture content was maintained by the addition of sterile distilled water as necessary (usually once each week).

DT_{50} and Kd values were determined for each soil site and depths combination. In addition, the number of mecoprop-P degrading micro-organisms was determined at 0% and at 100% degradation time points. In order to study the potential correlation between mecoprop-P soil degradation and *tfdA*-like genes, the following DNA analysis were undertaken:

- *tfdA* and *tfdAα* genes sequencing in pooled 0-10 cm soil samples at 0% and at 100% mecoprop-P degradation time points. It provided a Phylogenetic tree of the cloned *tfda*-like sequences present in soil.

- Quantitative PCR of *tfdA* genes was undertaken on soil samples at 0% and at 100% mecoprop-P degradation time points. The melting curves allowed to determine the profile evolution in terms of class I, II and III of *tfdA* genes before degradation started and once it was completed;

- Denaturating gradient gel electrophoresis of *tfdA* genes was undertaken on soil samples at 0% and at 100% mecoprop-P degradation time points and confirmed the results from the quantitative PCR.

2. Sampling

The soils were sampled at regular intervals over a 3-month period (Figure B. 8.1).

3. Description of analytical procedures

Mecoprop-P was determined at each sampling point with extraction and HPLC analysis as described by Rodriguez-Cruz *et al*. (2006).

Sorption of mecoprop-P was determined using a batch mixing method, and adsorption distribution coefficients (Kd) measured as described by Rodriguez-Cruz *et al*. (2006).

The number of mecoprop-P degrading organisms was determined in soil immediately following mecoprop-P addition and at the point of 100% degradation. The size of the mecoprop-P degrading community was determined using the most probable number (MPN) method, as described in Bending *et al*. (2003).
DNA was extracted from 1 g fresh weight portions of soil taken immediately following mecoprop-P addition, and at the point of 100% degradation, by bead beating using a MoBio (Carlsbad, California, USA) Ultraclean soil DNA extraction kit as described by the manufacturer.

Sequencing of *tfdA* and *tfdAα* genes: Initial studies used primers described by Itoh *et al*. (2002) to amplify both *tfdA* and *tfdAα* from DNA extracts. 10-fold diluted DNA extracts from pooled 0–10 cm depth samples, taken immediately following mecoprop-P addition or at the point of 100% degradation, were amplified using the primers 5'-AC(C/G)GAGTTC(G/T)(C/G)CGACATGCG-3' and 5'-GCGGTTGTCCCACATCAC-3'. The PCR reaction mixture and reaction conditions were as described by Bending *et al*. (2003) and Itoh *et al*. (2002) respectively. The PCR reactions were purified using a QIAquick PCR Purification Kit (Qiagen Ltd, Dorking, UK) and then cloned using a TOPO Cloning Kit (Invitrogen, Paisley, UK). For each sample, plasmid DNA was extracted from 25 clones containing an insert using a QIAprep Spin Miniprep Kit. Sequencing was performed using M13 forward and reverse primers and a PRISM BigDye Terminator Cycle Sequence Reaction Kit (Applied Biosystems, Warrington, UK), with products sequenced on an Applied Biosystems 3700 automated sequencer. *tfdAα* -like sequences cloned in this study were compared with selected reference *tfdA* and *tfdAα* sequences available in the Genbank database. A neighbour-joining dendrogram (Jukes–Cantor distances; Phylip 3.6a3) was constructed from common partial sequences (c. 356 bp) following alignment in ClustalX1.81. Bootstrap analysis (Seqboot, Phylip 3.6a3) was conducted with 1000 replicates. The resulting trees and consensus were viewed using TreeExplorer 2.12.

Quantitative PCR focussed on the *tfdA* gene group only. Primers used were selective for *tfdA* genes and did not amplify *tfdAα* (Bælum *et al*., 2006). *Cupriavidus necator* JMP134 (pJP4) (Pemberton *et al*., 1979) was used for standard curve preparation in the quantitative real time PCR assays. *C. necator* JMP134(pJP4), *Burkholderia sp*. RASC (Fulthorpe *et al*., 1995), and an unclassified bacterial strain (Tonso *et al*.,1995) were used for positive controls in melting curve analyses. All of the bacterial strains were propagated in MMO medium (Stanier *et al*., 1966) supplemented with 500 mg l^{-1} of 2,4-Dichlorophenoxyacetic acid (2,4-D). DNA sequence analysis confirmed that these strains contained *tfdA* class I, II and III genes, respectively. Standards for quantitative real time PCR (qPCR) with known quantities of the *bacterium C. necator* AEO106 harbouring the class I *tfdA* gene and qPCR with DNA from the standards and from the soils treated with mecoprop-P, were made as described previously (Fredslund *et al*., 2008). Briefly, the Quantitect SYBR green PCR kit (Qiagen, Crawley, UK) was used for the mastermix. The reaction contained 0.4mM of the *tfdA* primers5'-GAGCACTACGC(AG)CTGAA(CT) TCCCG-3' and 5'-GTC GCG TGC TCG AGA AG-3' and 1 ml of 10-fold diluted DNA extract. In order to ensure a highly specific reaction 25.5 mg bovine serum albumin (Amersham Bioscience, Buckinghamshire, UK) was added to each reaction mixture to avoid unspecific bindings and to ensure as efficient reaction conditions as possible. The PCR conditions were as follows: 6min at 95°C; 50 cycles of 45 s at 94°C, 30 s at 64°C, and 2 min at 72°C; and a final step of 6 min at 72°C. Subsequently, temperature ramping was performed to analyse melting curve profiles of the PCR products. The conditions were as follows: 80 cycles of 30 s starting at 58°C with an increase in temperature of 0.5°C for every cycle to a temperature of 98°C at the final cycle. The melting curves were used to verify presence of the specific real time PCR product.

Denaturing gradient gel electrophoresis of *tfdA* genes: to provide phylogenetic information about the *tfdA* genes associated with mecoprop-P degradation, *tfdA* genes were amplified from soil taken immediately following mecoprop-P addition, and at the point of 100% degradation, using GC clamped *tfdA* primers. PCR products were separated by Denaturing Gradient Gel Electrophoresis (DGGE), as described previously (Bælum *et al*., 2006) except that PuReTaq[TM] Ready-To-Go PCR beads (GE Healthcare, Buckinghamshire, UK) were used to produce the PCR product. Bands excised from the gel were re-amplified and sequenced by MWG (Ebersberg, Germany).

II.   RESULTS AND DISCUSSION

A.   DATA

Table B. 8.55. Soil properties and degradation parameters of top-soil and sub-soil samples

Soil depth (cm)	Organic matter (%)	Biomass (mg C kg^{-1} soil	DT_{50} (days)	Lag phase (days)	Log MPN (g^{-1} dw soil)[a, b]	*tfda* copy No. (g^{-1} dw soil)[a, c]	Ratio MPN degraders: *tfdA* copy no.
0-10	2.7	68.8	12.3	0.0	5.1	76591	3.1
20-30	2.4	66.9	12.7	0.0	5.9	47369	12.5
40-50	2.2	45.6	30.8	28.0	5.0	70800	11.0
60-70	1.5	16.3	61.7	23.3	4.0	67156	0.2
70-80	1.1	9.5	83.6	33.4	4.4	51244	0.8

[a] At the point of 100% mecoprop-P degradation.
[b] Number of degraders at time 0 were below detection limits.
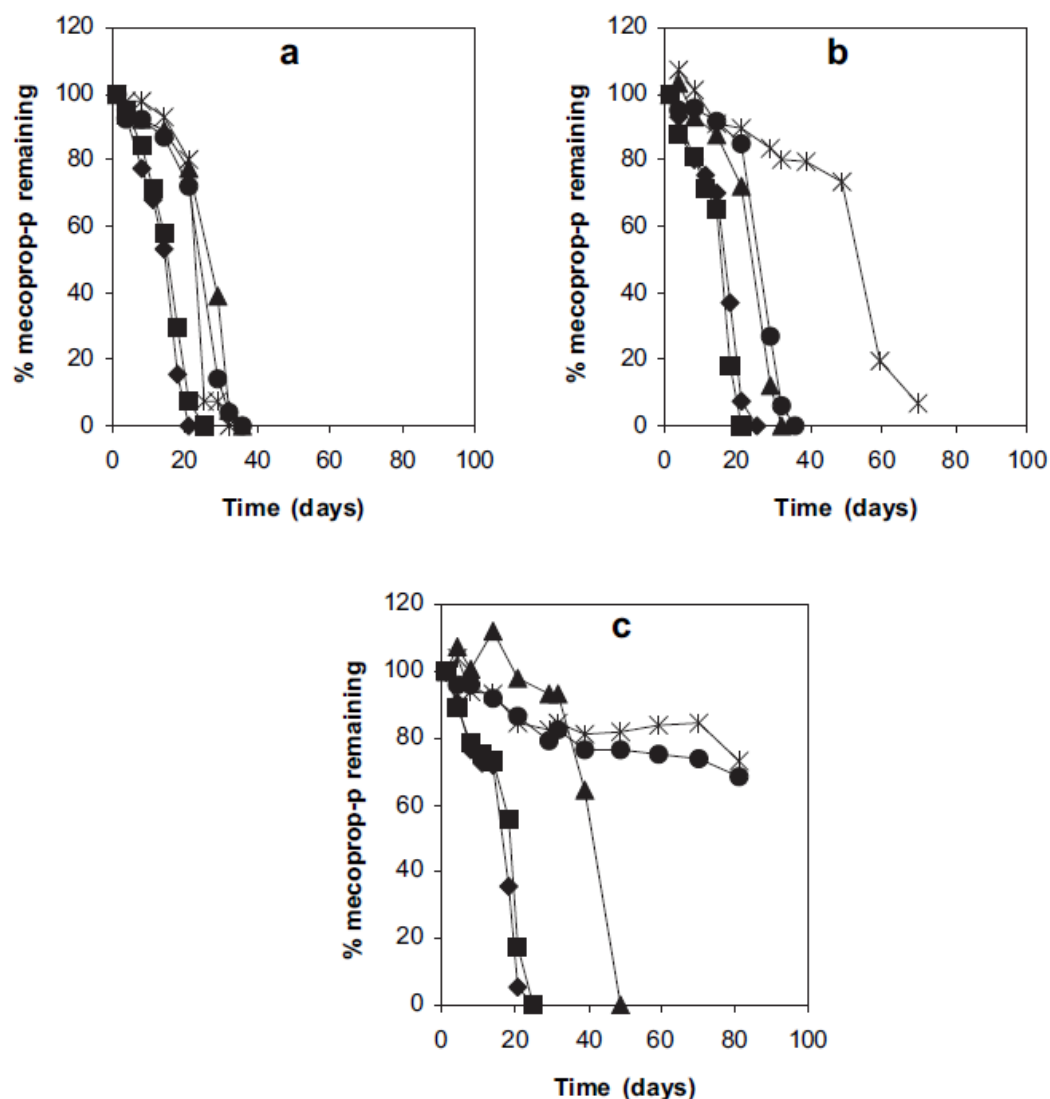[c] tfdA copy number at time 0 <400 g^{-1} dw soil.

Figure B. 8.1. Degradation of mecoprop-P in top- and sub-soil samples for the three sampling locations (a, b ,c) studied. Soil depth: 0–10 cm (♦); 20–30 cm (■); 40–50 cm (▲); 60–70 cm (●); 70–80 cm (X).

There were significant progressive declines in percentage of organic matter (OM) and biomass down the soil profile, demonstrating a clear gradient in soil chemical and biological properties with depth (Table B. 8.55). In top-soil (depths above 30 cm), mecoprop-P degradation rates were similar in soil from all three sampling locations and proceeded rapidly without a lag phase (Figure B. 8.1. a–c). Top-soil biodegradation kinetics were most closely fitted to a linear model, and DT_{50} occurred within 13 d (Table B. 8.55). In sub-soil (depths below 30 cm), kinetics most closely followed the Gompertz model (Figure B. 8.1). There was a lag phase of between 23.3 and 33.4 d prior to a phase of rapid degradation (Figure B. 8.1and Table B. 8.55). However, there was substantial variability in degradation rate between the sampling locations and at site 3 in samples taken from below 60 cm depth, there had been no rapid phase of degradation after 80 d (Figure B. 8.1. c). DT_{50} in sub-soils increased from 30.8 d at 40–50 cm depth to 83.6 d at 70–80 cm depth. Soil depth had no significant effect on the maximum degradation rate, which averaged at 0.59 µg mecoprop-P g^{-1} soil d^{-1}.

Kd averaged 0.15 ml g^{-1} and was not significantly affected by depth.

B.   NUMBER OF MECOPROP-P DEGRADERS

Prior to mecoprop-P application the most probable number (MPN) of mecoprop-P degrading organisms was

lower than the detection limit of 100 degraders g^{-1} soil in all samples. At the point of 100% degradation numbers of mecoprop-P degrading organisms had increased in all samples to between 4.0 and 5.9 log cells g^{-1} soil, although there were no significant differences in the number proliferating at the different soil depths (Table B. 8.55), and no relationship between the number of degraders and DT_{50}.

C.   DIVERSITY AND RELATIVE ABUNDANCE OF TFDAα AND TFDA GENES

Phylogenetic analysis of cloned sequences is shown in Figure B. 8.2. The data indicates that the soil supported diverse *tfdAα* and *tfdA* sequences, although some of the branches of the phylogenetic tree were not well supported using the neighbour-joining method with bootstrap percentages less than 50%. Clones with high homology to the *tfdAα* gene were found with the same abundance prior to and after the degradation of mecoprop-P. The tree shows fairly strong support (92%) for 27 of the soil clones from both mecoprop-P treated and untreated soil clustering with between 69% (clone U20) and 91% (clone M22) identity to known *tfdAα* sequences from *bradyrhizobial* isolates (e.g. *Bradyrhizobium* strain RD5-C2) and also with sequences amplified from enrichment cultures from other UK soils. There was also strong support (100%) for one clone sequence from mecoprop-P treated soil (clone M1) clustering with 99% identity to the *tfdA* of *Achromobacter xylosoxidans* EST4002, a known class III *tfdA*, and, with 78% identity to *tfdA* from *C. necator* JMP134 pJP4 (class I). The analysis also identified that the remainder of the clones (both mecoprop-P treated and untreated; M20, U15, U26, U14, M23, U18, U1, M15, U17, M9, M24) did not cluster with *tfdA* or *tfdAα* from cultured strains.
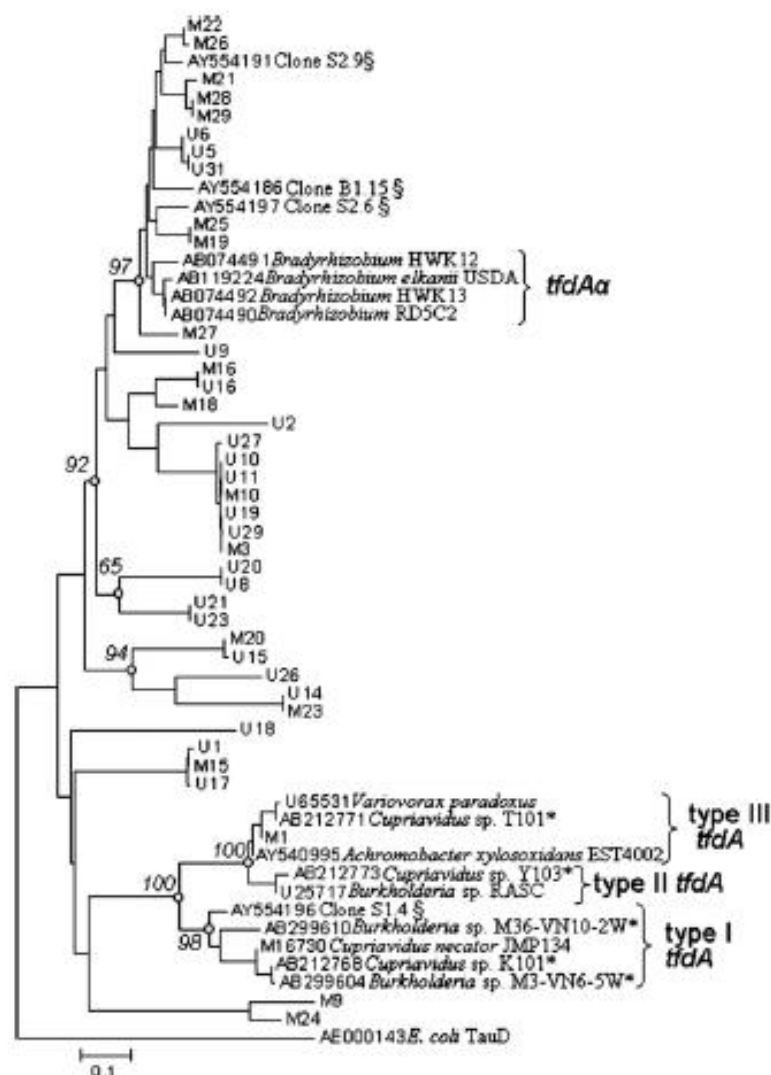

Figure B. 8.2. Phylogenetic analysis of soil *tfdAα* and *tfdA* cloned sequences. Samples prior to mecoprop-P addition: U. Samples at the point of 100% mecoprop-P degradation: M

D.   QUANTITATIVE PCR OF TFDA GENES

The number of *tfdA* genes in the soils increased from an amount between the limit of detection and the limit of quantification (400 g^{-1} soil) to numbers ranging from 4.74 x 10^4–7.66 x 10^4 genes g^{-1} soil (Table B. 8.55). ANOVA revealed that there was no significant difference in the number of *tfdA* genes in soil from different depths. Furthermore there was no significant relationship between the number of *tfdA* genes and DT_{50} or the MPN of mecoprop-P degrading organisms. In addition to the quantitative data obtained from the real time PCR, the authors were able to investigate diversity in the *tfdA* genes present prior and subsequent to mecoprop-P degradation (Figure B. 8.3). Prior to the mecoprop-P treatment class I as well as class III *tfdA* genes were detectable in the soils. However only the class III *tfdA* gene was detectable at the point of 100% mecoprop-P degradation, although the possible presence of class I sequences cannot be excluded. Identical melting curve profiles were obtained for all samples prior to and after degradation.
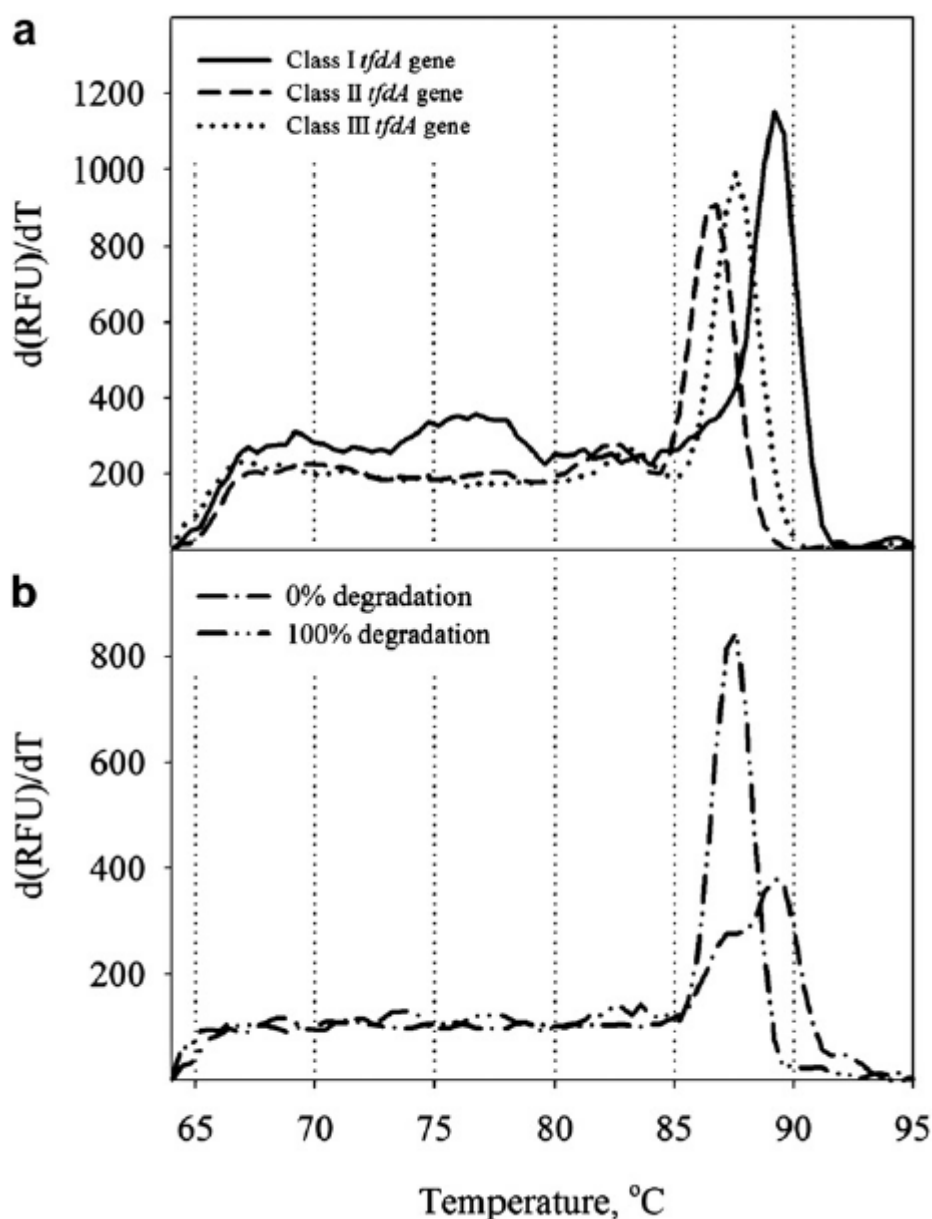

Figure B. 8.3. Melting curve profiles of real time PCR amplification products using a) standard sequences as template and b) soil sample prior to and following mecoprop-P addition.

E.   **DENATURING GRADIENT GEL ELECTROPHORESIS OF TFDA GENES**

In order to investigate the dynamics of *tfdA* genes during mecoprop-P degradation DGGE analysis was performed. Samples had between 4 and 5 separate DGGE bands (data not shown), but there was no difference in banding number or pattern either between sampling times, depth or location. However, bands were observed to be stronger in samples taken at 100% degradation than at 0% degradation. BLAST searching showed that all bands present on DGGE gels in samples at 100% mecoprop-P degradation showed >99% homology to *Burkholderia cepacia* plasmid pIJB class III *tfdA* (EMBL accession U87394), with bands also showing >99% homology to *tfdA* Class III DGGE bands A2-6 and B1 (EMBL accessions DG272406–DG272414) described by Bælum *et al.* (2006).

III.   CONCLUSIONS

Mecoprop-P degradation rates were slower in sub-soils relative to top-soils. The calculated average DT_{50} ranged from 12.3 days in soil surface to 83.6 days in the 70-80 cm soil layer. Lag phases ranging from 0 (surface soil) to 33.4 days (70-80 cm layer) were also observed. There was a clear trend of slower degradation and longer lag phases with soil depth. Kd averaged 0.15 ml g^{-1} and was not significantly affected by depth. The genetic analysis revealed that *tfdA*-like genes are involved in mecoprop-P degradation, in particular class III *tfdA* genes. The lack of significant difference in MPN of mecoprop-P degraders and *tfdA* gene concentration from one soil layer to another indicates that other genes or other mechanisms influence the degradation of mecoprop-P in subsoil. The authors suggest that the tfdA gene did not contribute to the degradation of mecoprop-P, despite the fact that tfdA appeared to be abundant in the soil community.

Assessment of methodological quality

	Relevance	Reliability	Transparency & repeatability
Material	Mecoprop-P formulation was used	No GLP certificate	Nominal concentration is mentioned. No Mecoprop-P analysis in Duplosan sample was undertaken prior to the study.
	The soil tested received Mecoprop-P and other phenoxyalkanoic acid treatments in the year before sampling.	Micro-organism population should be adapted to degradation of phenoxyalkanoic acid herbicides. Therefore the soils should be suitable for studying the genes involved in Mecoprop-P degradation.	Location, soil class (sandy loam), organic matter content and biomass were reported. However, other soil parameters are missing.
Method	Extraction and HPLC analysis is relevant for Mecoprop-P analysis in soil.	No validation is referenced. FOCUS (2006) Kinetic guideline not followed for DT_{50} determination	The analytical method used is described in another reference: Rodriguez-Cruz *et al.* (2006).
	Kd determination was not conducted acc. to OECD guideline.	Kd determination was not conducted acc. to OECD guideline.	The Kd method used is described in another reference: Rodriguez-Cruz *et al.* (2006).
	MPN method is relevant to study the increase of Mecoprop-P degrading μ-org. with time.	MPN method is described in Bending *et al.* (2003).	MPN method is described in Bending *et al.* (2003).

	Relevance	Reliability	Transparency & repeatability
	DNA analysis was relevant to study *tfdA* (and to a lesser extend *tfdAα* genes). It did not study any other class of genes.	DNA sequencing use primers cited by other authors for *tfdA* and *tfdAα* genes. The material used seems reliable. qPCR was calibrated using a standard with known amount of bacteria harbouring *tfdA* genes. Qualitative standards for Class I, II and III *tfdA* genes were used as well. DGGE and sequencing of the excised bands is reliable to sequence the different *tfdA* genes amplified from soil samples.	The method for DNA sequencing was detailed and should be reproducible. Method, primers and standard bacteria used for qPCR were well referenced. Methodoly for DGGE was well referenced.
Results & interpretation	The results indicate a trends of DT_{50} and lag phase increase with soil depths. It also shows that a soil adapted to phenoxyalkanoic acid degradation will degrade Mecoprop-P in subsoil layer, even if after a longer lag phase. DT_{50} and Koc calculated should not be used as endpoint (lack of GLP statement, no OECD method stated)	DT_{50} and Kd determination are in the range of that recovered using OECD methods. The observed increased of DT_{50} and lag phase in soil depth is consistent with other references.	The results were reported transparently, except for Kd determination (only final result stated). DT_{50} is known to be a variable parameter. However, the trends are in agreement with other references. Therefore, repeating this study should provide results in the same order of magnitude.
	The genetic analysis was relevant to *tfdA*-like genes analysis only. Impact of other genes was not studied.	Results were found reliable as far as *tfdA* genes are concerned. Class III tfdA genes were found to be associated with Mecoprop-P degradation.	The finding should be repeatable if duplicating the study on soil adapted to phenoxyalkanoic acid degradation. Otherwise, it is not certain that *tfdA* gene harbouring micro-organisms would be present in subsoil layers.

Soil accumulation studies (CA 7.1.2.2.2)

No data required – soil dissipation studies were not triggered.

B.8.1.2. **Adsorption and desorption in soil**

Adsorption and desorption of active substance (CA 7.1.3.1.1)

RMS comments:	Two studies were assessed and considered acceptable for the original approval of mecoprop-P: - Matla and Vonk, 1993, assessed sorption of mecoprop-P to soils with pH <5 according to OECD guideline 106. - Obrist, 1986e, assessed sorption of racemic mecoprop to soils with pH >5.5. One study has been submitted for the purpose of renewal – Simmonds, 2010, which assesses sorption of mecoprop-P to soils with pH >5.5 according to OECD 106. Two papers were identified as potentially relevant by the applicant from the literature search – Nolan, 2007, and Piwowarczyc, 2013.

Report:	**Matla, Y & Vonk, J (1993)**
Title	Adsorption of mecoprop-P to soil particles in three soil types. TNO Report IMW-R 93/035
Guidelines:	OECD 106
GLP:	Yes
Deviations	0.05 M CaCl$_2$ was used instead of 0.01 M CaCl$_2$ solutions.

Previous evaluations:	In DAR for original approval (1998). The original evaluation has been reproduced below. The RMS has briefly reviewed the study and added some additional information. The soils used in the study are all sandy soils with low pHs (4.3 to 4.4). The results indicate mecoprop-P is mobile and with highly non-linear sorption at these low pH's. Sorption to soil was calculated from the solution concentrations. Given the high mobility of mecoprop-P, direct analysis of the soil residue would have been more appropriate to obtain accurate sorption results.

Methods

The adsorption/desorption of ^{14}C-mecoprop-P (ring labelled, 98% pure) to three sandy soil types was determined essentially according to OECD 106. The soils were sieved to remove coarse particles greater than 2 mm. One g dry weight of soil were added 5, 10, 20 and 50 µg test substance/vial and CaCl$_2$ solution (0.05 M CaCl$_2$) to a total volume of 10 ml. The vials were shaken for 48 hours at 20°C. After centrifugation duplicate samples of the supernatant were analyzed by LSC. The soils from the 5 mg/l test solution (50 µg test substance/vial) were extracted with methanol and analyzed by LSC.

Table B. 8.56. *Soil characteristics*

Soil type	pH (KCl)	Sand % >50 µm	Silt % 2-50 µm	Clay % < 2 µm	OM %
Sandy soil A (Zeist)	4.3	89.2	7.0	3.8	5.6
Sandy soil B (De Krakeling)	4.4	91.4	4.8	3.8	3.6
Sandy soil C (Maarn)	4.3	85.4	6.7	3.9	4.2

Results

The amount of test material sorbed was calculated from the initial concentration of the test solution and the concentration remaining in the supernatant at equilibrium. The adsorption constant values based on total soil ranged 3.2 to 4.5 ml/g soil. Adsorption constants calculated on organic matter base (Kom) ranged 78 to 97. Mass balances for the 5 mg/l test solution (50 µg test substance/vial) were reported as 94%, 99% and 98%AR for soils A, B and C respectively. Mass balances for the other test solution concentrations were not calculated. Desorption studies were not performed because the adsorption at the 5 mg/l level was less than 25%.

Table B. 8.57. Adsorption of mecoprop-P to three soils

Amount of mecoprop-P (µg)		Soil A (Zeist)		Soil B (De Krakeling)		Soil C (Maarn)	
Nominal	Found	Solution (µg/ml)	Adsorbed (µg/g)	Solution (µg/ml)	Adsorbed (µg/g)	Solution (µg/ml)	Adsorbed (µg/g)
5	5.05	0.30	2.05	0.34	1.65	0.35	1.52
10	10.04	0.67	3.35	0.72	2.87	0.74	2.62
20	19.78	1.38	5.92	1.50	4.78	1.50	4.74
50	48.45	3.78	10.68	3.94	9.05	3.94	9.10

Table B. 8.58. *Linear regression analysis*

Soil type	OM %	K (ml/g)	1/n	r^2	Kom	Koc
Sandy soil A (Zeist)	5.6	4.5	0.66	0.99	80	139
Sandy soil B (De Krakeling)	3.6	3.5	0.69	0.99	97	167
Sandy soil C (Maarn)	4.2	3.3	0.75	0.99	78	135

1998 Evaluation Comments

The study is acceptable. The pHs of the soils were lower than recommended by the guideline and pH would be expected to have an influence of the adsorption by a weak acid such as mecoprop-P; the adsorption is expected to be higher the lower the pH is. Soils with a lesser content of organic matter should have been included. Comparing to the study on MCPP (Obrist 1986e) the MCPP-P seems to be better adsorbed than mecoprop but the conditions, especially the pH were different. However, the value is still low and indicating a mobility potential.

Report:	**Obrist (1986e)**
Title	Adsorption/desorption of mecoprop on representative agricultural soils. Study No 6015-324
Guidelines:	US-EPA 40 CFR 160 and N, 163-1
GLP:	Yes
Deviations	Hagerstown silty clay loam was used in place of Kewaunee silty clay loam due to availability. The concentrations of mecoprop used in this study were specified in the protocol to be approximately 10, 5, 1 and 0.5 ppm. The actual concentrations used were 11.6, 5.82, 1.16 and 0.582 ppm in the preliminary study and 12.0, 5.92, 1.24 and 0.606 ppm in the definitive study.

Previous evaluations:	In DAR for original approval (1998)
	The original evaluation has been reproduced below. The RMS has briefly reviewed the study and added some additional information.
	The study shows that mecoprop is highly mobile with almost linear sorption isotherms. The study was on racemic mecoprop rather than mecoprop-P, however the results are within the same range as those in the newly submitted study (Simmonds, 2010), indicating that the adsorption process is not stereoselective. The soils used in the study cover a range of soil types with a reasonable pH range (5.6 to 7.6), however, the linear fit for the sandy soil

(Plainfield) was relatively poor (r^2 0.95) and will be taken into account when considering the adsorption/desorption data set as a whole. Sorption to soil was calculated from the solution concentrations. Given the high mobility of mecoprop-P, direct analysis of the soil residue would have been more appropriate to obtain accurate sorption results.

Methods

The adsorption/desorption of mecoprop was studied on 4 soils according to US-EPA 40 CFR 160 and N, 163-1. The equilibrium concentrations in soil/water systems were measured and calculated using Freundlich isotherms to Freundlich correlation coefficients. ^{14}C-Mecoprop (ring label) >96% pure were added in duplicate to each soil at 0.606, 1.24, 5.92 and 12.0 mg/l in 0.01M $Ca(NO_3)_2$ solution. 10 ml of the solution were added to 3 g of the soil. The samples were shaken for 1 hour (equilibrium time) at 25^oC before centrifugation and analysis of supernatant. Desorption study was carried out after replacing 7 ml solution with pure solution.

Table B. 8.59. *Soil characteristics*

Soil type	pH (solution not reported)	Sand %	Silt %	Clay %	OM %	FMC %	CEC
Sand (Plainfield)	5.6	90	8	2	0.8	20.3	1
Sandy loam (Fox)	7.6	56	34	10	2.3	15.2	9
Silty clay loam (Hagerstown)	6.6	24	42	34	2.5	31.0	14.7
Silt loam (Plano)	6.8	6	74	20	5.9	29.3	13

Results

Freundlich constant (K_d) values ranged from 0.20 to 0.69. Desorption of adsorbed mecoprop was usually in the range of 25% to 50%.

Table B. 8.60. *Linear regression analysis. K_d: Freundlich constant, Kom: adsorption coefficient related to soil organic matter content. Koc: adsorption coefficient related to soil organic carbon content.*

Soil type	OM %	K_d	1/n	r^2	Kom	Koc
Sand (Plainfield)	0.8	0.199	1.093	0.950	24.9	42.9
Sandy loam (Fox)	2.3	0.298	0.942	0.996	12.9	22.3
Silty clay loam (Hagerstown)	2.5	0.428	1.012	0.997	17.1	29.5
Silt loam (Plano)	5.9	0.687	0.961	0.999	11.6	20.1

1998 Evaluation Comments

The study was performed on racemate mecoprop.

The Freundlich constant K_d-values ranged from 0.2 to 0.7 and the corresponding Koc values ranged from 20 to 43 which indicate that mecoprop has a low adsorption ability and thus a high mobility potential. The equilibrium time of 1 hour was below the recommended 16 hours of the OECD guideline but was supported by an equilibrium study. The soil/water relation 3:10 was also supported by a preliminary study.

Report:	CA 7.1.3.1.1/01, Simmonds, M. (2010)
Title	$[^{14}C]$-Mecoprop-P: adsorption to and desorption from four soils
	Report No. QC/09/001

Guidelines:	OECD 106
	OPPTS 835.1230
GLP:	Yes
Deviations	None

| Previous evaluations:	None: Submitted for the purpose of renewal under Regulation 844/2012.
	The study was generally well reported and demonstrates that mecoprop-P is highly mobile. Three of the soils used in the study were of similar pH(H$_2$O) (5.7 and 5.8) with only one with a higher pH (7.3). All soils have similar organic carbon contents so any correlation between Kf and OC cannot be clearly established from this study. Sorption to soil was calculated from the solution concentrations. Given the high mobility of mecoprop-P, direct analysis of the soil residue would have been more appropriate to obtain accurate sorption results.

Executive Summary

In an adsorption/desorption study, 3 UK soil types and 1 German soil (pH(H$_2$O) range of 5.7 - 7.3) were used to assess the adsorption behaviour of mecoprop-P in soil. In all soil types tested mecoprop-P was very highly mobile. There was some degree of correlation between adsorption constants and soil organic matter and soil pH. Determined Koc values ranged 12 to 34 (mean = 21) indicating very high potential soil mobility for mecoprop-P based on the McCall classification system. Once adsorbed by soil mecoprop-P was readily desorbed (Koc = 24 to 54 (mean = 37)). Due to significant breakdown of the test item observed in the soil:solution ratio preliminary tests, subsequent tests were performed using soils that had been sterilised by gamma irradiation. The mass balance at the end of the study ranged from 94.3 to 105.8 %.

I.   MATERIALS AND METHODS

A.   MATERIALS

1.   Test materials: Mecoprop-P / ^{14}C-Mecoprop-P
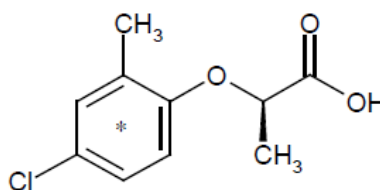
*denotes position of radiolabel in ^{14}C-Mecoprop-P

Description:	White solid
Lot/Batch #:	AC529/9 / 3668DCP001-7
Purity:	99.8% / 97.87%
CAS #:	16484-77-8
Stability of test compound:	Stable in sterilised soil
	Stable in 0.01M calcium chloride for at least 6 days

2.   Soils:

Four agricultural soils collected from various sites in the UK and Germany were used for the study. Soils were classified according to the USDA system. A summary of the physical and chemical properties of the soils is provided in

Table B. 8.61.

Table B. 8.61. Soil physiochemical properties

Soil Reference (Batch ID)	Calke (10/001)	South Witham (10/002)	Lockington (10/003)	Hagen (Refesol 04-A) (10/005)
Source Geographic Location	Site D, Calke, Derbyshire, UK	South Witham Quarry, South Witham, Lincolnshire, UK	Site G2, Lockington Ground Farm, Leicestershire, UK	Schmallenberg Nordrein-Westphalia, Germany
Collection Date	5 January 2010	5 January 2010	5 January 2010	5 January 2010
Textural classification (USDA)	Sandy loam	Clay loam	Sandy clay loam	Loamy sand
Sand (50-2000 μm)	69%	41%	47%	87%
Silt (2-50 μm)	18%	26%	22%	8%
Clay (< 2 μm)	13%	33%	31%	5%
pH				
1:1 Soil:H$_2$O Ratio	5.8	7.3	5.7	5.7
1N KCl	5.4	6.9	5.1	5.3
0.01M CaCl$_2$ (1:2)	5.6	7.2	5.6	5.5
Organic Carbon % [a]	3.13	3.71	3.07	2.90
Organic Matter %	5.4	6.4	5.3	5.0
Cation Exchange Capacity (meq/100g)	12.1	25.6	22.9	10.1
Water holding capacity				
pF 2.0 – WHC 0.1 bar	20.9	27.2	28.2	11.5
pF 2.5 – WHC 0.33 bar	15.7	23.2	24.4	6.1
Moisture content (% w/w)	14.78	22.05	22.55	11.33
Bulk Density (Disturbed) (gm/cc)	1.12	1.13	1.12	1.36

[a] = organic matter/1.724

B. STUDY DESIGN

1. Dates of experimental work

19 January 2010 – 03 March 2010

2. Experimental conditions:

Preliminary tests:

Tests were carried out in PTFE tubes. Preliminary testing demonstrated recovery of mecoprop-P from the tubes was quantitative (mean 99.6%). Background radioactivity was negligible in all soils therefore no background correction was necessary. Soil solution ratios of 1:2 were selected for the Calke, South Witham and Hagen soils and a 1:3 ratio selected for the Lockington soil based on preliminary testing to give adsorptions of between 20% and 80%. HPLC analysis of the supernatants indicated significant breakdown of the test item during the soil:solution ratio tests, therefore soils sterilised by gamma irradiation were used for all further tests. The adsorption equilibrium of mecoprop-P was reached after 48 hours for Calke, South Witham and Lockington soils. Adsorption continued to increase between 48 hours and 72 hours for the Hagen soil therefore an adsorption time of 72 hours was selected for the definitive phase of the study. Desorption was found to be complete after 2 hours.

Definitive tests:

The test item, nominally 3.1 mg of [^{14}C]-mecoprop-P was diluted to approximately 10 mL with 2 mL acetonitrile and 8 mL of de-ionised water to give the treatment stock solution. A 200 µL aliquot of this solution was taken and diluted accurately to 10 mL with acetonitrile and 100 µL aliquots were removed and counted by LSC to determine the exact concentration. The concentration of this stock solution was determined to be 0.36 mg mL^{-1}.

For the absorption phase, treatment solutions were prepared by dispensing 1.38 mL, 550 µL, 138 µL, 55 µL and 14 µL of the stock solution and diluting to 25 mL with 0.01M calcium chloride solution (<0.1% v/v acetonitrile in test solutions). Uniquely labelled duplicate PTFE tubes were prepared for each soil at each of five concentrations. Approximately 10 g oven-dried equivalent (ode) portions of the Calke, South Witham and Hagen (Refesol 04-A) loamy sand soil and 6.7g ode portions of the Lockington soil were weighed into pre-weighed tubes. The tubes were capped and re-weighed. Calcium chloride solution (19 mL minus the soil moisture content) was added and the mixture was shaken for ca.16 hours to pre-equilibrate prior to treatment. Following pre-equilibration, 1 mL of the appropriate treatment solution was added to each tube to allow treatment at nominal concentrations of 1.0, 0.4, 0.1, 0.04 and 0.01 mg L^{-1} [^{14}C]-mecoprop-P. The soil solutions were mixed and slurried for 72 hours on an end-over-end shaker in the dark at 20±1°C.

The tubes were removed from the shaker, weighed and centrifuged for 10 minutes at 2390 rcf. The supernatant solutions were removed by decanting and the tubes containing the soil pellets were reweighed. Aliquots of each supernatant were weighed and the radioactivity determined by LSC.

Following removal of the adsorption supernatant, an additional portion of fresh calcium chloride solution (approximately equal to the volume removed) was added to each tube, which was capped and weighed. Each tube was placed on an end-over-end shaker. After approximately 2 hours, the tubes were removed, weighed and centrifuged for 10 minutes. The supernatant (desorbate) was removed and the tubes were reweighed.

Following desorption, all tubes were solvent extracted. Approximately 20 mL of acetonitrile was added to each tube and the tubes weighed. The tubes were placed on the end-over-end shaker for ca.30 minutes, removed, reweighed, centrifuged for 10 minutes and the supernatants decanted. Following removal of the supernatant, the tube and soil pellet were re-weighed to enable the weight of each supernatant to be calculated.

3. Description of analytical procedures

Radiopurity of the treatment solution was determined as 97.87% by HPLC. Comparison of LC/MS data with that of a certified reference standard demonstrated that the test item was mecoprop-P.

Aliquots of each supernatant were weighed and the radioactivity determined by LSC. The LOQ for LSC was determined to be 0.000019 µg g^{-1}, representing 0.19% AR for the lowest concentration test solution (0.01 µg g^{-1}).

HPLC was used for the analysis of aqueous supernatants and solvent extracts in order to confirm the stability of the test item. HPLC column recoveries were good – 99.4% and 95.4%. The test item was found to be stable in 0.01M calcium chloride for at least 6 days.

All tubes, containing soil, were allowed to air dry, reweighed without the cap prior to homogenisation and combustion.

All samples were analysed within 3 days of generation.

II.   RESULTS AND DISCUSSION

A.   MASS BALANCE

The recovery of radioactivity was quantitative, with all recoveries within the acceptable range of 90-110% of applied radioactivity. The overall material balance for individual samples was in the range of 94.3-99.2% for the Calke sandy loam (mean 96.8%), 97.1-101.0% for the South Witham clay loam (mean 98.3%), 97.6-105.8% for the Lockington sandy clay loam (mean 99.9%), and 94.9-99.3% for the Hagen (Refesol 04-A) loamy sand (mean 97.0%).

Table B. 8.62 shows the results of the mass balance.

Table B. 8.62. Overall recovery expressed as percentage of applied radioactivity after adsorption and desorption

Concentration	% Applied Radioactivity			
	Calke	**South Witham**	**Lockington**	**Hagen**
1 mg L^{-1}	98.5	98.8	99.5	97.9
	94.3	98.7	105.8	97.8
0.4 mg L^{-1}	95.1	97.1	98.4	95.2
	95.1	97.6	97.6	99.3
0.1 mg L^{-1}	98.3	98.3	99.8	94.9
	97.7	97.8	98.5	97.2
0.04 mg L^{-1}	96.3	98.3	99.3	98.5
	96.1	98.1	99.2	96.8
0.01 mg L^{-1}	97.0	97.5	99.1	95.4
	99.2	101.0	101.5	96.6
Mean	96.8	98.3	99.9	97.0
sd (±)	1.67	1.07	2.34	1.47

B.   TRANSFORMATION OF PARENT COMPOUND

The adsorption equilibrium determination proved greater than 90% of [^{14}C]-mecoprop-P was extracted from the soil after 48 hours adsorption. [^{14}C]-mecoprop-P accounted for greater than 97% of the region of interest in the HPLC radiochromatogram for all samples run during the preliminary and definitive study. It was concluded that no significant degradation of [^{14}C]-mecoprop-P occurred over the duration of the study. Therefore no adjustment to the adsorption or desorption coefficients was necessary.

C.   FINDINGS

The amount of test material sorbed was calculated from the initial concentration of the test solution and the concentration remaining in the supernatant at equilibrium. The amount of applied test material adsorbed ranged from 19.3 to 33.7% in the Calke sandy loam, 17.7 to 26.8% in the South Witham clay loam, 17.8 to 30.6% in the Lockington sandy clay loam and 32.1 to 40.6% in the Hagen (Refesol 04-A) loamy sand.

The calculated adsorption constants (Kf) of the Freundlich isotherms for the soils ranged from 0.46 mL g^{-1} in the South Witham clay loam to 0.98 mL g^{-1} in the Hagen (Refesol 04-A) loamy sand. The Freundlich exponents (1/n) ranged from 0.852 in the Calke sandy loam to 0.926 in the Hagen (Refesol 04-A) loamy sand. The adsorption Koc values ranged from 12 mL g^{-1} in the South Witham clay loam to 34 mL g^{-1} in the Hagen (Refesol 04-A) loamy sand.

At the end of the desorption phase, the amount of test material desorbed, expressed as a percentage of the initial amount adsorbed, ranged from 31.0 to 34.9% in the Calke sandy loam, 32.1 to 35.4% in the South Witham clay loam, 33.4 to 38.4% in the Lockington sandy clay loam and 33.9 to 38.3% in the Hagen (Refesol 04-A) loamy sand.

The desorption K$_{des}$ values ranged from 0.88 mL g^{-1} in the South Witham clay loam to 1.55 mL g^{-1} in the Hagen (Refesol 04-A) loamy sand.

Table B. 8.63 summarises the key data for this study.

Table B. 8.63. Adsorption and desorption endpoints

Soil	Calke (Soil 10-001)	South Witham (Soil 10-002)	Lockington (Soil 10-003)	Hagen (Refesol 04-A) (Soil 10-005)
Texture (USDA)	sandy loam	clay loam	sandy clay loam	loamy sand
pH 0.01M CaCl$_2$	5.6	7.2	5.6	5.5
Organic Carbon (%)	3.1	3.7	3.07	2.9
Kf (mL g^{-1})	0.56	0.46	0.64	0.98
Koc (mL g^{-1})	18	12	21	34
1/n (adsorption)	0.852	0.892	0.853	0.926
Correlation (R^2)	0.99	1.00	1.00	1.00
Kdes (mL g^{-1})	1.00	0.88	1.15	1.55
Kocdes (mL g^{-1})	32	24	38	54
1/n (desorption)	0.869	0.915	0.866	0.936
Correlation (R^2)	0.99	1.00	1.00	1.00

For all soils the data fit to a linear equation was good for both adsorption and desorption with correlation coefficients of 0.99 to 1.00.
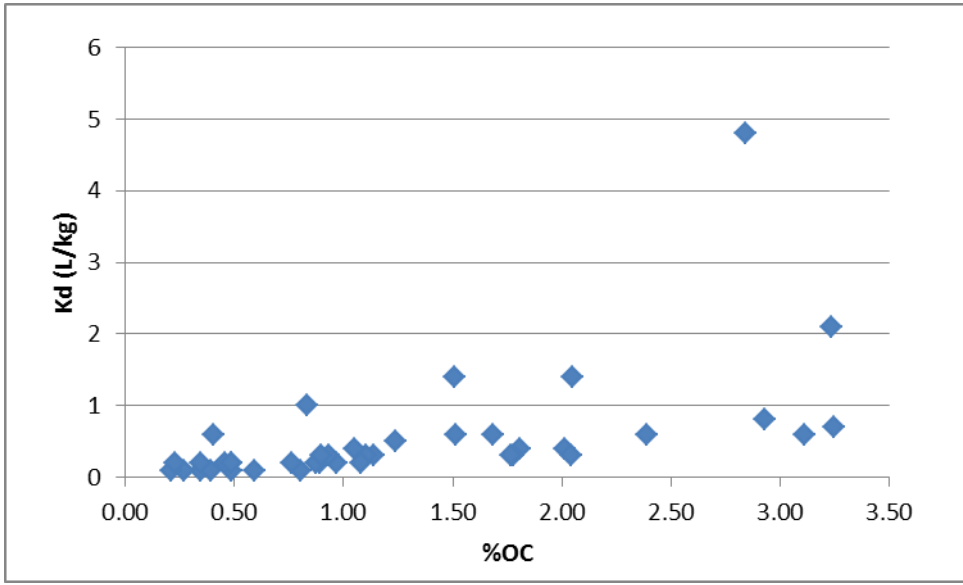
III. CONCLUSIONS

The K$_{oc}$ values obtained ranged from 12 to 34 mL g^{-1} (mean = 21 mL g^{-1}). Freundlich exponents were non-linear for all of the soils, with 1/n values of 0.85 to 0.93, indicating significant change in the relationship between the amount adsorbed onto the soil and the amount in solution through the concentration range.

The K$_{oc\ des}$ values ranged from 24 to 54 mL g^{-1} (mean 37 mL g^{-1}).

The determined Koc values indicate that mecoprop-P can be classified as being mobile in soil according to the Briggs classification and as having a very high mobility in soil according to the McCall classification.

Report:	CA 7/03, Nolan, B.T. *et al.* (2007) XIII Symposium Pesticide Chemistry - Environmental fate and ecological effects of pesticides, pp187-194
Title	Sorption of 7 weak-acid pesticides in 41 European soils: controlling factors and empirical modelling
Guidelines:	None
GLP:	Not applicable
Deviations	Not applicable

Report:	CA 7/04, Surdyk, N. *et al.*, (2008) Rapport d'avancement du projet BRGM RP-56702-FR. BRGM, Orléans
Title	Estimation de la mobilité dans les sols de molécules ioniques à caractère acide faible : application à ml'évaluation des risques environnementaux dans le cadre de l'homologation de produits phytosanitaires
Guidelines:	Not specified, batch equilibrium similar to OECD TG 106 for K$_D$ determination
GLP:	Not specified, but assumed not GLP

Deviations	Not applicable

| Previous evaluations	None: Submitted for the purpose of renewal under Regulation 844/2012.
	This paper was identified by the applicant as potentially relevant during the literature review.
	The paper summary and relevance/reliability assessment provided by the applicant have been reproduced below. Nolan, 2007, refers to a paper by Surdyk *et al*, 2006. In order to make the summary more complete, the applicant obtained a newer version of the paper by Surdyk *et al.,* 2008 and the results were tabulated from Appendix 2 and 5. The following is a joint summary of the papers.
	The RMS agrees with the applicant's assessment that there is uncertainty in the reliability of the Kd values reported in Surdyk, 2008, so cannot be used to derive endpoints. However, the paper presents a relatively large data set over a comprehensive range of pHs (3.87 to 7.78) and OM contents (3.68 to 82.9 g/kg) allowing general trends to be observed. From the reported data, Koc values have been calculated to range from 12 L/kg to 169 L/Kg by the RMS. Some correlation in Kd with OC is evident for mecoprop-P as shown in Figure B. 8.4. A plot of Koc vs pH shows a general decrease in sorption with increasing pH (Figure B. 8.5).
	Figure B. 8.4. Kd vs %OC for mecoprop-P
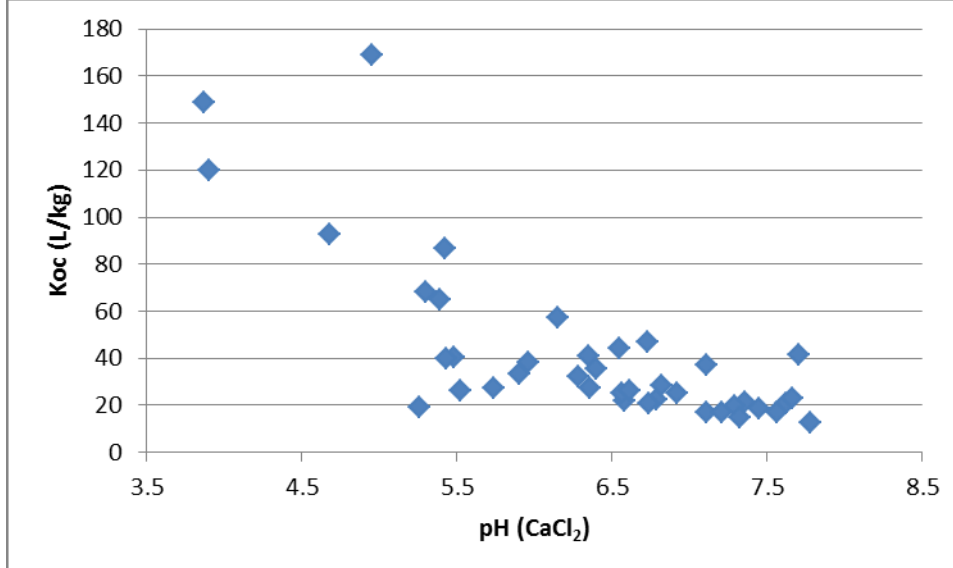
Figure B. 8.5. Koc vs pH for mecoprop-P

Executive summary

The paper by Nolan *et al*., 2007 describes an empirical model to determine the sorption coefficient K_D of a weak-acid pesticide in function of the soil properties (among 32 properties) and the pesticide properties (among 447 properties) based on a data set of 266 values of K_D obtained on 7 pesticides, including mecoprop-P.

The sorption data consisted in 266 couples of K_D values measured for 7 pesticides at two different concentrations (0.05 mmol/l and 0.005 mmol/l) and 41 soils, after eliminating invalid data. The best subsets regression was applied to this data using organic matter, pH and 447 pesticide properties (including 5 readily available properties from the FOOTPRINT Pesticides Properties Database: molecular mass, water solubility, dissociation constant, bulk density and octanol-water partition coefficient).

Prior to best subsets regression spearman correlations were used as a screen to identify variables reasonably correlated with K_D. Performance of the resulting models was assessed through the coefficient of determination, root square error, plots of measured versus predicted K_D, probability plots of model residuals and the significance of independent variables. Subsets of 3-7 parameters were tested. Log transforms of independent variables were considered on a case-by-case basis. Since small differences, were observed for K_{D1} and K_{D2} (two concentrations), a mean value of K_D was used.

Simple models developed by integrating both organic matter and pH explained up to roughly 90% of the variation in K_D for individual pesticides. Considering a 3-parameters model, the three best parameters to predict K_D were the organic matter content, the soil pH and a molecular property called "Moran lag 7 autocorrelation coefficient". The model predicts log K_D against the measured log K_D with $R^2 = 0.812$ and the root mean square error (RMSE) = 0.561. Considering a 7-parameter model using the 2 dominant soil properties (pH and OM) and the 5 readily available pesticides properties from the FOOTPRINT (molecular mass, water solubility, dissociation constant, bulk density and octanol-water coefficient), log K_D is estimated with $R^2 = 0.825$ and RMSE = 0.541. The 7-parameter model is considered to be more useful as it takes into account additional substance specific parameters.

I.   MATERIALS AND METHODS

A.   MATERIALS

1. Test materials: Mecoprop-P and 6 other weak acid pesticides: dichlorprop, 2,4-D, 2,4,5-T, dicamba, MCPA and metsulfuron-methyl.

Purity: >95 %[1]
CAS #: 16484-77-8 (Mecoprop-P)

2. Soils: 41 European soil types (FR + UK) characterized by 32 physical and chemical properties including sand, silt and clay content, pH, cation exchange content, and CaCO$_3$, P, Ca, Mg, K, Na, Mn, Al, Si, Fe concentrations

B. STUDY DESIGN

1. Experimental conditions

The paper refers to a non-peer-reviewed report for the description of experimental conditions: Surdyk, N., Dubus, I.G., Crouzet, C., Gautier, A., Flehoc, C., 2006a. *Estimation de la mobilité dans les sols de molécules ioniques à caractère acide faible : application à ml'évaluation des risques environnementaux dans le cadre de l'homologation de produits phytosanitaires*. Rapport d'avancement du projet BRGM PDR04EAU19. BRGM, Orléans. The following information was retrieved and translated from the definitive version of the original report (Surdyk *et al.,* 2008).

The soils were dried in open air and sieved to retain only particles < 2 mm. The marked parent solution of mecoprop-P was prepared in an adequate solvent (either acetonitrile, methanol, water or MilliQ, the specific one used for mecoprop-P was not reported). The radiochemical purity of the pesticide was verified by comparing the concentration read by a liquid scintillation counter and those obtained by HPLC/UV. Where purity rates below 90 % were reported, the solutions were purified by HPLC (up to 7 runs) to obtain purity >95%. Specific activity of the parent solutions were comprised between 1.4E10 to 1.22E11 dpm mol^{-1}. To the exception of Bignan soil and three soils from La jaillère, 5 g of sieved soil were put into contact with 10 mL of a pesticide solution, for 24 h at 20°C in the dark (liquid/solid fraction = 1/2). The soils from Bignan and the three remaining soils from La Jaillère were treated identically but with a sample of only 2.5 g due to limited availability. Containers were Corex tubes of 15 mL. All pesticide solutions were prepared in a CaCl$_2$ matrix 10^{-2}M to approximate at best the soil solution conditions. Soils without pesticides were also included with unmarked solutions in order to take account of the natural soil radioactivity. The initial concentrations of the pesticides were 0.005 and 0.05 mmol/L. A warm/cold mix (2000 dpm/ML warm and the rest cold) was used. Samples were agitated for 24 h.

2. Description of analytical procedures

The agitated samples were centrifuged and a sample of the supernatant liquid as taken for radioactivity analysis with a liquid scintillation counter (Tricarb 2300 TR). The pH of the supernatant was measured (Mettler SevenMulti with Mettler INLAB422 electrode). Adsorbed concentrations were determined by difference between initial concentrations and supernatant concentrations. Kd was reported as the ratio of Solid Concentration / Liquid Concentration. All experiments were performed in duplicate.

II. RESULTS AND DISCUSSION

Individual results of sorption experiments were not reported for mecoprop-P in the paper, and the following information was retrieved from the definitive version of the original report (Surdyk *et al.,* 2008). There is contradictory information about which initial concentration corresponds to these results.

Table B. 8.64. Sorption coefficients of mecoprop-P on 41 European soils (from Appendix 2 and 5 of Surdyk *et al.,* 2008), initial concentration is either 0.005 mol L^{-1} (reported in the table in Appendix 5 of Surdyk *et al.,* 2008) or 0.05 mol L^{-1} (reported in the text)

Soil	Organic matter (g kg^{-1})	pH (CaCl$_2$)	Kd (L kg^{-1})
Boigneville (FR) - 1	15.4	6.79	0.2
Boigneville (FR) - 2	8.41	6.35	0.2

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[1] From the definitive version of the original report, published in 2008 : Surdyk, N., Dubus, I.G., Crouzet, C., Gautier, A., Flehoc, C., 2008. *Estimation de la mobilité dans les sols de molécules ioniques à caractère acide faible : application à ml'évaluation des risques environnementaux dans le cadre de l'homologation de produits phytosanitaires*. Rapport d'avancement du projet BRGM RP-56702-FR. BRGM, Orléans, publicly available at http://infoterre.brgm.fr/rapports/RP-56702-FR.pdf

Soil	Organic matter (g kg^{-1})	pH (CaCl$_2$)	Kd (L kg^{-1})
Boigneville (FR) - 3	6.02	6.82	0.1
Boigneville (FR) - 4	31.2	6.58	0.4
Boigneville (FR) - 5	8.36	6.74	0.1
Boigneville (FR) - 6	6.82	6.92	0.1
La Jaillère (FR) - 1	21.4	5.48	0.5
La Jaillère (FR) - 2	7.85	6.55	0.2
La Jaillère (FR) - 3	4.64	7.11	0.1
La Jaillère (FR) - 4	3.68	6.73	0.1
La Jaillère (FR) - 5	26.10	5.43	0.6
La Jaillère (FR) - 6	19.60	5.52	0.3
La Jaillère (FR) - 7	6.02	6.15	0.2
La Jaillère (FR) - 8	3.98	5.42	0.2
Roujan (FR) - 1	16.70	7.62	0.2
Roujan (FR) - 2	8.37	7.70	0.2
Roujan (FR) - 3	13.90	7.78	0.1
Kerlavic (FR) -	49.00	4.95	4.8
Kerguehennec (FR)	35.30	5.30	1.4
Rennes (FR)	19.00	6.36	0.3
Lorraine (FR)	18.10	5.96	0.4
La Jaillère (FR) - 9	53.60	5.26	0.6
Bignan (FR) - 1	82.90	5.88	-
Bignan (FR) - 2	50.50	5.74	0.8
Banyuls (FR) -	14.40	3.90	1.0
Vias (FR)	6.96	3.87	0.6
Feucherolles (FR)	16.10	6.28	0.3
England	30.70	7.56	0.3
England	56.00	7.36	0.7
England	18.60	7.45	0.2
England	34.70	7.29	0.4
England	41.20	6.56	0.6
England	13.20	6.61	0.2
England	29.00	6.40	0.6
England	55.80	5.39	2.1
England	26.00	4.68	1.4
Bréville (FR) - 1	35.20	7.32	0.3
Bréville (FR) - 2	15.10	7.66	0.2
Bréville (FR) - 3	15.50	5.90	0.3
Bréville (FR) - 4	30.50	7.11	0.3
Bréville (FR) - 5	10.20	7.21	0.1

The results of the modelling by the current paper (Nolan *et al,* 2007) indicate that pH and organic matter content, combined with pesticides properties are good predictors of the sorption coefficient K_D of weak acid pesticides, such as mecoprop-P.

III.   CONCLUSIONS

The authors conclude that a large number of potential explanatory variables were screened with uni-variate and multi-variate statistical analyses, to identify reliable predictors of adsorption in the case of ionisable pesticides. Explanatory variables consisted of 32 soils properties and 447 pesticide properties. Simple models integrating both organic matter and pH explained up to about 90% of the variation in log transformed, average K_D for individual pesticides. Subsequent models consisting of both soil and pesticide properties confirmed that organic matter and pH are dominant soil characteristics. Parsimonious models consisting of 3 variables and a full model consisting of 7 variables were developed using hest subsets regression. The two best models performed comparably and explained over 80% of the variability in Koc. However, the full model (adjusted R^2=0.825, root mean square error = 0.541) is considered more useful because, in addition to organic matter and pH, it is based on pesticide properties that are readily available in on-line databases (molecular mass, solubility in water, dissociation constant, bulk density, and octanol-water partition coefficient). Following verification, they believe that the model would be broadly applicable for the purpose of generating K_D values to parameterize fate models for ionisable compounds.

The applicant considers that from a regulatory point of view, the results of the study are not suitable to derive sorption endpoints for mecoprop-P, unless a non-peer-reviewed project report (Surdyk *et al.,* 2008) is considered and included. In that case, K_D values range from 0.1 to 4.8 L kg^{-1}. The method used (batch equilibrium method) to derive sorption coefficients did not provide information about transformation of parent compound, and adsorption/desorption were not differentiated. Koc values were not derived from K_D values.

The model presented in the current paper (Nolan *et al.*, 2007) was built with multiple pesticide data and not specific to mecoprop-P.

Assessment of methodological quality

	Relevance	Reliability	Transparency & repeatability
Material	Data obtained with mecoprop-P are relevant but presented only in the original research report[3].	Pure or purified mecoprop-P (> 95 %) was used.	Soil properties and origins were extensively and accurately documented in the original research report[3].
Method	Not fully peer-reviewed[2]. The method used to estimate the sorption coefficients does not provide all data such as sorption / desorption curves. The model developed is relevant when considering soil properties, but the scope of the study is too large and the relevant data is not highlighted.	Modelling: there is some risk of data over-fitting[4]. May not be peer-reviewed[2].	Except for the solvent used and minor details, sorption experiments were accurately described in the original research report[3]. Modelling: not enough details are given to ascertain the reliability of the statistical methodology with such a high number of parameters.

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[2] The paper is from the "XIII Symposium Pesticide Chemistry". The peer-review process is not well described (at the website of the Symposium[2]). Some level of control and filtering was probably applied to accept the paper at the Symposium and a scientific committee evaluate the papers and decides which one are to be orally presented, but without more details it cannot be considered as fully peer-reviewed.

	Relevance	Reliability	Transparency & repeatability
Results & interpretation	Relevant results presented only in the original research report[3].	The provided Kd values are not sufficient to provide Koc values without further data interpretation. Only one set of results is reported in the original research report, while two initial concentrations are cited. Modelling: Additional validation and tests are missing to obtain a reliable model[4]. Negative values of K_D were discarded without assessing if they were possibly equal to 0.	Appears correct.

Report:	**CA 7/05, Piwowarczyk, A. _et al._ (2013)** Chemosphere, 90, 535-541
Title	Phenoxyalkanoic acid herbicide sorption and the effect of co-application in a Haplic Cambisol with contrasting management
Guidelines:	OECD TG 106, standard batch equilibrium
GLP:	Not specified, but assumed not GLP
Deviations	None

Previous evaluations	None: Submitted for the purpose of renewal under Regulation 844/2012. This paper was identified by the applicant as potentially relevant during the literature review. The paper summary and relevance/reliability assessment provided by the applicant have been reproduced below. The RMS agrees with the applicant's assessement. The study follows the OECD guideline; however the study is not reported in sufficient detail to be relied upon for endpoints (i.e. mass balances not reported, only average values reported). The Kf and 1/n values reported for mecoprop-P on the two soils tested are in line with those from the other studies and demonstrate high mobility with almost linear sorption at pH(CaCl$_2$) 5.1 and 5.7.

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[3] (Surdyk, N., Dubus, I.G., Crouzet, C., Gautier, A., Flehoc, C., 2006a. Estimation de la mobilité dans les sols de molécules ioniques à caractère acide faible : application à l'évaluation des risques environnementaux dans le cadre de l'homologation de produits phytosanitaires. Rapport d'avancement du projet BRGM PDR04EAU19. BRGM, Orléans). A definitive version of the report is publicly available: Surdyk, N., Dubus, I.G., Crouzet, C., Gautier, A., Flehoc, C., 2008. Estimation de la mobilité dans les sols de molécules ioniques à caractère acide faible : application à ml'évaluation des risques environnementaux dans le cadre de l'homologation de produits phytosanitaires. Rapport d'avancement du projet BRGM RP-56702-FR. BRGM, Orléans, publicly available at http://infoterre.brgm.fr/rapports/RP-56702-FR.pdf.

The methodology selected subsets of parameters (3-7 parameters) that achieved satisfactory performance (i.e. parameters which can be used to predict/estimate Kd) with readily available pesticide properties, among 447 pesticides properties. By doing this, it is possible that some subsets would give "satisfactory" performance by accident, and over-fitting of the data (i.e. the data used to fit the model) to the parameters cannot be excluded. With the original number of data (n = 266), it is not reliable to test more than 50-100 parameters to fit a model. Even if the individual models contain only 3-7 parameters, over-fitting can occur if too many sets of parameters are tested. In other words, by selecting the "Moran lag 7 autocorrelation coefficient" among a total number of 477 parameters with n = 266, it is possible that the predictive value of the "Moran lag 7 autocorrelation coefficient" was overestimated.

This potential over-fitting problem does not affect the relevant data which are the sorption properties of Mecoprop-P in relationship with soil properties such as the dependency to organic matter content and pH. Unfortunately, the statistical interpretation presented in the paper does not allow to interpret the relevant results adequately and to derive endpoints for the risk assessment of Mecoprop-P. The original sorption data (K_D) for Mecoprop-P should only be interpreted in relationship to concentration and soil properties.

Executive summary

The adsorption and desorption behaviour of mecoprop-P (and MCPA, but not discussed in this summary except for the mix of both substances) in a Haplic Cambisol with tillage and grassland management was examined using the batch equilibrium method OECD TG 106. Mecoprop-P was stable over the experimental period. Adsorption and desorption kinetics were tested with an initial concentration of 40 mg L^{-1}. The sorption equilibrium was reached within 24 h for adsorption and desorption. The experimental sorption data for mecoprop-P fitted the linear adsorption isotherm well (R² > 0.99). The Freundlich exponent values of the adsorption isotherm ranged from 0.96 to 0.99. The tested concentrations for Kd and Koc estimation were 1, 10, 20, 40 and 100 mg L^{-1}. The adsorption of mecoprop-P was low (Kd = 1.09 ± 0.14 and 1.71 ± 0.20 L kg^{-1} under tillage and grassland, respectively). Corresponding values of Koc were 30.45 and 43.57 L kg^{-1}, but Koc may not always be a good predictor of sorption and transport for mecoprop-P. Low adsorption may be related to their dissociation (deprotonation). Additionally, the effect on adsorption of the simultaneous presence of the two herbicides was also studied. The mecoprop-P adsorption coefficient and exponent (1/n ≈ 1) remained unaffected by the presence of MCPA. (Kd = 0.91± 0.09 and 1.60 ± 0.20 L kg^{-1} under tillage and grassland, respectively, Koc = 25.42 and 40.76 L kg^{-1}).

I.   MATERIALS AND METHODS

A. MATERIALS

1. Test materials: Mecoprop-P and MCPA
              Purity: Analytical grade; 99.0 % (Mecoprop- P), 99.5 % (MCPA)
              CAS #:   16484-77-8 (Mecoprop-P), 94-74-6 (MCPA)
              Stability of test compound: Stable over the experimental period

2. Soils: The study was conducted with a Haplic Cambisol (Oakpark series) with representative sites under tillage (N 52°51', W 006°55', devoted mainly to wheat production) and permanent grassland (N 53°51', W 007°54') management. Five sub-samples per site were removed at random locations from the surface layer of 0-15 cm depth with a Dutch auger. Each subsample was air dried, crushed and sieved to 2-mm and then bulked to create a composite sample. The composite samples were stored in the dark at 20 ± 2°C under low humidity. The soil was analysed for properties thought to be related to adsorptive capacity. Particle size distribution was determined by the pipette method (Gee and Or, 2002[5]), organic carbon content by dry combustion using a Skalar Primacs^{SLC} TOC analyser (Skalar Analytical, Breda, The Netherlands), cation exchange capacity by the method of Metson (1956[6]), pH using slurries of 5 g of soil in 10 mL 0.01 M CaCl$_2$ and gravimetric water content by oven drying for 24 h at 105°C. These properties are provided in Table B. 8.65.

Table B. 8.65.   Soil physiochemical properties

Soil	pH (0.01 M CaCl$_2$)	% OC	CEC (cmol kg^{-1})	% sand	% silt	% clay	Texture
OT (tillage)	5.7	3.6	15.6	68	27	5	Sandy loam
OG (grassland)	5.1	3.9	17.0	68	19	13	Sandy loam

B.   STUDY DESIGN

1. Experimental conditions

The experiment was conducted by the standard batch equilibrium method (OECD TG 106) using 25 mL glass centrifuge tubes with Teflon-lined screw caps. Duplicate soil samples (5 g) were pre-equilibrated overnight in 0.01 M CaCl$_2$ solution on an overhead shaker at 20 ± 2 °C. Working dilutions were prepared in 0.01 M CaCl$_2$

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[5] Gee, G.W., Or, D., 2002. Particle-size analysis. In: Dick, W.A. (Ed.) . Methods of soil Analysis, Part 4. Physical methods. Soil Science Society of America, Inc., Madison, WI, pp. 201-228.
[6] Metson, A.J., 1956. Methods of Chemical Analysis for Soil Survey Samples. DSIR, Soil Bureau Bulletin No. 12, New Zealand, pp. 193-204.

(10 mL) by spiking with herbicide stock solutions in methanol to a final concentration of 1.01, 10.09, 20.22, 40.90 and 100.89 mg L^{-1} MCPA and 1.01, 10.07, 20.12, 40.29 and 100.71 mg L^{-1} mecoprop-P.

The kinetic study was run at a single herbicide concentration of 40.29 mg L^{-1} mecoprop-P. At 2, 4, 6, 8, 12 and 24 h tubes were removed from the shaker and centrifuged at 4500 rpm for 30 min. The supernatants were recovered and extracted. The adsorption isotherm study was similar to the kinetic study except that the experimental samples were spiked with five mecoprop-P concentrations in the single compound study; or with a mix of mecoprop-P and MCPA (the mix study), and analysed at the previously established equilibrium time in the kinetic experiment. Tubes with herbicide CaCl$_2$ (0.01 M) solution, but without soil, served as control samples. Blank samples (soil, 0.01 M CaCl$_2$ and methanol) were handled identically to the experimental samples and the results showed no MCPA or mecoprop-P presence in the soils or interfering peaks. The adsorption experiment was repeated twice.

Desorption isotherms were determined immediately from all equilibrium points of the adsorption isotherm for individual compounds as a single step desorption process in duplicates. The time needed to reach desorption equilibrium was determined beforehand in a desorption kinetic experiment, in which the samples were analysed at 2, 4, 6, 8, 12 and 24 h. At adsorption equilibrium the supernatants were removed as much as possible, replaced by the same amount of herbicide free aqueous 0.01 M CaCl$_2$, agitated to disperse the sediment pellets, shaken until an approximate desorption equilibrium time and centrifuged as before. All supernatants were extracted immediately and analysed.

2. Description of analytical procedures

Mecoprop-P and the mix of mecoprop-P + MCPA were extracted from supernatants manually using a vacuum manifold and reversed phase Strata X 60 mg cartridges (Phenomenex, UK). The supernatants were acidified with HCl to pH 2 prior to extractions. Isocratic solution (2 mL) of methanol and 0.025 M H$_3$PO$_4$ was applied for conditioning, followed by the same volume of Milli-Q water (pH ~ 2) at a flow rate of 6 mL min^{-1}. Samples were loaded at a flow rate of 2 mL min^{-1} and washed at the same rate with Milli-Q water (2 mL, pH ~ 2). The cartridges were dried under vacuum for about 10 min after which, the herbicide residues were pre-concentrated by elution with 4 mL methanol (adsorption) or 2 mL methanol (desorption) at a flow rate of 1 mL min^{-1}. The elutions were homogenised using vortex and samples (2 x 1 mL) were injected to HPLC-DAD (Agilent Technologies). An aqueous 0.025 M H$_3$PO$_4$ and acetonitrile (ratio = 55:45) were used as the mobile phases. The aqueous H$_3$PO$_4$ mobile phase was filtrated beforehand under vacuum using HNWP 0.45 μm filter (Millipore, USA). The analyses were performed on a Synergi 4 tm Hydro-RP, 150 x 4.6 mm (Phenomenex, UK) at 22 °C and a flow rate of 1.5 mL min^{-1}. The herbicides were analysed at the wavelength of maximum adsorption (230 nm). The lowest limit of detection achieved was 100 μgL^{-1}. The standard range used to build the calibrations curves was 500 μgL^{-1} to 300 mgL^{-1}. The study states that several standard samples in 0.01 M CaCl$_2$ of the same herbicide concentration range used to study adsorption-desorption isotherms were also extracted along the experimental samples and injected to the HPLC-DAD to evaluate whether the extraction recovery was acceptable, although the results of this are not reported. The HPLC-DAD performance was examined by injecting the MCPA and mecoprop-P standards in methanol at different concentrations.

II.   RESULTS AND DISCUSSION
A. MASS BALANCE

Mass balances are not reported. Results of the control samples in the adsorption kinetics experiment indicate that approximately 95% of the initial concentration was recovered after 24hrs. The study author attributes the <100% recovery to losses during sample extraction.

B.   FINDINGS

1.   Kinetic experiment

Preliminary adsorption and desorption kinetic experiments showed both adsorption and desorption to be rapid and equilibrium reached within 24 hours.

2.   Adsorption - desorption experiments

Adsorbed amount onto soil was plotted against the solution concentration. Adsorption isotherms were obtained by plotting the amount of MCPA and mecoprop-P adsorbed per unit weight of the soil (oven dry basis) (C_s, mg kg^{-1}) against the amount of herbicides in the remaining solution at equilibrium (C_e, mg L^{-1}). This can be described by the linear isotherm:

$$C_s = K_d C_e \qquad\qquad (1)$$

Adsorption distribution coefficients (K_d, L kg^{-1}) were calculated from the Eq. (1) for all five concentrations used in the study. The average K_d value for adsorption was normalised to the organic carbon content (%OC) by calculating K_{oc} (L kg^{-1}),

$$K_{oc} = (K_d/\%OC) \times 100 \qquad\qquad (2)$$

Adsorption–desorption data were also fitted to the linearised form of the Freundlich isotherm:

$$\log C_s = \log K_f + 1/n \ \log C_e \qquad\qquad (3)$$

where K_f and $1/n$ are the empirical Freundlich constants representing intercept and slope of the isotherm respectively.

Table B. 8.66. displays the resulting Kd, Kf, Koc and 1/n values.

Table B. 8.66.   Mecoprop-P adsorption-desorption parameters for the linear and the Freundlich isotherms in Oakpark tillage (OT) and Oakpark grassland (OG) soil.

Type	Soil	Linear isotherm		R²	Freundlich isotherm		R²
		Kd (L kg^{-1})	Koc (L kg^{-1})		Kf (mg 1-1/n kg^{-1}) (L)$^{1/n}$	1/n	
Mecoprop-P alone Adsorption	OT	1.09 ± 0.14	30.45	0.992	1.08 ± 0.14	0.99 ± 0.03	0.998
	OG	1.71 ± 0.20	43.57	1.000	1.87 ± 0.13	0.96 ± 0.02	0.999
Mecoprop-P alone Desorption	OT	3.58 ± 0.65	nc	0.999	3.50 ± 0.47	1.01 ± 0.12	0.999
	OG	4.98 ± 0.67	nc	0.999	4.87 ± 0.34	1.03 ± 0.08	1.000
Mecoprop-P in presence of MCPA Adsorption	OT	0.91 ± 0.09	25.42	0.999	0.97 ± 0.13	0.98 ± 0.04	1.000
	OG	1.60 ± 0.21	40.76	0.999	1.72 ± 0.24	0.97 ± 0.03	0.999

The graphical adsorption isotherm for mecoprop-P indicated that adsorption tended towards linear (0.96 to 0.99). This suggests a constant partitioning of mecoprop-P between adsorption sites and the solution and that the adsorption was not affected by concentration. The experimental adsorption data fitted both the Freundlich and the linear models very well ($R^2 > 0.99$).

Desorption data fitted the Freundlich and the linear model well ($R^2 > 0.99$). The Kf desorption values were greater than the corresponding Kf adsorption values, indicating that the adsorption of the two phenoxyalkanoic acid herbicides could not be fully reversed during one washing cycle. Mecoprop-P adsorption remained unaltered by the presence of MCPA.

III.   CONCLUSION

The study authors conclude that adsorption of mecoprop-P in the Haplic Cambisol seems to be governed by soil organic content and pH, as greater sorption and lower desorption were observed in samples with lower pH (OG - grassland managed soil). They also emphasize the fact that Koc may not be a good predictor of sorption and transport as cited by Buss *et al.* (2006) and that site-specific Kd values should be obtained instead.

Assessment of methodological quality

	Relevance	Reliability	Transparency & repeatability
Material	Irish soil used relevant for EU.	Reliable as cited.	No issue.
Method	Appropriate OECD guideline.	OECD guideline, but not cited as GLP-compliant.	Correctly described and repeatable as much as it is possible with sampled soil studies.
Results & interpretation	Results provide data within the same range as GLP studies already available on mecoprop-P.	Reliable, assuming that results were accurately reported.	Transparent only if the storage and handling of data were compatible with GLP practices.

Summary of adsorption

Table B. 8.67 summarises the sorption data from Matla & Vonk (1993), Obrist (1986) and Simmonds (2010). mecoprop-P has low adsorption to soil with Kf observed from 0.199 ml/g to 4.5 ml/g in 11 soils. Only a weak correlation between Kf and OC is evident (Figure B. 8.6) which is similar to that observed with the data from Surdyk (2008) (Figure B. 8.4).

Table B. 8.67. Summary of adsorption studies on mecoprop-P

Soil	pH (KCl)	pH (CaCl$_2$)	pH (H$_2$O)	OC %	Kf (ml/g)	Kfoc (ml/g)	1/n	R^2	Reference
Zeist	4.3	-	5.2*	3.2	4.5	139	0.66	0.99	Matla & Vonk, 1993
De Krakeling	4.4	-	5.3*	2.1	3.5	167	0.69	0.99	Matla & Vonk, 1993
Maarn	4.3	-	5.2*	2.4	3.3	135	0.75	0.99	Matla & Vonk, 1993
Plainfield	-	-	5.6**	0.5	0.199	42.9	1.093	0.950	Obrist, 1986
Fox	-	-	7.6**	1.3	0.298	22.3	0.942	0.996	Obrist, 1986
Hagerstown	-	-	6.6**	1.5	0.428	29.5	1.012	0.997	Obrist, 1986
Plano	-	-	6.8**	3.4	0.687	20.1	0.961	0.999	Obrist, 1986
Calke	5.4	5.6	5.8	3.1	0.56	18	0.852	0.99	Simmonds, 2010
South Witham	6.9	7.2	7.3	3.7	0.46	12	0.892	1.00	Simmonds, 2010
Lockington	5.1	5.6	5.7	3.1	0.64	21	0.853	1.00	Simmonds, 2010
Hagen	5.3	5.5	5.7	2.9	0.98	34	0.926	1.00	Simmonds, 2010
				Mean (pH <5.5), (n = 3)		146[†]	0.70[#]		
				Mean (pH >5.5), (n = 7)		21[†]	0.92[#]	Plainfield soil excluded	

%OC = %OM/1.724
* Calculated from pH(H$_2$O) = 0.820pH(KCl) + 1.69
** Solution not reported in study, assumed to be H$_2$O
#Arithmetic mean
†Geometric mean, according to EFSA Journal 2014:12(5): 3662
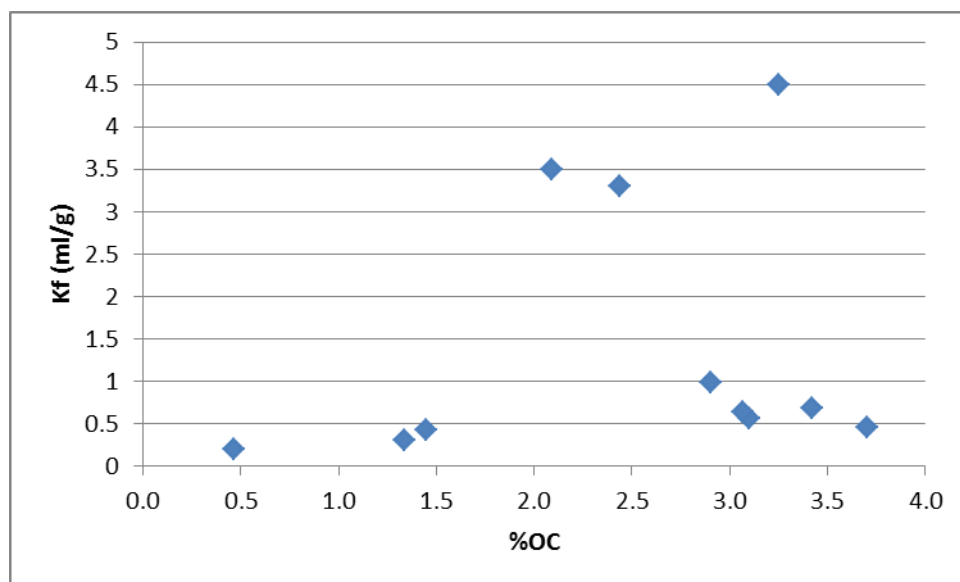
Figure B. 8.6. Variation in Kf with %OC

The solution used to measure soil pHs in Obrist (1986) is not reported, so has been assumed to be H$_2$O by the RMS. For comparison purposes, pH(H$_2$O) values have been calculated from the pH(KCl) reported in Matla & Vonk (1993) as outlined in FOCUS Groundwater guidance (2014). Plots of Kfoc and 1/n versus pH(H$_2$O) are shown below (Figure B. 8.7 and Figure B. 8.8) in which variation in both Kfoc and 1/n with pH is evident. The applicant proposes that the Kfoc data are clustered above and below approximately pH 5.5, with sorption

increased at lower pH. The RMS notes that the variation in Kd with pH observed with the data from Surdyk (2008) supports this observation (Figure B. 8.5). The applicant proposes using a mean 1/n value for all soils; however, the 1/n values show a similar pH variation to Kfoc, with markedly lower 1/n values at pHs below 5.5. The data for the Plainfield soil has been excluded as an outlier from the calculated means by the RMS due to the poor correlation coefficient (R^2 0.95) reported in Obrist (1986). This is particularly evident for the 1/n value as shown in Figure B. 8.8.

Figure B. 8.7. Variation in Kfoc with pH. Value for Plainfield soil circled in red

Figure B. 8.8. Variation in 1/n with pH. Value for Plainfield soil circled in red

Adsorption and desorption of metabolites, breakdown and reaction products (CA 7.1.3.1.2)
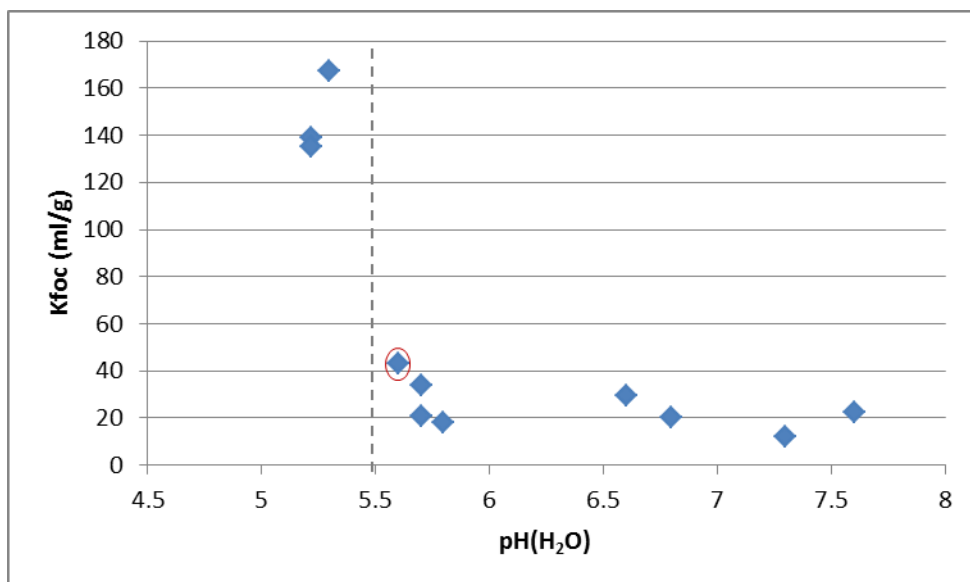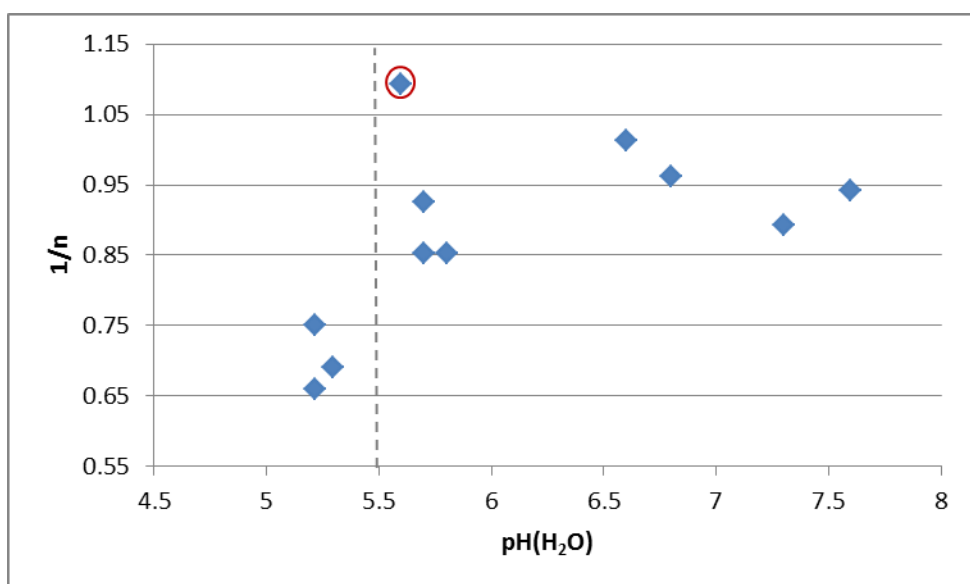
No data required – no metabolites to consider.

Aged sorption (CA 7.1.3.2)

No data required

B.8.1.3. **Mobility in soil**

Column leaching of the active substance (CA 7.1.4.1.1)

RMS Comments:	For the purpose of renewal, column leaching studies are not required as reliable batch equilibrium adsorption studies on are available. No new data have been submitted. For the original approval of mecoprop-P, two soil thin layer chromatography studies and a column leaching study of aged residues on racemic mecoprop were assessed (DAR for original approval (1998), Obrist 1986b, c and Zohner 1990). As these studies were on racemic mecoprop rather than mecoprop-P and are not required for renewal purposes, they are not relied on for the risk assessment.

Column leaching of metabolites, breakdown and reaction products (CA 7.1.4.1.2)

No data required

Lysimeter studies (CA 7.1.4.2)

RMS Comments:	In DAR for original approval (1998) a lysimeter study on mecoprop-P was assessed and considered acceptable (Herrchen, 1991). This study provides supporting information for renewal purposes. A lysimeter study on racemic mecoprop (Kubiak, 1991) and data from two further lysimeter studies on racemic mecoprop obtained from the literature were also considered (Helweg, 1992 and Odgaard, 1993). These studies are not relied on as they consider racemic mecoprop rather than mecoprop-P. No new studies have been submitted however two papers were identified as potentially relevant by the applicant from the literature search.

Report:	Hercchen 1991
Title	Outdoor lysimeter study on mecoprop-P
Guidelines:	BBA guideline IV 4-3
GLP:	Yes
Deviations	None reported

Previous evaluations:	In DAR for original approval (1998) The original evaluation has been reproduced below.

Methods

The fate of ^{14}C-mecoprop-P (ring label, >97% pure) in two outdoor lysimeters consisting of undisturbed sandy loam soil monoliths and its uptake by plants was investigated over two years. The lysimeter study was performed at Fraunhofer Institute at Schmallenberg, North-Rhine Westphalia, Germany according to BBA guideline IV 4-3.

The lysimeters contained a sandy soil (see the table below) and were of 1 m^2 surface and 1.2 m depth. The soil surface were applied with 120 mg a.i./m^2 (equivalent to 1.2 kg ai/ha) formulated as SL type (Duplosan KV product type) at May 18, 1989.

The culture summer wheat, winter wheat and winter rape were seeded as first (10/4-1989, 30 g/m^2), second (28/9-1989, 20 g/m^2) and third (18/9-1990, 2 g/m^2) rotational crop.

Climate: The air temperature averaged 8.9^{o}C in 1989 and 8.5^{o}C in 1990. Temperatures, precipitation and amount leachate are given in the table next page.

Table B. 8.68. *Soil characteristics*

Soil depth (cm)	pH	Sand %	Silt %	Clay %	OC %	FMC %	CEC
0 - 30	5.7	68.3	24.5	7.2	1.5	20-30	9.2
30 - 57	4.9	67.0	26.3	6.7	1.0	18-31	6.3
57 - 73	4.9	96.2	2.9	0.9	0.2	13-30	ND
73 - 90	5.0	99.8	0.2	0.0	0.0	10-25	ND
90 - 110	4.8	100.0	0.0	0.0	0.0	10-28	ND

Results

MCPP-P was not detected in the leachate. The potential degradation product 4-chloro-2-methylphenol was not detected.

The radioactivity is expressed as a.i. equivalents. The detection limit = 0.03 µg/l. When MCPP-P was not detected the calculations were based on the maximum concentration 0.03 µg/l (DL).

Amount and concentrations of the unidentified radioactive material in the leachate are given in the tables below (as "Rad") expressed as MCPP-P equivalents. The respective values are calculated by subtraction of the amount of a.i. plus the metabolite from the total radioactivity. No significant amount of $^{14}CO_2$ could be detected at the beginning of the study (till 03/90), no other samples were investigated for $^{14}CO_2$. The author characterises the unidentified radioactivity as being "volatile and polar indicating the formation of short-chain carboxylic acids as final degradation products".

Table B. 8.69. *Lysimeter A (13). Amount and concentrations of radioactive material in the leachate expressed as MCPP-P equivalents.*

Period	Precipitation mm	Leachate (mm=l)	Rad µg/l	Rad µg	MCPP-P µg/l	MCPP-P µg
1st year	937.4	467.5	0.54	253.72	<0.03	<13.25
2nd year	797.9	417.8	0.20	81.53	<0.03	<12.54
Sum	1735.3	885.3	0.38	335.25	<0.03	<25.79

Table B. 8.70. *Lysimeter B (14). Amount and concentrations of radioactive material in the leachate expressed as MCPP-P equivalents.*

Period	Precipitation mm	Leachate (mm=l)	Rad µg/l	Rad µg	MCPP-P µg/l	MCPP-P µg
1st year	937.4	482.5	0.44	210.58	<0.03	<13.66
2nd year	797.9	404.4	0.18	70.83	<0.03	<12.14
Sum	1735.3	886.6	0.32	281.41	<0.03	<25.80

Table B. 8.71. *Climatic data, and recoveries in leachate*

Year Month	Mean air temp.	Soil temperature,°C, at soil depth			Precipita-tion	Amount of leachate (mm = l)	
	°C	10 cm	30 cm	60 cm	mm = l	Lys A	Lys B
1989							
May	13.4	11.4	10.4	11.4	0.3	0.0	0.0
June	14.5	13.3	12.9	13.2	28.0	0.0	0.0
July	16.8	15.4	14.9	15.2	93.7	0.0	0.0
August	15.9	15.5	14.5	15.3	93.2	0.0	0.0
September	13.3	13.5	13.8	13.3	102.4	0.0	0.0
October	9.8	8.8	9.1	9.1	146.2	61.7	65.8
November	3.0	4.0	5.2	6.5	25.4	55.3	48.8
December	2.6	2.4	2.8	3.7	125.5	124.2	116.8
1990							
January	1.9	1.2	1.5	2.5	52.3	48.7	50.5
February	4.9	3.1	3.1	3.6	129.2	57.7	59.6
March	5.8	4.3	4.1	4.3	56.1	100.2	124.0
April	6.2	5.8	5.5	5.7	49.0	19.7	16.7
May	12.7	11.9	11.1	10.6	36.1	0.0	0.0
June	13.5	12.9	12.1	11.7	83.0	0.0	0.0
July	15.0	14.8	14.1	13.7	51.0	0.0	0.0
August	17.5	16.4	15.9	15.6	69.1	0.0	0.0
September	10.1	10.9	11.2	12.1	92.1	0.0	0.0
October	10.2	9.2	9.3	10.0	77.9	0.0	32.3
November	3.5	4.6	5.0	6.0	108.7	111.1	87.0
December	0.2	0.7	0.7	2.0	87.4	143.1	135.2
1991							
January	0.6	1.3	1.1	2.2	86.2	102.1	91.5
February	-2.8	-0.9	-1.0	0.2	24.0	0.0	0.0
March	6.2	3.6	2.4	3.1	47.4	61.5	33.8
April	5.9	5.6	4.7	5.3	34.7	0.0	0.0
May					36.4	0.0	24.6

The soil was segmented and analyzed after two year. The distribution of [14]C- radioactivity in the soil layers are given in the table below.

Table B. 8.72. *Distribution of ^{14}C- radioactivity in soil layers two years after application in % of initial total radioactive residues (or µg/kg soil). Below 40 cm depth, the result was based on NaOH extraction (Unid: unidentified radioactivity. NER: Non-extractable residues. Rad.: Radioactivity)*

Soil depth	Lys A				Lys B			
cm	MCPP-P	Unid.	NER	Total rad. %	MCPP-P	Unid. %	NER %	Total rad. %
0-10 % (µg/kg)	0.20 (1.76)	3.48	4.91	8.59	0.10 (0.88)	2.03	2.34	4.47
10-20 % (µg/kg)	0.09 (0.77)	1.65	1.76	3.50	0.04 (0.35)	0.55	0.44	1.03
20-30	<0.03	0.10	0.07	0.17	<0.03	0.07	0.08	0.16
30-40	<0.03	0.04	0.00	0.05	<0.03	0.08	0.03	0.11
40-50	NA	0.04		0.04	<0.03	0.05	0.04	0.10
50-60	NA	0.06		0.06	<0.03	0.09	0.09	0.19
60-70	NA	0.04		0.04	<0.03	0.07	0.08	0.16
70-80	NA	0.01		0.01	<0.03	0.03	0.08	0.12
80-90	NA	0.00		0.00	<0.03	0.00	0.09	0.10
90-100	NA	0.02		0.02	<0.03	0.00	0.10	0.10
100-110	NA	0.01		0.02	<0.03	0.00	0.14	0.14
110-120	NA	0.02		0.02	<0.03	0.00	0.21	0.21
Total	0.29	5.47	6.74	12.51	0.14	2.97	3.72	6.89

At termination of the study, the soil contained 7 to 13% of the applied radioactivity. Mecoprop-P was present at 0.1 to 0.3%, unidentified radioactivity at 3 to 5% and non-extractable residues (NER) at 4 to 7% of the initial dose. The radioactivity in plants was negligible and amounted to a total of 0.1% for all rotational crops.

1998 Evaluation Comments
Neither mecoprop-P nor the metabolite 4-chloro-2-methylphenol could be detected in any leachate sample in concentrations > 0.03 µg/l. Unidentified compounds were present at 0.4-0.5 and 0.1-0.2 µg/l (expressed as MCPP-P equivalents) 1. and 2. year after application, respectively.
It is interesting that 5-9% of the applied radioactivity was still present in the top soil layers after two years. The MCPP-P was applied in the spring where leaching may be expected to be low compared to the situation with fall application. The winter 1989-90 was mild (c.f. table on climatic conditions). The study was performed under aerobic conditions. Thus, the study may not represent realistic worst case conditions for a Nordic climate.

The BAS Task Forces points out that the study was carried out according to an existing, valid guideline (BBA-guideline) and represents realistic worst case conditions on spring application. The RMS opinion is that the lysimeter study can cover a wide range of regions but not necessarily the Nordic climate. Especially, it can not represent the situation concerning fall application, where leaching is expected to be higher because the soil temperature is low and the precipitation surplus often is high.

Article:	*CA 7/06, Idowu, I.A. et al.* **(2014)**
	Environmental Technology, 35, pp2055-2067
Title	Possible source term of high concentration of mecoprop-P in leachate and water quality: impact of climate change, public change, public and disposal
Guidelines:	None
GLP:	Not applicable
Deviations	Not applicable

Previous evaluations	None: Submitted for the purpose of renewal under Regulation 844/2012.
	This paper was identified by the applicant as potentially relevant during the literature review.
	The paper summary and relevance/reliability assessment provided by the applicant have been reproduced below. The RMS agrees with the applicants' assessment. The study provides a qualitative study on the potential sources of mecoprop-P in ground and surface water but does not provide new endpoints or change the risk assessment.

Executive summary

The paper aimed to identify the non-agricultural sources of mecoprop-P contamination of ground and surface water in England. A route map for mecoprop-P herbicide source term contamination was developed with emphasis on both consumer and producer responsibility towards use of mecoprop-P product. The impact of future climate changes on this contamination was estimated.

The available literature shows that mecoprop-P herbicide is often found in wells and water abstractions in many areas around Europe, including the UK. There is a growing environmental and public health concern about mecoprop-P pollution in ground and surface water in England. Reviews suggest that extensive work has been carried out on the contribution of mecoprop-P herbicides from agricultural use, whilst more work needs to be carried out on the contribution of mecoprop-P herbicide from non-agricultural use.

The study covers two landfill sites in Weaver/Gowy Catchment. Mecoprop-P herbicide concentrations in the leachate quality (from literature) range between 0.06 and 290 μg L^{-1} in cells. High concentration of mecoprop-P herbicide in the leachate quality suggests that there is a possible source term in the waste stream.

This paper addresses the gap by exploring possible source terms of mecoprop-P herbicide contamination on landfill sites and evaluates the impact of public purchase, use and disposal alongside climate change on seasonal variations in mecoprop-P concentrations. Mecoprop-P herbicide was found to exceed the EU drinking water quality standards at the unsaturated zone/aquifer with observed average concentrations (from literature) ranging between 0.005 and 7.96 μg L^{-1}.

A route map for mecoprop-P herbicide source term contamination is essential for mitigation and pollution management with emphasis on both consumer and producer responsibility towards use of mecoprop-P product. In addition, improvement in data collection on mecoprop-P concentrations and detailed seasonal herbicide sales for non-agricultural purposes are needed to inform the analysis and decision process.

Impacts of climate change on water contamination by mecoprop-P have been assessed based on the UK Climate Impacts Programme (UKCIP) and their most recent scenarios (UKCP09), and a summary of impacts of climate changes on factors affecting source term and herbicide pathways. Three impacts were identified that would increase the pesticide concentration in surface water with moderate confidence level, while the effect of climate change on groundwater could not be reliably predicted.

I.   MATERIALS AND METHODS

A.   MATERIALS

1. Main information sources

No experiment was conducted in the frame of this article. However, a scientific literature review of mecoprop-P leaching and drainage was undertaken. The following sources of information were consulted:

- Literature data, on mecoprop-P (CAS #:16484-77-8) water contamination on landfills sites in the location or in similar geological locations, resulting in a semi-hypothetical case landfill site;

- Leachate quality and groundwater quality (2009-2011) and hydrological assessments data for 2009 from the Environment Agency Office for three landfill sites in the Weaver-Gowy Catchment (Cheshire);

- Flow rate data for the River Gowy (Huxley and bridge Trafford stations) for the period 2008-2012 provided by the Centre for Ecology and Hydrology;

- Weather data from 03/04/2009 to 03/08/2011 on the selected area from the Met office (see below);

- UKCP09 scenarios of the UK Climate Impacts Programme;

- A focus group discussion with stakeholders: regulators, water companies, waste management companies and the public.

2. Area of study

The study area is located in Gowy catchment, Cheshire, UK, and covers an area of about 28.80 km. The Gowy catchment aims to give a representative sample of the North West region. The catchment is characterized by low-lying rolling countryside and plains. The soil is predominantly loamy and clayey soil, which might suggest a slow permeability and impeded drainage. The catchment, a growing economy with many heavy industries, is situated by two river basin catchments. The Gowy River runs to the east of Chester and meets the Mersey Estuary near the oil refinery at Stanlow. The land cover comprises grassland, some arable and woodland. Tiles drains are present in all arable fields in the catchment. The landfill sites comprise cells in the age range of 8–25 years old and essentially accept non-hazardous waste.

B.   STUDY DESIGN

The authors gathered data as described above and grouped data from a series of landfill sites in similar geological locations to build a semi-hypothetical case landfill site.

Hypotheses on the lining of the landfill site were made. It was considered that cell 1 is unlined and fully capped, cell 2 is un-lined and still operational, and cells 3-6 are lined.

The possible sources of mecoprop-P in leachate quality were investigated based on a survey on public use and disposal of pesticide, the availability of mecoprop-P in comparison with other pesticides and the actual and past waste management practices. A route map was built.

The public use, storage and disposal methods were discussed using a structured focus group discussion technique.

The effect of precipitation, temperature and river flow rates on mecoprop-P concentration was assessed on the basis of graphs: plot of temperature, precipitation and Gowy at Huxley flow rates in the area of study and during the study period as cited above. Concentrations of mecoprop-P measured in the landfill cells were plotted against temperature, precipitation and flow rate.

The variation in mecoprop-P concentrations in old and new cells was discussed by the authors.

The climate change scenarios and impacts on land use in the UK was a three-step procedure. At the first step, a summary of climate changes was reported from the UKCIP09 summary. Each change is labelled with a confidence level: "High", "Medium", or "Low". At second step, a summary of impacts of climate changes on factors affecting source term and herbicide pathways was built, with each impact labelled as "Low", "Medium" or "High" based on expert judgment. At the third step, the expected climate changes are compared with their expected impact and their confidence levels to produce a table of probable impacts of climate changes to herbicide concentrations in ground water and surface water, with a combined confidence level.

II.   RESULTS AND DISCUSSION

The investigation of possible source term of mecoprop-P in leachate quality led to a route map for possible source term of mecoprop as follows:
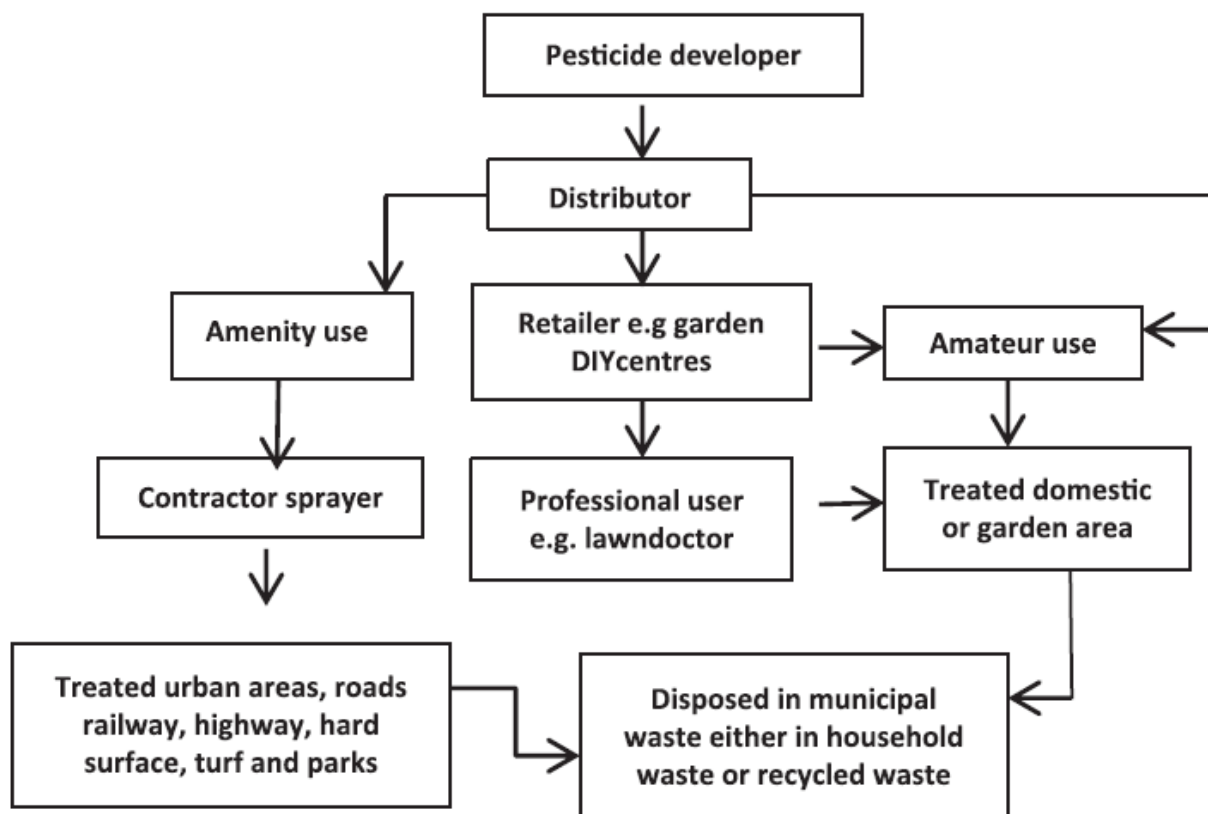
Figure B. 8.9. Route map for possible source term of mecoprop (Fig. 4, Idowu *et al.*, 2014)

The main findings of the discussion about the public use, storage and disposal methods were the following:
- Amenity and household use might be significant but agriculture still contributes a major proportion of mecoprop-P into water bodies usually as run-off;

- The proportion of disposed empty herbicide containers, including mecoprop-P, disposed of into general waste bins account for 48 % of the total amount of containers;

- Favourable climate conditions promote increased prevalence of weeds during summer and hence more frequent application for garden and household use;

- Various stakeholders are involved in the sustainable water management: UK National action plan for sustainable use of pesticides, the Pesticide Safety Directorate, the Amenity Forum, the Amateur Use Action Plan Implementation Group and the voluntarily initiative and water catchment project.

The effect of precipitation, temperature, river flow rates and season on mecoprop-P concentrations were the following:
- Consistent decrease of mecoprop-P concentrations (in landfill cells) during summers;

- Increase of temperature and precipitation result in a decrease in concentration of mecoprop-P;

- General increase of mecoprop-P concentrations in autumn;

- Flow rate seemingly increases as mecoprop-P concentrations decreases over the period of study;

- Higher concentrations of mecoprop-P in 2010, hypotheses for the origin are

  o More application in the autumn period with potential runoff possibility from adjacent arable lands and, in addition, some containers disposed in the general waste bin

  o Time of leachate sampling

  o Age of the cell and landfill

  o Soil permeability

  o Poor drainage tiling

  o Ineffective capping

  o Week EBS (a liner)

No statistical analysis of the data or graphs was provided to confirm these claims.

The variation in mecoprop-P concentrations in old and new cells raises a concern since high concentrations were observed in newer cells, which indicates that improper disposal of containers is still an issue, citing significant contribution from garden and household users.

The climate change scenarios and impacts on land use led to the following summary of impacts of climate change on factors affecting receptor (Table B. 8.73):

Table B. 8.73.   Summary of impacts of climate change on factors affecting receptor (Table 5, Idowu *et al.*, 2014)

Factors affecting receptor	Summary of impacts	Confidence level
Surface water	Small changes in mean river flows are unlikely to lead to significant changes in the effect of dilution on surface water concentrations	M (medium)
	Low flows in summer may cause a significant reduction in dilution potential and could give rise to increased pesticide concentrations if runoff or spray events occurred	M
	Where landfills is lined this results in runoff, and if occur in the summer, concentrations in water bodies are likely to be higher	M
Groundwater	The overall impact of climate change on the groundwater receptor is likely to be limited	L (low)
	Where landfill is lined, impact of climate change on ground water is likely to be limited	L

II. CONCLUSION

The study identified the possible source terms, using a map to route the transport of mecoprop to landfill sites, starting with the manufacturer to amenity use, garden and household use (excluding agricultural use) and the municipal landfill as the possible final destination. Importantly, high concentrations of mecoprop obtained from data (in landfill) could have potential impact on both surface and ground water. In addition, it is suggested that daily rainfall, temperatures and river flow rates are significant factors that directly or indirectly contribute to the high concentrations of mecoprop-P in leachate.

The authors suggest that the manufacturers should be responsible for providing clear and practical advice to householders, or, as a drastic approach, that the use of mecoprop for amenity, garden and household use be withdrawn. Also the study authors point out that caution should be taken when considering mecoprop-P as non-hazardous substance and its presence or absence on the List I and List II substances.

The applicant concludes the following; that from a regulatory point of view, the paper is mainly an interpretation of existing data, even if some data were not published in peer-reviewed papers previously. An attempt is made of interpreting inadequate data about contamination of landfill cells by mecoprop, weather, river flow, pesticide uses, waste management practices and even climate changes to highlight the contamination of ground and surface water arising from the non-agricultural uses of mecoprop-P. The results point mainly at improper waste disposal by the end user, the landfill systems in the UK, and weather events. The impact of climate change is maybe too long-term to be taken into account in the risk assessment, since 2080 is cited compared to the ten years of length for a pesticide approval. In addition, climate change is a controversial issue. The qualitative results of this study should be taken as hypotheses to be tested with further, more specific studies intended to clarify each aspect separately and thoroughly. The paper does not provide usable new data about the link between landfill cells contamination and the contamination of groundwater and surface water. Finally, the claim that the onus is on the manufacturer to provide clear and practical advice to householders must be complemented by adequate waste disposal and waste management legislation and its enforcement by authorities.

Assessment of methodological quality

	Relevance	Reliability	Transparency & repeatability
Material	UK, relevant but data inadequate for full interpretation.	Depends on the various literature sources, not assessed. Most sources are peer-reviewed; other data originate from government agencies.	Literature data is retrievable.
Method	Expert judgment may be considered as relevant in combination with other methods, but may not be sufficient by itself.	Qualitative approach, not validated and therefore unreliable, no statistical analysis of the data, trends on graphs are not clear enough to draw conclusions based on visual assessment.	The participants in the focus group discussion are not detailed.
Results & interpretation	Relevant	Unreliable due to methodology and lack of data, but not without interest, findings ought to be confirmed by further studies.	No particular issue, the authors cited the reasons for each conclusion drawn.

Report:	**CA 7/07, Van Beinum, W. *et al.* (2007)** XIII Symposium Pesticide Chemistry - Environmental fate and ecological effects of pesticides, pp366-373
Title	The effect of soil type on pesticide leaching
Guidelines:	None stated
GLP:	Not stated, but assumed not GLP
Deviations	Not applicable

Previous evaluations	None: Submitted for the purpose of renewal under Regulation 844/2012. This paper was identified by the applicant as potentially relevant during the literature review. The paper summary and relevance/reliability assessment provided by the applicant have been

| | reproduced below. The RMS generally agrees with the applicant's assessment. The study describes a two year lysimeter study on 8 different soil types. Overall no clear correlation between soil type and leaching could be established. The applicant highlights that applications were made at later timings (autumn) than for the representative use (spring), so represents a more vulnerable time. However, the results demonstrate that heavy rainfall close to the application timing results in leaching of mecoprop-P. The results are not sufficiently reported to provide new endpoints and do not change the risk assessment. |

Executive summary

The paper assesses the relationship between clay content (8 soils) and maximum concentration in leachate for four herbicides, including mecoprop-P (only data relevant to mecoprop-P will be cited further), with the aim to determine if it is possible to reduce pesticide transport to surface waters via drainflow. In order to achieve this lysimeter experiments were carried out during two consecutive years on winter wheat in the UK. The maximum concentration in leachate was negatively correlated to the clay content during the dry year (2005-06) and positively correlated to the clay content during the wet year. Therefore, the results do not support mitigation based on a restriction of pesticide use by soil type.

Large amounts of pesticides have been found in discharge from agricultural fields with subsurface drainage systems. Large concentrations in drainflow often coincide with rainfall events just after application and have been connected to preferential flow. Soils with high clay content that are prone to preferential flow due to crack formation are also likely to have subsurface drainage systems installed to support field drainage. A restriction on the use of certain pesticides according to soil type could potentially decrease the risk of pesticide contamination of surface water whilst allowing use in less vulnerable areas.

Top soil half-life and Koc of mecoprop-P were estimated using a degradation study and a batch sorption experiment, respectively. DT_{50} values ranged from 7.3 to 14.5 d, while Koc values ranged from 20.2 to 35.0 mL g^{-1}.

Mecoprop-P was applied to 48 lysimeters from eight contrasting soils for two consecutive years. There was a large difference in rainfall amount and intensity between the two years. The first year was abnormally dry, while in the second year a rain event > 10 mm occurred 10 days after the pesticide application.

The concentration of pesticides in leachate was much larger in the wetter year than in the relatively dry year. The maximum concentrations of mecoprop-P in leachate showed a decrease with clay content in the first year, but an increase with clay content in the second year. The results do not support mitigation based on a restriction of pesticide use by soil type. In this case restriction would not result in reduces transport of pesticides to surface waters, this is however, not to say that such restrictions are not useful under other circumstances.

I. MATERIALS AND METHODS

A.   MATERIALS

1. Test materials: Optica: commercial formulation of mecoprop-P (and 3 other pesticides, not summarized)
Purity: Commercial formulation, not specified
CAS #: 16484-77-8 (mecoprop-P)

2. Soils: Agricultural fields in the UK representing eight contrasting soil types, 6 replicates. The physical and chemical properties of the soil are provided in

Table B. 8.74

Table B. 8.74.   Soil physiochemical properties (Table 1, Van Beinum *et al.*, 2007)

Soil series	Clay (%)	OC (%)	pH (H$_2$O)
Denchworth	64.8	4.1	6.7
Evesham	59.2	3.4	7.9
Hanslope	46.2	2.7	8.0
Brockhurst	36.4	2.5	6.7
Ragdale	33.7	2.6	7.0
Salop	22.6	1.5	7.0
Clifton	15.9	1.9	6.3
Quorndon	15.7	1.7	6.9

B.   STUDY DESIGN

a) Degradation rate (laboratory)

The authors referred to measurements of the degradation rate of mecoprop-P, but the method was only briefly described.

Duration: 15 weeks
Temperature: 15°C
Sampling times: 12 times, 3 replicates
Moisture content of the soil: adjusted to the water holding capacity at a suction of -50 cm H$_2$0.
The authors do not state that the DT$_{50}$ was corrected for temperature.

b) Koc (laboratory)

The authors referred to measurements of the Koc range of mecoprop-P, but the method was only briefly described.

Method: batch sorption experiment
Sampling: single concentration, 3 replicates

The sorption coefficients were normalised to the organic carbon content of each soil to yield a range of Koc values.

c) Lysimeter study

1. Dates of experimental work

Lysimeter experiments: 16 November 2005 - 16 April 2006 and 16 November 2006 - 16 April 2007.

2. Experimental conditions

A lysimeter study was performed over two consecutive years. Six replicate lysimeters were taken from agricultural fields in the UK representing eight contrasting soil types. The soil cores were extracted in PVC pipes (40 cm length and 24 cm inner diameter). The pipes were attached to a cutting ring and driven vertically into the ground using a JCB excavator. A 5 cm layer of soil at the bottom of the core was replaced by a layer of fine sand and a layer of gravel to aid drainage before attaching a bottom plate with outlet. The lysimeters were installed outdoors at the Central Science Laboratory in crates filled with sand for insulation. Rainfall and temperature were recorded by a weather station on site. To aid drainage from the lysimeters, a weak suction (50 cm H$_2$O) was periodically applied at the outlets using hanging water columns. Winter wheat was sown at the end of October and a commercial formulation of mecoprop-P was applied on 16 November in both years (2240 g a.s. ha^{-1} in the first year and 1890 g a.s. ha [-1] in the second year). The application solution was distributed manually across the soil surface with a Pasteur pipette. The target dose was 2000 g a.s. (similar to recommended field rates).

3. Sampling

All leachate from the lysimeters was collected and analysed until flow of leachate stopped in spring of the following year to cover the main part of the leaching period. The duration of the sampling intervals was controlled by the amount of rainfall.

4. Description of analytical procedures

The volume of leachate was determined and up to 500 mL of the leachate was concentrated by solid phase extraction (SPE). The leachate was acidified with 0.1 % H_3PO_4 (v/v), (purity 80-85%, Fluka) and concentrated onto Supelco Supelclean Envi-I8 SPE cartridges (1000 mg, 6 mL) that had been preconditioned with 3 mL acetonitrile followed by 3 mL acidified water (0.1% H_3PO_4). Leachate was drawn through the cartridge at approximately 4 mL min^{-1}. The loaded cartridges were eluted with acetonitrile. The eluate was made up to 5 mL in a volumetric flask and stored at 4°C prior to analysis by HPLC. Recovery rate (with the standard deviation in brackets) was 99.2% (±2.7%) for mecoprop-P.

II.   RESULTS AND DISCUSSION

FINDINGS

1. Pesticide properties

Degradation rates and sorption properties for mecoprop-P on the test soils are reported as:

DT_{50} 7.3-14.5 days
K_d 0.3-1.2 mL g^{-1}
K_{oc} 20.2-35.0 mL g^{-1}

2. Rainfall pattern

Figure B. 8.10 shows the cumulative rainfall for the first three months after application in both years. The winter of 2005 was exceptionally dry in comparison to the local average. Only 97.6 mm of rain fell in the first three months of the monitoring period. Twice as much rain fell in the first three months of the 2006/07 season, a total of 197.6 mm.
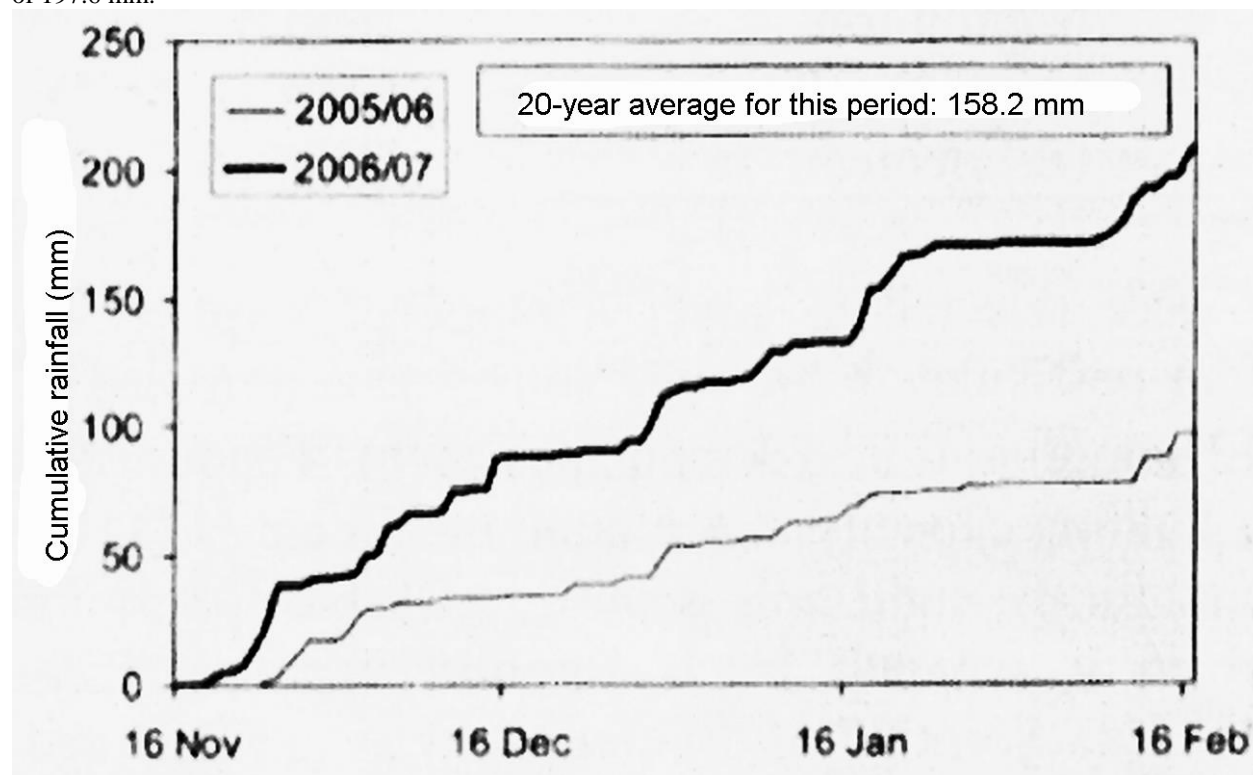
Figure B. 8.10. Cumulative rainfall during the first three months of the lysimeter experiments (Figure 2, Van Beinum *et al.*, 2007)

3. Mecoprop-P concentrations

Concentrations in leachate at 35 cm depth were much smaller in 2005/06 than in 2006/07. Early breakthrough of pesticide (< 5 days after application) in the Hanslope soil was observed in 2006/07 which indicates rapid movement to depth via preferential flow. The maximum concentrations (average of 6 replicates) are reported in Table B. 8.75 for each soil type.

Table B. 8.75. Maximum concentrations of mecoprop-P in leachate at 35 cm depth, mean of 6 replicates (µg L^{-1}). Approximate values extrapolated from Figure B. 8.11)

Year	Denchworth	Evesham	Hanslope	Brockhurst	Ragdale	Salop	Clifton	Quorndon
2005/06	< 5	55	< 5	50	10	25	70	125
2006/07	no data[7]	900	500	500	550	375	125	350

[7] The Denchworth column stopped flowing soon after application and was excluded

4. Relationship between maximum leachate concentration and soil clay content

The maximum concentrations of mecoprop-P in leachate collected in 2005/06 and 2006/07, reported in Table B. 8.75, were plotted against the clay content of the soils in Figure B. 8.11.
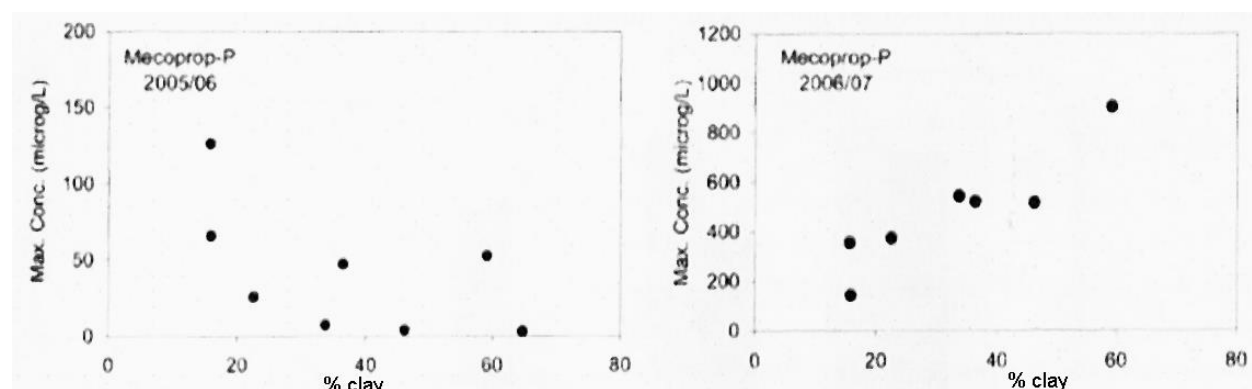
Figure B. 8.11. Maximum concentrations of mecoprop-P in leachate collected in 2005/06 and 2006/07, plotted against the clay content of the soils (Extract from Figure 5, Van Beinum *et al.*, 2007)

An apparent decrease of the maximum leachate concentration with increasing clay content was observed for the 2005/06 period (note: the decrease is only significant due to a single soil whose max. leachate concentration was above 100 µg L^{-1} and should be considered with care). An increase of the leachate concentration with increasing clay content was observed for the wetter 2006/07 period.

III.   CONCLUSIONS

An extensive set of leachate data was collected over two years from 48 small lysimeters of eight contrasting soil types from the UK. Rainfall was the most important factor that determined the concentrations that were found in leachate. Concentrations were much larger in the year with more intensive rainfall than in the relatively dry year. Large concentrations of mecoprop-P were found in leachate from the lysimeters. There was no consistent effect of clay content on the maximum concentration in leachate. A weak, negative correlation between leaching of the weakly sorbed pesticides and soil clay content was found in the dry year.

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[7] The Denchworth column stopped flowing soon after application and was excluded

Applicant's conclusions: From a regulatory point of view, the study is not fully peer-reviewed (Symposium paper) and should be considered with caution. The study show potential high concentrations of Mecroprop-P at 35 cm depth for a large array of UK soils, but the small size of the lysimeters may have interfered with the soil behaviour, especially the cracking and swelling of clay. Preferential flow should be more unpredictable with small lysimeters than in real soils. Preferential flow may have been either non-existent due to the swelling of clay or exaggerated since a single crack has the potential to by-pass the entire column height. Also, the application date is especially unfavourable due to low temperature, autumn and winter rain. Within this submission it is only proposed that mecoprop-P be applied in the spring. The application of suction at the bottom of the column to facilitate leaching may have affected the results. The authors conclude that the results do not support mitigation based on a restriction of pesticide use by soil type, due to inconsistent correlation between the clay content and the maximum leachate concentration of mecoprop-P. However, the 2005/06 period was exceptionally dry. It is possible that, considering only normal or wet years, which are the most significant for risk assessment, the positive relationship between maximum leachate concentration and soil clay content, seen on the "wet" experimental period would be more consistent.

In conclusion, the high concentrations of mecoprop-P in the leachates show that leaching potential of mecoprop-P is clearly a critical aspect of the risk assessment, but the absolute values given in the paper are not reliable. The possibility of a restriction based on soil clay content should not be discarded without further experiments performed only during non-dry years which are the most relevant for leaching potential. It is probable that the application dates extended as late as mid-November in the UK would give unfavourable results for leaching simulations, lysimeter and field studies, and that any field experiments in the UK should be carried out only with a more reasonable assumption on the application date.

The Koc and DT_{50} additional studies are unfortunately not documented enough to be reliable. They show similar results compared to the already known properties of mecoprop-P.

Assessment of methodological quality

	Relevance	Reliability	Transparency & repeatability
Material	Relevant: contrasted UK soils.	No particular issue.	No number of lot/batch for the commercial preparation used.
Method	Not fully peer-reviewed. The application date was very late (16 Nov) and the effective depth of the lysimeter was only 35 cm. Application rate is high but reasonable[8].	Method for Koc and DT_{50} determination are not fully described. The sampling process if fully described but the HPLC analysis was not. Suction is applied at the bottom of the lysimeter Not fully peer-reviewed.	Method for Koc and DT_{50} determination are not fully described. The sampling process is fully described but the HPLC analysis was not.
Results & interpretation	Relevant, but not completely reported. Leaching concentrations measured at shallow depth (35 cm).	Abnormally high results[9]. Uncertain due to inadequate reporting of analytical method.	Reporting of results is not complete, only the mean of peak values are reported for most soils. Unsure if handling of data were compatible with GLP practices.

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[8] 1.44 kg a.s./ha is given by EFSA[8] as the most critical use for wheat in Northern Europe, against 2 kg a.s. /ha in the summarized paper.

[9] The study gives peak concentration for Diflufenican, another pesticide tested in the same experimental conditions with an initial concentration of 250 g a.s./ha, up to 1 μg L^{-1}, while the EFSA Conclusions on Diflufenican (EFSA Scientific report (2007) 122, 1-84, Conclusion on the peer review of diflufenican) present a lysimeter study (application rate: 185 g a.s./ha) with an individual mean annual concentration in leachate < 0.003 μg L^{-1} during the first year. The study of Van Beinum *et al.* (2007) does not provide average values, which makes any comparison difficult.

Field leaching studies (CA 7.1.4.3)

No data required

B.8.2. FATE AND BEHAVIOUR IN WATER AND SEDIMENT

B.8.2.1. **Route and rate of degradation in aquatic systems (chemical and photochemical degradation)**

Hydrolytic degradation (CA 7.2.1.1)

| RMS Comments: | In DAR for original approval (1998) two aqueous hydrolysis studies were considered acceptable (Anon, 1982 and Obrist, 1986a, 1988, 1990). Both studies were conducted on racemic mecoprop however differences in hydrolysis between mecoprop and mecoprop-P are not expected. Mecoprop was found to be stable to hydrolysis at both 70°C over 8 days and 25°C over 31 days. Studies were carried out at pH 5, 7 and 9 rather than the recommended pH's of 4, 7 and 9. The applicant considers that since no degradation was observed at any pH, this difference in pH is not considered to significantly affect the overall result. The pKa of mecoprop-P is 3.7 so will be largely ionised at both pH 4 and 5, therefore the RMS agrees with the applicant.

No new hydrolysis studies have been submitted, however, dark controls in the newly submitted aqueous photolysis study (Connor, 1996b) provide additional evidence of the stability of mecoprop-P to hydrolysis at pHs 5, 7 and 9 at 25°C. |
|---|---|

Report:	**Anonymous 1982**
Title	Behaviour of pesticides in water
Guidelines:	BBA Merkblatt 55
GLP:	No
Deviations	Not applicable

| Previous evaluations: | In DAR for original approval (1998)

The original evaluation has been reproduced below. |
|---|---|

Methods
The hydrolytical stability of mecoprop, >99.5% pure, was studied during 8 days at pH 5, 7, and 9 according to BBA Merkblatt 55. The concentration was 400 mg/l and the temperature was 70°C. The detection limit was 8 µg/l.

Results
Mecoprop was stable to hydrolysis. During the 8 days, no degradation was observed at any pH.

Table B. 8.76. *Hydrolysis at different pH's. Recovery % after 0-8 days*

pH	% of active substance after:			
	0 days	2 days	4 days	8 days
5	98.6	102	95.3	103
7	104	103	94.5	103
9	102	102	92.0	102

1998 Evaluation Comments
The results and information are presented on a standard form without detailed information.

Report:	**CA 7.2.1.1, Obrist 1986a, 1988 and 1990 (Supplement)**
Title	Photodegradation and hydrolysis of mecoprop in aqueous buffer and Supplement to final report
Guidelines:	US-EPA Subdivision N161-1 and 161-2
GLP:	Yes
Deviations	pH 9 day 4 sample taken on day 3 (after 66 hours)

Previous evaluations:	In DAR for original approval (1998)
	The original evaluation has been reproduced below.

Methods
The photodegradation of ^{14}C-mecoprop, ring labelled 96.9% pure, was studied in aqueous solutions according to US-EPA Subdivision N 161-1 and 161-2. The solutions were buffered to pH 5, 7 and 9. The vials contained 4 ml mecoprop solution at the concentration 51-52 mg/l. One set of glass vials was sensitized by adding 1% acetone. Half of the cells were exposed to Chroma 50 artificial sunlight with the light intensity of 320 µWatt/cm^2 for 31 days. The rest of the vials was used for dark control and in the hydrolysis study. The temperature was 25°C. Analysis were performed by LSC and TLC.

Results
The photodegradation half-life was calculated to be 1000, 1060 and 770 hours at pH 5, 7 and 9, respectively. Mecoprop was stable in dark controls and hydrolytical stable for the duration of the study.

Table B. 8.77. *Photolysis and hydrolysis. NC: not calculated. At pH 9 the recoveries at day 0 was low due to inadequate mixing and day 4 was sampled at day 3 (after 66 hours).*

Photolysis		% recovery of MCPP after day					Half-life	
Hydrolysis		0	4	8	14	31	Hours	Days
Non-sensitized	pH 5	104	102	93.7	89.7	62.6	1000	42
	pH 7	107	102	96.3	88.5	66.8	1060	44
	pH 9	NC	103	89.3	64.2	55.1	770	32
Sensitized	pH 5	102	32.6	29.0	3.7	_*	72	3
	pH 7	103	47.1	40.2	3.8	ND	70	3
	pH 9	103	70.4	13.9	3.1	ND	44	2
Dark control	pH 5	109	105	97.9	106	99.1	Stable	
	pH 7	103	101	98.8	104	99.1		
	pH 9	NC	99.6	104	114	103		
Hydrolysis	pH 5	102	103	98.1	104	103	Stable	
	pH 7	108	106	99.8	104	101		
	pH 9	NC	108	111	104	110		

1998 Evaluation Comments
MCPP was hydrolytically stable and was degraded photolytically at half-lives of 32 - 44 days when not sensitized and at 2 - 3 days when sensitized.

Supplement:

Methods
The non-sentized samples were re-analysed using HPLC and TLC. Based on the further separation of radioactive components, the photolysis degradation half-lives at pH 5, 7 and 9, were recalculated to be 680, 1019 and 415 hours, respectively.

Results
At least 11 components were indicated to be present in the original study. The region with about 14% of applied radioactivity consisted of at least 10 components. No degradation product consisted of more than 7.3% of applied radioactivity.

Table B. 8.78. *Recalculation of photolysis results based on further chemical analysis of the non-sensitized samples*

Photolysis		MCPP in % of applied after day:					Half-life	
		0	4	8	14	31	Hours	days
Non-sensitized	pH 5	96.2	90.1	87.3	77.8	45.7	680	28
	pH 7	96.7	90.2	86.3	77.5	58.3	1019	42
	pH 9	95.9	91.0*	70.7	57.5	NC	415	17

1998 Evaluation Comments
The light intensity used was 320 µW/cm^2. Natural sunlight at the testing facility was measured to vary between 1100 and 3500 µW/cm^2 on overcast to clear days around noon. That is a ratio of natural to artificial light of 3.4 to 11. The photodegradtion may be assumed to proceed faster than indicated in the study. But even assuming 12 hour sunlight/day, the photolysis may not be considered the most essential degradation route in water.

Direct photochemical degradation (CA 7.2.1.2)

RMS	In DAR for original approval (1998) three studies were assessed;

Comments:	- Klopffer 1991 and Maestracci 1991 are not to current guideline and therefore not relied on.
	- Obrist 1986a, 1988 and 1990 (Supplement) was a combined hydrolysis and photolysis study at pH 5, 7 and 9 using racemic mecoprop (the original evaluation has been reproduced above). The applicant considers that Obrist 1986a, 1988 and 1990 provides supplementary information as it was conducted on racemic mecoprop. Given that studies on racemic mecoprop have been accepted for hydrolysis on the basis that substantial difference between the stereoisomers is considered unlikely for an abiotic process, the RMS does not consider this sufficient reason to disregard the study. The RMS has briefly reviewed the study. Photolysis was evident in non-sensitised samples exposed to artificial light. Low mass balance was obtained for the pH 9 time zero sample reportedly due to inadequate mixing of the test systems. The supplementary report (1990) re-analysed selected samples to identify photodegradates. No degradation product was repoted at >10% (max 7.3%AR), however, not all samples were analysed. For the original approval of mecoprop-P, the 1998 RMS considered the study sufficient to show that photodegradation may occur and noted that photolysis would be expected to be faster under sunlight. The RMS considers the study does not meet current standards and therefore is not relied on for the risk assessment.
	For the purpose of renewal a new aqueous photolysis study on mecoprop-P has been submitted: Connor 1996b

Report:	**CA 7.2.1.1/01, Connor, S.R. (1996b)**
Title	MCPP-P – aqueous photolysis study
	Report No. 96-1-6341
Guidelines:	FIFRA Subdivision N: § 161-2
GLP:	Yes
Deviations	The temperature exceeded 26ºC on several occasions.
	The test solution for one sample evaporated to dryness on 2 occasions.

Previous evaluations	None: Submitted for the purpose of renewal under Regulation 844/2012
	A kinetics assessement for the data in Connor (1996b) is given in Hazlerigg, 2015.

Executive Summary

The aqueous phototransformation of mecoprop-P was studied at pH 5, 7 and 9 under artificial light (xenon arc) with a 12 hour light/dark cycle for 30 days at 25ºC. Mass balances for mecoprop-P were 73.6-103 % and 94.3-104 % for the irradiated and dark control samples respectively.

Evolution of CO_2 accounted for ~10 % of the radioactivity, with volatile organic compounds accounting for 11.0%. The metabolite *o*-cresol was detected at up to 30.4 % of the applied radioactivity. Degradation of mecoprop-P was not observed in dark control samples.

I.   MATERIALS AND METHODS

A.   MATERIALS

1.	**Test materials:**	Mecoprop-P / ^{14}C-Mecoprop-P
	Description:	White solid
	Lot/Batch #:	39-170-3 / 515-02
	Purity:	99.3% / 99.2%, 48.2 mCi/mol
	CAS #:	16484-77-8

Stability of test compound:	Stable

2.   Buffers: pH 5 – 200 mL 0.01M sodium acetate + 200 mL 0.01M acetic acid and diluted to 600 mL with reagent water.

pH 7 – 300 mL 0.01M potassium phosphate monobasic + 300 mL 0.01M potassium phosphate dibasic and diluted to 675 mL with reagent water.

pH 9 – 100 mL 0.01M HCl + 375 mL 0.01M sodium tetraborate decahydrate and diluted to 675 mL with reagent water.

Sterilisation: Autoclaved at 121°C, 30 minutes

Aeration: Saturated with bacteria-free air for approximately 20 minutes prior to use.

B.   STUDY DESIGN

1. Dates of experimental work

17 July 1995 – 17 December 1995

2. Experimental conditions:

Aqueous photolysis of mecoprop-P was studied at a nominal concentration of 10.0 mg/L. A stock solution of the test item was prepared in acetonitrile at a concentration of 0.959 mg/ml.   Test solutions were prepared in sterile 200 mL volumetric flask with 2 ml stock solution and diluted to volume with buffer solution at either pH 5, 7 or 9. The acetonitrile co-solvent was present at 1% v/v in the test solutions.

Test vessels (borosilicate glass vials) and buffer solutions were autoclaved prior to the addition of the test solution.   Dark control samples were prepared, wrapped in aluminium foil and incubated in the same environmental chamber as the irradiated samples.

Irradiation was provided by a Heraeus Suntest Accelerated Exposure Unit with a xenon arc lamp fitted with a filter preventing transmission of light below 300 nm. The xenon arc lamp was suspended directly above the test vessels. The light source operated on a 12 h light / 12 h dark cycle. Test samples were irradiated for 30 days at 25±1°C. Spectral profiles and total integrated light intensities of the artificial light source and natural sunlight were recorded over a 250 to 700 nm range. Artificial light values were recorded before and after the study period at two representative positions within the test unit in which samples were incubated (6 and 10.5 inches from the xenon arc lamp). Sunlight measurements were recorded on 1st August, 1995, at 12:17 pm on a clear, sunny day outside Wareham, Massachusetts laboratory, USA (42° N latitude).

A preliminary test was performed at pH 7 to estimate the rate of photolysis and to set appropriate sampling intervals for the definitive study.   For the definitive study, samples were taken after 0, 1, 3, 7, 14 and 30 days. Duplicate vials of irradiated and dark control test solutions were taken at each time point. Samples were either stored in the fridge or frozen for no more than 4 days prior to analysis.

Sterility of the test solutions were established by standard plate counts for irradiated and dark control samples for pH 5, 7 and 9 test solutions on days 0 and 30. The study author states that plate counts were zero for all samples with the exception of day 30, pH 5 samples for which a maximum of 60 cfu/ml is reported. Plate count data for each pH and time point are not reported in the study.

3. Description of analytical procedures

Prior to test initiation, duplicate 10 mg/L solutions of racemic mecoprop in pH 5, 7 and 9 buffer solutions were prepared and UV-visible absorption spectra were recorded over a 280 to 900 nm range. No absorption exceeding 0.05 absorbance units at any wavelength longer than 290 nm was observed.

Volatile organic compounds were trapped for a pair of test vessels (aerated samples) for each buffered test solution by passing the air flow through two polyurethane foam plugs, two sulphuric acid traps and an ethylene glycol trap. $^{14}CO_2$ was trapped using two potassium hydroxide solutions in succession. Volatile traps were analysed and replaced at each sampling interval.

The polyurethane plugs and traps were radio-assayed using LSC to quantify the overall radioactivity. Trapped $^{14}CO_2$ in the potassium hydroxide trapping solution was precipitated using 5.0 mL of saturated barium hydroxide. The precipitate was separated and dried and analysed by LSC.

Irradiated and dark control samples were analysed by LSC (LOD 0.43%AR) and profiled using HPLC-RAM/UV (LOD 1.9%AR, RAM - Radiometric Detection). Residual mecoprop-P was confirmed using LC-ES/MS. The identity of metabolite *o*-cresol was confirmed using GC-MS.

II.   RESULTS AND DISCUSSION

A. EXPERIMENTAL CONDITIONS

Light Intensity

The total intensity of natural sunlight at midday and 42° N latitude was recorded as 1.67×10^{-2} Watts/cm^2. The light intensities received by samples at two distances from the xenon lamp ranged from 36.5% to 52.9% of natural sunlight. Artificial light values recorded before and after the study were reasonably comparable indicating a consistent artificial light source during the 30 day light exposure period.

Table B. 8.79. Total light intensities of the xenon arc lamp before and after the study period compared to sunlight intensity

Distance of probe from xenon lamp	Total intensity (Watts/cm^2)		Percent of sunlight	
	Before	**After**	**Before**	**After**
6 inches	8.30×10^{-3}	8.84×10^{-3}	49.7	52.9
10.5 inches	6.10×10^{-3}	8.17×10^{-3}	36.5	48.9

Temperature

Test solutions were generally maintained within the specified range (25 ± 1^oC). Minimum and maximum temperatures recorded for the irradiated samples were 22.0 and 28.7^oC. Minimum and maximum temperatures recorded for the dark control samples were 24.0 and 26.5^oC. The RMS considers that the deviations from the specified temperature range will not significantly impact the overall study results.

pH maintenance

pH records demonstrate that that pH of the solutions were stable throughout the study period. The test solution for a pH 7, dark control, aerated sample was reported to have evaporated to dryness on two occasions. By day 30 the pH for this sample had decreased to 2.99. Given that no degradation of mecoprop-P was observed in the dark control samples and the aerated sample was used for the assessment of volatile degradation products, the RMS does not consider that this deviation in pH impacts the overall study results.

Table B. 8.80. Solution pH

pH	Condition	Rep	Day						
			0	**1**	**3**	**7**	**14**	**30**	**30 (aerated)***
5	Light	A	4.98	5.09	4.99	5.08	5.17	5.04	5.30
		B	N.A	5.02	4.97	5.04	5.12	5.02	5.19
	Dark	A	N.A	5.00	4.97	5.04	5.10	5.01	5.54
		B	N.A	5.00	4.96	5.01	5.12	5.01	5.68
7	Light	A	6.93	6.92	6.93	6.91	6.99	6.99	7.00

		B	N.A	6.93	6.95	6.96	6.99	6.97	7.00
	Dark	A	N.A	6.91	6.93	6.91	6.99	6.99	2.99**
		B	N.A	6.92	6.93	6.92	7.01	6.99	6.99
9	Light	A	8.77	8.81	8.74	8.72	8.83	8.80	8.73
		B	N.A	8.75	8.78	8.73	8.82	8.82	8.77
	Dark	A	N.A	8.74	8.77	8.73	8.82	8.83	8.77
		B	N.A	8.74	8.77	8.76	8.83	8.83	8.75

N.A – not analysed
*Volatile collection samples
**sample evaporated to dryness on days 13 and 18. HPLC-RAM analysis indicated no mecoprop-P breakdown

B.   MASS BALANCE

The material balance for the non-aerated, pH 7 irradiated and dark control samples ranged from 75.6 to 103 % (one sample <90%) and 94.4 to 103 % respectively over the 30 day study. Recovery in the 30 day aerated (i.e. volatile collection) averaged 77.9 and 97.8 % for the irradiated and dark controls respectively.

The material balance for the non-aerated, pH 5 irradiated and dark control samples ranged from 73.6 to 100 % (3 samples <90%) and 94.3 to 100 % respectively over the 30 day study. Recovery in the 30 day aerated (i.e. volatile collection) averaged 64.1 and 98.5 % for the irradiated and dark controls respectively.

The material balance for the non-aerated, pH 9 irradiated and dark control samples ranged from 95.6 to 103 % and 98.8 to 104 % respectively over the 30 day study. Recovery in the 30 day aerated (i.e. volatile collection)

averaged 83.1 and 102 % for the irradiated and dark controls respectively.

The study author attributes the low material balance in the irradiated aerated samples as due to difficulty in maintaining the efficiency of the volatile trapping system over the 30 day period.

Evolution of CO_2 accounted for ~10 % of the radioactivity, with volatile organic compounds accounting for 11.0%.

Table B. 8.81. Material balance for pH 7 test systems

		%AR					
		Irradiated Samples			Dark Controls		
Day	Rep	Test solution	Volatile traps	Mass balance	Test solution	Volatile traps	Mass balance
0	A	100	N.A	100	100	N.A	100
	B	100	N.A	100	100	N.A	100
1	A	98.0	N.A	98.0	99.7	N.A	99.7
	B	102	N.A	102	94.4	N.A	94.4
3	A	103	N.A	103	102	N.A	102
	B	102	N.A	102	99.1	N.A	99.1
7	A	99.6	N.A	99.6	100	N.A	100
	B	75.6	N.A	75.6	103	N.A	103
14	A	97.3	N.A	97.3	101	N.A	101
	B	96.4	N.A	96.4	100	N.A	100
30	A	90.0	N.A	90.0	102	N.A	102
	B	93.4	N.A	93.4	99.7	N.A	99.7
30 (aerated)*	A	63.6	10.1	73.7	95.5	0	95.5
	B	70.2	11.9	82.1	100	0	100

N.A – not analysed

*Volatile collection samples

Table B. 8.82. Material balance for pH 5 test systems

Day	Rep	%AR					
		Irradiated Samples			Dark Controls		
		Test solution	Volatile traps	Mass balance	Test solution	Volatile traps	Mass balance
0	A	100	N.A	100	100	N.A	100
	B	100	N.A	100	100	N.A	100
1	A	97.6	N.A	97.6	99.5	N.A	99.5
	B	94.3	N.A	94.3	96.1	N.A	96.1
3	A	93.7	N.A	93.7	94.3	N.A	94.3
	B	95.9	N.A	95.9	96.8	N.A	96.8
7	A	91.8	N.A	91.8	95.7	N.A	95.7
	B	93.3	N.A	93.3	97.5	N.A	97.5
14	A	89.2	N.A	89.2	98.0	N.A	98.0
	B	90.3	N.A	90.3	96.8	N.A	96.8
30	A	73.6	N.A	73.6	96.1	N.A	96.1
	B	77.8	N.A	77.8	97.5	N.A	97.5
30 (aerated)*	A	50.0	11.5	61.5	97.0	0	97.0
	B	53.5	13.3	66.8	99.9	0	99.9

N.A – not analysed
*Volatile   collection   samples

Table B. 8.83. Material balance for pH 9 test systems

Day	Rep	%AR					
		Irradiated Samples			Dark Controls		
		Test solution	Volatile traps	Mass balance	Test solution	Volatile traps	Mass balance
0	A	100	N.A	100	100	N.A	100
	B	100	N.A	100	100	N.A	100
1	A	100	N.A	100	98.9	N.A	98.9
	B	100	N.A	100	101	N.A	101
3	A	99.6	N.A	99.6	99.0	N.A	99.0
	B	103	N.A	103	102	N.A	102
7	A	101	N.A	101	102	N.A	102
	B	100	N.A	100	103	N.A	103
14	A	97.3	N.A	97.3	103	N.A	103
	B	100	N.A	100	101	N.A	101
30	A	95.6	N.A	95.6	98.8	N.A	98.8
	B	96.1	N.A	96.1	104	N.A	104
30 (aerated)*	A	72.4	8.68	81.1	100	0	100
	B	75.5	9.61	85.1	103	0	103

N.A – not analysed
*Volatile collection samples

B.   FINDINGS

Degradation of mecoprop-P was observed at pHs 5, 7 and 9, reaching <10% AR within the 30 day study period (Table B. 8.84). No significant degradation of mecoprop-P was observed in the dark control samples at any of the tested pHs demonstrating an absence of hydrolysis.

Table B. 8.84. Degradation of mecoprop-P in test systems

Day	Rep	Mecoprop-P (%AR)					
		pH 7		pH 5		pH 9	
		Irradiated	Dark	Irradiated	Dark	Irradiated	Dark
0	A	100	100	100	100	100	100
	B	100	100	100	100	100	100
1	A	89.3	99.7	85.4	99.5	90.5	98.9
	B	92.8	94.4	76.5	96.1	93.5	101
3	A	69.1	102	49.8	94.3	72.1	99
	B	79.8	99.1	49.9	96.8	79.0	102
7	A	52.0	100	37.5	95.7	29.2	102
	B	39.0	103	47.5	97.5	48.7	103
14	A	30.8	101	13.9	98.0	20.1	103
	B	27.1	100	23.8	96.8	35.3	101
30	A	2.98	102	1.69	96.1	2.43	98.8
	B	8.79	99.7	0.871	97.5	9.04	104

The photodegradate profile is reported for the pH 7 irradiated test system only (Table B. 8.85). The study author reports that HPLC photodegradate profiles for pH 5 and 9 were similar to pH 7 although the data is not provided in the study report. For the pH 7 system, data for days 0, 1, 3, 7 and 14 are reported for one replicate only. Data

for both replicates are reported for day 30. The RMS asked the applicant to provide the full data sets for all pH tested, but the data is not available due to the age of the study.

For the pH 7 irradiated test system, the metabolite *o*-cresol was detected at up to 30.4 % of the applied radioactivity on day 30. Unknown metabolite 3 was initially identified at 18.6% on day 30 but subsequent HPLC profiling confirmed that no single metabolite represented >10%. There were no other metabolites accounting for more than 10% of the applied dose.

Table B. 8.85. Photodegradate profile of pH 7 irradiated test systems (non aerated samples)

	Days after application						
	0	**1**	**3**	**7**	**14**	**30 Rep A**	**30 Rep B**
o-cresol	ND	3.7	13.2	15.1	26.0	26.0	30.4
Unknown 1	ND	ND	ND	1.1	2.5	5.7	5.1
Unknown 2	ND	ND	ND	1.6	ND	ND	ND
Unknown 3	ND	ND	ND	ND	6.0	18.6*	15.1*
Unknown 4	ND	ND	ND	ND	1.7	5.1	4.0
Unknown 5	ND	ND	ND	1.6	ND	1.0	ND
Unknown 6	ND	ND	ND	ND	1.2	4.2	1.6
Unknown 7	ND	ND	ND	ND	4.1	6.3	6.1
Unknown 8	ND	ND	ND	ND	2.0	2.4	2.3
Unknown 9	ND	ND	ND	ND	1.2	2.1	2.7
Unknown 10	ND	ND	ND	ND	1.4	1.8	ND
Unknown 11	ND	ND	ND	1.1	1.5	2.0	3.3
Unknown 12	ND	ND	ND	ND	1.4	2.2	3.4
Unknown 13	ND	ND	ND	ND	1.3	2.5	ND
Unknown 14	ND	ND	1.5	ND	1.5	1.07	4.8
Unknown 15	ND	ND	ND	ND	3.9	ND	ND
Unknown 16	ND	3.9	8.2	4.3	1.2	0.9	ND
Unknown 17	ND	ND	ND	ND	ND	1.1	ND
Unknown 18	ND	ND	ND	ND	ND	1.6	ND
Unknown 19	ND	ND	ND	ND	1.7	ND	1.34
Unknown 20	ND	ND	ND	ND	1.3	1.1	1.6

*HPLC chromatograms show Unknown 3 as unresolved peaks. Subsequent HPLC profiling showed no individual degradate accounting for >10% of the applied dose

An updated kinetics assessment to FOCUS 2006 and 2014 is given in Hazlerigg, 2015. The results are summarised in

Table B. 8.86. Overall, the RMS considers the study methodology to be acceptable, but the data reporting to be insufficient. Based on the reported data, aqueous photolysis of mecoprop-P occurs relatively rapidly (DT_{50} 3.39 to 4.65 days in natural sunlight at $42^{o}N$) with o-cresol formed as the major metabolite observed at a maximum of 30.4%.

Table B. 8.86. Summary of kinetic endpoints for aqueous photolysis of mecoprop-P

	pH	Fit	Artificial light		Sunlight 42°N	
			DT$_{50}$ (days)	DT$_{90}$ (days)	DT$_{50}$ (days)	DT$_{90}$ (days)
Mecoprop-P	7	SFO	7.04	23.4	4.65	15.44
	5	SFO	5.13	17.1	3.39	11.29
	9	SFO	6.38	21.2	4.21	14.0
O-Cresol (formation fraction 0.38)	7	SFO	63.5	211	41.91	139.26

Indirect photochemical degradation (CA 7.2.1.3)

No data required – mecoprop-P is readily degraded in aquatic systems.

B.8.2.2. **Route and rate of biological degradation in aquatic systems**

Ready biodegradability (CA 7.2.2.1)

RMS Comments:	In DAR for original approval (1998), one ready biodegradeability study was assessed (Berge & Blok, 1978). The 1998 evaluation reported that the study was not to guideline and therefore was not relied on. A new study has been submitted for the purpose of renewal: Feil, 2010.

Report:	**CA 7.2.2.1/01, Feil, N. (2010)**
Title	Ready biodegradability of mecoprop-P in a manometric respirometry test. Report No. 55481163
Guidelines:	OECD 301 F Commission Regulation 440/2008/EC, Method C.4-D
GLP:	Yes
Deviations	None

Previous evaluations:	None: Submitted for the purpose of renewal under Regulation 844/2012 The study follows the guideline and was generally well reported. The validity criteria were passed. Mecoprop-P can be classified as readily biodegradeable under the test conditions.

Executive Summary

A study was conducted to determine the ready biodegradability of mecoprop-P in a manometric respirometry test over 28 days in accordance with OECD test guideline 301 F. Aqueous test solutions of mecoprop-P at a concentration of 83 mg/L were inoculated with aerobic activated sludge from a wastewater treatment plant treating predominantly domestic wastewater. Samples were incubated in airtight flasks under aerobic conditions in the dark at 22 ± 1°C, and oxygen consumption over the 28-day test period was measured using the manometric method. Procedure controls containing a readily biodegradable reference compound, sodium benzoate, were tested simultaneously under the same conditions, and controls containing inoculum (but without test substance) were run to determine oxygen blanks.

At the end of the 28-day incubation period, mecoprop-P was 85% biodegraded under the test conditions. The pass level for ready biodegradability (biodegradation ≥60% of the chemical oxygen demand [COD] of the test item in a 10-day window within the 28-day test period) was reached. Mecoprop-P can therefore be classified as readily biodegradable under the test conditions.

I.   MATERIALS AND METHODS

A.   MATERIALS

1.	**Test materials:**	Mecoprop-P
	Description:	Yellow solid
	Lot/Batch #:	20043
	Purity:	91.7% as Mecoprop-P
	CAS #:	16484-77-8
	Empirical Formula / Mw	$C_{10}H_{11}ClO_3$ / 214.65 g/mol
	Stability of test compound:	Stable
	ThOD$_{NH4}$	1.640 mg oxygen/mg test item
	Reference item:	Sodium benzoate
2.	**Test species:**	Aerobic activated sludge (micro-organisms from domestic wastewater treatment plant) supplied by the sewage works of Darmstadt, Germany.
	Test item loading rate:	83 mg/L corresponding to an oxygen demand of approximately 136 mg/L (ThOD$_{NH4}$)
	Reference item loading rate:	83 mg/L corresponding to an oxygen demand of approximately 138 mg/L (ThOD$_{NH4}$)
	Temperature:	22 ±1°C
	Light/dark cycle:	Darkness

B.   STUDY DESIGN

1. Dates of experimental work

14 January 2010 – 11 February 2010

2. Experimental conditions

The ready biodegradability of mecoprop-P was determined in aqueous mineral solutions at a concentration of 83 mg/L. Samples of mecoprop-P were weighed directly into the test flasks and test water was added. No emulsifiers or solvents were used. The solutions were inoculated with the aerobic activated sludge and incubated in airtight flasks under continuous stirring in the dark at 22°C for 28 days.

Inoculum controls containing inoculum, but without test item, were run to determine oxygen blanks. Procedure controls containing the reference item sodium benzoate, which is known to be readily biodegradable, were tested simultaneously under the same conditions. An abiotic control, without the activated sludge, was run to check the baseline oxygen demand. A toxicity control containing the test and reference items was run to determine whether there was any inhibitory effect on the aerobic activated sludge micro-organisms. pH's of the test solutions at the start of the test were 7.5-7.6.

A summary of the contents of each of the test flasks used in the study is provided in Table B. 8.87.

Table B. 8.87. Contents of the prepared test flasks

Treatment	Flask	Test item (mg)	Reference item[1] (mg)	HgCl$_2$ (mL)	Activated sludge[2] (mL)	Test water (mL)	Final volume (mL)
Mecoprop-P	1	19.9	-	-	5	239	244
	2	20.4	-	-	5	239	244
Inoculum control	3	-	-	-	5	239	244

Treatment	Flask	Test item (mg)	Reference item[1] (mg)	HgCl$_2$ (mL)	Activated sludge[2] (mL)	Test water (mL)	Final volume (mL)
	4	-	-	-	5	239	244
Procedure control	5	-	20.2	-	5	239	244
Abiotic control	6	20.5	-	5	-	239	244
Toxicity control	7	20.0	20.2	-	5	239	244

[1] Sodium benzoate
[2] Stock suspension of 1.5 g/L on dry matter basis (final concentration: 31 mg/L)

Oxygen consumption was measured using an electrode-type manometer, and measurements were recorded manually by taking a daily reading on each working day. The biochemical oxygen demand (BOD) and percentage biodegradation of the test and reference item were calculated according to the test guidelines.

## II.	RESULTS AND DISCUSSION

### A.	FINDINGS

Biochemical oxygen demand of the inoculum control (medium and inoculum) was 35 mg O$_2$/L in both flasks on day 28 and is therefore within the 60 mg O$_2$/L limit stipulated by the guideline. Oxygen demand in the abiotic control was zero throughout the 28 day period. pH's of the test solutions at the end of the 28 day test ranged from 6.8 to 7.4.

The percentage biodegradation calculated for each of the test systems throughout the study is presented in Table B. 8.88. The biochemical oxygen demand of mecoprop-P in the test media increased significantly from Day 8 onwards, and by the end of the 28-day exposure period, mean biodegradation was 85%. The criterion for ready biodegradability (biodegradation ≥60% of the COD in a 10-day window within the 28-day test period) was reached. Mean biodegradation increased from 20.5% at Day 8 to 81% at Day 18. Mecoprop-P can therefore be classified as readily biodegradable under the conditions of the test. In the procedure controls, the mean biodegradation of the reference item sodium benzoate was 87% at Day 14 and Day 28, thus confirming the suitability of the activated sludge. In the toxicity control containing both the test item (mecoprop-P) and the reference item (sodium benzoate), 75% biodegradation was noted within 14 days and 83% biodegradation after 28 days incubation. Therefore, mecoprop-P can be assumed to not be inhibitory to the aerobic activated sludge micro organisms.

Table B. 8.88. Percentage biodegradation based on ThOD$_{NH4}$

Time (days)	Mecoprop-P		Sodium Benzoate	Toxicity Control
	Flask 1 (%)	Flask 2 (%)	Flask 5 (%)	Flask 7 (%)
1	0	0	40	18
2	2	2	56	27
3	0	4	62	33
4	4	4	69	37
5	4	4	73	37
6	4	7	76	39
7	7	11	76	40
8	19	22	76	50
9	37	40	80	57
10	52	55	83	66
11	71	73	83	72

Time (days)	Mecoprop-P		Sodium Benzoate	Toxicity Control
	Flask 1 (%)	**Flask 2 (%)**	**Flask 5 (%)**	**Flask 7 (%)**
12	75	73	83	73
13	78	77	83	75
14	82	80	87	75
15	82	80	87	79
16	84	78	85	78
17	82	80	87	79
18	82	80	87	79
19	86	84	87	81
20	86	84	87	81
21	86	84	87	83
22	86	84	91	83
23	84	82	89	82
24	86	80	87	83
25	86	84	87	83
26	86	84	87	83
27	84	82	85	82
28	86	84	87	83

III.   CONCLUSIONS

The ready biodegradability of the mecoprop-P was determined in a manometric respirometry test over 28 days in accordance with OECD test guideline 301 F. Under valid test conditions, mecoprop-P was 85% biodegraded within the 28-day exposure period, and it was shown that mecoprop-P can be classified as readily biodegradable according to the conditions of the test.

Aerobic mineralisation in surface water (CA 7.2.2.2)

Report:	CA 7.2.2.2/01, Traub, M. (2014)
Title	Aerobic mineralisation of [^{14}C]Mecoprop-P in surface water Report No. S13-00242
Guidelines:	OECD 309
GLP:	Yes
Deviations	None

Previous evaluations:	None: Submitted for the purpose of renewal under Regulation 844/2012 Aerobic mineralisation in surface water is a new data requirement under Regulation 1107/2009. Consequently a new study has been conducted. The study is acceptable. No degradation of mecoprop-P was observed within the study period so DT$_{50}$ cannot be reliably calculated. Mecoprop-P is considered to be persistent in surface waters.

Executive Summary

^{14}C-Mecoprop-P was applied at two test concentrations of 10 µg/L and 100 µg/L to surface water taken from Rhineland-Palatinate (67374 Hanhofen, Germany, 49°31'N, 08°32'O). Surface water dissolved organic carbon content was 8.6 mg/L and BOD5 was <3 mg/L. The water system was incubated in the dark at 20 ± 2°C under constant bubbling of air through the water for 58 days. Organic volatiles and carbon dioxide were trapped.

Duplicate samples were taken for analysis at specified intervals up to 58 days after application. The radioactivity was quantified by liquid scintillation counting and characterised by normal phase thin layer chromatography. Reversed phase thin layer chromatography was used for confirmation of metabolites in selected samples. The mean recoveries of both test concentrations were within the range 97% to 101% of the applied radioactivity (AR). The mineralisation rate was negligible for both tested concentrations. The amount of CO_2 in the sodium hydroxide traps was negligible (<2%AR). Organic volatiles were detected at <1% AR. For both concentrations no metabolites were formed during the incubation period in the water system.

Due to the negligible mineralisation of mecoprop-P, degradation rates cannot be reliably calculated. However, mecoprop-P is considered persistent in surface water.

The test system was validated using reference substance sodium benzoate. After 13 days 82-87% of the reference material was mineralised which demonstrates that the surface water contained active microbial populations.

I.   MATERIALS AND METHODS

A.   MATERIALS

1.   Test materials: Mecoprop-P / ^{14}C-Mecoprop-P (ring labelled)
     Description: White solid
     Lot/Batch #:   DC/532/22 / 7178RDB001-4
     Purity: 99.71 % / 100 %, 1782 MBq/mmol
     CAS #:   16484-77-8
     Water solubility: 860 mg/L (20°C, pH 3.1)
     Stability of test compound: Stable
     Storage: Ambient / Glass bottle, -18°C

     Reference item: ^{14}C-sodium benzoate (ring labelled)
     Description: White solid
     Storage: -18°C

2.   Water:
     Location: Sampled from the Rhineland-Palatinate (67374 Hanhofen, Germany, 49°31'N, 08°32'O) a natural aerobic surface water body. The study states that the use of phenoxy herbicides in the surrounding agricultural areas is considered unlikely.
     Sampling: Top 6cm of water body. Transported in polyethylene containers.
     Storage: 7 days, 4°C in the dark under aeration. Particles removed by sedimentation prior to use.
     Characteristics: Characteristics at time of sampling and at start of study are given in Table B. 8.89 and Table B. 8.90.

Table B. 8.89. Characteristics of the water at the time of sampling

Temperature (°C)	17.7
pH	8.28
Oxygen (below water surface) (mg/l)	8.82
Oxygen (water/sediment interface) (mg/l)	6.38
Colour	Light yellow/brown, cloudy
Smell	No smell

Table B. 8.90. Characteristics of the water system at the start of study

TOC [mg/L]	9.0
DOC [mg/L]	8.6
Total nitrogen [mg/L]	1.2
Total phosphorus [mg/L]	<0.05
Total ammonium [mg/L]	0.03
Total nitrite [mg/L]	<0.01
Total nitrate [mg/L]	<0.5
Dissolved Orthophosphate [mg/L]	<0.03
Turbidity [NTU]	1.3
BOD5 [mg/L]	<3
Suspended Solids	<10

TOC = Total Organic Carbon
DOC = Dissolved Organic Carbon

B.   STUDY DESIGN

1. Dates of experimental work

11 September 2013 – 20 November 2013

2. Experimental conditions

Test vessels (1000 ml all glass metabolism flasks, 10.1 cm inner diameter) were filled with 500ml surface water and acclimated at $20 \pm 2°C$ under aerobic conditions in the dark for one day. The test vessels were treated once with mecoprop-P in acetonitrile at 10 or 100 µg/L (58 and 582 µl of test solution/test vessel respectively) onto the water surface. Assuming a specific activity of 8.24 MBq/mg this corresponds to a spiked radioactivity of approximately 0.04 MBq and 0.41 MBq per vessel, respectively. The concentration of acetonitrile was <0.2% of the amount of water present. Reference samples were prepared using ^{14}C-sodium benzoate treated at a concentration of 10 µg/l. Solvent blank controls and two reference samples were spiked with 582 µl acetonitrile to monitor the influence of the solvent on the biodegradability.

Test vessels were incubated for a period of 58 days in the dark at $20 \pm 2°C$, under constant air flow (moistened). Any carbon dioxide generated in the flasks was trapped by two sodium hydroxide reservoirs. Any organic volatiles generated in the flasks were trapped by Tenax adsorbent.

Two test sample flasks were taken for analysis on days 0, 2, 7, 13, 19, 29 and 58 to determine mineralisation and degradation pathways in the water. pH and dissolved oxygen concentrations were monitored from the blank controls once a week.

Table B. 8.91. Prepared test flasks

Sample	Test item concentration	Reference item concentration	Comment	Number of sample units	Sampling times (days)
Test samples	10 µg/l	-	-	14	0, 2, 7, 13, 19, 29, 58
Spare samples	10 µg/l	-	-	4	-
Test samples	100 µg/l	-	-	14	0, 2, 7, 13, 19, 29, 58
Spare samples	100 µg/l	-	-	4	-
Sterilised test samples	100 µg/l	-	-	2	58
Reference samples	-	10 µg/l	-	6	13
Solvent reference samples	-	10 µg/l	Spike with solvent	6	13

| Blank controls | - | - | Filled with test water | 2 | 0 |
| Solvent blanks | - | - | Filled with test water and spiked with solvent | 2 | 0 |

3. Description of analytical procedures

RP-HPLC was used to check the purity of the application solution. Test solution purity was determined to be 100%.

The organic volatile traps (Tenax) were extracted with acetone and the amount of radioactivity was determined by liquid scintillation counting (LSC). Evolved $^{14}CO_2$ was trapped by sodium hydroxide (2 M) solution in two separate reservoirs connected to the flask (each 60 mL). Traps were monitored for radioactivity by LSC at the sampling date of the corresponding flask. Limits of detection for the LSC are not given in the study report.

The radioactivity in the water was determined directly by LSC of an aliquot (2 x 1 mL) taken from the water phase before it was poured out of the incubation flask. To two aliquots a further 100 µL acetic acid was added and an hour later the radioactivity remaining in the aliquots was measured by LSC to determine the amount of carbon dioxide which was dissolved in the water phase. The remaining water was concentrated by rotary evaporation and characterised by normal phase thin layer chromatography (NP-TLC). Radioactivity on TLC plates was determined optically by digital autoradiography (LOD 25 dpm, LOQ 50 dpm). Reversed phase thin layer chromatography was used as a confirmatory method.

Samples were analysed immediately by LSC. Samples were stored in a freezer at -18°C. Stability of the stored samples was demonstrated by re-measuring samples stored frozen for 68 days.

II.   RESULTS AND DISCUSSION

A.   MASS BALANCE

Mean recoveries from the water system during the 58 days of incubation were 97-102% AR and 100-101% for the 10 µg/L and 100 µg/L tests respectively.

B.   FINDINGS

Weekly pH and oxygen levels recorded in the blank controls during the study demonstrate the system was stable and aerated throughout the study period.

The mineralisation rate of ^{14}C-mecoprop-P was negligible. Only small amounts (<2% AR) were detected as CO_2. Organic volatiles were detected at <1% AR. No metabolites were observed.

Table B. 8.92 and Table B. 8.93 summarise the key data for this study.

Table B. 8.92. Distribution of radioactivity between water phase, total carbon dioxide and organic volatiles (%AR) for the applied amount of 10 µg/L

	Sampling interval (days)						
	0	2	7	13	19	29	58
Radioactivity in water phase	98 100	115* 79*	97 97	102 100	99 93	98 96	N.A. 97
Mean	99	97*	97	101	96	97	97
Mecoprop-P	98 100	97 97	97 97	102 100	99 93	98 96	N.A. 97
Mean	99	97	97	101	96	97	97
CO_2	2 N.D.	<1 <1	1 2	<1 <1	<1 <1	<1 <1	N.A. 2
Mean	2	<1	2	<1	<1	<1	2
Volatiles	N.A. N.A.	<1 <1	<1 <1	<1 <1	<1 <1	<1 <1	N.A. <1
Mean	N.A.	<1	<1	<1	<1	<1	<1
Mean Recovery	100	99*	99	102	98	98	97**

N.A.   Not analysed
N.D.   Not detected
*   Samples of DAT 2 flowed together during the experiment. Replicate 1 of DAT 58 was not used for metabolite characterisation, because water was lost during treatment of sample.
**   Replicate 1 of DAT 58 was not used for evaluation for experimental reasons.

Table B. 8.93. Distribution of radioactivity between water phase, total carbon dioxide and organic volatiles (%AR) for the applied amount of 100 µg/L

	Sampling interval (days)						
	0	2	7	13	19	29	58
Radioactivity in water phase	101 99	100 101	100 97	99 101	99 98	99 100	101 98
Mean	100	101	99	100	99	99	99
Mecoprop-P	101 99	100 101	100 97	99 101	99 98	99 100	101 98
Mean	100	101	99	100	99	99	99
CO_2	N.D. N.D.	<1 <1	<1 <1	<1 2	<1 1	<1 <1	<1 <1
Mean	N.D.	<1	<1	2	1	<1	<1
Volatiles	N.A. N.A.	<1 <1	<1 <1	<1 <1	<1 <1	<1 <1	<1 <1
Mean	N.A.	<1	<1	<1	<1	<1	<1
Mean Recovery	100	101	100	101	100	100	100

N.D.   Not detected
N.A.   Not analysed

The sterilised test samples were analysed 58 days after treatment. The radioactivity in the water phase of the sterilised test samples showed a mean recovery of 100%AR (Table B. 8.94). The amount of CO_2 in the sodium hydroxide traps was neglible. Organic volatiles were <1%AR. No transformation products were observed therefore the hydrolysis rate of mecoprop-P is considered negligible.

Table B. 8.94. Distribution of radioactivity in the water phase (%AR) for applied amount of 100μg/l test item (sterilised test samples)

Sampling interval (days)	58
Radioactivity in water phase	100 99
Mean	99
CO_2	1 <1
Mean	1
Volatiles	<1 <1
Mean	<1
Mean Recovery	100

The reference samples and the solvent containing reference samples were analysed 13 days after treatment. The study author reports that all samples showed mean recoveries of mass 93-97%, although the data for these test systems is not provided in the study report. Mineralisation was 82-87% indicating microbiological activity of the test water. The solvent did not influence the activity of the test system.

III.   CONCLUSIONS

The study determined the DT_{50} of mecoprop-P in surface water as 2,501 days (10 µg/L) and 9,621 days (100 µg/L) using SFO kinetics. The RMS considers that degradation rates cannot reliably be calculated given the negligible mineralization observed in the study period, however, mecoprop-P can be considered persistent in surface water.

Water/sediment studies (CA 7.2.2.3)

RMS comments:	In DAR for original approval (1998) two studies were assessed; - Bieber and Krohn, 1991 was not considered guideline compliant and therefore was not relied on. - Balk and Stroo, 1985, assessed degradation of racemic mecoprop and therefore is not relied on for the purpose of renewal. In Addendum II to DAR, July (2002) a further water/sediment study was evaluated and considered acceptable (Cooper & Unsworth, 1996). No metabolites >10% were identified. Unidentified metabolites were noted at >5%, therefore an additional water/sediment study has been conducted to address this (Roohi, 2015). An updated kinetics assessment for Copper & Unsworth, 1996, has been submitted (Hazlerigg & Garratt, 2014). Additionally, two papers were identified by the applicant as potentially relevant during the literature reviews (Degenhardt, 2011 and Bromilow, 2006).

Report:	**Cooper, J.L.D. and Unsworth, R.H. (1996)**
Title	Mecoprop-P degradation in two water/sediment systems. Study No.: P 95/123, Rhône-Poulenc Agriculture Ltd. Essex UK. (BASF Doc ID 1996/1000348).
Guidelines:	Guideline BBA, Part IV, Section 5.1
GLP:	Yes
Deviations	None

Previous evaluations:	In Addendum II to DAR (July 2002) The original evaluation has been reproduced below. The RMS has briefly reviewed the study and added some additional information. A new analysis of the data has been submitted to FOCUS kinetics guidance (Hazelrigg & Garratt, 2014), therefore the discussion of kinetics from the original evaluation has been struckthrough. The RMS notes the following: - The systems were acclimatised for 6 weeks prior to the study. This is longer than the maximum 4 weeks recommended in the current guideline (OECD 308). However, microbial biomass measurements taken at the start and end of the study suggest that the systems were microbially viable throughout the study period. - Unknown metabolite 1 was identified at >5% at two time points in the Ongar system and at >5% at one time point in the Manningtree system. At the time of the original assessment metabolites were not considered relevant at this level and was therefore not identified. Roohi, 2015, was undertaken to identify the metabolites, however no metabolites were observed at >5% in either system. The RMS notes that the dose applied in Cooper & Unsworth, 1996, would have resulted in a water column concentration of 0.449 mg/l, whilst the dose applied in Roohi, 2015, was 0.138mg/l. The RMS considers the dose rate used in Roohi, 2015, to be appropriate for the representative use, therefore, the higher levels of metabolite observed in Cooper & Unsworth, 1996, can be ascribed to the exaggerated dose rate used. Overall the RMS considers study acceptable to assess degradation of the parent, mecoprop-P.

Methods

The degradation of ^{14}C-mecoprop-P (phenyl-ring labelled) in two aquatic sediment systems was undertaken to meet the requirements of BBA guideline, part IV, section 5-1, 1990.

Two water/sediment systems consisting of water and sediments from a stream in Manningtree and from the river Roding in Ongar, both locations in Essex UK, were collected. The surface water was characterised immediately prior to sampling. The sediments were collected and sieved to 5 mm at the site. Sediment and water were stored at 4°C in the dark prior to use. The physico-chemical properties of the waters and sediments are given in the tables below.

Table B. 8.95. *Characterisation of surface water at the time of collection.*

Surface water	pH	Redox potential (mV)	Oxygen content (%)	Total N (mg/l)	Total P (mg/l)	TOC (mg/l)	Water hardness (mg CaCO$_3$/l)
Manningtree	5.57	248	63	24.9	0.68	18.59	319
Ongar	6.94	225	82	20.2	0.24	59.46	413

Table B. 8.96. *Characterisation of sediments.*

Sediment	pH (H$_2$O)	Sand % 63-2000 µm	Silt %*		Clay % <2 µm	OC (%)	CEC (meq/100 g)	Biomass**	
			50-63 µm	2-50 µm				at start	at end
Manningtree (Sandy Silt Loam)	6.7	40.09	8.51	36.21	15.18	5.3	11.9	349	390
Ongar (Clay Loam)	8.6	33.90	4.98	29.03	32.08	3.1	63.2	219	222

*: silt fraction divided at 63 µm in the BBA and at 50 µm in the USDA sediment classification system. Totals of fractions are 99.99%. **: Microbial biomass, µg C/g.

The sediments were sieved to 2 mm and added to 80 glass flasks, approx. 7.5 cm internal diameter, to a depth of 2-2.5 cm. Surface water filtered by 0.2 mm was added to an approximate depth of 5 cm. A low flow of CO$_2$-free air passed the system during a 6-week acclimatisation period before the experiment started. The air stream was low enough to allow aeration and gentle movement but to avoid mixture of the two phases. The effluent air current passed through ethylene glycol and two 2M potassium hydroxide traps to trap volatiles and ^{14}CO$_2$, respectively.

^{14}C-mecoprop-P was added dropwise to the water phase on a single occasion at 99.2 µg/flask (100 µl of 0.992 mg/ml solution in acetonitrile), equivalent to 1.123 kg ai/ha. Based on a 7.5cm ID flask and a 5cm water depth, this dose rate results in a water phase concentration of 0.449 mg/l. The incubation temperature was 20ºC±2ºC in the dark. Duplicate samples of each sediment were removed for analysis at intervals 0, 24 and 48 hours, 7, 14, 22, 30, 61 and 100 days after application. An extra sampling point at 80 days was added for the Manningtree system due to poor replication of samples. The water fraction was sampled by decanting and centrifugation and analysed by LSC (radioactivity) and HPLC and TLC for identification. The sediments were dried and measured by combustion. If >5% of dose was identified in the sediment by combustion, sediments were rehydrated, sequentially extracted and analysed for MCPP-P and degradation products by HPLC and TLC. Procedural recoveries were monitored at all stages of the sequential extraction and are reported as generally greater than 85%.

Limits of detection are not clearly stated in the study report. An LOD of 0.01%AR is reported as a footnote to the results tables for the Ongar system.

Results
Monitoring results of system pH, redox potential and % oxygen saturation demonstrate that the conditions were stable throughout the experimental period. The recovery of radioactivity was high in both systems. The overall mean recovery was 110.0% (range 114.0-103.7%) for the stream system (Manningtree) and 105.5% (range 112.6-87.4%) for the river system (Ongar). One replicate in the Ongar system at 100 days resulted in a mass balance of 66.9% which was ascribed to poor ^{14}CO$_2$ trapping (

Table B. 8.101). All remaining mass balances for the Ongar system were between 99.05 and 114.68%.

The distribution of the radioactivity over time showed that the radioactivity with time was transferred from the water phase to the sediments phase. After 100 days, the radioactivity in the water phase in the Manningtree system was 15.4% and in Ongar system 1.8% of applied. At the same time the radioactivity in the sediments was increased to approx. 30% in both systems (cf. table below).

The main fraction of the recovered radioactivity in water and extracted from sediment was MCPP-P. Only minor fractions of 3 unknown degradation products were observed.   Metabolite 1 was detected in the water column at 5.46%AR on day 61 in the Manningtree system and on day 30 and 61 in the Ongar system at 8.40 and 7.04%AR respectively. Metabolite 1 was below detection in the water column at all other time points for both systems. Metabolites 2 and 3 were below detection in the water column for both systems. No metabolites were identified in the sediment at >5%AR. The degradation to CO_2 increased to 55% in the Manningtree and 58% in the Ongar system during 100 days. The non-extractable residues in the sediment increased to 24-28% of applied radioactivity.

Table B. 8.97. *Radioactivity distribution and balance in the Manningtree system.*

	Recovered radioactivity in % of applied after day:									
	0	1	2	7	14	22	30	61	80	100
Water	111.29	110.03	106.38	105.75	92.41	94.65	88.32	42.73	42.98	15.43
MCPP-P	111.29	110.03	106.38	105.75	92.41	94.65	88.32	37.27	42.98	14.68
met.1								5.46		
Sediment	0.77	3.93	5.75	7.46	18.31	11.59	18.61	32.40	37.74	33.47
MCPP-P	n.a.	n.a.	0.58	0.82	13.48	0.41	8.39	9.04	12.72	4.95
met.2			0.07							
met.3										0.54
NER	0.77	3.93	5.01	6.63	4.83	10.60	10.22	23.36	25.02	27.98
Volatiles	n.a.	0.06	0.15	0.76	1.93	2.28	2.95	33.70	22.99	55.29
CO_2		0.06	0.14	0.73	1.91	2.27	2.79	33.64	22.98	55.29
Total rec.	112.06	114.03	112.27	113.96	112.64	108.52	109.87	108.83	103.70	104.19
MCPP-P	111.29	110.03	107.13	106.57	105.88	95.05	96.71	46.31	55.70	20.37

NER: non-extractable residues. met: unknown degradation product.

Table B. 8.98. Mass balance and distribution of radioactivity in Manningtree system

		%AR					
		Surface Water	Sediment Extract	Sediment Residue	Volatile Traps		Mass Balance
Day	Rep				KOH	Ethylene Glycol	
0	A	114.79	0.00	0.64	-	-	115.43
	B	107.79	0.00	0.89	-	-	108.68
1	A	110.48	0.00	4.37	0.07	nd	114.92
	B	109.57	0.00	3.50	0.05	nd	113.12
2	A	106.08	0.86	4.86	0.15	0.02	111.97
	B	106.69	0.74	5.01	0.13	0.00	112.57
7	A	105.77	0.74	6.19	0.68	0.03	113.41
	B	105.72	0.92	7.06	0.78	0.03	114.51
14	A	93.56	13.48	4.80	2.04	0.01	113.89
	B	91.25	13.47	4.87	1.78	0.02	111.39
22	A	93.32	1.08	11.12	1.60	0.00	107.12
	B	95.98	0.91	10.08	2.94	0.01	109.92
30	A	87.75	8.47	10.56	3.05	0.01	109.84
	B	88.89	8.29	9.89	2.54	0.30	109.91

61	A	56.80	10.71	22.79	18.16	0.07	108.53
	B	28.65	7.38	23.93	49.12	0.04	109.12
80	A	30.30	10.67	27.03	34.85	0.01	102.86
	B	55.65	14.77	23.00	11.11	0.00	104.53
100	A	1.49	2.35	18.79	78.91	nd	101.54
	B	29.36	8.62	37.17	31.67	nd	106.82

-   not analysed
nd not detected

Table B. 8.99. Identification of radioactivity in the water column and sediment extracts by HPLC for the Manningtree system

Day	Rep	%AR							
		Surface Water				Sediment			
		Mecoprop-P	Met 1	Met 2	Met 3	Mecoprop-P	Met 1	Met 2	Met 3
0	A	114.79	nd	nd	nd	-	-	-	-
	B	107.79	nd	nd	nd	-	-	-	-
1	A	110.48	nd	nd	nd	-	-	-	-
	B	109.57	nd	nd	nd	-	-	-	-
2	A	106.08	nd	nd	nd	0.54	nd	0	nd
	B	106.69	nd	nd	nd	0.62	nd	0.13	nd
7	A	105.77	nd	nd	nd	0.73	nd	nd	nd
	B	105.72	nd	nd	nd	0.91	nd	nd	nd
14	A	93.56	nd	nd	nd	13.48	nd	nd	nd
	B	91.25	nd	nd	nd	13.47	nd	nd	nd
22	A	93.32	nd	nd	nd	0.45	nd	nd	nd
	B	95.98	nd	nd	nd	0.37	nd	nd	nd
30	A	87.75	nd	nd	nd	8.48	nd	nd	nd
	B	88.89	nd	nd	nd	8.29	nd	nd	nd
61	A	51.57	5.23	nd	nd	10.71	nd	nd	nd
	B	22.96	5.69	nd	nd	7.37	nd	nd	nd
80	A	30.3	nd	nd	nd	10.67	nd	nd	nd
	B	55.56	nd	nd	nd	14.77	nd	nd	nd
100	A	nd	nd	nd	nd	2.35	nd	nd	nd
	B	29.36	nd	nd	nd	7.54	nd	nd	1.08

-    not analysed
nd not detected

Table B. 8.100. *Radioactivity distribution and balance in the Ongar system.*

	Recovered radioactivity in % of applied after day:									
	0	1	2	7	14	22	30	61	80	100
Water	109.16	108.14	105.29	101.73	97.39	92.15	11.37	7.04		1.80
MCPP-P	109.16	108.14	105.29	101.73	97.39	92.15	2.97	<dl		<dl
met.1							8.40	7.04		
Sediment	2.80	4.37	4.46	7.57	10.56	10.68	32.43	44.42		27.68
MCPP-P	n.a.	n.a.	n.a.	1.13	6.64	0.74	2.12	4.74		2.16
met.1				0.08			1.59			
others							0.56			1.20
NER	2.80	4.37	4.46	6.35	3.92	9.94	28.16	39.67		24.32
Volatiles	n.a	0.06	0.14	1.13	2.17	3.31	56.52	55.28		57.94
CO_2		0.05	0.13	1.11	2.16	3.29	56.45	55.26		57.94
Total rec.	111.96	112.57	109.88	110.43	110.12	105.79	100.32	106.73	n.a.	87.41
MCPP-P	109.16	108.14	105.29	102.86	104.03	92.89	5.09	4.74		2.16

NER: non-extractable residues. met: unknown degradation product. n.a.: not analysed. < DL: <0.01%.

Table B. 8.101. Mass balance and distribution of radioactivity in Ongar system

Day	Rep	%AR					
		Surface Water	Sediment Extract	Sediment Residue	Volatile Traps		Mass Balance
					KOH	Ethylene Glycol	
0	A	110.95	0.00	3.73	-	-	114.68
	B	107.37	0.00	1.87	-	-	109.24
1	A	107.64	0.00	4.46	0.08	0.01	112.19
	B	108.64	0.00	4.28	0.03	0.01	112.96
2	A	104.39	0.00	4.55	0.15	0.01	109.10
	B	106.19	0.00	4.36	0.11	0.01	110.67
7	A	99.87	1.62	6.97	1.09	0.02	109.57
	B	103.59	0.81	5.74	1.13	0.02	111.29
14	A	96.65	6.46	5.47	2.81	nd	111.39
	B	98.12	6.82	2.37	1.51	0.02	108.84
22	A	88.49	0.81	11.08	4.06	0.02	104.46
	B	95.80	0.68	8.10	2.51	0.02	107.11
30	A	9.73	4.72	26.72	57.81	0.07	99.05
	B	13.01	3.82	29.60	55.09	0.07	101.59
61	A	8.78	4.86	40.36	52.99	0.02	107.01
	B	5.29	4.62	38.99	57.52	0.01	106.43
100	A	1.56	2.34	20.53	42.41	nd	66.84
	B	2.03	4.37	28.11	73.47	nd	107.98

- not analysed
nd not detected

Table B. 8.102. Identification of radioactivity in the water column and sediment extracts by HPLC for the Ongar system

Day	Rep	Surface Water				Sediment			
		Mecoprop-P	Met 1	Met 2	Met 3	Mecoprop-P	Met 1	Met 2	Met 3
0	A	110.95	nd	nd	nd	-	-	-	-
	B	107.37	nd	nd	nd	-	-	-	-
1	A	107.64	nd	nd	nd	-	-	-	-
	B	108.64	nd	nd	nd	-	-	-	-
2	A	104.39	nd	nd	nd	-	-	-	-
	B	106.19	nd	nd	nd	-	-	-	-
7	A	99.87	nd	nd	nd	1.61	nd	nd	nd
	B	103.59	nd	nd	nd	0.66	0.15	nd	nd
14	A	96.65	nd	nd	nd	6.58	nd	nd	nd
	B	98.12	nd	nd	nd	6.7	nd	nd	nd
22	A	88.49	nd	nd	nd	0.81	nd	nd	nd
	B	95.8	nd	nd	nd	0.68	nd	nd	nd
30	A	2.4	7.33	nd	nd	2.35	2.37	nd	nd
	B	1.77	4.74	nd	nd	1.89	0.81	nd	nd
61	A	nd	8.78	nd	nd	4.86	nd	nd	nd
	B	nd	5.29	nd	nd	4.62	nd	nd	nd
100	A	nd	nd	nd	nd	nd	nd	nd	nd
	B	nd	nd	nd	nd	nd	nd	nd	nd

- not analysed
nd not detected

The recovery of total MCPP-P was reduced to 20.4 and 2.2% in the Manningtree and Ongar systems, respectively. Together with the mineralisation (development of $^{14}CO_2$) this demonstrates that degradation took place.

2002 Evaluation Comments
The study is acceptable.
The recovery of radioactivity was high in both systems with an overall mean of 110% for Manningtree and 105% for the Ongar system. The lower rate in the Manningtree system may be caused by a more acidic water phase and/or a lesser content of total organic carbon TOC than in the Ongar water. After 100 days, the mineralisation and the amount of non-extractable residues are approximately the same in the two systems. However, it was observed that the mineralisation increased strongly already at day 30 in Ongar where it first accelerated at day 60 in the Manningtree system. The mineralisation half-lives were not calculated, but based on the tabular values appears to be approximately 90 days in the Manningtree system and 30 days in the Ongar system.

Report:	CA 7.2.2.3/01, Hazlerigg, C. & Garratt, J. (2014)
Title	Kinetic analysis of mecoprop-P degradation in water-sediment studies Report No. E2014-25
Guidelines:	FOCUS
GLP:	No – not applicable (calculation)
Deviations	None

Previous evaluations:	None: Submitted for the purpose of renewal under Regulation 844/2012 This study provides updated kinetics for the mecoprop-P data from Cooper & Unsworth, 1996.

In Hazlerigg 2014, data from Cooper & Unsworth (1996) were re-analysed in accordance with FOCUS guidance using Kingui2 v2.2012.320.1629 for P1 and P2 levels. Parameters were optimised using Iteratively Reweighted Least Squares (IRLS). Endpoints for the P1 levels proposed by the study are given in
Table B. 8.103. The study author notes that values for sediment were poorly supported by the data with large χ^2 errors in all models used.

Table B. 8.103. Summary of DissT$_{50}$ and DissT$_{90}$ for mecoprop-P at Level P1 proposed by the study author

System	Endpoint	Water (Dissipation)	Sediment (Dissipation)	Whole System (Degradation)
Manningtree	DT$_{50}$ trigger [d]	49	130	59
	DT$_{90}$ trigger [d]	161	432	196
	DT$_{50}$ modelling [d]	49	130	59
	Best fit kinetics	SFO	SFO	SFO
	χ^2 % error	8.212	21.63	8.8
Ongar	DT$_{50}$ trigger [d]	30	12	35
	DT$_{90}$ trigger [d]	100	131	117
	DT$_{50}$ modelling [d]	30	40†	35
	Best fit kinetics	SFO	FOMC	SFO
	χ^2 % error	13.69	60.26	12.01
Geometric Mean	DissT$_{50}$ trigger [d]	38	39	46
	DissT$_{90}$ trigger [d]	127	238	152
	DissT$_{50}$ modelling [d]	38	72	46

†Back calculated from FOMC DT$_{90}$ / 3.32

Data used by Hazlerigg in kinetic modelling are given in Table B. 8.104 and Table B. 8.105. The study presents statistics for the fitted models, but not plots of the fits or residuals. The RMS notes that data points on day 30 and 61 from the Ongar system were omitted as outliers and that data points for day 80 were included although they were not recorded for the Ongar system at that time point.

Table B. 8.104. Manningtree system recorded data and data used for kinetics modelling by applicant

Time	Recorded data (%)			Data used for kinetics modelling (%)		
Point	Water	Sediment	Whole System	Water	Sediment	Whole System
0	114.79	NA^	114.79	114.79	-#	114.79
0	107.79	NA^	107.79	107.79	-#	107.79
1	110.48	NA^	110.48	110.48	-	110.48
1	109.57	NA^	109.57	109.57	-	109.57
2	106.08	0.54	106.62	106.08	0.54$	106.62
2	106.69	0.62	107.31	106.69	0.62$	107.31
7	105.77	0.73	106.5	105.77	0.73$	106.5
7	105.72	0.91	106.63	105.72	0.91$	106.63
14	93.56	13.48	107.04	93.56	13.48	107.04
14	91.25	13.47	104.72	91.25	13.47	104.72
22	93.32	0.45	93.77	93.32	0.45	93.77
22	95.98	0.37	96.35	95.98	0.37	96.35
30	87.75	8.48	96.23	87.75	8.48	96.23
30	88.89	8.29	97.18	88.89	8.29	97.18
61	51.57	10.71	62.28	51.57	10.71	62.28
61	22.96	7.37	30.33	22.96	7.37	30.33
80	30.3	10.67	40.97	30.3	10.67	40.97
80	55.56	14.77	70.33	55.56	14.77	70.33
100	ND*	2.35	2.355	0.005 +	2.35	2.355
100	29.36	7.54	36.9	29.36	7.54	36.9

^NA = not analysed
*ND = not detected (below detection limit)
$Data-points excluded for P1 analysis of sediment kinetics, curve-fitting conducted on decline phase only
#Data-points set to 0 for P2 analysis of two compartment kinetics
+Data-point set to ½ Limit of Detection (LOD)

Table B. 8.105. Ongar system recorded data and data used for kinetics modelling by applicant

Time	Recorded Data (%)			Data used in kinetics modelling (%)		
Point	Water	Sediment	Whole System	Water	Sediment	Whole System
0	110.95	NA^	110.95	110.95	-&	110.95
0	107.37	NA^	107.37	107.37	-&	107.37
1	107.64	NA^	107.64	107.64	-	107.64
1	108.64	NA^	108.64	108.64	-	108.64
2	104.39	NA^	104.39	104.39	-	104.39
2	106.19	NA^	106.19	106.19	-	106.19
7	99.87	1.61	101.48	99.87	1.61$	101.48
7	103.59	0.66	104.25	103.59	0.66$	104.25
14	96.65	6.58	103.23	96.65	6.58	103.23
14	98.12	6.7	104.82	98.12	6.7	104.82
22	88.49	0.81	89.3	88.49	0.81	89.3
22	95.8	0.68	96.48	95.8	0.68	96.48
30	2.4	2.35	4.75	-#	2.35	-#
30	1.77	1.89	3.66	-#	1.89	-#
61	ND*	4.86	4.865	0.005+	4.86	-#

Time	Recorded Data (%)			Data used in kinetics modelling (%)		
Point	Water	Sediment	Whole System	Water	Sediment	Whole System
61	ND*	4.62	4.625	0.005+	4.62	-#
80	ND*	ND*	ND*	-	0.005+	0.005+
80	ND*	ND*	ND*	-	0.005+	0.005+
100	ND*	ND*	ND*	-	-	-
100	ND*	ND*	ND*	-	-	-

^NA = not analysed

*ND = not detected (below detection limit)

$Data-points excluded for P1 analysis of sediment kinetics, curve-fitting conducted on decline phase only

&Data-points set to 0 for P2 analysis of two compartment kinetics

#Data-points considered outliers and removed from the kinetics analysis

+Data-points set at ½ Limit of Detection (LOD)

No clear decline phase is discernible from the sediment data for either the Manningtree or the Ongar system over the time period of the study (see Figure B. 8.12 and Figure B. 8.13). Therefore, the RMS considers that robust kinetic fits cannot be obtained for the sediment data.
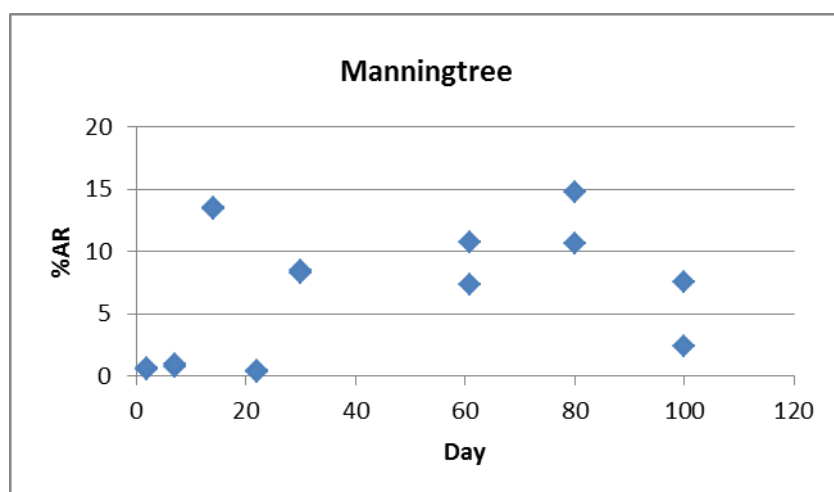
Figure B. 8.12. Mecoprop-P in sediment for the Manningree system
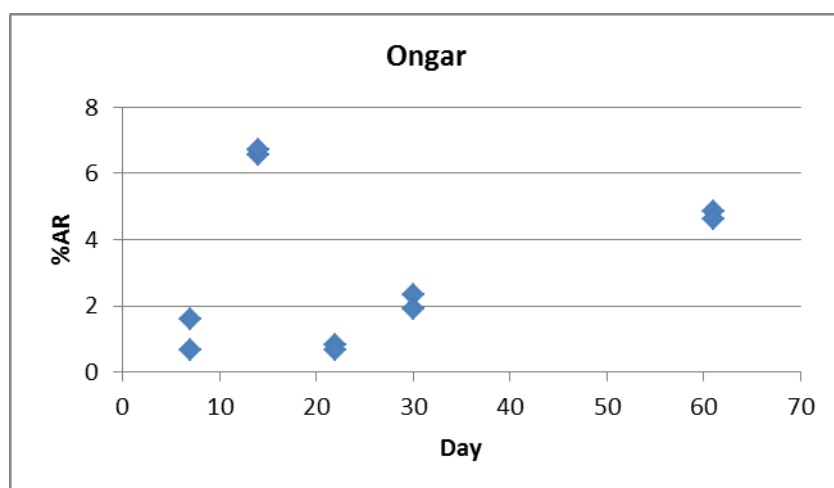
Figure B. 8.13. Mecoprop-P in sediment for the Ongar system

RMS kinetic modelling

P1 level

The RMS has repeated the kinetic modelling for P1 level using CAKE v2.0 for the whole system and water. All recorded data were included and were unweighted. Time zero values were set to the recorded mass balance and all radioactivity was considered to be in the water column. Values below LOD were set to ½LOD. M_0 was not fixed for model fitting. The data was fitted with SFO, FOMC and HS models optimised using OLS in the first instance. For the whole system data for both Manningtree and Ongar systems and the water data for the Manningtree system, the RMS was unable to obtain FOMC fits using OLS so optimised the fits using IRLS.

Manningtree System

Recorded data in the water column and sediment extracts along with the data used by the RMS in kinetic modelling are listed in Table B. 8.106.

Table B. 8.106. Manningtree system recorded data and data used for kinetics modelling by RMS

Time Point	Recorded data (%AR)				Data used for kinetics modelling (%AR)	
	Mass Balance	**Water**	**Sediment (extract)**	**Whole System**	**Water**	**Whole System**
0	115.43	114.79	NA	114.79	115.43	115.43
0	108.68	107.79	NA	107.79	108.68	108.68
1	114.92	110.48	NA	110.48	110.48	110.48
1	113.12	109.57	NA	109.57	109.57	109.57
2	111.97	106.08	0.54	106.62	106.08	106.62
2	112.57	106.69	0.62	107.31	106.69	107.31
7	113.41	105.77	0.73	106.5	105.77	106.5
7	114.51	105.72	0.91	106.63	105.72	106.63
14	113.89	93.56	13.48	107.04	93.56	107.04
14	111.39	91.25	13.47	104.72	91.25	104.72
22	107.12	93.32	0.45	93.77	93.32	93.77
22	109.92	95.98	0.37	96.35	95.98	96.35
30	109.84	87.75	8.48	96.23	87.75	96.23
30	109.91	88.89	8.29	97.18	88.89	97.18
61	108.53	51.57	10.71	62.28	51.57	62.28
61	109.12	22.96	7.37	30.33	22.96	30.33
80	102.86	30.3	10.67	40.97	30.3	40.97
80	104.53	55.56	14.77	70.33	55.56	70.33
100	101.54	ND	2.35	2.355	0.005*	2.355
100	106.82	29.36	7.54	36.9	29.36	36.9

NA – not analysed

ND – not detected (below LOD of 0.01 %AR)

*Data point set to ½LOD

Manningtree – Whole System

Plots of fitted models and residuals are given in Table B. 8.107 and parameters are listed in Table B. 8.108.

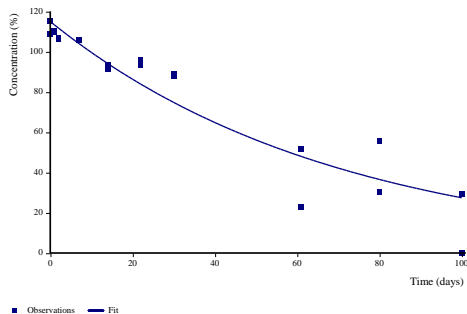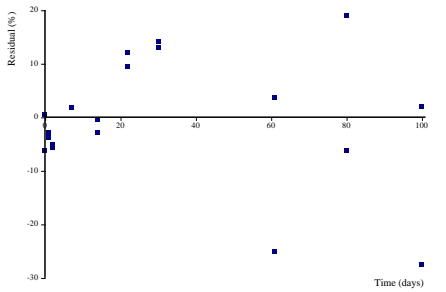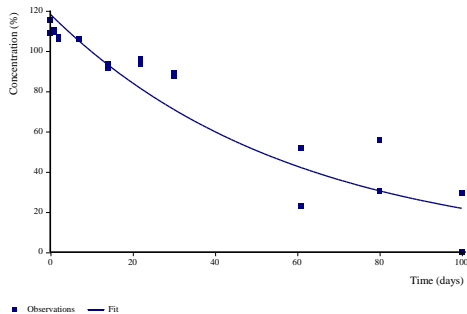Table B. 8.107. Fitted models and residual plots for Manningtree Whole System data
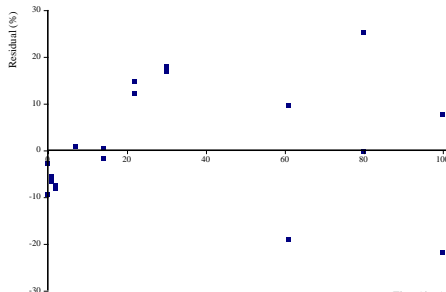
	Observations and Fitted Model	**Residuals**
SFO		
FOMC		
HS		
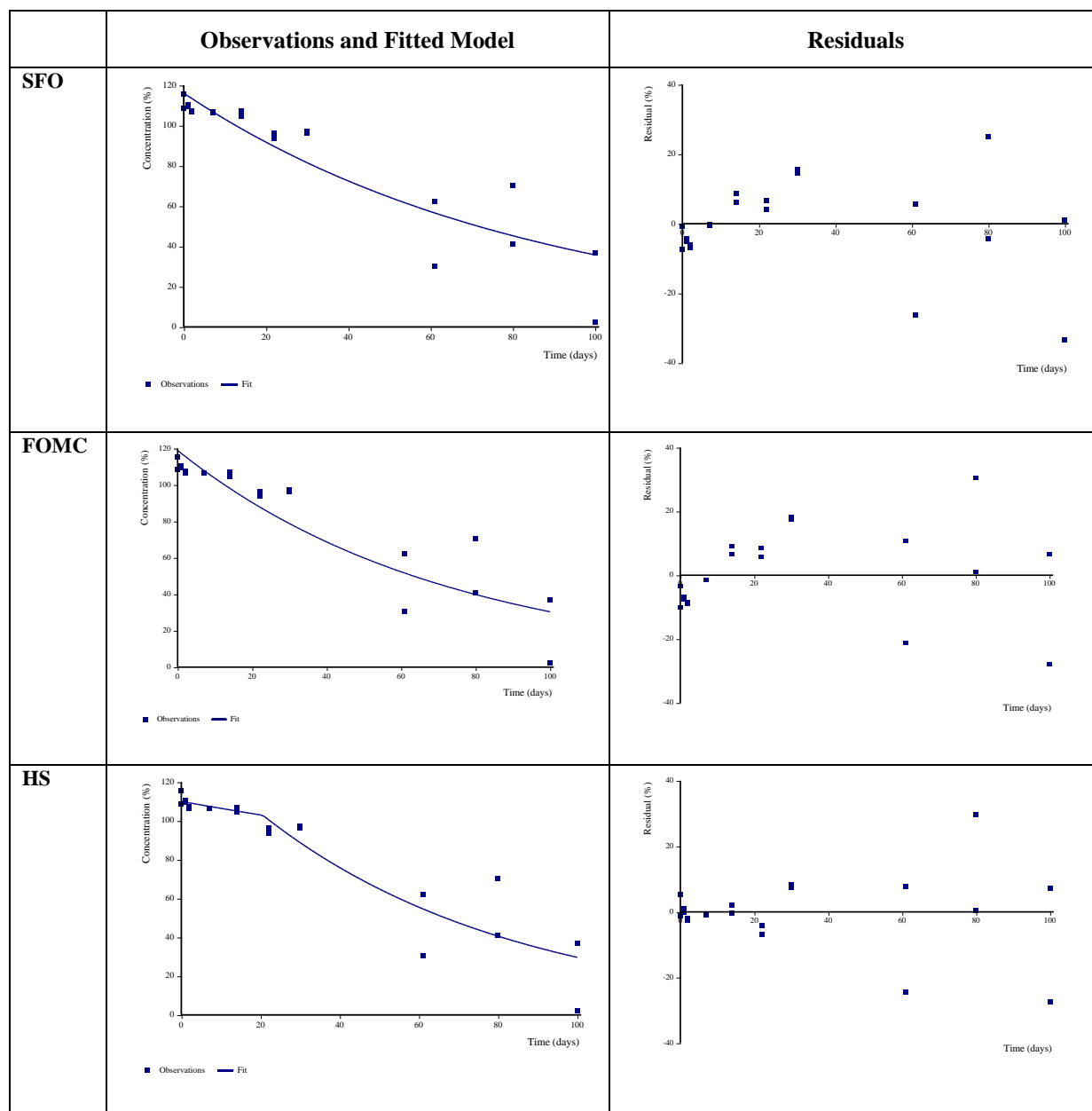
Table B. 8.108. Kinetic fit parameters for Manningtree whole system data

	SFO with OLS	**FOMC with IRLS**	**HS with OLS**
M_0	116.1	118.9	110
k	0.01177		k1 0.00326 k2 0.01565
alpha		82.45	
beta		6.00E+003	
tb			20.61
Visual fit	Acceptable	Acceptable	Good
χ^2 % error	8.76	9.88	7.39
Prob. > t	4.74E-007		k1 0.3292 k2 1.44E-005
Lower (90%) CI		α 30.93 β 2.23E+003	

Upper (90%) CI		α 134 β 9.76E+003	
DT_{50} (days)	58.9	50.6	60.6*
DT_{90} (days)	196	170	163*
k1 DT_{50} (days)			213
k2 DT_{50} (days)			44.3

*Overall

Visually SFO fits the data reasonably well given the variation at later time points. χ^2 % error is 8.76% and it passes the t-test (P<0.1). The RMS was unable to get a fit for FOMC with OLS optimisation but achieved a fit with IRLS optimisation. Visually FOMC fits the data similarly to SFO. The confidence intervals show that α and β are different to zero. χ^2 % error is higher than SFO, 9.88%. HS visually fits the data well, particularly for the early time points. χ^2 % error is lower than that for SFO, 7.39%. The t-test is passed for k_2 but failed for k1 (P=0.3292). On balance the RMS agrees with the study author that SFO is the most appropriate fit for Manningtree whole system data for both modelling and persistence endpoints; DT_{50}(whole system) 58.9 days, DT_{90}(whole system) 196 days.

Manningtree – Water

Plots of fitted models and residuals are given in Table B. 8.109 and parameters are listed in Table B. 8.110.

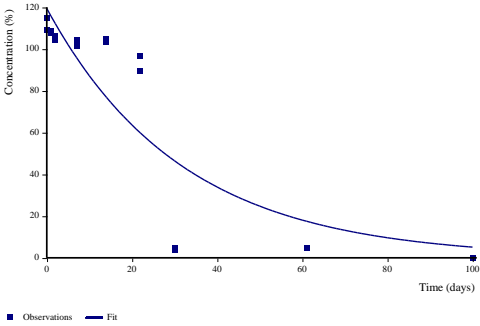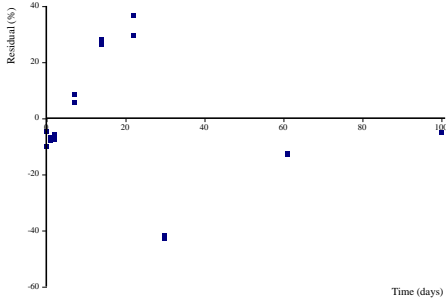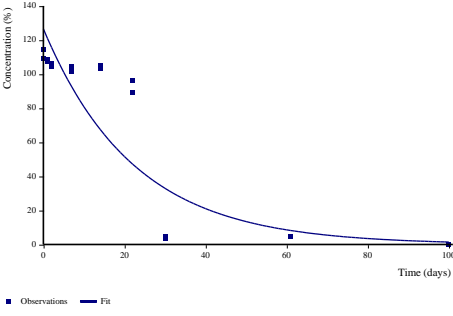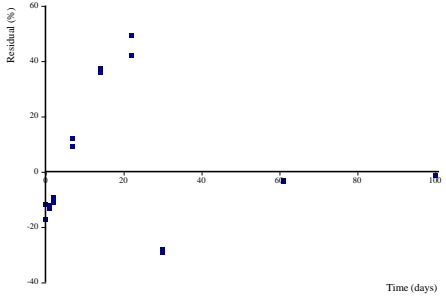Table B. 8.109. Fitted models and residual plots for Manningtree Water data
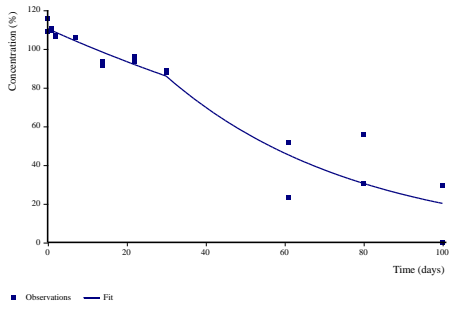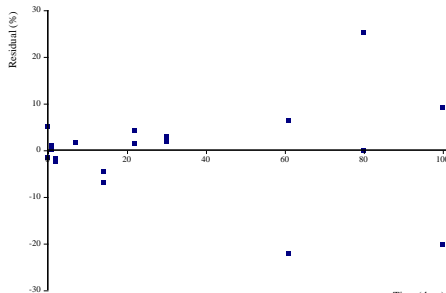
Table B. 8.110. Fitted models and residual plots for Manningtree Water data

	SFO with OLS	**FOMC with IRLS**	**HS with OLS**
M_0	115	118.2	110.4
k	0.01433		k1 0.008351 k2 0.02073
alpha		85.99	
beta		5.04E+003	
tb			30
Visual fit	Acceptable	Acceptable	Good
X^2 % error	8.17	9.66	6.12
Prob. > t	4.66E-008		k1 0.02416 k2 1.21E-005
Lower (90%) CI		α 59.45 β 3.45E+003	
Upper (90%) CI		α 112.5 β 6.62E+003	
DT_{50} (days)	48.4	40.8	51.4*
DT_{90} (days)	161	137	129*
k1 DT_{50} (days)			83
k2 DT_{50} (days)			33.4

*Overall

Visually SFO fits the data reasonably well given the variation in the data at later time points. χ^2 % error is 8.17% and the t-test is passed (P<0.1). The RMS was unable to get a fit for FOMC with OLS optimisation but achieved a fit with IRLS optimisation. Visually FOMC fits the data similarly to SFO. The confidence intervals show that α and β are different to zero. χ^2 % error is higher than SFO, 9.66%. HS visually fits the data well, particularly for the early time points. χ^2 % error is lower than that for SFO, 6.12% and the t-test is passed for both k1 and k2. The RMS considers HS the best fit model for persistence endpoints; DT_{50} 51.4 days, DT_{90} 129 days. For modelling purposes DT_{50} for the HS slow phase represents a conservative value; DT_{50} 83 days.

Ongar System

Recorded data in the water column and sediment extracts along with the data used by the RMS in kinetic modelling are listed in Table B. 8.111.

The RMS does not agree with the study author that values at day 30 and 61 should be omitted as outliers. It is evident from the data that there is a slow degradation phase followed by a very rapid degradation phase.

Table B. 8.111. Ongar system recorded data and data used for kinetics modelling by RMS

Time Point	**Recorded Data (%AR)**				**Data used in kinetics modelling (%AR)**	
	Mass Balance	**Water**	**Sediment (extract)**	**Whole System**	**Water**	**Whole System**
0	114.68	110.95	NA	110.95	114.68	114.68
0	109.24	107.37	NA	107.37	109.24	109.24
1	112.19	107.64	NA	107.64	107.64	107.64
1	112.96	108.64	NA	108.64	108.64	108.64
2	109.10	104.39	NA	104.39	104.39	104.39
2	110.67	106.19	NA	106.19	106.19	106.19
7	109.57	99.87	1.61	101.48	99.87	101.48
7	111.29	103.59	0.66	104.25	103.59	104.25
14	111.39	96.65	6.58	103.23	96.65	103.23
14	108.84	98.12	6.7	104.82	98.12	104.82

Time Point	Recorded Data (%AR)				Data used in kinetics modelling (%AR)	
	Mass Balance	**Water**	**Sediment (extract)**	**Whole System**	**Water**	**Whole System**
22	104.46	88.49	0.81	89.3	88.49	89.3
22	107.11	95.8	0.68	96.48	95.8	96.48
30	99.05	2.4	2.35	4.75	2.4	4.75
30	101.59	1.77	1.89	3.66	1.77	3.66
61	107.01	ND	4.86	4.865	0.005*	4.865
61	106.43	ND	4.62	4.625	0.005*	4.625
100	66.84	ND	ND	ND	-	0.005
100	107.98	ND	ND	ND	-	0.005

NA – not analysed

ND – not detected (below LOD of 0.01 %AR)

*Data point set to ½LOD

Ongar - Whole System

Plots of fitted models and residuals are given in Table B. 8.112 and parameters are listed in Table B. 8.113.

Table B. 8.112. Fitted models and residual plots for Ongar Whole System data
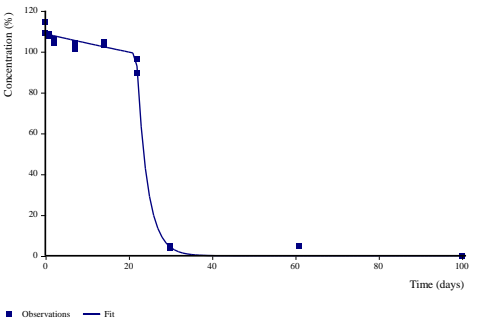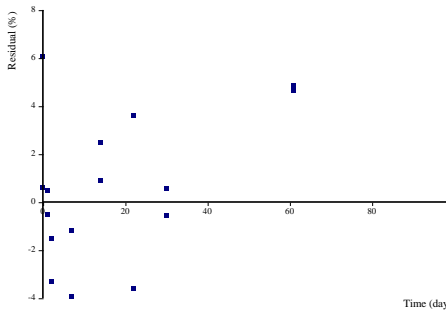
	Observations and Fitted Model	Residuals
SFO		
FOMC		
HS		

Table B. 8.113. Fitted models and residual plots for Ongar Whole System data

	SFO with OLS	FOMC with IRLS	HS with OLS
M_0	119.4	126.6	108.6
k	0.03147		k1 0.004265 k2 0.3869
alpha		1.26E+003	
beta		2.80E+004	
tb			21.84
Visual fit	Poor	Poor	Good
χ^2 % error	24	27.9	2.99
Prob. > t	2.68E-004		k1 0.02008

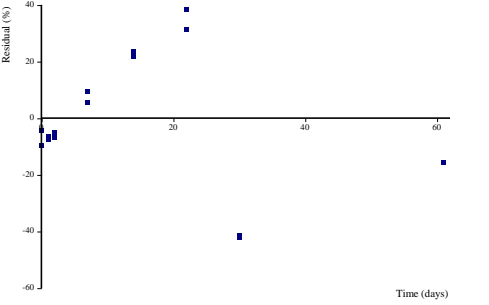|	SFO with OLS	FOMC with IRLS	HS with OLS
			k2 2.80E-005
Lower (90%) CI		α -1850 β -4.124E+04	
Upper (90%) CI		α 4.36E+003 β 9.73E+004	
DT_{50} (days)	22	15.5	23.4*
DT_{90} (days)	73.2	51.4	27.6*
k1 DT_{50} (days)			163
k2 DT_{50} (days)			1.79
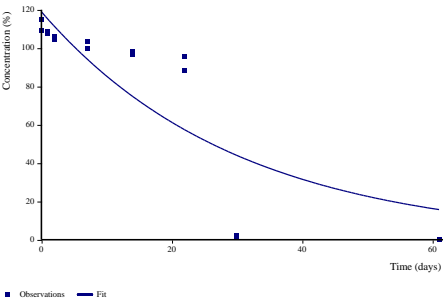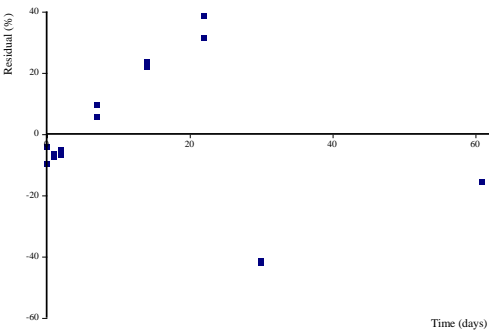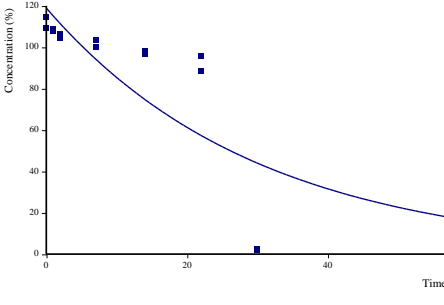
*Overall

Visually SFO fits the data poorly and χ^2 % error is large, 24%. The t-test is passed for SFO (P<0.1). The RMS was unable to get a fit for FOMC with OLS optimisation but achieved a fit with IRLS optimisation. Visually FOMC fits the data similarly to SFO. The confidence intervals for α and β contain zero and the χ^2 % error is larger than for SFO, 27.9%.   Visually HS fits the data well, χ^2 % error is small (2.99%) and the t-test is passed for both k1 and k2. The RMS considers HS the best fit for persistence endpoints; DT_{50} 23.4 days, DT_{90} 27.6 days. For modelling purposes DT_{50} for the HS slow phase represents a conservative value; DT_{50} 163 days.

Ongar – Water

Plots of fitted models and residuals are given in Table B. 8.114 and parameters are listed in Table B. 8.115.

Table B. 8.114. Fitted models and residual plots for Ongar Water data
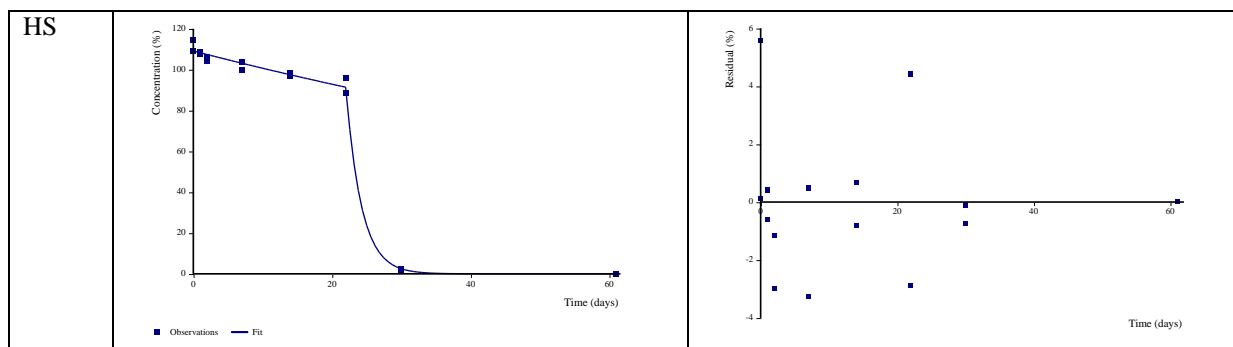
HS

Table B. 8.115. Fitted models and residual plots for Ongar Water data

	SFO with OLS	**FOMC with OLS**	**HS with OLS**
M_0	118.9	118.9	109.1
k	0.03317		k1 0.008068 k2 0.45
alpha		4.82E+005	
beta		1.45E+007	
tb			22
Visual fit	Poor	Poor	Good
X^2 % error	22.8	24.3	1.63
Prob. > t	6.60E-004		k1 1.26E-004 k2 6.07E-004
Lower (90%) CI		α -2.95E+07 β -8.901E+08	
Upper (90%) CI		α 3.05E+007 β 9.19E+008	
DT_{50} (days)	20.9	20.9	23.2*
DT_{90} (days)	69.4	69.4	26.7*
k1 DT_{50} (days)			85.9
k2 DT_{50} (days)			1.54

*Overall value

Visually SFO fits the data poorly and χ^2 % error is large, 22.8%. The t-test is passed for SFO (P<0.05). Visually FOMC fits the data similarly to SFO. The confidence intervals for α and β contain zero and the χ^2 % error is larger than for SFO, 24.3%. Visually HS fits the data well, χ^2 % error is small (1.63%) and the t-test is passed for both k1 and k2. The RMS considers HS the best fit for persistence endpoints; DT_{50} 23.2 days, DT_{90} 26.7 days. For modelling purposes DT_{50} for the HS slow phase represents a conservative value; DT_{50} 85.9 days.

P2 Level

Hazlerigg, 2014, also analysed the data for a two compartment model with transfer between the water and sediment phases – P2 level.   A summary of the results are given in

Table B. 8.116.

Table B. 8.116. Results of the assessment criteria for SFO kinetics fitted to both Manningtree and Ongar data-sets at Level P2

Assessment Criteria	Manningtree	Ongar
Visual Fit:		
For water	Pass	Pass
For sediment	Pass	Pass
Distribution of the residuals:		
For water	Pass	Pass
For sediment	Pass	Pass
Confidence interval around the kinetic parameters:		
Degradation in aqueous phase	Pass	Pass
Degradation in sediment phase	Fail	Fail
Transfer co-efficient from water to sediment	Pass	Pass
Transfer co-efficient from sediment to water	Fail	Fail
χ^2 error test:		
For water	8.622	14.79
For sediment	27.92	70.92
For whole system	11.381	21.17
Back-transfer rate (sediment to water):		
Is the value positive	Yes, Pass	Yes, Pass
***Fsed* test**	0.99, Fail	0.99, Fail

The results at level P2 show that the kinetic fit for two compartment analysis is not acceptable for either Manningtree or Ongar data-sets. The RMS has not repeated the P2 Level fitting.

Summary - P1 level

Table B. 8.117. Persistence (best fit) endpoints

	Manningtree	Ongar
DT_{50} Whole System (d)	58.9 (SFO)	23.4 (HS)
DT_{90} Whole System (d)	196 (SFO)	27.6 (HS)
$DissT_{50}$ Water (d)	51.4 (HS)	23.2 (HS)
$DissT_{90}$ Water (d)	129 (HS)	26.7 (HS)

Table B. 8.118. Modelling endpoints

	Manningtree	Ongar
DT_{50} Whole System (d)	58.9 (SFO)	163 (HS, slow phase)
$DissT_{50}$ Water (d)	83 (HS, slow phase)	85.9 (HS, slow phase)

Report:	CA 7.2.2.3/02, Roohi, A. (2015)
Title	[^{14}C]-mecoprop-P: Route and Rate of Degradation in Two Water/Sediment Systems at 20 ± 2°C Laboratory: Battelle UK Ltd. Report No. WU/14/004
Guidelines:	OECD 308
GLP:	Yes
Deviations	None

Previous evaluations:	None: Submitted for the purpose of renewal under Regulation 844/2012

Executive Summary

The route and rate of degradation of ^{14}C-mecoprop-P was investigated under aerobic conditions at 20 ± 2 °C in two contrasting water/sediment systems in the dark according to OECD 308. [^{14}C]-mecoprop-P was applied to the water surface of individual water sediment systems at a target application rate of 0.138 mg/L in the water phase. The systems were then incubated for up to 98 days, with sampling points at time 0, 7, 14, 29, 56, 81 and 98 days. The overall recovery of radioactivity was good, with mean values of 96.9% AR for Calwich Abbey and 99.7% AR for Swiss Lake. Recoveries within individual flasks were all within the acceptable range of 90-110% AR. In both the Calwich Abbey and Swiss Lake systems, the applied mecoprop-P degraded to form minor metabolites, none exceeding 5% AR. Some partitioning to sediment was observed (max 22.73% AR and 14.91% AR in Calwich Abbey and Swiss Lake systems respectively).

The dissipation of mecoprop-P from the water phase and degradation in the total system was evaluated according to FOCUS (2006) guidance. Under aerobic conditions in the Calwich Abbey system, [^{14}C]-mecoprop-P dissipated rapidly from the water phase after an initial lag phase with a best-fit overall DT_{50} value of 72.5 days (HS model). Dissipation from the water phase was slower in the Swiss Lake system with a DT_{50} of 171 days (SFO). The degradation in the total water/sediment systems again showed differences in the two systems, with best fit DT_{50} values of 83.2 (HS model, overall) and 244 days (SFO) for the Calwich Abbey and Swiss Lake systems, respectively.

In conclusion, [^{14}C]-mecoprop-P in natural water/sediment systems was shown to degrade ultimately to carbon dioxide and unextractable sediment bound residues.

I. MATERIALS AND METHODS

A. MATERIALS

1.	**Test materials:**	Mecoprop-P // [^{14}C]-Mecoprop-P (ring labelled)
	Description:	White solid
	Lot/Batch #:	CN/588/6 // 8113JYC001-3
	Purity:	99.64 % // 99.5 %, 8.24 MBq/mg
	CAS #:	16484-77-8
2.	**Aquatic sediment systems:**	Two natural aquatic sediment systems were sampled from the following locations:

-Calwich Abbey Lake, Ashbourne, Staffordshire, UK (Calwich Abbey), sampled 26th August 2014

- Swiss Lake, Chatsworth, Derbyshire, UK (Swiss Lake), sampled 27th August 2014

- sediment was sieved to <2mm before use

- water was sieved to <212 μm before use

Supplier: Land Research Associates, Derby, UK

Table B. 8.119. Sampling:

	Calwich Abbey	Swiss Lake
Site description	Perennial lake (500x150m) fed by stream from River Dove. Woodland & ley grassland vegetation.	Shallow lake at 250m fed by surface water run-off originating from moorlands, woodland & upland pastures.
Weather conditions	Cloudy, 17°C, following heavy rain for 2 days	Cloudy, 17°C, following heavy rain for 1 day
Collection: sediment	Scooped from top 5cm of sediment	Scooped from top 5cm of sediment
Collection: water	Taken from lake by bucket	Scooped from lake
Shipping conditions	Courier, ambient	
Storage length	9 days	
Storage conditions upon receipt	*ca* 5°, dark	

Table B. 8.120. Sediment:

	Calwich Abbey		Swiss Lake	
	USDA	ADAS	USDA	ADAS
Sand [%]	39	37	87	83
Silt [%]	52	54	8	12
Loam [%]	9	9	8	5
Textural Class	Silt loam	Sandy silt loam	Loamy sand	Loamy sand
CEC* [meq/100 g]	10.7		3.1	
Organic carbon [%]	5.0		0.71	
pH in 1:1 soil:water ratio	7.2		6.6	
pH in 1N KCl	7.1		6.2	
pH in 0.01M CaCl$_2$	7.1		6.1	
Nitrogen [%]	0.42		0.04	
Phosphorus [ppm]	919		142	
Base saturation data [%]:				
- Calcium	80.6		53.9	
- Magnesium	6.3		11.8	
- Sodium	0.9		1.4	
- Potassium	1.0		1.9	
- Hydrogen	11.2		31.0	

* CEC = Cation Exchange Capacity

Table B. 8.121. Water:

	Calwich Abbey	**Swiss Lake**
pH	8.2	7.1
Calcium [ppm]	87	9.1
Magnesium [ppm]	9.6	2.9
Hardness [mg CaCO$_3$/L]	257	35
Alkalinity [mg CaCO$_3$/L]	203	21
Total organic carbon [ppm]	2.6	17.7
Dissolved organic carbon [ppm]	1.6	8.7
Total Nitrogen [ppm]	3.1	1.2
Nitrate-Nitrogen [ppm]	2.7	<0.1*
Total Phosphorus [ppm]	0.3	0.5

* Below limit of detection of 0.1 ppm

Table B. 8.122. Microbial biomass:

Microbial biomass as mg C/kg sediment	**Calwich Abbey**	**Swiss Lake**
Initial (post acclimatisation)	752.1	108.7
Final	891.0	129.5

B.   STUDY DESIGN
1. Dates of experimental work

2 September 2014 – 16 January 2015

2. Experimental conditions

Samples of each water/sediment system were incubated in individual glass flasks with screw top and straight sides of approximately 600 mL capacity (*ca* 6.0 cm diameter). Each flask had an associated air-tight flask head with side-arm fittings to permit the passage of air through the flask. The flasks were connected to a series of trap vessels.

For each water/sediment system 18 flasks were prepared for treatment with [^{14}C]-mecoprop-P, allowing for duplicate samples to be taken at each of the 6 specified time points, whilst leaving 6 spare flasks. Additionally, 4 flasks were prepared and remained untreated.

Approximately 58g oven-dried equivalent of Calwich Abbey sediment and 105g oven dried equivalent of Swiss Lake sediment (each sieved to 2 mm) along with *ca* 340 mL of the associated water, was dispensed into the flasks. A resulting sediment:water ratio of 1:4 v/v was achieved (*ca* 3-4cm depth of sediment with 12cm overlying water).

Once prepared the samples were acclimatised under study conditions for 7 days prior to application of the test item. Study conditions included:
  - Attachment to an incubation system, through which moistened air was bubbled, to allow aeration of the water. Air flow rate was maintained at a uniform flow rate, ensuring that the sediment was not disturbed.
  -Connection to a series of three traps, the first containing ethylene glycol (organic volatiles) and the second and third containing 2M potassium hydroxide (carbon dioxide).
  - Temperature: 20 ± 2°C
  - Light regime: constant darkness

Eight control flasks were prepared for each sediment type for determination of sediment biomass (four for initial and four for final). The four flasks for the final biomass determination were treated with 320 μL of water:acetonitrile 90:10 to mimic test item application. The control flasks were also used to measure water and sediment conditions (pH, oxygen, redox potential) throughout the duration of the study.

3. Preparation and application of the test item

A target dose rate of 0.138 mg/l was calculated based on consideration of direct overspray of a water body of 100cm depth at a treatment rate of 1380 g/ha.

The test item treatment was prepared by transferring 2 mL of supplied stock solution to a 20 mL volumetric flask, making to volume with acetonitrile:water 10:90. Aliquots (100 μL) of this solution were diluted to 25 mL with acetonitrile and triplicate 100 μL aliquots of this solution were counted by LSC to determine the exact concentration. The treatment solution concentration was determined to be 0.145 mg/mL.

The water/sediment systems were treated with the [^{14}C]-mecoprop-P solution (320 μL) using a positive displacement pipette, adding the solution drop-wise to the surface.

4. Sampling

Measurements were taken from the control flasks to determine the redox potential and pH of both the water and sediment phases. The dissolved oxygen content was also measured for the water phase.

The trapping solutions were connected in series to the incubation flasks. Moist air was bubbled constantly, at a consistent rate, through the flasks and trap vessels during the course of the study. The traps were removed and replaced at appropriate intervals to ensure efficient trapping of evolved volatile metabolites.

Samples were taken for analysis at the following time points: 0, 7, 14, 29, 56, 81, 98 days.

Water and sediment samples were processed on the day of sampling and generally profiled by HPLC on the same day, with the exception of the water samples for day 56, which were analysed ca 24 hours after generation. Prior to analysis the samples were kept refrigerated (< 5°C).

5. Description of analytical procedures

<u>Analytical techniques</u>

Quantitative measurement of radioactivity was carried out by liquid scintillation counting (LSC) following solubilisation of the samples in an LSC cocktail. The limit of quantitation for LSC analysis is reported as 0.2ng.

With the exception of time zero samples, trap solutions were removed for analysis at each sampling interval and the radioactivity present was determined by LSC. The radioactivity collected in the potassium hydroxide traps was confirmed to be $^{14}CO_2$ by barium carbonate precipitation.

For determination of unextractable radioactivity the sediment samples were air-dried (until day 29) or not dried (day 56 onwards) and ground into a fine powder. The samples were then weighed and combusted. The combustion products were absorbed in Carbosorb E and mixed with Permafluor E+ prior to quantification of the radioactivity by LSC.

<u>Sample analysis</u>

When sampling the water phase the water was poured into a glass measuring cylinder, taking care not to disturb the sediment. The volume was measured and aliquots taken for LSC.

Sediment was extracted with ca 100 mL of acetonitrile, shaken, centrifuged (ca 2500 rpm for 10 minutes) and the supernatant was decanted. The process was then repeated with two 100 mL portions of acetonitrile:water (80:20 v/v). The three extracts were combined and radioactivity determined by LSC.

Following extraction and quantification of the levels of radioactivity remaining unextracted, the sediment residues were further characterised by organic matter fractionation. For this Sodium hydroxide (0.5M, 20 mL) was added to a portion (*ca* 10 g) of extracted air-dried sediment, shaken (24 hours), centrifuged (2000 rpm for 10 minutes) and the dark coloured supernatant removed. The remaining sediment was washed with sodium hydroxide solution (0.5M, 2 x 10 mL) followed by distilled water (3 x 10 mL). The sodium hydroxide extract and washings were combined, the volume measured and aliquots taken for LSC. The aqueous solution was then acidified to pH 2 with hydrochloric acid, centrifuged (2000 rpm for 10 minutes), measured and assayed for radioactivity by LSC (fulvic acid fraction). The remaining precipitate (humic acid fraction) was re-dissolved in sodium hydroxide (0.5M), the volume was measured and the radioactivity assayed by LSC. The humin fraction was determined as the difference between the radioactivity in the original sediment sample and that in the fulvic acid and humic acid fractions.

Chromatographic and spectroscopic procedures

Water and sediment extracts were analysed by high performance liquid chromatography (HPLC) using the conditions specified in Table B. 8.123. The limit of quantitation is reported as 0.28%AR for HPLC analysis. To verify that all radioactive material injected onto the HPLC column was eluted, column recoveries were carried out for selected samples (range 98.2% to 110.5%, mean 104.1%).

Table B. 8.123. HPLC conditions for water and sediment extract analysis

Column	Phenomemex Kromasil C18, 250 x 4.6 mm i.d		
Mobile phase	A) 1.5% formic acid (v/v) in 80/20 water/acetonitrile (v/v)		
	B) 1.5% formic acid (v/v) in 30/70 water/acetonitrile (v/v)		
	Time (minutes)	A%	B%
	0	100	0
	23	0	100
	28	0	100
	32	100	0
	40	100	0
Temperature	Ambient		
Injection volume	Standards 10 µL, samples generally 200 µL		
Flow rate	1 mL/min		
Scintillant	FloLogic; flow rate 1.5 mL/min		
UV wavelength	254 nm		

LC-MS was used to confirm the identity of the [^{14}C]-mecoprop-P in the application solution at the start of the study and in selected water samples and sediment extracts. Analyses were carried out on a Thermo Q-Exactive Orbitrap mass spectrometer in negative ion Heated Electrospray Ionisation (HESI-) mode using the HPLC conditions and the mass spectrometric conditions given in Table B. 8.124 and Table B. 8.125, respectively.

Table B. 8.124. HPLC conditions for confirming the identity of [^{14}C]-mecoprop-P

Column	Kromasil C18 5µm (250 x 4.6 mm)		
Mobile phase	A) 0.2% acetic acid in water		
	B) 0.2% acetic acid in acetonitrile		
	Time (minutes)	A%	B%
	0	80	20
	23	30	70
	28	30	70
	32	80	20
	40	80	20
Injection volume	20 – 100 µL		
Flow rate	1 mL/min with ca 200 µL/min into MS ion source		
Scintillant	FloLogic; flow rate 1.5 mL/min		
[14C]-detection	LabLogic β-Ram model 3 radiodetected fitted with a 0.5 mL liquid flow cell utilising Pro Flo G+ liquid scintillation cocktail at 1.5 mL/minute		

Table B. 8.125. Mass spectrometric conditions for confirming the identity of [^{14}C]-mecoprop-P

Tune parameters	
Ion source	Heated electrospray ionisation (HESI)
Spray voltage	Negative 2.5 kV
Capillary temperature	300°C
Sheath gas	65
Aux gas	25
Probe heater temp.	350°C
S-lens RF level	55
Full MS Conditions	
Polarity	Negative
In source CID	0.0 eV
Resolution	70,000
AGC target	1e6
Max IT	130 ms
Scan range	100 to 500 m/z

For identification and confirmation analyses the standards and samples were analysed using LC-FTMS HR/AM (High Resolution/Accurate Mass).

6. Degradation kinetics

DT_{50} and DT_{90} values for the degradation of [^{14}C]-mecoprop-P in the water phase and in the total water/sediment systems were determined following the recommendations of the FOCUS work group. The degradation kinetics were estimated according to FOCUS recommended procedures, using the software CAKE v2.0. A model input data set was derived from the individual data for each time point, for both the water phase and the total system.

The models SFO, FOMC, DFOP and HS were tested in order to determine the best-fit kinetic model. The best-fit kinetic model was selected based upon a visual assessment of the goodness of fit and the χ^2 scaled-error criterion. The significance of the estimated parameters was also confirmed by a single-sided t-test. A t-test probability of <0.05 (>95% parameter significance) is usually considered sufficiently small.

II.   RESULTS AND DISCUSSION

A. EXPERIMENTAL CONDITIONS

Water pH averaged 7.7 for the Calwich Abbey system and 7.4 for the Swiss Lake system. Oxygen measurements demonstrate that the water column remained aerobic throughout the study period (mean 8.8 and 8.6 mg/l for Calwich Abbey and Swiss Lake systems respectively). Sediment biomass results demonstrate the viability of the systems (Table B. 8.122).

B. DISTRIBUTION OF RADIOACTIVITY & MASS BALANCE

The recovery and distribution of the applied radioactivity in the water/sediment systems are summarised in

Table B. 8.126 and Table B. 8.127.

Table B. 8.126. Distribution and recovery of radioactivity in Calwich Abbey system (as % of applied radioactivity)

Incubation time (days)	Water	Sediment extracts (1-3)	Unextracted	Total in sediment (extracted + unextracted)	Total volatiles	Total
0	101.98	0.01	0.00	0.01	-	101.98
	100.66	0.00	0.00	0.00	-	100.66
Mean	**101.32**	**0.00**	**0.00**	**0.00**	**-**	**101.32**
7	92.36	8.94	0.52	9.46	0.10	101.92
	97.88	2.53	0.10	2.63	0.04	100.54
Mean	**95.12**	**5.74**	**0.31**	**6.05**	**0.07**	**101.23**
14	81.04	14.06	1.78	15.85	0.32	97.21
	84.98	11.58	1.34	12.92	0.73	98.63
Mean	**83.01**	**12.82**	**1.56**	**14.38**	**0.53**	**97.92**
29	75.10	19.16	1.61	20.77	0.38	96.25
	72.17	20.21	2.19	22.40	0.03	94.59
Mean	**73.63**	**19.69**	**1.90**	**21.59**	**0.20**	**95.42**
56	60.19	22.48	7.37	29.85	3.80	93.84
	57.12	23.59	7.16	30.76	6.04	93.91
Mean	**58.65**	**23.04**	**7.27**	**30.30**	**4.92**	**93.87**
81	46.36	20.13	13.65	33.78	16.00	96.13
	50.08	21.30	10.02	31.32	13.62	95.01
Mean	**48.22**	**20.71**	**11.83**	**32.55**	**14.81**	**95.57**
98	4.15	6.36	33.19	39.56	49.34	93.05
	4.06	6.89	31.44	38.34	50.76	93.16
Mean	**4.11**	**6.63**	**32.32**	**38.95**	**50.05**	**93.10**
					Average	**96.89**

Table B. 8.127. Distribution and recovery of radioactivity in Swiss Lake system (as % of applied radioactivity)

Incubation time (days)	Water	Sediment extracts (1-3)	Unextracted	Total in sediment (extracted + unextracted)	Total volatiles	Total
0	100.58	0.00	0.00	0.00	-	100.58
	101.67	0.00	0.00	0.00	-	101.67
Mean	**101.12**	**0.00**	**0.00**	**0.00**	**-**	**101.12**
7	88.42	10.78	0.71	11.49	0.25	100.16
	94.65	6.26	0.43	6.69	0.16	101.49
Mean	**91.53**	**8.52**	**0.57**	**9.09**	**0.20**	**100.83**
14	81.91	14.91	2.27	17.18	0.79	99.88
	82.21	11.12	2.42	13.54	2.31	98.06
Mean	**82.06**	**13.02**	**2.35**	**15.36**	**1.55**	**98.97**
29	86.59	11.88	0.75	12.63	0.24	99.46
	86.71	12.45	1.00	13.45	0.15	100.31
Mean	**86.65**	**12.17**	**0.88**	**13.04**	**0.19**	**99.88**
56	79.06	12.19	3.82	16.01	4.58	99.65
	74.51	13.43	7.78	21.21	5.51	101.24
Mean	**76.79**	**12.81**	**5.80**	**18.61**	**5.04**	**100.44**
81	71.68	10.32	4.53	14.85	10.88	97.42
	73.08	12.64	4.22	16.86	9.70	99.65
Mean	**72.38**	**11.48**	**4.37**	**15.86**	**10.29**	**98.53**
98	63.38	11.21	7.06	18.27	13.68	95.33
	61.96	11.73	13.64	25.37	13.21	100.54
Mean	**62.67**	**11.47**	**10.35**	**21.82**	**13.45**	**97.93**

Average	99.67

The mean recovery from the systems during the 98 day incubation period were 96.9% and 99.7% for Calwich Abbey and Swiss Lake, respectively. Calwich Abbey recoveries ranged from 92.7% to 102.0% and Swiss Lake recoveries ranged from 95.3% to 101.7%. The levels of recovery were therefore acceptable for the study.

In the Calwich Abbey system the levels of radioactivity in the water declined steadily from 101.3% AR to 48.2% AR at day 81. After this initial lag phase, however, the rate of decline from the water accelerated rapidly, reaching 4.1% AR at day 98. The total extractable radioactivity in the sediment rose from 0.0% AR at time zero to a maximum of 23.0% at day 56 before declining to 6.6% at the end of the study at day 98. The unextracted radioactivity rose from 0.0% at time zero to 32.3% at day 98. The presence of an initial metabolic lag phase was also evident in the evolution of CO_2. Over the first 56 days only 4.9% CO_2 was released, however, this had increased to 14.8% AR by day 81 and reached 50.1 % AR by day 98.

In the Swiss Lake system there was a slower transfer of the applied radioactivity from the water to the sediment, when compared with Calwich Abbey system, and thus resulting in a much greater percentage of applied radioactivity remaining in the water at the end of the incubation period. The radioactivity in the water declined from 101.1% AR at time zero to 62.7% AR by day 98. The total radioactivity in the sediment increased from 0.0% at time zero to 21.8% by day 98, with the extractable portion reaching a maximum of 12.8% AR at day 56 and the unextractable reaching a maximum of 10.4% AR at day 98. The degree of mineralisation to CO_2 was less than in the Calwich Abbey system accounting for 13.5% AR by day 98.

Unextracted residue fractionation was conducted on individual selected samples to assess the composition. The results of the fractionation are presented in Table B. 8.128 below.

Table B. 8.128. Results of unextracted residue fractionation

Sample	As % of applied radioactivity			
	Fulvic acid	**Humic acid**	**Humin**	**Total**
Calwich Abbey Day 98	0.10	8.02	15.22	23.34
Swiss Lake Day 98	0.05	3.97	4.51	8.53
	As % of total non-extractable			
Calwich Abbey Day 98	0.43	34.35	65.22	100
Swiss Lake Day 98	0.61	46.53	52.87	100

C.   PROFILE OF COMPONENTS

Whole System

The profile of components extracted from the whole system (water and sediment) of Calwich Abbey and Swiss Lake   systems   are   summarised   in

Table B. 8.129 and Table B. 8.130 respectively.

In the total Calwich Abbey system, comprising sediment and overlying water, mecoprop-P declined from 101.3% AR at time zero to 66.8% AR at day 81. After day 81, degradation accelerated rapidly such that only 8.7% AR remained as mecoprop-P by day 98.

In the total Swiss Lake system, the applied mecoprop-P declined more steadily, from 101.1% AR at time zero to 73.4% AR at day 98.

Several minor metabolites were detected throughout the course of the study but none exceeded 5% AR at any time point in the total system (combined water and sediment) of either system (max reported; 1.81% AR, Calwich Abbey system, day 81).

Table B. 8.129. Composition of radioactivity in total water/sediment system, Calwich Abbey (as % of applied radioactivity by HPLC)

Incubation time (days)	% AR	Unknown RRT 0.35-0.64	Unknown RRT 0.94-0.96	Mecoprop-P RRT 1.00
0	101.98	-	-	101.98
	100.66	-	-	100.66
Mean	**101.32**	**-**	**-**	**101.32**
7	101.30	0.14	-	101.16
	100.41	0.45	-	99.96
Mean	**100.85**	**0.29**	**-**	**100.56**
14	95.10	-	0.40	94.70
	96.56	-	0.25	96.32
Mean	**95.83**	**-**	**0.32**	**95.51**
29	94.27	-	0.56	93.71
	92.38	-	0.61	91.76
Mean	**93.32**	**-**	**0.59**	**92.73**
56	82.67	0.22	0.96	81.49
	80.71	0.16	0.86	79.69
Mean	**81.69**	**0.19**	**0.91**	**80.59**
81	66.49	1.01	1.03	64.45
	71.37	0.48	1.81	69.08
Mean	**68.93**	**0.75**	**1.42**	**66.76**
98	10.52	0.00	1.53	8.99
	10.96	0.79	1.72	8.45
Mean	**10.74**	**0.39**	**1.63**	**8.72**

Table B. 8.130. Composition of radioactivity in total water/sediment system, Swiss Lake (as % applied radioactivity by HPLC)

Incubation time (days)	% AR	Unknown RRT 0.35-0.64	Unknown RRT 0.94-0.96	Mecoprop-P RRT 1.00	Unknown RRT 1.06
0	100.58	-	-	100.58	-
	101.67	-	-	101.67	-
Mean	**101.12**	**-**	**-**	**101.12**	**-**
7	99.20	-	-	99.20	-
	100.91	-	-	100.91	-
Mean	**100.05**	**-**	**-**	**100.05**	**-**
14	96.82	-	-	96.82	-
	93.33	-	-	93.33	-
Mean	**95.07**	**-**	**-**	**95.07**	**-**
29	98.47	-	-	98.47	-
	99.16	-	-	99.16	-
Mean	**98.82**	**-**	**-**	**98.82**	**-**
56	91.25	-	-	91.25	-
	87.94	-	-	87.94	-
Mean	**89.60**	**-**	**-**	**89.60**	**-**
81	82.01	1.06	0.23	80.51	0.20
	85.72	0.43	0.00	85.29	0.00
Mean	**83.87**	**0.75**	**0.11**	**82.90**	**0.10**
98	74.60	0.51	0.16	73.92	0.00
	73.68	0.72	0.00	72.96	0.00
Mean	**74.14**	**0.62**	**0.08**	**73.44**	**0.00**

Water

The profile of components extracted from the water phase of Calwich Abbey and Swiss Lake systems are summarised in Table B. 8.131 and Table B. 8.132, respectively.

In the Calwich Abbey system, mecoprop-P declined steadily from 101.3% AR at time zero to 47.5% AR at day 81 but degradation then accelerated rapidly with only 3.7% AR remaining as mecoprop-P at day 98. In the Swiss Lake system, mecoprop-P declined at a steadier rate from 101.1% at time zero to 62.1% by day 98. In both systems, several minor metabolites were observed, none of which accounted for more than (mean) 0.8% AR (max reported; 1.06 %AR, day 81, Swiss Lake system).

Table B. 8.131. Composition of radioactivity in water phase, Calwich Abbey system (as % applied radioactivity by HPLC)

Incubation time (days)	% AR	Unknown RRT 0.35-0.64	Unknown RRT 0.94-0.96	Mecoprop-P RRT 1.00
0	101.98	-	-	101.98
	100.66	-	-	100.66
Mean	**101.32**	**-**	**-**	**101.32**
7	92.36	0.00	-	92.36
	97.88	0.45	-	97.43
Mean	**95.12**	**0.23**	**-**	**94.89**
14	81.04	-	-	81.04
	84.98	-	-	84.98
Mean	**83.01**	**-**	**-**	**83.01**
29	75.10	-	-	75.10
	72.17	-	-	72.17
Mean	**73.63**	**-**	**-**	**73.63**
56	60.19	0.22	-	59.97
	57.12	0.16	-	56.96
Mean	**58.65**	**0.19**	**-**	**58.46**
81	46.36	1.01	-	45.35
	50.08	0.48	-	49.60
Mean	**48.22**	**0.75**	**-**	**47.47**
98	4.15	0.00	-	4.15
	4.06	0.79	-	3.28
Mean	**4.11**	**0.39**	**-**	**3.71**

Table B. 8.132. Composition of radioactivity in water phase, Swiss Lake system (as % applied radioactivity by HPLC)

Incubation time (days)	% AR	Unknown RRT 0.35-0.64	Unknown RRT 0.94-0.96	Mecoprop-P RRT 1.00	Unknown RRT 1.06
0	100.58	-	-	100.58	-
	101.67	-	-	101.67	-
Mean	**101.12**	**-**	**-**	**101.12**	**-**
7	88.42	-	-	88.42	-
	94.65	-	-	94.65	-
Mean	**91.53**	**-**	**-**	**91.53**	**-**
14	81.91	-	-	81.91	-
	82.21	-	-	82.21	-
Mean	**82.06**	**-**	**-**	**82.06**	**-**
29	86.59	-	-	86.59	-
	86.71	-	-	86.71	-
Mean	**86.65**	**-**	**-**	**86.65**	**-**
56	79.06	-	-	79.06	-

Incubation time (days)	% AR	Unknown RRT 0.35-0.64	Unknown RRT 0.94-0.96	Mecoprop-P RRT 1.00	Unknown RRT 1.06
	74.51	-	-	74.51	-
Mean	**76.79**	**-**	**-**	**76.79**	**-**
81	71.68	1.06	0.23	70.19	0.20
	73.08	0.43	0.00	72.65	0.00
Mean	**72.38**	**0.75**	**0.11**	**71.42**	**0.10**
98	63.38	0.51	-	62.87	-
	61.96	0.72	-	61.23	-
Mean	**62.67**	**0.61**	**-**	**62.05**	**-**

Sediment

The profile of components extracted from the sediment phase of Calwich Abbey and Swiss Lake systems are summarised in Table B. 8.133 and

Table B. 8.134, respectively.

In the Calwich Abbey system, HPLC analysis showed that mecoprop-P reached a maximum level of 22.1% AR at day 56 and subsequently declined to 5.0% AR by day 98. Two minor metabolites were detected, neither accounting for (mean) >1.6% AR (max reported; 1.81%AR, day 81).

In the Swiss Lake system, HPLC analysis showed that mecoprop-P reached a maximum level of 13.0% AR at day 14 and declined to 11.4% AR by the end of the study. A single minor metabolite was observed at (mean) 0.1% AR at day 98 (max reported; 0.16%AR, day 98).

Table B. 8.133. Composition of radioactivity in combine sediment extracts, Calwich Abbey system (as % applied radioactivity by HPLC)

Incubation time (days)	% AR	Unknown RRT 0.46-0.64	Unknown RRT 0.94-0.96	Mecoprop-P RRT 1.00
0	0.01	<4% AR – not analysed		
	0.00			
Mean	**0.00**			
7	8.94	0.14	-	8.80
	2.53	0.00	-	2.53
Mean	**5.74**	**0.07**	**-**	**5.67**
14	14.06	-	0.40	13.66
	11.58	-	0.25	11.34
Mean	**12.82**	**-**	**0.32**	**12.50**
29	19.16	-	0.56	18.60
	20.21	-	0.61	19.60
Mean	**19.69**	**-**	**0.59**	**19.10**
56	22.48	-	0.96	21.52
	23.59	-	0.86	22.73
Mean	**23.04**	**-**	**0.91**	**22.13**
81	20.13	-	1.03	19.10
	21.30	-	1.81	19.48
Mean	**20.71**	**-**	**1.42**	**19.29**
98	6.36	-	1.53	4.84
	6.89	-	1.72	5.17
Mean	**6.63**	**-**	**1.63**	**5.00**

Table B. 8.134. Composition of radioactivity in combined sediment extracts, Swiss Lake system (as % applied radioactivity by HPLC)

Incubation time (days)	% AR	Unknown RRT 0.94-0.96	Mecoprop-P RRT 1.00
0	0.00	<4% AR – not analysed	
	0.00		
Mean	**0.00**		
7	10.78	-	10.78
	6.26	-	6.26
Mean	**8.52**	**-**	**8.52**
14	14.91	-	14.91
	11.12	-	11.12
Mean	**13.02**	**-**	**13.02**
29	11.88	-	11.88
	12.45	-	12.45
Mean	**12.17**	**-**	**12.17**
56	12.19	-	12.19
	13.43	-	13.43
Mean	**12.81**	**-**	**12.81**
81	10.32	-	10.32
	12.64	-	12.64
Mean	**11.48**	**-**	**11.48**
98	11.21	0.16	11.05
	11.73	0.00	11.73
Mean	**11.47**	**0.08**	**11.39**
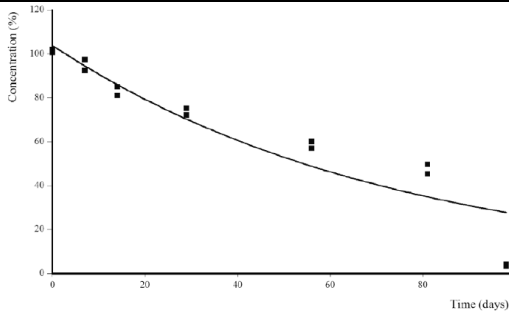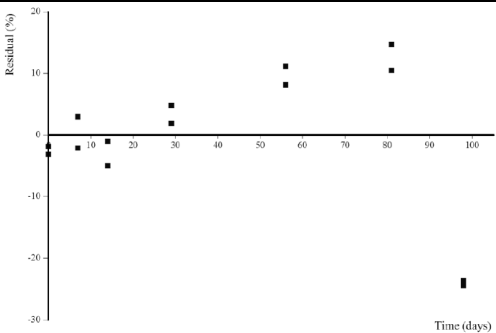
D.   DEGRADATION RATE

Degradation rates were modelled using CAKE v2.0. Fits were optimised using IRLS. All recorded data were included and were unweighted. Time zero values were set to the recorded mass balance and all radioactivity was considered to be in the water column. M_0 was not fixed for model fitting.

Calwich Abbey – Water

Plots of fitted models and residuals are given in Table B. 8.135 and parameters are listed in Table B. 8.136.

Table B. 8.135. Fitted models and residual plots for water in the Calwich Abbey system
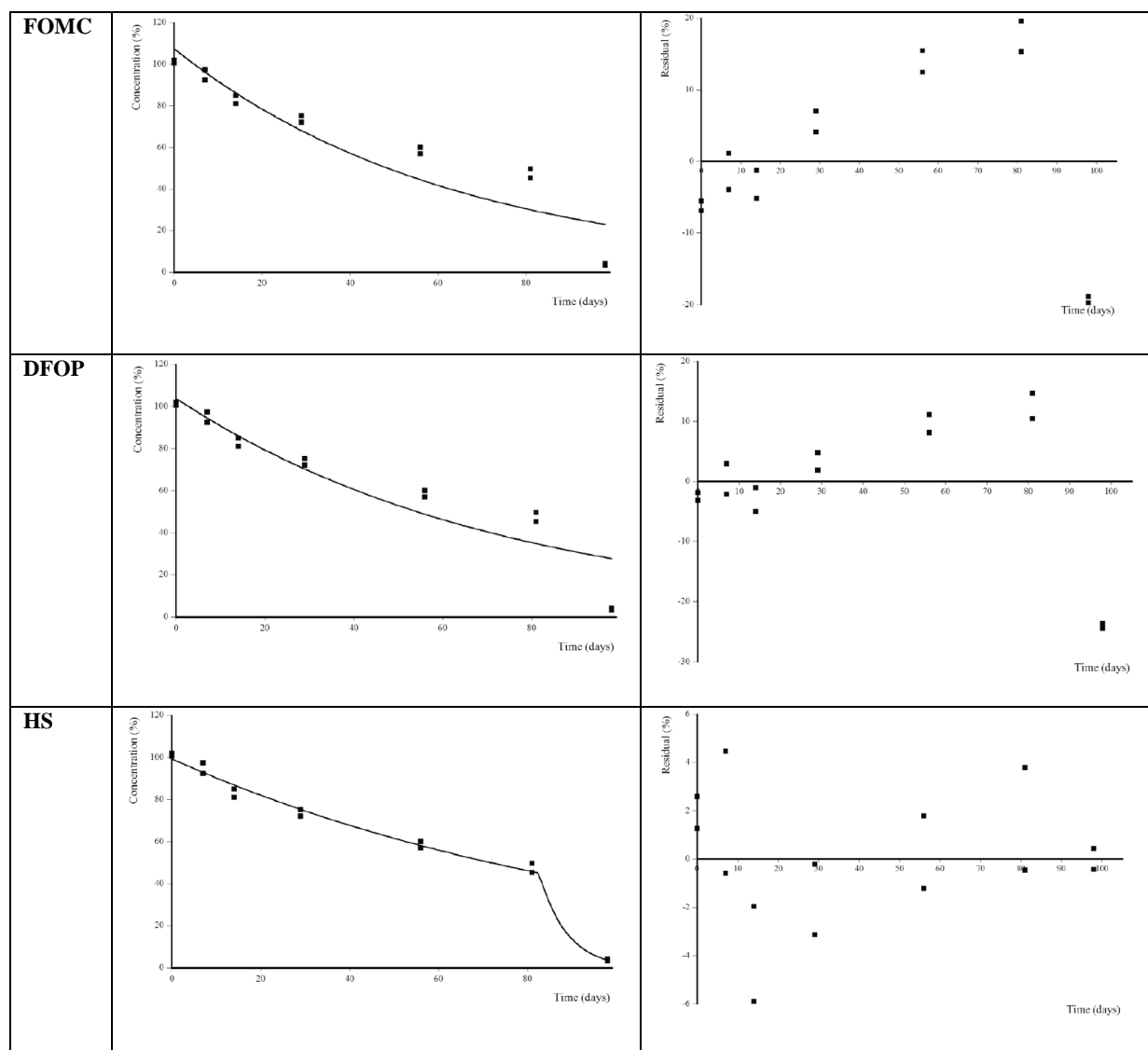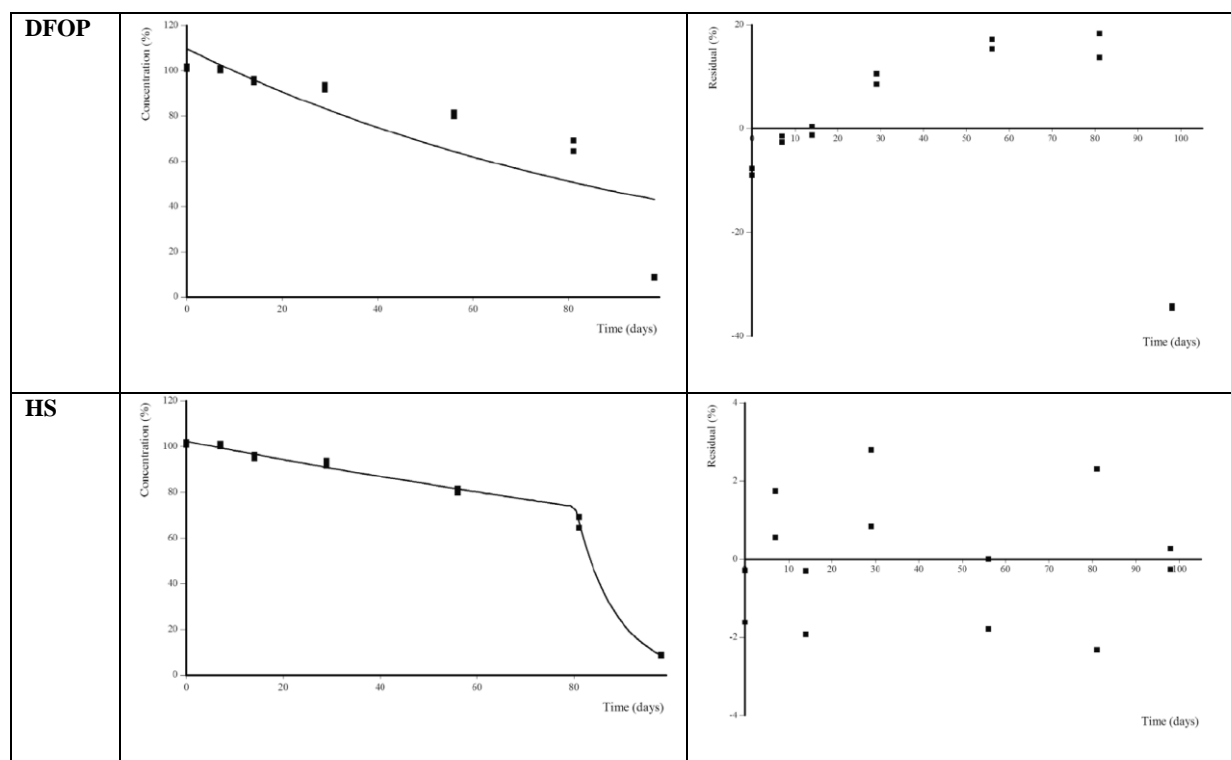
FOMC		
DFOP		
HS		

Table B. 8.136. Kinetic fit parameters for water in the Calwich Abbey system

Fit (Optimisation)	SFO (IRLS)	FOMC (IRLS)	DFOP (IRLS)	HS (IRLS)
M_0	103.8	107.5	103.8	99.38
k	0.01346		k1 0.01346 k2 0.01346	k1 0.009564 k2 0.1619
alpha		206.5		
beta		1.31E+004		
g			0.2341	
tb				82.58
Visual fit	Poor	Poor	Poor	Good
χ^2 % error	13.3	15.2	15.8	2.89
Prob. > t	9.90E-006		k1 0.5 k2 0.5	k1 1.50E-009 k2 0.4714
Lower (90%) CI		α -727.3 β 4.623E+04		
Upper (90%) CI		α 1.14E+003 β 7.24E+004		
DT_{50} (days)	51.5	44	51.5*	72.5*
DT_{90} (days)	171	147	171*	91.9*

Fit (Optimisation)	SFO (IRLS)	FOMC (IRLS)	DFOP (IRLS)	HS (IRLS)
k1 DT_{50} (days)			51.5	72.5
k2 DT_{50} (days)			51.5	4.28

*Overall

SFO: Visually fits the data poorly. χ^2 % error is acceptable (13.3%) and the t-test is passed (P<0.1).

FOMC: Visually fits the data poorly. χ^2 % error is higher than for SFO (15.2%) and the confidence interval for α contains zero.

DFOP: Visually fits the data poorly. χ^2 % error is higher than for SFO (15.8%). The t-test is failed for both k1 and k2.
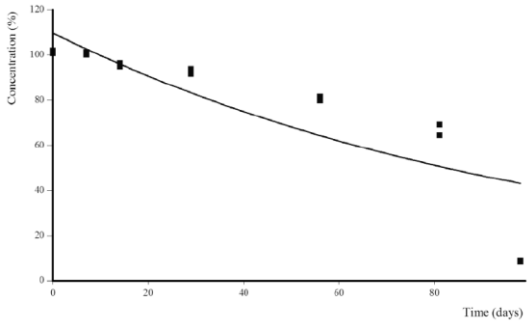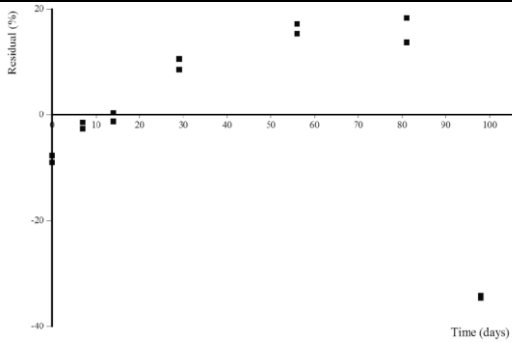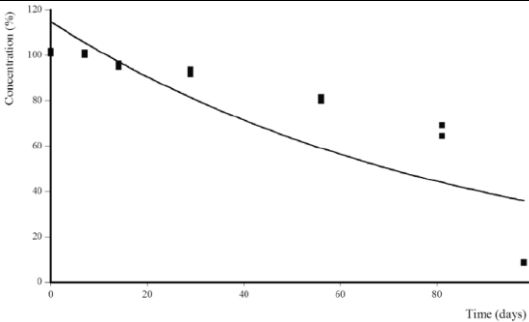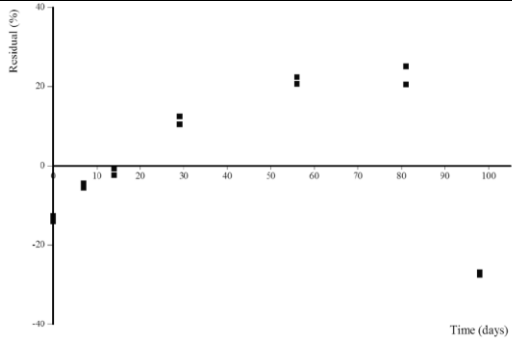
HS: Visually fits the data well. χ^2 % error is low (2.89%). The t-test is passed for k1 but not for k2.

The RMS has validated the study modelling using OLS optimisation and achieved the same kinetic fits. The RMS agrees with the study author that Hockey Stick is the best-fit model for persistence endpoints for the Calwich Abbey water column; DT_{50} 72.5 days, DT_{90} 91.9 days. For modelling purposes, the study author has calculated the DT_{50} from the overall HS $DT_{90}/3.32$, however, the RMS considers the DT_{50} for the HS slow phase should be used as a conservative value; DT_{50} 72.5 days.

Calwich Abbey – Total System

Plots of fitted models and residuals are given in Table B. 8.137 and parameters are listed in Table B. 8.138.

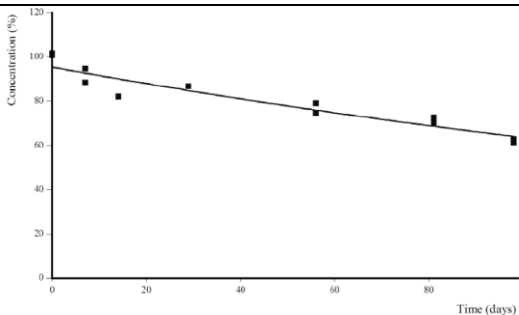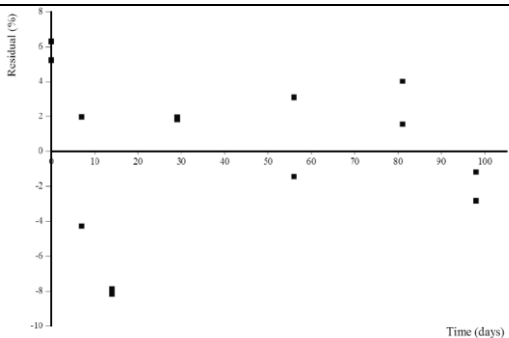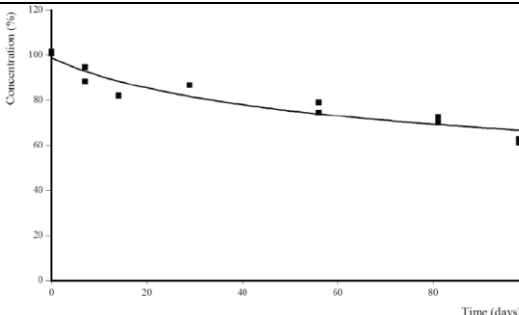Table B. 8.137. Fitted models and residual plots for the total system in the Calwich Abbey system
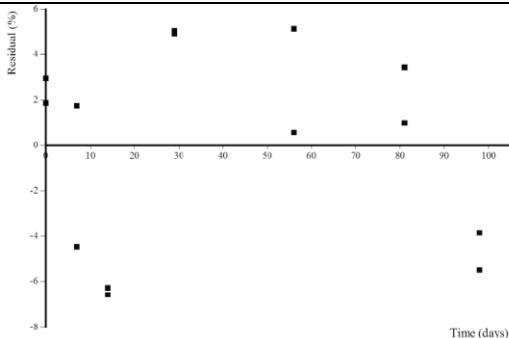
DFOP		
HS		

Table B. 8.138. Kinetic fit parameters for the total system in the Calwich Abbey system

Fit (Optimisation)	SFO (IRLS)	FOMC (IRLS)	DFOP (IRLS)	HS (IRLS)
M_0	109.7	114.7	109.7	102.3
k	0.009523		k1 0.009524 k2 0.009523	k1 0.00406 k2 0.1197
alpha		152.2		
beta		1.28E+004		
g			0.1498	
tb				80.16
Visual fit	Poor	Poor	Poor	Good
χ^2 % error	16.7	18.9	19.8	1.26
Prob. > t	4.25E-004		k1 0.5 k2 0.5	k1 2.38E-007 k2 3.37E-008
Lower (90%) CI		α -362.1 β -3.062E+04		
Upper (90%) CI		α 666.5 β 5.63E+004		
DT_{50} (days)	72.8	58.5	72.8*	83.2*
DT_{90} (days)	242	195	242*	96.7*
k1 DT_{50} (days)			72.8	171
k2 DT_{50} (days)			72.8	5.79

*Overall

SFO: Visually fits the data poorly. χ^2 % error is 16.7% and the t-test is passed (P<0.1).
FOMC: Visually fits the data poorly. χ^2 % error is higher than for SFO (18.9%) and the confidence interval for α and β contain zero.
DFOP: Visually fits the data poorly. χ^2 % error is higher than for SFO (19.8%). The t-test is failed for both k1 and k2.
HS: Visually fits the data well. χ^2 % error is low (1.26%). The t-test is passed for k1 and k2.

The RMS has validated the study modelling using OLS optimisation and achieved the same kinetic fits. The RMS agrees with the study author that Hockey Stick is the best-fit model for persistence endpoints for the Calwich Abbey total system; DT_{50} 83.2 days, DT_{90} 96.7 days. For modelling purposes, the study author has calculated the DT_{50} from the overall HS $DT_{90}/3.32$, however, the RMS considers the DT_{50} for the HS slow phase should be used as a conservative value; DT_{50} 171 days.

Swiss Lake - Water

Plots of fitted models and residuals are given in Table B. 8.139 and parameters are listed in Table B. 8.140.

Table B. 8.139. Fitted models and residual plots for water in the Swiss Lake system

Table B. 8.140. Kinetic fit parameters for water in the Swiss Lake system

Fit (Optimisation)	SFO (IRLS)	FOMC (IRLS)
M_0	95.37	98.71
k	0.00406	
alpha		0.2456
beta		24.95
Visual fit	good	good
χ^2 % error	3.95	4.14
Prob. > t	8.58E-007	
Lower (90%) CI		α 0.001968 β -23.45
Upper (90%) CI		α 0.4892 β 73.35
DT_{50} (days)	171	395
DT_{90} (days)	567	2.95E+05

SFO: Visually fits the data well. χ^2 % error is low (3.95%) and the t-test is passed (P<0.1).
FOMC: Visually fits the data well. χ^2 % error is marginally higher than for SFO (4.14%) and the confidence interval for βcontains zero.

The RMS has validated the study modelling using OLS optimisation and achieved the same kinetic fits. The RMS agrees with the study author that SFO is the best-fit model for persistence and modelling endpoints for the Swiss Lake water column; DT_{50} 171 days, DT_{90} 567 days.

Swiss Lake - Total System

Plots of fitted models and residuals are given in Table B. 8.141 and parameters are listed in

Table B. 8.142.

Table B. 8.141. Fitted models and residual plots for the total system in the Swiss Lake system

	Observations and Fitted Model	Residuals
SFO		
FOMC		
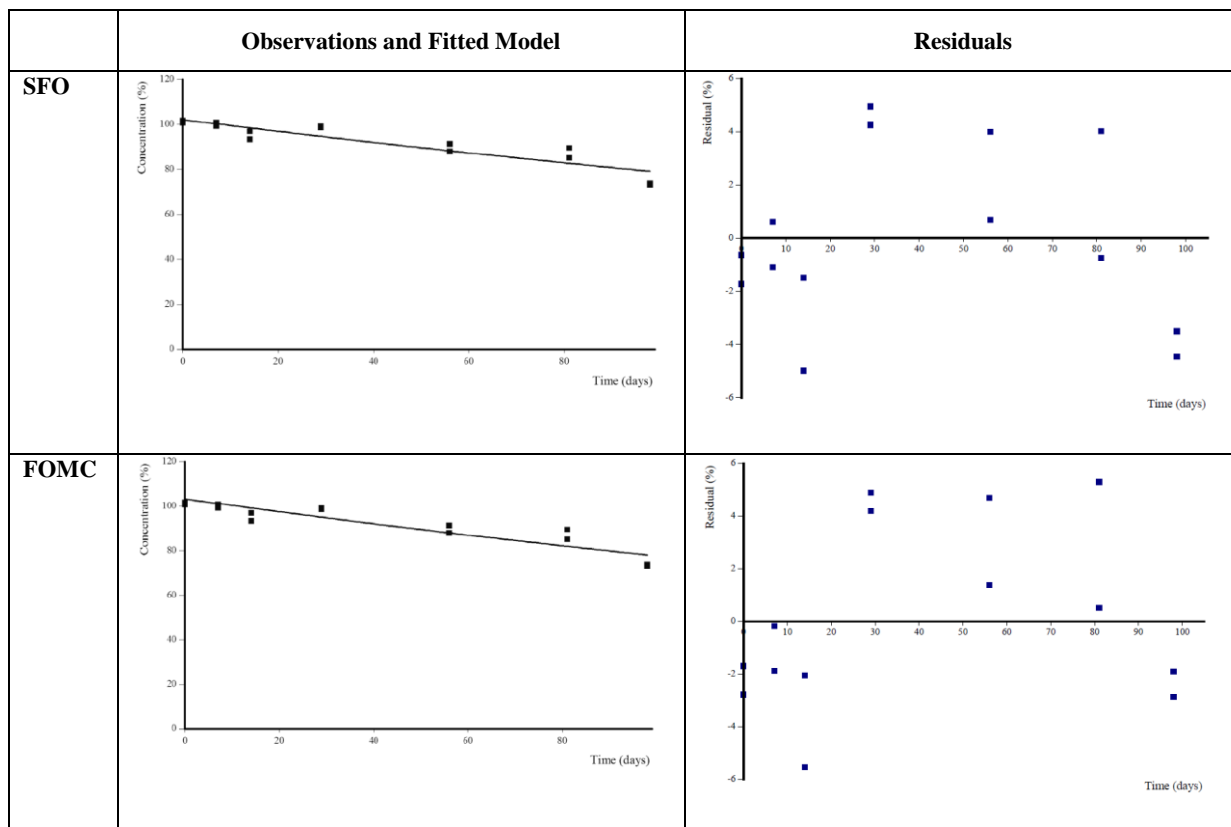
Table B. 8.142. Kinetic fit parameters for the total system in the Swiss Lake system

Fit (Optimisation)	SFO (IRLS)	FOMC (IRLS)
M_0	102.3	103.4
k	0.002844	
alpha		26.05
beta		8.19E+003
Visual fit	good	good
χ^2 % error	2.48	2.84
Prob. > t	5.93E-007	
Lower (90%) CI		α 13.7 β 4.29E+003
Upper (90%) CI		α 38.39 β 1.21E+004
DT_{50} (days)	244	221
DT_{90} (days)	810	757

SFO: Visually fits the data well. χ^2 % error is low (2.48%) and the t-test is passed (P<0.1).

FOMC: Visually fits the data well. χ^2 % error is marginally higher than for SFO (2.84%) and the confidence interval for α and β do not contain zero.

The RMS has validated the study modelling using OLS optimisation and achieved the same kinetic fits. The RMS agrees with the study author that SFO is the best-fit model for persistence and modelling endpoints for the Swiss Lake water column; DT_{50} 244 days, DT_{90} 810 days.

Sediment

Sediment dissipation DT50 values are calculated as decline from the maximum residue. For Calwich Abbey the maximum residue occurs at day 56, with a total of three time points for fitting. For Swiss Lake the maximum residue occurs at day 81, with a total of two time points for fitting. According to FOCUS Kinetics (2006) a minimum of 5 time points are required, therefore, whilst an SFO model can be fitted to these data, the derived DT_{50} values are not robust and therefore not reported.

Degradation rate summary

A summary of the kinetic evaluation of the degradation of [14C]-mecoprop-P in the two water/sediment systems is   provided   in

Table B. 8.143. This represents the endpoints relevant for trigger for further studies. The endpoints for use within modelling are presented in Table B. 8.144.

In the Calwich Abbey system, degradation of [^{14}C]-mecoprop-P exhibited a lag-phase of moderate degradation followed by rapid decline. The hockey-stick (HS) model was selected as the best-fit to the data for the water phase and the total system. No meaningful kinetic work could be conducted on the sediment phase due to the lack of data points. The resulting DT_{50}(overall) and DT_{90}(overall) values were 72.5 and 91.9 days in the water phase and 83.2 and 96.7 days in the total system, respectively.

In the Swiss Lake system the single first order (SFO) model was selected as best-fit for the degradation in the water phase and the total system. Similarly to Calwich Abbey, no meaningful kinetic work could be conducted on the sediment phase due to a lack of data points. The resulting DT_{50} and DT_{90} values were 171 and 567 days in the water phase and 244 and 810 days in the total system, respectively.

Table B. 8.143. Summary of persistence endpoints (best fit)

System	Phase	Kinetic model	DT$_{50}$ (days)	DT$_{90}$ (days)	χ^2	t-test	Visual fit
Calwich Abbey	Water	HS	72.5	91.9	2.9	K$_1$ 1.50E-09 K$_2$ 0.4714	Good
	Total system	HS	83.2	96.7	1.3	K$_1$ 2.380E-07 K$_2$ 3.37E-08	Good
Swiss Lake	Water	SFO	171	567	4.0	8.58E-07	Good
	Total system	SFO	244	810	2.5	3.39E-06	Good

Table B. 8.144. Summary of degradation endpoints for modelling

System	Phase	Kinetic model	DT$_{50}$ (days)
Calwich Abbey	Water	HS (slow phase)	72.5
	Total system	HS (slow phase)	171
Swiss Lake	Water	SFO	171
	Total system	SFO	244

Report:	**CA 7/08, Degenhardt, D. *et al*. (2011)** Environmental Toxicology and Chemistry, 30, pp1982-1989
Title	Dissipation of six acid herbicides in water and sediment of two Canadian prairie wetlands
Guidelines:	None stated
GLP:	Not stated, but assumed not GLP
Deviations	Not applicable

Previous evaluations	None: Submitted for the purpose of renewal under Regulation 844/2012.
	This paper was identified by the applicant as potentially relevant during the literature review.
	The paper summary and relevance/reliability assessment provided by the applicant have been reproduced below. The RMS generally agrees with the applicant's assessment. The applicant considers the dose rates used in the study to be exaggerated. The study states that target concentrations of herbicides were based on recommended application rates, but these are not clearly stated in the study so it is difficult to relate this to the dose rates proposed for the representative use. However, direct overspray does represent a worst case exposure scenario. The study does not provide new endpoints and has not been relied on for the risk assessment.

Executive summary

The dissipation of mecoprop-P (and five other herbicides) was evaluated in the water and sediment of an ephemeral and a semi-permanent wetland of about 54 m³ and 1136 m³ respectively. 15.8 g and 360 g of mecoprop-P were dispersed into the water of an ephemeral (E) and a semi-permanent (SP) wetland (respectively) at time 0. Concentrations of mecoprop-P in the water and sediment, as well as the total mass of the pesticide in the water and sediment, were evaluated between t = 1 d and t = 77 d. Analysis was performed using liquid chromatography tandem mass spectrometry. Dissipation half-lives in water were estimated at 16 d and 13 d for the ephemeral and semi-permanent wetland, respectively.

An E and an SP wetland were divided into halves using a polyvinyl curtain and one-half of each wetland was treated with dicamba, bromoxynil, MCPA, 2,4-D, mecoprop-P, and dichlorprop [(RS)-2-(2,4-dichlorophenoxy)propionic acid] such that concentrations in the water simulated an over-spraying event, thus

representing a worst-case scenario for wetland contamination. Only experiments and results relevant with mecoprop-P will be described further.

Water and sediment samples were taken from the control and treated portions of each wetland over the 77-d study period to monitor herbicide concentrations. Water samples were maintained at 4°C until analysis. Sediment samples were frozen at -10°C on site and at -20°C in the laboratory until analysis.

A solid-phase extraction of each water sample was performed for the free-acid form of the herbicide. Recovery of mecoprop-P was 100 %. On the other hand, sediment samples (5 g) were mixed with Ottawa sand (40 g) and extracted with acetonitrile:water (10:90, v/v). Two extraction cycles were performed to obtain a 60 mL extract and water added to obtain a 100 mL extract. Solid-phase extraction was carried out on that extract. Recovery rate of mecoprop-P in sediment was 65.2 % at 20 µg/kg and 59.2 % at 5 µg/kg. See "Method of analysis" below for a more complete description.

The dissipation of mecoprop-P could be described by first-order reaction kinetics. In water, the field half-life (DT_{50}) values ranged from 13 d (SP) to 16 d (E). Mecoprop-P was detected in sediment samples from both wetlands. Use of bromide ion as a conservative tracer indicated that infiltration through sediment was an important route of water loss in both wetlands, especially in wetland E. Because strong correlations were found between the mass of each herbicide and bromide ion mass in wetland SP ($r^2 = 0.59\text{-}0.76$ - the range presented is for six herbicides, no individual value is given for mecoprop-P) and wetland E ($r^2 = 0.80\text{-}0.95$**Error! Bookmark not defined.**), it is likely that herbicide dissipation was due, in part, to mass lost by way of infiltration through sediment.

I. MATERIALS AND METHODS

A. MATERIALS

1. Test materials: Commercial formulation of mecoprop-P, Potassium salt, supplied by United Agri Products (field). No concentration stated.

       Analytical grade herbicide standard (for laboratory control) supplied by Chem Service

       Purity: Commercial formulation (purity not stated)

        > 98 % (analytical standard)

       CAS #: 16484-77-8 (Mecoprop-P)

Five other pesticides (dicamba, MCPA, bromoxynil, 2,4-D and dichlorprop) were also tested but not cited in the summary except where it is relevant or necessary for understanding.

2. Water/sediment

The study site was the Manitoba Zero Till Research Farm (49° 53'N latitude, 99° 58'W longitude) located approximately 20 km north of Brandon, Manitoba, Canada.. Two wetlands within a cultivated field, each with a riparian zone, were selected for study at this site: a smaller ephemeral wetland (wetland E) and a larger semi-permanent wetland (wetland SP). In wet years, wetland E would exist as a single wetland. However, 2007 was a dry year so that in 2008 when the study was carried out, it consisted of two separate smaller wetlands. These wetlands, typical of those found in the prairie pothole region, differed not only in size and water permanence but also in water chemistry and sediment characteristics. Herbicide products containing 2,4-D and MCPA had been applied annually to the catchments of both wetlands at recommended label rates for at least seven years prior to initiation of the present study. No herbicides were applied to the catchments in 2008 when the study took place. Laminated polyvinyl curtains were installed in May 2008, approximately one month prior to herbicide treatment, to divide wetland SP into control and treated halves and to prevent the separate components of wetland E from merging if there was sufficient rainfall. The control portions of each wetland were used by collaborators on this project to investigate the effects of herbicide mixtures on aquatic biota.

The wetland area and volume calculations were based on a digital elevation model (DEM) of the site which included measured wetland bathymetry, surrounding catchment topography, as well as water level measurements taken throughout the study. The algorithm for area and volume calculation was based on an algorithm given in

Planchon and Darboux[10]. According to this algorithm, the wetland and its catchment are initially inundated with a thick layer of water and excess water is removed in 0.1mm increments until the water depth equals the measured wetland water depth. The depth of water in each DEM cell (5 x 5 m in the present study) was then calculated from wetland bathymetry. The sum of the cell volumes (product of depth multiplied by area) is the wetland volume at a given time. Wetland volume calculation by this method is accurate because it is based on actual wetland bathymetry rather than an idealized elliptical basin form (Shenk Li, University of Manitoba, personal communication).

B.   STUDY DESIGN

1. Experimental conditions

Sodium bromide was added on 6th June 2008 to the half of the wetlands to be treated at a target concentration of 20 mg/L. Bromide acts as a conservative tracer to determine water movement between the treated and control halves of each wetland and to delineate the various hydrological transport and herbicide dissipation processes.

The herbicide application was conceived in order to simulate over-spraying which represents a worst-case scenario for prairie wetland contamination. The target concentration for each herbicide was calculated by assuming that a typical prairie wetland of 0.5-m depth was inadvertently over-sprayed at the corresponding recommended application rate. Due to an error in estimating the volume of wetland SP that was not discovered until after herbicide treatment, the target concentration of each herbicide for this wetland was 1.28 times greater than that for wetland E**.** On June 9 (day 0), using commercially available formulations, one half of each wetland was treated with a mixture of dicamba, bromoxynil, MCPA, 2,4-D, mecoprop-P, and dichlorprop (Table B. 8.145). The herbicides were mixed into approximately 30 L of water in the tank of a manually pressurized backpack sprayer equipped with a 1.5 m wand attached to a flat-fan nozzle. For wetland SP, an inflatable raft was used to inject herbicide solution at varying depths by moving the wand from just beneath the water surface to a depth of 1.5 m. To ensure a more homogeneous application of herbicide, the raft was pulled in a zigzag pattern over the width and length of the wetland using ropes. Wetland E was too shallow to deploy an inflatable raft and the herbicide solution was similarly applied from the edge of the wetland by moving the wand in a zigzag pattern to increase homogeneity of the herbicide application.

Table B. 8.145.   Herbicide active ingredients of commercial products added to wetlands E and SP (from Table 1 in Degenhardt *et al.*, 2011)

Commercial product	Herbicide active ingredients	Formulation	Herbicide mass added to wetland (g)		Herbicide mass on day 1 (g)		Target concentration of free acid ($\mu g\ L^{-1}$)	
			E	SP	E	SP	E	SP
Oracle	Dicamba	Dimethylamine salt	6.8	152	3.8	74	95	121
MCPA Amine	MCPA [(4-chloro-2-methylphenoxy) acetic acid]	Dimethylamine salt	9.0	203	11.8	291	127	162
Mecoprop-P	Mecoprop-P	Potassium salt	13	274	15.8	360	181	230
Pardner	Bromoxynil	*Iso*-octyl ester	4.4	100	3.7	52	26	80
Estaprop	2,4-D [(2,4-dichlorophenoxy) acetic acid	2-Ethylexyl ester	7.1	160	5.2	84	100	128
Estaprop	Dichlorprop	2-Ethylexyl ester	7.6	170	2.3	44	106	136

E = ephemeral, SP = semi-permanent wetlands

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[10] Planchon O, Darboux F. 2001. A fast, simple and versatile algorithm to fill the depressions of digital elevation models. Catena 46:159–176.

2. Sampling

In water: to establish bromide ion as well as herbicide residue levels prior to herbicide treatment, water samples were collected centrally from both halves of each wetland on June 5. After treatment with sodium bromide and the six herbicides, water samples were similarly collected from the treated and control halves of both wetlands. Water samples were collected through a polyethylene tube (4-mm interior diameter) into a 1-L polyethylene bottle at a rate of 300 to 400 mL/min using a variable speed peristaltic sampling pump placed 40 to 60 cm below the water surface. Each sample was filtered on site through a 153-µm mesh screen, transferred to a 1-L amber glass bottle equipped with a Teflon-lined cap and then acidified to pH 3.5 with concentrated sulphuric acid. The day after herbicide treatment (June 10), three water samples were collected from different points in the treated half of each wetland to determine the homogeneity of both the herbicide and bromide ion concentrations. Subsequent samples for herbicide analysis were similarly collected from the treated and control sides of each wetland on days 2, 3, 5, 7, 14, 21, 28, 42, 56, 63, and 77. The water samples were maintained at 4°C in an on-site refrigerator and later shipped on ice to the National Hydrology Research Centre, Saskatoon, Saskatchewan, where the samples were maintained at 4°C until analysis. Water samples for bromide ion analysis were collected on days 1, 2, 3, 5, 7, 14, 21, 28, 35, 42, 49, 56, 63, and 77.

In sediment: bottom sediment sampling was achieved using a hand-core sediment sampler (Wildco) in wetland E and a Kajak-Brinkhurst corer (Wildco) in wetland SP. On June 5, 2008, four sediment cores from different locations within the treated and control halves of each wetland were collected to establish background herbicide residue levels before herbicide treatment. Sediment samples from both treated and control halves of the wetland were then collected 1, 3, 7, 14, 21, 28, 42, 56, and 77 d after herbicide treatment as follows: a sediment core was collected at the centre and three peripheral locations from the treated and control halves of each wetland, and the top 5 cm of each core was placed in a Whirl-Pak polyethylene bag (Nasco), which was then placed in an amber polyethylene bag. The composite samples were kept on site in a freezer maintained at -10°C, and then were shipped on dry ice to the National Hydrology Research Centre, Saskatoon, Saskatchewan. The samples were freeze-dried using a Lab-Conco freeze-dry system and maintained at -20°C prior to residue extraction.

3. Description of analytical procedures

Preparation of standard solution: stock solutions (50 mg L^{-1}) of each acid herbicide as well as the surrogate and internal standards were prepared in acetonitrile and stored in the dark at 4°C. A calibration stock solution, containing all six herbicides at 100 µg L^{-1}, and the surrogate standard solution [Bromoxynil (ring-$^{13}C_6$)] at 50 µg L^{-1}, was also prepared in acetonitrile.

Water extraction: the solid-phase extraction (SPE) of each water sample for the free acid form of each herbicide was conducted within 24 h after collection according to the protocols established by Raina and Etter[11]. Solid-phase extraction of the water samples was achieved using Supelco Superclean ENVI-Chrom-P cartridges (1 g, 6 mL; Sigma-Aldrich). The water sample (250 mL) was passed through the cartridge at a rate of 200 mL/h under vacuum using a Supelco DL SPE extraction manifold (Sigma-Aldrich). The herbicide residues were eluted from the cartridge with 8 mL of 60/40 % (v/v) methanol/ethyl acetate and concentrated to approximately 0.95 mL and the surrogate standard (50 µL of 50 mg L^{-1}) was added to give a total volume of 1 mL. Surface water samples collected from storm water ponds were fortified with the six acid herbicides at 75 ng L^{-1} (n=10). Recovery of mecoprop-P was determined (see "Mass Balance" in Results section). A detailed description of the SPE clean-up can be found in Raina and Etter11.

Sediment extraction: freeze-dried sediment (5 g) was mixed with approximately 40 g of Ottawa sand and transferred to a 33-mL stainless steel accelerated solvent extraction (ASE) cell equipped with two GF/X filter papers at both the inlet and the exit end of the cell. The sample was extracted with acetonitrile:water (10:90 v/v) using an ASE system (ASE 200; Dionex) under the following operating conditions: temperature, 70°C; static mode time, 2 min at 1500 pounds per square inch; two static cycles; 90% flush volume with each cycle; and 60 s purge time with ultrahigh purity nitrogen at the end of each run. After two extraction cycles, the combined volume of extract was approximately 60 mL. The extract was diluted with deionised water to approximately 100 mL and then acidified by the addition of 3 M sulphuric acid (0.5 ml) prior to solid-phase extraction. Recovery experiments for the six acid herbicides from sediment were conducted using control sediment collected from a

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[11] Raina R, Etter M. 2010. Liquid chromatography with post-column reagent addition of ammonia in methanol coupled to negative ion electrospray ionization tandem mass spectrometry for determination of phenoxyacidic herbicides and their degradation products in surface water. Anal Chem Insights 5:1–14.

wetland situated within a catchment that had not received any pesticide application in the past five years. Sediment samples from this wetland (n=2) contained no detectable residue of any of the acid herbicides used in the present study. Freeze-dried sediment (5 g) was fortified at 5 and 20 ng g^{-1} (n= 6 for each level) by the addition of 25 and 100 ng of each acid herbicide (plus 50 ng of Bromoxynil (ring-$^{13}C_6$) dissolved in methanol) and extracted within 48 h. Blank sediment was treated similarly with methanol only. Recovery of mecoprop-P was determined (see "Mass Balance" in Results section).

Liquid chromatography tandem mass spectrometry: a Waters liquid chromatography system interfaced to a Quattro Premier triple quadrupole mass spectrometer (Waters-Micromass) equipped with an electrospray ionization interface set to negative ion mode was used for the analysis of both the sediment and water extracts. Based on the minimum standard concentration showing 25% deviation of peak area from the best-fit regression line of the calibration curves determined over 2 to 150 ng L^{-1}, the method detection limit (MDL) for the water samples was 10 ng L^{-1} for mecoprop-P.

4. Calculations

Herbicide and conservative ion mass in water: the mass of each herbicide or bromide ion ($mass_t$) at a given sampling time (t) was calculated using Equation (1):

$$mass_t = concentration_t \times volume_t \quad (1)$$

where $concentration_t$, is the concentration of each analysis at time t and $volume_t$, is the volume of water in the treated or control half of each wetland at time t.

Herbicide mass in sediment: the mass of each herbicide ($mass_t$) in the surficial sediment (0 to 5 cm) at a given sampling time (t) was calculated using Equation (2):

$$mass_t = \text{wetland area} \times \text{sediment depth} \times \text{sediment bulk density} \times concentration_t \quad (2)$$

Where: wetland area is the maximum area underwater on the treated half of wetland E or SP.

In order to account for all of the surficial sediment that could have been under water at any point during the 77-d study, the maximum area was used instead of the area at each sampling event. The bulk density of the upper 5 cm of the sediment was determined in a previous study[12], and concentration, is the concentration of each herbicide at time (t).

Field DT_{50} values: the field DT_{50} value for each herbicide is the time required for 50% of its concentration or mass to dissipate from the water column of the treated half of each wetland. Using a first-order kinetics approximation, the field DT_{50} value for the herbicide was calculated using Equation (3):

$$DT_{50} = Ln2 / k \quad (3)$$

where k is the dissipation rate (d^{-1}) obtained from the linear correlation between Ln [concentration/initial concentration(C_0)] and time, or Ln [mass/initial mass (m_0)] and time.

II. RESULTS AND DISCUSSION

A. MASS BALANCE

Recovery of mecoprop-P was 100 % for water samples. For sediment samples, recovery of mecoprop-P was 65.2 ± 3% at 20 ng g^{-1} and 59.2 ± 11% at 5 ng g^{-1}.

B. FINDINGS

1. Hydrology

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[12] XuD,MeyerS, Gaultier J, Farenhorst A, Pennock DJ. 2009.Land use and riparian effects on prairie wetland sediment properties and herbicide sorption coefficients. J Environ Qual 38:1757–1765.

In general, wetlands E and SP were hydrologically similar throughout the 77-d study. With approximately 245 mm of precipitation during the study, water volumes in both wetlands generally increased or decreased concurrently. This was most evident during the first week after herbicide treatment, when the study site received approximately 90 mm of rain and rainfall/ runoff events increased volumes of wetland E and SP by 330 and 30%, respectively. Maximum water volumes occurred in both wetlands on day 7. However, because of the semi-arid climate in this region, evapotranspiration and infiltration in both wetlands exceeded rainfall/runoff inputs and, by day 65, wetland E was dry and wetland SP had lost approximately 35% of its maximum volume at the end of the study. According to the bromide ion concentration and water volume data, water loss from wetland E was dominated by infiltration, whereas evapotranspiration also contributed significantly to water loss from wetland SP. The bromide ion concentration data also indicated that, with the large amount of rainfall and accompanying runoff which occurred during the study, the wetlands may not have been homogeneously mixed when samples for residue analysis were collected. This was evident for day 2 in wetland E and day 1 in wetland SP. Thus, incomplete mixing of the wetlands may explain some inconsistencies observed in the herbicide concentration data. Because of possible inconsistencies in the concentration data, dissipation of the herbicides in the water column of these wetlands was also determined using herbicide mass calculated as the product of the estimated volume of the wetland and herbicide concentration.

2. Dissipation in water

No residues of any of the six herbicides were detected in either the treated or control half of wetland SP in pre-treatment samples collected 4 d prior to herbicide addition, nor in the control half of wetland E. However, MCPA, 2,4-D, and mecoprop-P were detected in the treated half of wetland E in relatively low concentrations (0.12-0.56 $\mu g \ L^{-1}$) compared to corresponding concentrations measured post-herbicide treatment (Figure B. 8.14)**.** Because wetland E existed as two separate wetlands during the study, contamination of only one of these wetlands most likely resulted because it received surface runoff from a different portion of the catchment. None of the six herbicides were detected in the control half of wetlands E and SP post-herbicide treatment.

The mean herbicide concentrations detected in the triplicate water samples collected from the treated half of both wetlands 24 h post-treatment (day 1) had standard deviation values as high as ±42% (data not shown). These values concur with the bromide ion data which suggested incomplete mixing of the wetlands, most likely because of the 40-mm rainfall and resulting runoff that occurred on days 0 and 1.

In general, mecoprop-P concentrations in both wetlands decreased throughout the 77-d study (Figure B. 8.14). Plotting the natural logarithm of herbicide mass versus time showed that dissipation of mecoprop-P in wetlands E and SP could be described by first-order reaction kinetics with regression correlations values(r^2) of 0.84 and 0.93, respectively (Table B. 8.146). Field DT_{50} (dissipation) of mecoprop-P was 16 d in wetland E and 13 d in wetland SP.

The two phenoxy-2-propionic acids (dichlorprop and mecoprop-P) demonstrated greater persistence in the water column of the two wetlands than the two phenoxyacetic acids (MCPA and 2,4-D) and were the only herbicides whose concentrations remained above the Canadian Water Quality Guidelines for the Protection of Aquatic Life on the last day of the study (Figure B. 8.14). The longer persistence of these compounds may result from resistance to microbial degradation due to their chemical structures. The commercial products used in the present study contained the herbicidally active R-(+)-isomer of mecoprop and the racemic mixture of dichlorprop. Photodegradation likely played a relatively minor role in the dissipation of the masses of these acid herbicides, because the photolysis of organic contaminants in wetland waters is expected to be relatively slow. Most prairie wetlands have high dissolved organic carbon (DOC >20 mg L^{-1}) content, which largely attenuates UV light transmission and decreases the rate of photolysis of dissolved contaminants. Other dissipation pathways that would decrease herbicide masses in the water column include volatilization and infiltration through bottom sediment. Herbicide loss by infiltration can be assessed by examining the correlation between the decrease in bromide ion mass and the decrease in herbicide mass over time Although relatively strong correlations (r^2 = 0.80-0.95[13]) were observed for wetland E, they were much weaker for wetland SP (r^2 = 0.59-0.76[13]). Stronger correlations were expected with wetland E because the majority of the water loss was by way of infiltration.

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[13] for the six herbicides: no individual data available for Mecoprop-P

Table B. 8.146. Dissipation rate and dissipation DT_{50} in water of mecoprop-P in wetlands E and SP (Data from Table 3 in Degenhardt *et al.*, 2011)

Wetland	E		SP	
Unit	concentration	mass	concentration	mass
r^2	0.62	0.84	0.92	0.93
C_0 ($\mu g\ L^{-1}$)	178	NA	231	NA
$Mass_0$ (g)	NA	12.9	NA	274
k	0.04	0.04	0.05	0.05
DT_{50} (d)	18	16	14	13
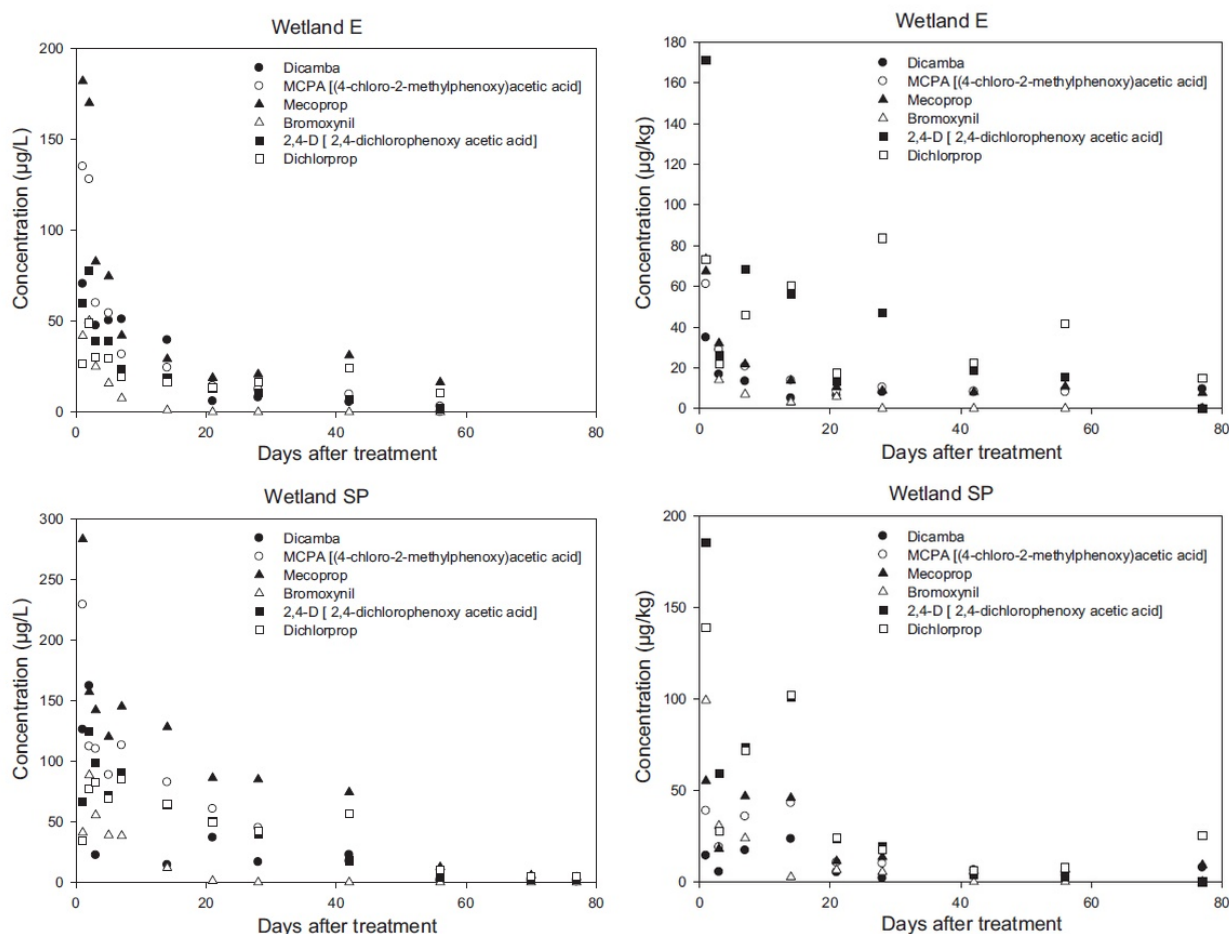
Figure B. 8.14.   Concentrations of the six herbicides in the water columns (left) and sediment (right) of the treated halves of the ephemeral (E) and semi-permanent (SP) wetlands with time (Fig 1. and Fig. 2, Degenhardt *et al.*, 2011)

3. Occurrence and dissipation in sediment

Bottom sediment was investigated to determine the extent of adsorption of the six herbicides to bottom sediment as the wetland water infiltrated through the sediment. None of the six herbicides were detected in sediment in either wetland prior to herbicide treatment nor were any of the six herbicides detected in sediment collected from the control half of either wetland throughout the 77-d study. In wetland E, herbicide concentrations in sediment were highest on day 1 and then generally decreased with time (Figure B. 8.14). In wetland SP, highest concentrations were similarly observed on day 1 for mecoprop-P. Mecoprop-P remained detectable in sediment

from both wetlands on the last day of the study (day 77). Using the maximum concentration for each herbicide detected in sediment (Figure B. 8.14) and the maximum area (the maximum area of the treated half of wetland E or SP that may have been under water at any point during the 77-d study) of each wetland, the maximum mass of mecoprop-P which was sorbed in the upper 5 cm of sediment during the study was calculated (Table B. 8.147). Based on the total herbicide mass added to wetland E, the upper 5 cm of sediment sorbed approximately 12% of mecoprop-P. Corresponding value for wetland SP was approximately 1% of mecoprop-P.

Although herbicide concentrations in sediment were similar between the two wetlands, sediment in wetland SP sorbed a smaller proportion of total herbicide added compared to wetland E. This is most likely due to the fact that a much smaller proportion of the maximum volume of wetland SP moved through the sediment, as well as the differences in the herbicide sorption capacity of the sediment in each wetland. Wetland SP was colonized by an aquatic moss (*Fontinalis antipyretica*), with an average density of 130 g (dry weight) per m^2 during the study period (P. Badiou, Ducks Unlimited, unpublished data). Herbicides taken up and metabolized by this moss by way of enzymatic metabolism would have resulted in less herbicide available for sorption to the sediment.

Table B. 8.147.   Calculated mass of mecoprop-P in bottom sediment of wetlands E and SP (Data from Tables 4 & 5 in Degenhardt *et al.*, 2011)

Wetland	E		SP	
Days after wetland treatment	Wetland area (m^3)	mass of mecoprop-P (top 5cm, g)	Wetland area (m^2)	mass of mecoprop-P (top 5cm, g)
-4 (June 05)	425	0.00	2300	0.00
0	475	NC	2300	NC
1	500	3.77	2175	2.89
3	750	0.58	2175	0.94
7	775	1.50	2375	2.45
14	725	1.23	2375	2.40
21	700	0.29	2350	0.59
28	650	1.04	2300	0.71
42	650	0.41	2175	0.30
56	475	0.34	2200	0.36
77	0 (dry)	0.00	2075	0.48

III.   CONCLUSION

The authors concluded that in water the dissipation of all six herbicides (including mecoprop-P) could be described by first-order reaction kinetics. The mean field DT_{50} values determined for mecoprop-P ranges 13 to 16 days. The two chiral herbicides tested, mecoprop-P and dichlorprop, were the most persistent acid herbicides in the water column. Infiltration through sediment with concomitant sorption to the sediment was an important dissipation route for the herbicides in water, especially in wetland E. Although not examined specifically in the present study, microbial degradation was most likely a major dissipation route for acid herbicides in wetlands. Given the findings, the authors believe herbicide guidelines are needed for sediment since a variety of aquatic organisms interact directly with sediments. Due to the cost and logistical challenges, very few studies have examined the field dissipation of acidic herbicides in wetlands. The authors have presented the dissipation behaviour of six acid herbicides in two prairie wetlands; they claim that replication of the present study on a wider range of wetlands is needed to create a larger dataset for pesticide fate modelling.

Applicants conclusions: From a EU regulatory point of view, the study gives an order of magnitude of the dissipation rate of mecoprop-P in wetland-type surface water (DT_{50} = 13-16 d) in semi-arid, temperate climatic conditions in summer, and an order of magnitude of its presence in sediment. As expected, mecoprop-P was found in relatively low amounts in sediment (1 % and 12 % of the total mass for the large and small wetland, respectively). No endpoint can be derived for modelling purposes. The level of contamination tested in the study is far higher than that expected to occur after the regular use of mecoprop-P in the EU. Since mecoprop-P has shown differentiated behaviour regarding to degradation (in soil) with different concentrations, this may also be

an issue in surface water. The proportion of the different routes of dissipation were not evaluated, which limits the scope of the study.

Assessment of methodological quality

	Relevance	Reliability	Transparency & repeatability
Material	Outside EU, but still relevant for dissipation processes and sorption to sediment evaluation and order of magnitude of dissipation time.	Seems correct, no issue.	Lot/batch numbers are not cited.
Method	Adequate for the claimed objectives.	Not GLP-compliant Application rates were very high, which could interfere with measured DT_{50}. The dissipation rate for a lower concentration could be different. Recovery rate of mecoprop-P in sediment is < 70 %.	Not repeatable since it concerns a field study on ephemeral and semi-permanent wetlands. Experiment is accurately described.
Results & interpretation	Same remarks as for material.	A lack of homogeneity of the mix of mecoprop-P in the water was reported. Reliable within the scope of the study, but no reliable endpoints for a EU risk assessment.	Unsure if handling of data were compatible with GLP practices.

Report:	**Bromilow R., de Carvalho R., Evans A., Nicholls P. (2006)**
Title	Behaviour of Pesticides in Sediment/Water Systems in Outdoor Mesocosms Journal of Environmental Science and Health, Part B:Pesticides, Food Contaminants, and Agricultural Wastes, 41:1–16, 2006
Guidelines:	None
GLP:	No, literature data

| Previous evaluations; | None: Submitted for the purpose of renewal under Regulation 844/2012.

This paper was identified by the applicant as relevant during the literature review.

The summary provided by the applicant has been reproduced below. The study is on mecoprop rather than mecoprop-P. It indicates that mecoprop degrades rapidly in water/sediment systems with little sorption to sediment observed.

The study does not provide new endpoints and has not been relied on for the risk assessment. |

Executive summary

The distribution of eight pesticides (including mecoprop) between sediment and water held in 1m^2 outdoor stainless-steel mesocosms was studied, simulating both spring and autumn applications. Pesticide behaviour was largely independent of rate of application, chosen in the experiments to be 4% or 40% of the normal field rate so as to simulate spray drift or partial overspray.

Following application by spray to the water surface, all compounds were uniformly distributed in the 30 cm of overlying water within 24 h. The lipophilic pesticides moved into the sediment within 30 d but with little penetration below 2.5 cm depth. Other, less sorptive compounds remained predominantly in the aqueous phase.

The polar mecoprop remained almost entirely in the water phase and was rapidly degraded. Two further experiments also examined the influence of the submerged plant *Lagarosiphon major* in the mesocosms, one of which included an application of mecoprop. Uptake into *L. major* was correlated with pesticide lipophilicity, but was only a small factor compared to uptake by sediment and degradation in these lightly vegetated systems.

Solely the results for mecoprop are reported below.

I.   MATERIALS AND METHODS

A.   Test item

Mecoprop (in formulation: Duplosan 600g/l SL).
Mecoprop standard was analytical grade.

B.   Substrate

Sampling time:
Experiment 3 (autumn/winter): 1, 7, 14, 28, 56, 90 and 118 days
Experiment 5 (late spring/early summer): 1, 7, 16, 25, 56 and 119 days

Water samples (1.0 L) were taken from 0–15 and 15–30 cm depth via a glass tube (3 mm i.d.) using a hand operated suction pump and glass receiving flask. These were stored in the dark at 4ºC prior to analysis, if necessary.

Sediment samples were taken at the same time from four to six random locations, using two ABS plastic rings (each 4.4 cm diameter and 2.5 cm deep, the lower one having a bevelled cutting edge) taped together, pressed into the sediment and lifted with the aid of a thin stainless-steel blade inserted under the lower edge. The two sections were separated (giving 0–2.5 and 2.5–5.0 cm depth sections) with the corresponding replicates combined.

For experiment 5, stems (four) of the *L. major* were removed at the same sampling times and surface dried with a tissue. The sediment and plant samples were stored in polyethylene bags at −10ºC until analysis.

C.   Test Conditions

Mesocosms
Stainless-steel tanks (10 in total), each 100×100×40 cm deep, were buried in soil to within 5 cm of their rim. Sediment was collected from a pristine site at Great Linford, Bedfordshire, UK, and sieved moist to 5 mm; it comprised 64% sand, 20% silt and 16% clay with 2.5% organic carbon and pH 7.32 (water). The sediment was placed to a depth of 5 cm in each tank and water (30 cm depth) was added. The tanks were then netted against birds and animals and left for several weeks to equilibrate. An overflow tap 5 cm below the rim allowed excess rainfall to be drained, but was kept closed during the experiments. In the tests including the plants (Experiments 5), 20 clumps of three stems (each 15 cm long) of *Lagarosiphon major* (syn *Elodea crispa*) were distributed in the tanks and allowed to root before the spray application. Tanks were unstirred.

D.   Dosing system

Application rates: 0.08 kg mecoprop/ha and 0.8 kg mecoprop/ha (4% and 40% of the typical field rates to represent spray drift or partial overspray) were made during Experiment 3 (28th October 2002) and Experiment 5 (12th May 2003). Applications were made using a hand held sprayer. Tanks were also dosed with chlorotoluron, isopruturon and pendimethalin. Two tanks were prepared per experiment.

E.   Analyses

Water
An aliquot of the water (500 mL) was drawn under vacuum through an Empore 47 mm diameter C-18 disc (disc prewashed with methanol). The aqueous filtrate was acidified (5.0 mL conc. HCl) and then extracted in a separating funnel with dichloromethane (3×50 mL). The combined dichloromethane extracts were rotary evaporated to dryness and taken up in methanol:water (70:30 v/v) (5.0 mL).

Sediment
Sediment as sampled (100 g) was extracted with methanol: 0.2 M $(NH_4) CO_3$ aq (270:130 v/v). An aliquot (50 mL) of the supernatant extract was evaporated to leave the aqueous phase, which was extracted with dichloromethane (3×15 mL) which was discarded. The aqueous phase (acidified with conc. HCl, 1.0 mL) was extracted again with dichloromethane (3×15 mL), which combined organic extracts were evaporated and the residue dissolved in methanol: water (70:30 v/v) (1.0 mL).

Plant material
The stems of *L. major* were cut into short lengths (sample weight 1.0 to 1.5 g) and macerated with a Silverson homogenizer in acetone (50 mL followed by 2×25 mL). The combined acetone extracts, filtered through a plug of cotton wool, were evaporated to dryness on a rotary evaporator; the residue was transferred to a SepPak to extract neutral compounds. A final elution with hexane:acetone:acetic acid (50:50:1 v/v) (5.0 mL) was performed to elute mecoprop. The fractions were evaporated to dryness and redissolved in HPLC mobile phase (1.0 mL).

HPLC analysis
The extracted samples were analyzed by HPLC equipped with a LicroCart C-18 reverse-phase column (20 cm $\times$ 4 mmi.d., particle size 10 μm) with solvent flow rate of 1.5 mL min^{-1}. Mobile phase and UV detection wavelengths for mecoprop were: methanol:water:acetic acid (65:35:1 v/v), 232nm (retention time 4.35 min).

Recovery tests were done in duplicate at two fortification levels chosen to reflect the application rates of the compound. For all matrices, recoveries were greater than 70%. All measurements were corrected for the appropriate recovery factor.

II. RESULTS

Experiment 3
The mass balance at 1 d was 70% for mecoprop. Movement into sediment and degradation over time were independent of the application rate; but analysis of the mecoprop at the lower rate was difficult, especially for the sediment due to interfering peaks, and so these results were not completely reliable.

Taking the 1 d measurements as the initial dose, DT_{50} values for mecoprop were between about 25 d and 40 d, with degradation subsequently slowing in the winter temperatures (application was made in late October). Amounts of mecoprop in sediment were small at a maximum of 5.2% at 118 d.
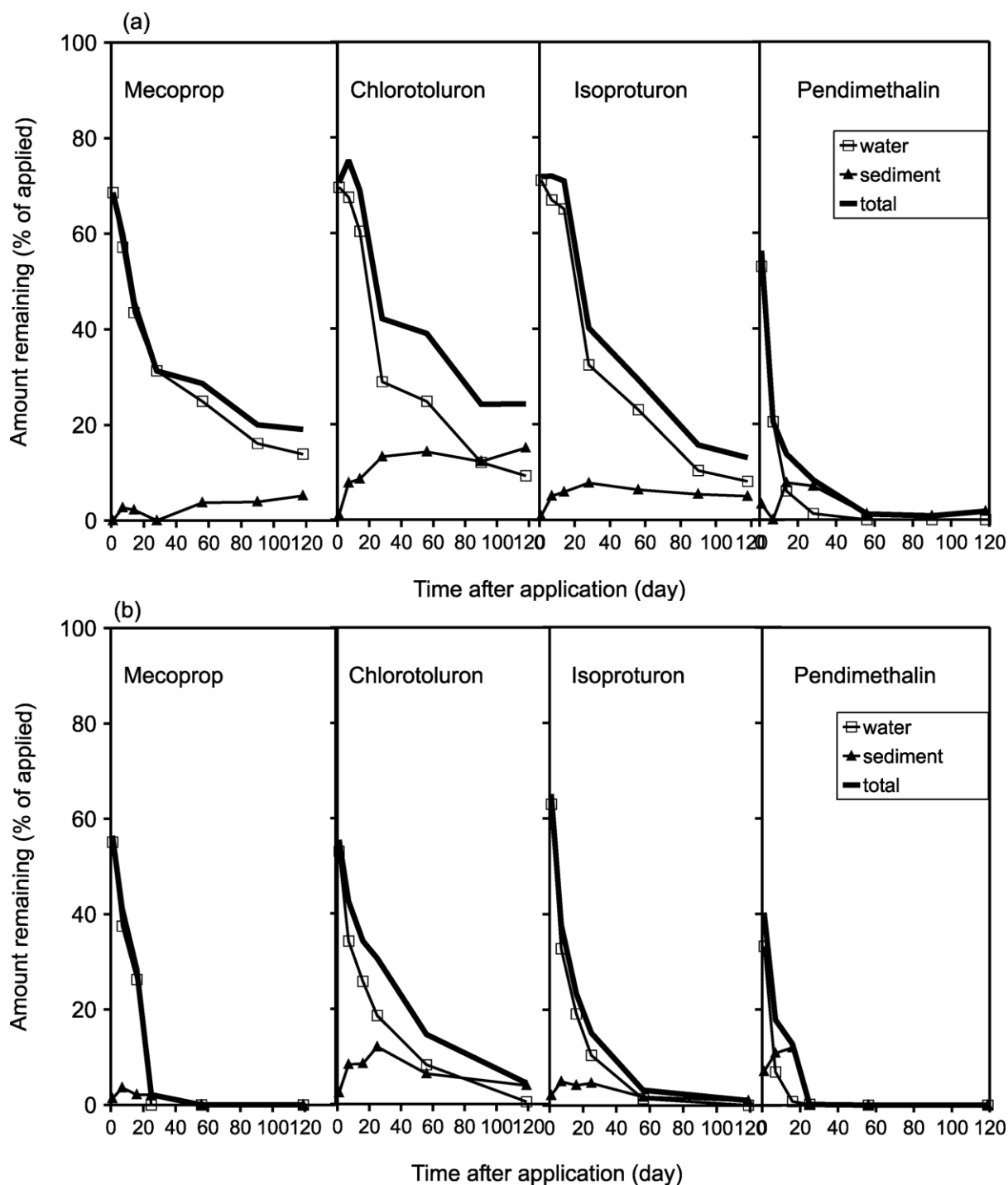
Figure B. 8.15 Dissipation of four pesticides (chlorotoluron, isoproturon, mecoprop, pendimethalin) applied to mesocosms at 40% of field rate: (*a*) Experiment 3, pesticides applied October 28, 2002; (*b*) Experiment 5, pesticides applied May 12, 2003 (amounts in the *Lagarosiphon major* plants were small and are not shown).

Experiment 5

The compound behaved as in Experiment 3, except that the mass balance at 1 d was less (approximately 55% by graphical interpolation) and that degradation was substantially faster in Experiment 5. Mecoprop was not detected in water after 25 d and was not detected in the plants. These differences reflect the differing climatic factors, with mecoprop being applied in mid-May.

III. CONCLUSION

The present study investigates the behaviour of mecoprop in outdoor mesocosms, in which conditions were not controlled and the pesticide was exposed to ambient conditions including wind and sunlight. The analytical methods and experiments description were well explained. Mecoprop remained almost entirely in the water phase and was rapidly degraded. The degradation was faster in spring/summer time, as expected due to the higher temperatures. Mecoprop was not detected in the plants.

Irradiated water/sediment study (CA 7.2.2.4)

No data – not required.

B.8.2.3. **Degradation in the saturated zone (CA 7.2.3)**

No data – not required. One study was identified as relevant during the literature review.

Report:	Barth, J. *et al* (2007)
Title	Deposition, persistence and turnover of pollutants: First results from the EU project AquaTerra for selected river basins and aquifers Science of the Total Environment 376, p40–50
Guidelines:	None
GLP:	No, literature data

Previous evaluations;	None: Submitted for the purpose of renewal under Regulation 844/2012. This paper was identified by the applicant as relevant during the literature review. The paper reports on an investigation of POPs in the EU. Mecoprop was not assessed in field samples but was investigated in laboratory experiments using aquifer and unsaturated zone material representing different depths below the surface. Mineralisation of mecoprop was measured via $^{14}CO_2$ production and was generally found to decrease with increasing depth. Mecoprop was not analysed directly and degradation products were not identified. Mass balances are not reported. The RMS considers the experiments are not sufficient to derive reliable degradation rates in the unsaturated zone. The study does not provide new endpoints and has not been relied on for the risk assessment.

Executive Summary

Deposition, turnover and movement of persistent organic pollutants (POP) were investigated in the EU integrated project "AquaTerra", which is among the first funded environmental projects within the 6th Framework Program by the European Commission. Project work integrates across various disciplines that range from biogeochemistry, environmental engineering, computer modelling and chemistry to socio-economic sciences. Field study areas are the river basins of the Ebro, the Meuse, the Elbe and the Danube as well as the 3-km^2 French catchment of the Brévilles Spring. Within the first 2 years of the project more than 1700 samples of atmospherically deposited particles, sediments, and water have been collected in the above-mentioned systems. Although a number of analytes were monitored in the field samples, mecoprop was not included in this. Laboratory studies were set up to investigate the degradation of mecoprop, among other herbicides, showing that this compound degrades in samples from up to 58 mbs (metres below surface).

Only the results for mecoprop are reported below.

I.　MATERIALS AND METHODS

A.　STUDY DESIGN

1.　Test substance

[14]C-labelled mecoprop. The purity is not specified in this paper.

2. Substrate

Laboratory experiments were set up to investigate the degradation of mecoprop in limestone and the aerobic sandy aquifer underlying the limestone. Drill cores were collected at the Brévilles site in plastic tubing, subsequently divided in suitable sections after visual inspection for contamination and transported to the laboratory under cooled conditions by overnight carrier. Water from the Brévilles spring was first treated with activated carbon to remove pesticides and then sterile-filtered before being added to the sediment (from the aquifer) samples in the microcosms.

With samples from the saturated zone, a total of 28 microcosms* including 7 biologically inhibited controls (autoclaved 20 min., 1.5 bar, 120°C, three times with one-day intervals) were set up to represent three different drilling locations and depths from 10.5 to 58.5 m below the surface (mbs).

Aquifer samples were added to 118-mL glass serum bottles with 40 g sediment (wet weight) and 60-mL water from the Brévilles spring before being sealed with a 1 cm butyl stopper and crimp caps. Samples from the unsaturated zone were collected from 4 drillings between 0.15 and 42.6 mbs and were set up similarly (70 microcosms* including 20 controls), but without extra water.

* The number of microcosms and control described here is the overall number to investigate the degradation of isoproturon, mecoprop and acetochlor.

3. Test conditions

Incubation took place in the dark at 10°C for up to 91 days.

4. Dosing system

0.5 mL of ^{14}C-labelled pesticide stock solutions was added to achieve a nominal initial concentration of 1 μg/L.

5. Analyses

Mineralisation of mecoprop was measured via $^{14}CO_2$ production only. Subsamples of 2 mL were filtered and transferred to a double-vial system consisting of a 20-mL-polyethylene scintillation vial that contained another 6-mL-scintillation vial with 1-mL 0.5 M NaOH where $^{14}CO_2$ was trapped after acidification of the samples. ^{14}C-activity was quantified with a liquid scintillation analyser (LSA). The accuracy of the analyses was ±2.5% or better for the counting of the $^{14}CO_2$-concentration.

Mecoprop was not analysed directly and degradation products were not identified. Mass balances are not reported.

II.   RESULTS AND DISCUSSION

Mecoprop could be biodegraded by bacteria present in soil (material from the unsaturated zone) and aquifer material from the Brévilles site. This process decreased in efficiency at greater depths. In the upper part (0.15–0.6 mbs) of the unsaturated zone a degradation of 9–16 % was indicated by $^{14}CO_2$-production already 14 days after initiation of the experiments. After 91 days 25–34% of the added ^{14}C-mecoprop was mineralized to $^{14}CO_2$ (Figure B. 8.16). After 78 days, degradation was also observed in greater depths around 19.5 mbs where 11–16% of the initially added ^{14}C-mecoprop was recovered as $^{14}CO_2$ (data not shown in the paper).

Mecoprop was observed to degrade in samples from up to 58 mbs for which a small, but noticeable $^{14}CO_2$-production was observed after more than 200 days of incubation.
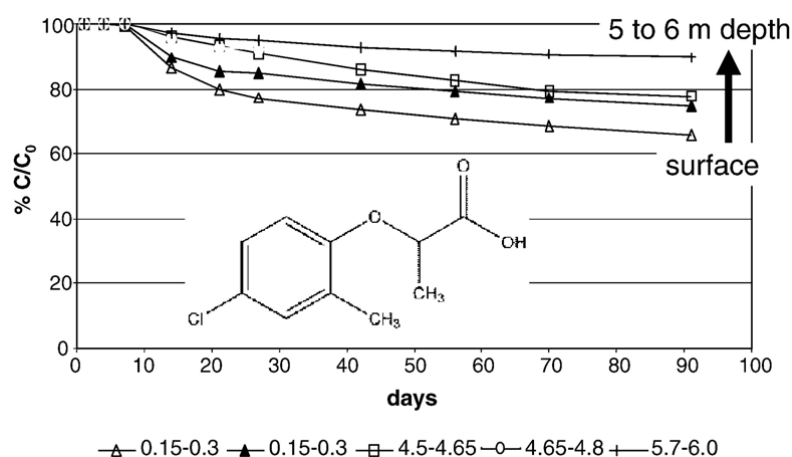
Figure B. 8.16. Mecoprop degradation as a function of soil depth. The different symbols represent samples taken in metres below ground (reproduced from Barth 2007).

III.   CONCLUSIONS

Laboratory studies with field samples from the Brévilles catchment demonstrated that mecoprop degrades in samples from up to 58 mbs, and that it has a clear tendency of declining degradation with depth. The authors suggest that natural attenuation in the saturated zone may have to be considered in mass balance considerations. They concluded that even though degradation rates are very low in greater depths, they should be considered in risk assessment and in modelling the fate of pesticides, particularly when considering the long hydraulic residence times of small aquifers such as the Brévilles. The authors presume that such residence times would be much longer in larger catchments and river basins and thus enable even slow rates of degradation.

Substances arising from water treatment processes

RMS comments:	This is a new requirement, under Article 4.3(b) of Regulation 1107/2009, which states that active substances shall not have harmful effects on human health, taking account of substances resulting from water treatment. There is no guidance available at present. The RMS has asked the applicant to provide a statement/reasoned case as to why it is expected that mecoprop-P will not produce any substances (e.g. degradation products) at levels harmful to health, as a result of water treatment processes.

Report:	Simmons, K., Hutton, L. and Heaton, S. (2015)
Title	Position Paper: Mecoprop-P – Effects of Water Treatment Processes Wyke_2015_028
Guidelines:	None
GLP:	No
Deviations	None

Previous evaluations:	None: Submitted for the purpose of renewal under Regulation 844/2012 The position paper provided by Nufarm has been reproduced below in full with RMS comments added where necessary.

Introduction

It was noted by the RMS UK that the dossier submitted for renewal of the active substance mecoprop-P did not contain information on the potential effects of water treatment processes. The following statement was made:
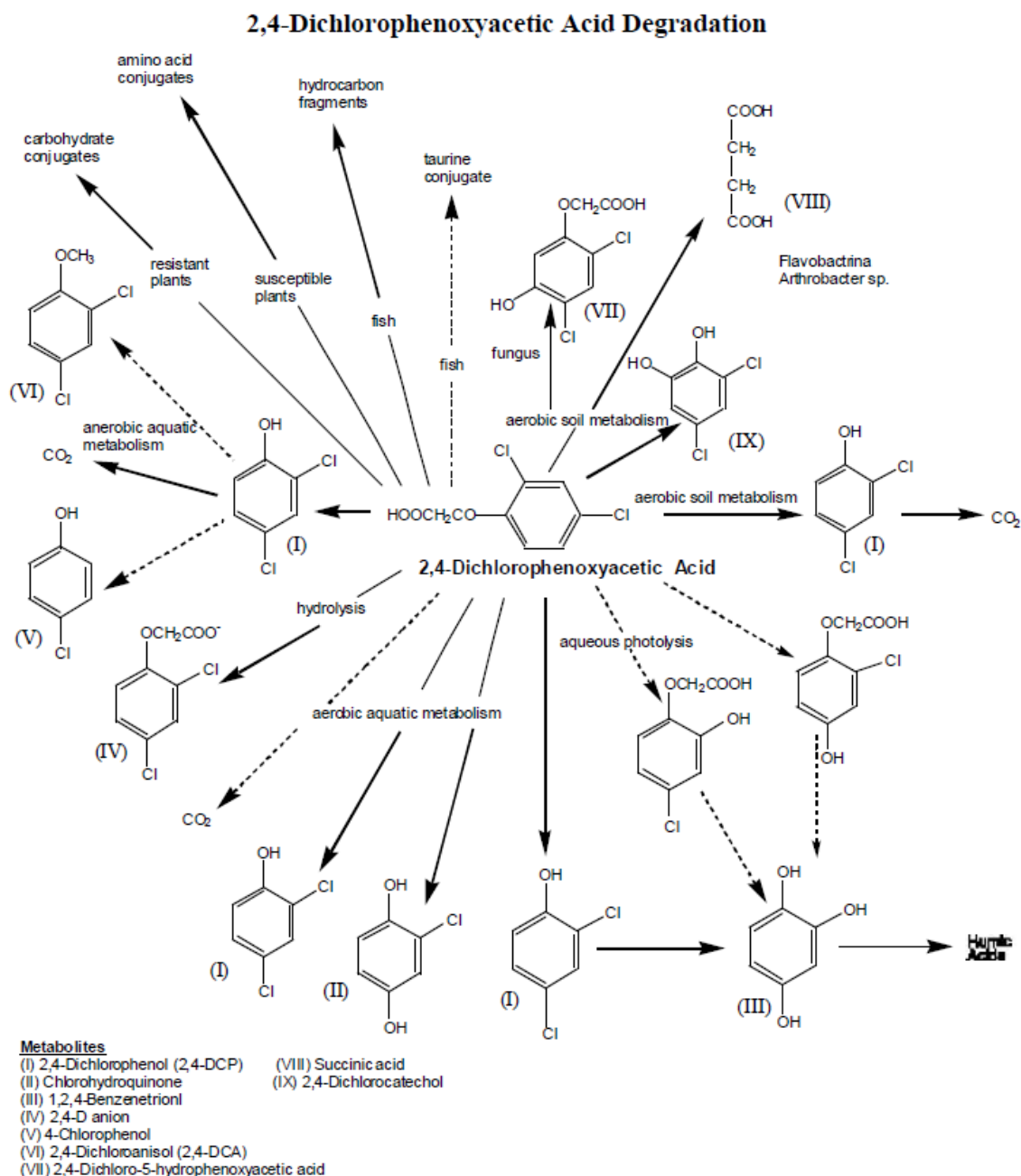
"Effects of Water Treatment Processes: Article 4.3(b) of Regulation 1107/2009 states that active substances shall not have harmful effects on human health, taking account of substances resulting from water treatment. Please provide a statement/reasoned case addressing the point that mecoprop-P will not produce any substances/degradation products at levels harmful to health as a result of water treatment processes." This position paper aims to make an assessment of the removal and potential metabolism of the active substance mecoprop-P during water treatment processes.

Environmental Fate Properties of Mecoprop-P

Mecoprop-P is to be applied as a foliar application to spring and winter cereals. As a result it is possible that mecoprop-P will reach the soil, surface water and groundwater. Thus it also has the potential to be present in drinking water, prior to treatment.

Mecoprop-P is rapidly degraded in soil, with a geometric mean DT50 of 6.0 days. Mecoprop-P can also be degraded relatively rapidly in water, largely dependent upon on the microbial population.

Based upon the environmental fate parameters of the active substance mecoprop-P, it is unlikely that it would persist within the environment and should have already degraded significantly before reaching a water treatment plant. As a result it is expected that levels of mecoprop-P entering water treatment plants would already be low. The environmental fate of the related 2,4-D molecule is the subject of many academic papers. The routes via which this model phenoxy acid breaks down to give primarily the parent phenol or other small molecules are discussed in an online review paper by the Californian Department of Pesticide Regulation in the USA (Walters). The many and varied degradation routes mentioned are just as applicable to the mecoprop-P molecule.

2,4-Dichlorophenoxyacetic Acid Degradation

Metabolites
(I) 2,4-Dichlorophenol (2,4-DCP)   (VIII) Succinic acid
(II) Chlorohydroquinone   (IX) 2,4-Dichlorocatechol
(III) 1,2,4-Benzenetrionl
(IV) 2,4-D anion
(V) 4-Chlorophenol
(VI) 2,4-Dichloroanisol (2,4-DCA)
(VII) 2,4-Dichloro-5-hydrophenoxyacetic acid

RMS comments:	The RMS agrees that from the available fate and behaviour studies, mecoprop-P is likely to degrade readily in soil under aerobic conditions. In water, mecoprop-P has been demonstrated to degrade in water/sediment systems following an initial lag phase and is readily biodegradeable according to CA 7.2.2.1/01 Feil (2010). However, in the surface waters mineralisation study, CA 7.2.2.2/02 Traub (2014), mecoprop-P was not found to degrade over the study period and therefore was considered persistent in surface waters.
	The online paper by Walters provides an overview of possible degradation processes that mecoprop-P could undergo in the environment and gives an indication of the types of breakdown products that could arise e.g. phenols and organochlorine compounds.

Water Treatment Process

Water treatment processes vary substantially throughout the EU. In order to make an assessment of the metabolism of mecoprop-P during water treatment numerous processes must be considered. There are several processes which appear to be common amongst water treatment, with some treatment plants using them all and

others using combination. The processes can be categorised into filtration, advanced treatment and disinfection. Each is described in the following paragraphs.

Filtration

Filtration sieves the water, removing any large particles. In addition to this the use of slow sand filters encourages bacteria to grow, which will break down organic compounds in the water.

Advanced Treatment

Granulated Activated Carbon (GAC) filters can be used. This is often in conjunction with ozone treatment. This process is intended to remove pesticides.

Disinfection

Chlorine disinfects the water, to eliminate potentially harmful micro-organisms such as bacteria. The water can also be passed through a UV light for disinfection.

Based upon the information above the following processes will be considered within this position paper:
- Sand filters
- GAC filters
- Ozonation
- Chlorination
- UV

Sand Filters

Slow sand filtration (or biological filtration) encourages the growth of micro-organisms within the filtration system. The bacterial population degradable organic matter present in the raw water is gradually broken down to water, carbon dioxide and innocuous inorganic salts (sulphates , nitrates and chlorides) which can go on to break down organic compounds in water. Their action is purely biological and does not require chemicals or pressure. Bacterial activity is most pronounced in the upper part of the filter bed under aerobic conditions.

Mecoprop-P is known to rapidly degrade under the presence of large microbial populations. This is demonstrated in the paper by Zipper *et al (1999)*, whereby the degradation of the herbicides mecoprop, dichlorprop and 2,4-D by activated sewage sludge was evaluated under aerobic and anaerobic conditions. This information indicates that mecoprop-P would be degraded rapidly by the microbial population within the sand filters.

RMS comments:	Zipper *et al* (1999): Fate of herbicides mecoprop, dichlorprop, and 2,4-D in aerobic and anaerobic sewage sludge as determined by laboratory batch studies and enantiomer-specific analysis.
	The purpose of the study was to evaluate the potential for degradation of mecoprop, dichloroprop, and 2,4-D in the aerobic and anaerobic compartment of a sewage treatment plant with particular emphasis on the stereochemistry of the compounds.
	Aerobic degradation experiments with the racemic mixtures of mecoprop and dichlorprop revealed that activated sludge collected from the aeration tank of a municipal waste water treatment plant degraded both enantiomers of mecoprop and dichlorprop within 7 days, albeit in an enantioselective manner; the (*S*) enantiomers were preferentially degraded. Degradation started after a lag-phase (104-149 h) and then commenced with rates of 174 – 225 µmol/h/g dry weight. Mecoprop, dichlorprop, and 2,4-D were completely metabolized under aerobic conditions, as shown by the 86–98% elimination of dissolved organic carbon. Neither 4-chloro-2-methylphenol nor 2,4-dichlorophenol (proposed initial metabolites of aerobic degradation of mecoprop and dichloroprop respectively) were detected by HPLC.
	Under anaerobic conditions, the concentration of 2,4-D decreased exponentially with a first-order reaction rate constant of 0.24 per day and without a lag phase. After an incubation time of 17 days,

	2,4-D was completely removed. 2,4-Dichlorophenol was the main metabolite of anaerobic 2,4-D degradation; only traces of 4-chlorophenol were detected. In contrast, the chiral phenoxypropionic acid herbicides mecoprop and dichlorprop persisted under anaerobic conditions during 49 days of incubation. The RMS agrees that mecoprop-P is likely to degrade in aerobic biological filtration systems/slow sand filters. Additionally, mecoprop-P is considered readily biodegradeable as demonstrated in CA 7.2.2.1/01 Feil (2010).

Granular Activated Carbon (GAC) Filters

Granular Activated Carbon (GAC) filters are used to adsorb organic substances. Water is passed through the filters and substances accumulate on the filter. The molecular weight and solubility of a compound is important when considering whether a compound will adsorb to GAC filters.

Mecoprop-P has a very high probability of being adsorbed by active carbon, according to its chemical properties. The adsorption of mecoprop-P to activated carbon is well known, with Petrie AJ *et al* (1993) confirming active carbon as a good method of removing phenoxy herbicides from water.

RMS comments	Sorption of compounds to activated carbon is dependent on the properties of the substance and surface characteristics of the activated carbon. The RMS does not agree that mecoprop-P has a very high probability of sorbing to activated carbon based on its chemical properties. Properties listed in SANCO/3065/99 (14th April 2003) indicate that mecoprop-P will be largely ionised at environmentally relevant pHs (pH > pKa of 3.86) and that partition coefficients of mecoprop-P decrease with increasing pH. Generally, more polar molecules (low logPow) are less likely to sorb to activated carbon. Physical-chemical parameters of mecoprop-P as listed in SANCO/3065/99 (14th April 2003) $\begin{array}{\|l\|l\|}\hline \textbf{Parameter} & \textbf{Value} \\\hline \text{Molecular mass (g/mol)} & 214.65 \\\hline \text{Water solubility (mg/l)} & 860 \text{ at pH } 3.1 \\\hline \text{pKa} & 3.86 \\\hline \text{logPow} & 1.43 \text{ at pH } 5 \\ & 0.02 \text{ at pH } 7 \\ & -0.18 \text{ at pH } 9 \\\hline \end{array}$ Petrie AJ et al (1993): the effectiveness of water treatment processes for removal of herbicides. The efficiencies of water treatment processes at removing herbicides (MCPA, mecoprop, isoproturon, linuron and chlortoluron) from freshwater samples (distilled water and river water) were investigated. Laboratory-based simulations of filtration treatments were carried out using a number of types of activated carbon, sand, clay and peat. Results of filtration experiments using activated carbon beds are shown in table 1 below indicate that at high flow rates and with solutions of high concentrations of herbicides as regards 'pollution' (i.e. 3 mg/l), activated carbon could remove 100% of the herbicide load.

TABLE 1

Filtration of herbicides through column beds of Norit ROW 0.8 SUPRA activated carbon

Herbicide load (µg)	Carbon bed dimensions		Filtration rate $(cm^3 min^{-1})$	EBCT % (min)	Removal of total herbicides
	Internal diameter (cm)	Height (cm)			
6	3	14	30	3.3	100
6	1.6	19	7	5	100
600	3	14	30	3.3	100
600	1.6	19	7	5	100

A volume (200 cm^3) of either 30 µg l^{-1} or 3000 µg l^{-1} distilled water solutions of mixtures of the three carbamate or the two chlorphenoxy acid herbicides were filtered through glass columns containing Norit ROW 0.8 SUPRA carbon (particle size 0.425–1.800 mm).

The paper concludes that activated carbon is a potentially useful means of removing chlorphenoxy acid and carbamate herbicides from freshwaters, with Norit the most effective brand of activated carbon used in the study.

The RMS considers that removal efficiency of granular activated charcoal filters towards mecoprop-P will be dependent on the type of activated carbon used and the conditions under which it operates. Sorption to activated carbon filters is unlikely to produce any degradation products that need to be considered further.

Ozonation

Ozone is a strong oxidising agent and is used in water treatment to react directly with the constituents in water.

Under ozonation mecoprop-P would be expected to undergo some oxidation up to its peroxy acid form (a minor reaction pathway, most likely via reaction with nascent hydrogen peroxide (Sauer, 1999) Figure 1 displays this reaction. The resulting 2-(4-chloro-2-methylphenoxy)propaneperoxoic acid would be highly unstable and liable to undergo homolytic bond fission to give free radicals; the further breakdown of which would be via a cascade radical mechanism similar to that induced by e.g. irradiation with UV light. In addition, if the conditions are found to be very forcing, the double bonds within the aromatic part of the molecule may be attacked directly by ozone to force ring opening of the phenol moiety to give ultimately carbon dioxide
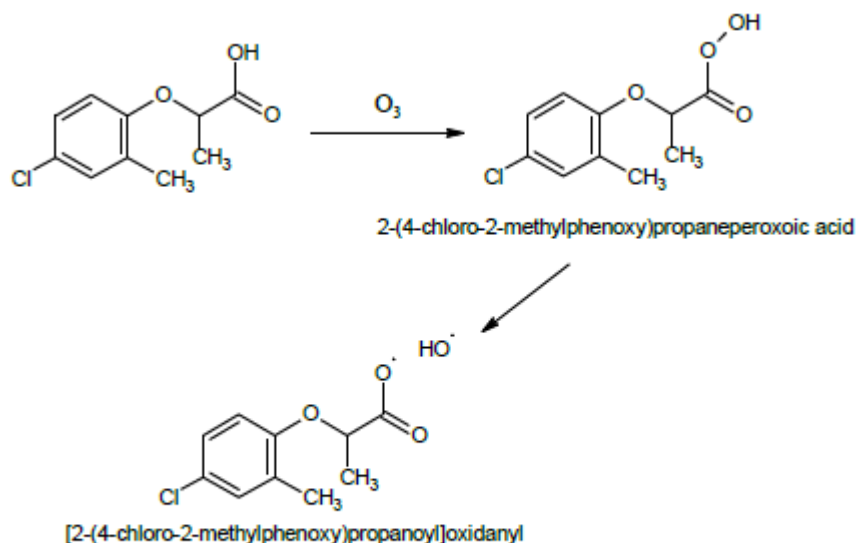
2-(4-chloro-2-methylphenoxy)propaneperoxoic acid

[2-(4-chloro-2-methylphenoxy)propanoyl]oxidanyl

Figure 1   Oxidation of Mecoprop-P with ozone (minor pathway) & unstable radical formation

RMS comments:	Sauer *et al* (1999): Formation of hydrogen peroxide and the ozonolysis of isoprene and simple alkenes under humid conditions
	Sauer (1999) investigates the gas phase ozonolysis of isoprene and simple alkenes under humid conditions and considers the atmospheric relevance of the results. It is unclear how this paper relates to the ozonolysis of mecoprop-P in water treatment systems. The reaction mechanism provided by the applicant in figure 1 (above) is not reported in the paper.
	Ozone reacts with most organic compounds either by direct attack or through the formation of hydroxyl radicals formed by the depletion of ozone. The RMS considers that mecoprop-P is likely to be oxidised during ozone treatment, but the identity and toxicity of the final reaction products likely to form under typical water treatment conditions are unclear from the information provided.

Chlorination

The introduction of elemental chlorine could give rise to the free radical induced degradation of mecoprop-P similar to that caused by e.g. irradiation with UV light (see below). Otherwise, HOCl (or chlorine water) is the major reactive species which is derived from elemental chlorine take-up into water. HOCl could degrade mecoprop-P via oxidation, addition or electrophilic substitution routes with the latter tending to dominate (Deborde M & Gunten UV, 2008).

RMS comments:	Deborde M & Gunten UV, 2008: Reactions of chlorine with inorganic and organic compounds during water treatment – Kinetics and mechanisms: A critical review
	The paper provides a review of the mechanisms and kinetics of reactions between chlorine and inorganic and organic compounds during water treatment. For most micropollutants, HOCl is the major reactive chlorine species during chlorination processes. In the case of organic compounds, second-order rate constants for chlorination vary over 10 orders of magnitude (i.e. $<0.1–10^9 M^{-1} s^{-1}$). Oxidation, addition and electrophilic substitution reactions with organic compounds are possible pathways. However, from a kinetic point of view, usually only electrophilic attack is significant. Chlorine reactivity limited to particular sites (mainly amines, reduced sulphur moieties or activated aromatic systems) is commonly observed during chlorination processes and small modifications in the parent compound's structure are expected for the primary attack. Linear structure–activity relationships can be used to make predictions/estimates of the reactivity of functional groups based on structural analogy. Furthermore, comparison of chlorine to ozone reactivity towards aromatic compounds (electrophilic attack) shows a good correlation, with chlorine rate constants being about four orders of magnitude smaller than those for ozone.

	Mecoprop is not considered directly in the paper by Deborde & Gunten, but the RMS considers it likely that it will react with chlorine to some extent. The identity of the final reaction products that are likely to form under typical water treatment conditions are unclear from the information provided.

UV

UV is normally used towards the end of the water treatment process as a final disinfecting stage. It is unlikely that pesticides would still be present at this stage of water treatment, but the potential metabolism under UV has still been considered to account for treatment plants operational differences.

Some information on the metabolism of mecoprop-P under UV light can be obtained from aqueous photolysis studies available on the active substance.

Klöpffer W (1991) assessed the phototransformation of mecoprop-P in water. This study was not conducted to current guidelines and was therefore only considered as supporting data under CA 7.2.1.2. However this study does provide some useful information on the behaviour of mecoprop-P under UV conditions (304 nm). It was concluded that, under the test conditions specified, mecoprop-P would be stable, with no significant decrease in the concentration of mecoprop-P during the irradiation time. This indicates that should mecoprop-P be exposed to UV irradiation it is unlikely to be degraded.

However, mecoprop has been shown to breakdown to its parent phenol and other small molecules when in aqueous media via photochemically induced free radical processes under some conditions (Boule *et al.* 2002), see Figure 2. Any phenols produced would be easily degraded by downstream biological treatment of waste waters.
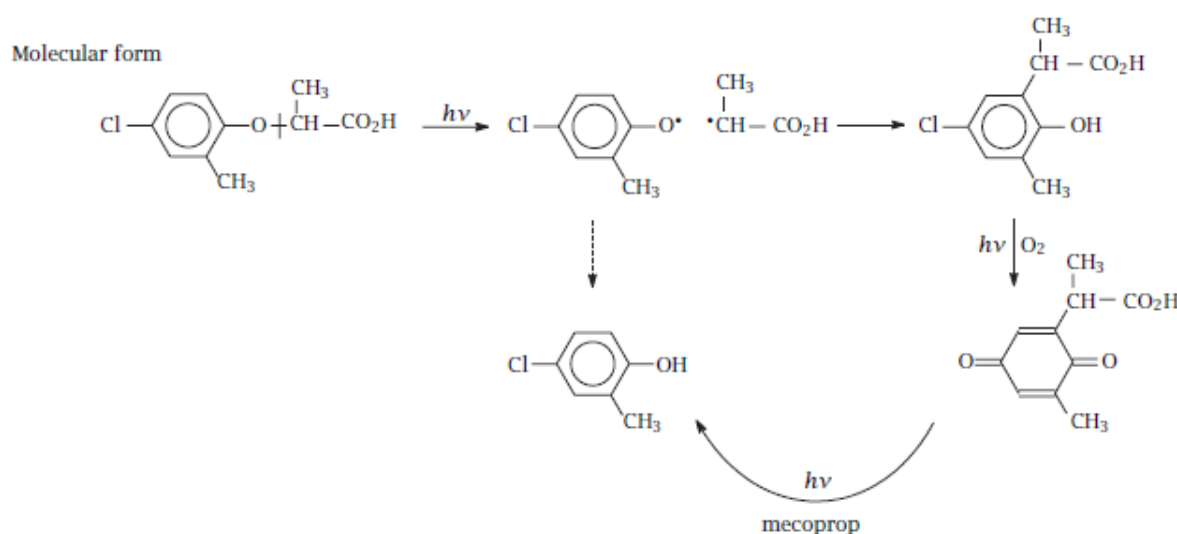
Figure 2. The UV induced degradation of mecoprop

It is difficult to predict what would happen under the specific conditions during the water treatment process, as data shows both degradation and stability to UV conditions (probably dependent upon the wavelength of the light mecoprop-P is exposed to), however indications are that if mecoprop is degraded, it would be to the parent phenol; a route which is well documented.

RMS comments:	UV/Vis absorption maximum for mecoprop-P as listed in SANCO/3065/99 (14th April 2003) show that mecoprop-P absorbs in the UV range (100-400nm): 203nm: ε 2.1 x 10^4 229nm: ε 9.8 x 10^3

280nm: ε 1.6 x 10^3
287nm: ε 1.5 x 10^3
290nm: ε 1.2 x 10^3

The applicant refers to Klopffer (1991) which was evaluated in the DAR for the original approval (1998). The concentration of mecoprop-P averaged 0.836 µg/ml over 144 hours of exposure to light with 304 nm wavelength, compared to a starting concentration of 0.9 µg/ml. Therefore, mecoprop-P was considered stable to photolysis in water at 304nm.

In addition to the aqueous photolysis study by Klopffer (1991), CA 7.2.1.1/01, Connor (1996)b was submitted for the purpose of renewal (see section B.8.2.1 for evaluation). Mecoprop-P was found to undergo photolysis in water following irradiation with light at wavelengths >300nm over 30 days. At pH 7, *o*-cresol was identified as a major degradation product at a maximum of 30.4% AR and a further 20 unidentified degradates were reported at <10% AR.
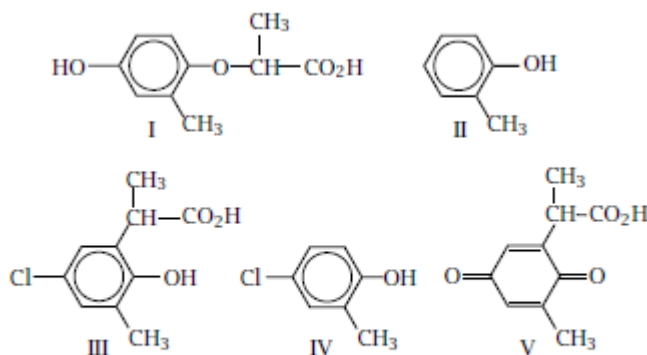
Boule et al. (2002): Direct photo transformation of aromatic pesticides in aqueous solution

The paper investigates the photochemical behaviour of a number of aromatic pesticides (including mecoprop). The main reactions can be separated into three different classes:
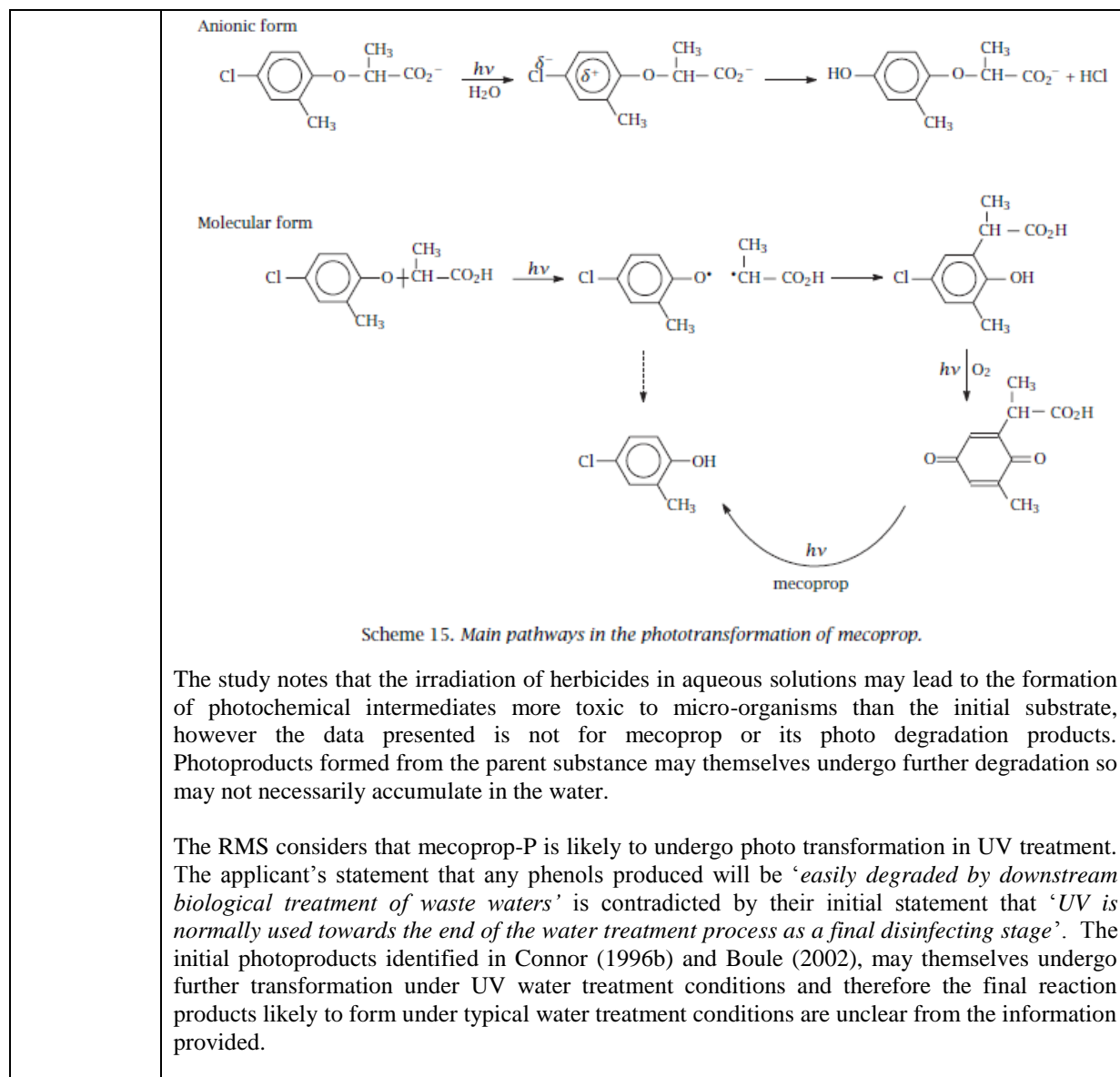1. Reactions involving carbon-halogen bonds
2. Reactions involving the aromatic ring
3. Reactions of the aliphatic moiety

The nature of substituents and their relative positions on the ring play a major role in the orientation of the reactions. The molecular and ionic forms of ionisable molecules may have different photochemical behaviour and a wavelength effect is observed with some compounds.

Mecoprop is presented as an example of a complex mechanism which depends on both pH and irradiation wavelength. When the anionic form (at pH = 5.5) is irradiated at λ < 350nm photo hydrolysis is reported to account for about 90% of the transformation (formation of I) (see scheme 14 below). The formation of 2-methylphenol (II) is also reported but as a minor pathway. I and II appear when an aqueous solution of the molecular form of mecoprop is irradiated (at pH = 2.15) but only account for a low percentage of the transformation. The main product (III) results from photo rearrangement. 4-chloro-2-methylphenol (IV) results from ether bond scission and the substituted quinone (V) is also detected. When an unbuffered solution of mecoprop is irradiated in sunlight or in near UV light (365nm with minor emission at 313 and 334 nm) the photo transformation is very slow and the main product is IV. The main photo transformation pathways are presented in scheme 15 below.

Scheme 14.

Scheme 15. *Main pathways in the phototransformation of mecoprop.*

The study notes that the irradiation of herbicides in aqueous solutions may lead to the formation of photochemical intermediates more toxic to micro-organisms than the initial substrate, however the data presented is not for mecoprop or its photo degradation products. Photoproducts formed from the parent substance may themselves undergo further degradation so may not necessarily accumulate in the water.

The RMS considers that mecoprop-P is likely to undergo photo transformation in UV treatment. The applicant's statement that any phenols produced will be '*easily degraded by downstream biological treatment of waste waters*' is contradicted by their initial statement that '*UV is normally used towards the end of the water treatment process as a final disinfecting stage*'. The initial photoproducts identified in Connor (1996b) and Boule (2002), may themselves undergo further transformation under UV water treatment conditions and therefore the final reaction products likely to form under typical water treatment conditions are unclear from the information provided.

Conclusions

After assessing the potential mechanisms of mecoprop-P removal in water treatment procedures, it can be concluded that it is likely mecoprop-P will be adsorbed onto Granular Activated Carbon (GAC) filters or degraded to CO_2 by micro-organisms present in slow sand filter beds.

Should any mecoprop-P remain through to ozonation, chlorination or UV treatments then the potential routes of metabolism are not expected to result in adverse degradation products.

RMS comments:	The RMS agrees that mecoprop-P is likely to undergo aerobic degradation in slow sand filter beds and could be removed by GAC filters. Any mecoprop-P present during ozonation, chlorination or UV treatment is likely to undergo transformation, probably via organochloride or substituted phenol intermediates. Whether these intermediates will react further or remain in the treated water at the end of the process, and the likely concentrations at which they will be formed, cannot be established from the available information.

References

Boule, P. *et al* (2002): Direct phototransformation of aromatic pesticides. Published in: International Journal of Photoenergy, Vol. 4. Pages 69-78

Deborde, M, van Gunten, U. (2008) Reactions of chlorine with inorganic and organic compounds during water treatment – kinetics and mechanisms: a critical review, Published in Water Research, Vol. 42. Pages 13-51

Klöpffer W (1991): Determination of the Phototransformation in water of Mecoprop-p According to UBA Test Guideline Direct Phototransformation, Unpublished report BE-P-49-91-PHO-02

Petrie AJ, Melvin MAL, Plane NH and Littlejohn JW (1993) The effectiveness of water treatment processes for removal of herbicides. *The Science of the Total Environment*; 135, 161-169

Sauer, F *et al* (1999): Formation of hydrogen peroxide in the ozonolysis of isoprene and simple alkenes under humid conditions, Published in Atmospheric Environment, Vol 33, Issue 2 pages 229-241

Walters, J: Environmental Fate of 2,4-Dichlorophenoxyacetic acid, Dept of Pesticide Regulation, Sacramento, California.

Zipper, Ch., *et al* (1999): Fate of the herbicides mecoprop, dichlorprop and 2,4-D in aerobic and anaerobic sewage sludge as determined by laboratory batch studies and enantiomer-specific analysis. Published in: Biodegradation, 10, pages

B.8.3. FATE AND BEHAVIOUR IN AIR

B.8.3.1. Route and rate of degradation in air (CA 7.3.1)

RMS comments:	7 studies were assessed for the original approval of mecoprop-P in the DAR (1998) and Addendum II to DAR (2002). No new data have been submitted.

Report:	**Kubiak, 1994a**
Title	Investigation of the volatilization of ^{14}C-MCPP-P and ^{14}C-Bifenox formulated according to Foxtril super (RPA30535H) from plant surfaces under laboratory conditions. Study No RPA15
Guidelines:	BBA guidelines IV 6-1 (phase 2)
GLP:	Yes
Deviations	None reported

Previous evaluations:	In DAR for original approval (1998). The original evaluation has been reproduced below.

Methods

The volatilization of ^{14}C-MCPP-P, 99.5% pure, from plant surfaces was studied according to BBA guidelines IV 6-1 (phase 2).

In the study, a mixture of mecoprop-P and Bifenox formulated according to Foxtril Super was used. In a volatilization chamber, the test substance was applied to French beans which were at the state of blossom and formation of fruit. The sprayed surface was 0.5 m^2 equivalent to 876 g MCPP-P/ha. The soil were covered with filter paper during application. In the chamber, the temperature was maintained at 20°C and the relative humidity at 50%. The wind speed was 1 m/s above the plants and 0.3 m/s in the plant height. Volatile substances were collected from the two air channels in PU-foams, water traps (freezing) and CO$_2$ traps at the sampling times after 1, 2, 3, 18 and 24 hours. Analyses were performed by LSC and HPLC.

Two experiments were performed: PI and PII.

Results

PI:

After deduction of application losses and the radioactivity adhering to the soil cover, the calculated amount of radioactivity applied to the plants were 32.25 mg MCPP-P equivalents.

The total air volume of the upper channel was 302.28 m^3/h and the sample volume was 17.49 m^3/h. The total air volume in the lower channel was 123.83 m^3/h and the sample volume was 9.33 m^3/h. No ^{14}C-MCPP-P was found in the PU foams at any sampling time. In the water traps the recovery of MCPP-P was below the detection limit, DL, which was <8.6×10^{-6} mg (20 dpm above background). $^{14}CO_2$ was not detected in the CO_2 traps.

After 24 hours, 91.7% of the ^{14}C-MCPP-P applied to the plants could be determined in the plant extracts and 17.8% were estimated after combustion to be non-extractable residues.

PII:

In the second experiment, the applied ^{14}C-MCPP-P to plants were 60.11 mg MCPP-P equivalents. The air volume were comparable to the previous study. No ^{14}C-MCPP-P was recovered from the air. After 24 hours, 78.7% of the applied amount was extracted from the plants and 17.8% was non-extractable residues.

In both studies < 0.1% of the applied ^{14}C was measured at the walls of the volatilization chambers and the channels.

Table B. 8.148. *Volatilization of MCPP-P formulated as Foxtril Super from plant surfaces. * Upper and lower air channels*

Experiment	Applied MCPP-P	Total air m^3/h	Air sample m^3/h	Plants		
	mg	Upper* Lower	Upper Lower	Extract mg eqv. (%)	NER (%)	Total (%)
PI	32.25	302.28 123.88	17.49 9.33	26.58 91.7%	5.73 17.8%	35.37 109.7%
PII	60.11	308.31 119.39	17.61 9.15	47.33 78.7%	10.71 17.8%	58.06 96.6%

1998 Evaluation Comments

The study is a thorough study showing that no volatilization took place during the laboratory study. The study was performed in the dark. In natural environment, the sun would have increased the temperature and the volatilization potential on the plant surfaces.

Report:	Kubiak, 1994b
Title	Investigation of the volatilization of ^{14}C-MCPP-P and ^{14}C-Bifenox formulated according to Verigal D (RPA44040H) from plant surfaces under laboratory conditions. Study No RPA14
Guidelines:	BBA guidelines IV 6-1 (phase 2)
GLP:	Yes
Deviations	None reported

Previous evaluations:	In DAR for original approval (1998). The original evaluation has been reproduced below.

Methods

The volatilization of ^{14}C-MCPP-P, 99.5% pure, from plant surfaces was studied according to BBA guidelines IV 6-1 (phase 2).

In the study, a mixture of mecoprop-P and bifenox formulated according to Verigal D was used. In a volatilization chamber, the test substance was applied to French beans which were at the state of blossom and formation of fruit. The sprayed surface was 0.5 m^2, equivalent to 924 g MCPP-P/ha. The soil were covered with filter paper during application. In the chamber, the temperature was maintained at 20°C and the relative humidity at 50%. The wind speed was 1 m/s above the plants and 0.3 m/s in the plant height. Volatile substances were collected from the two

air channels in PU-foams, water traps (freezing) and CO_2 traps at the sampling times after 1, 2, 3, 18 and 24 hours. Analyses were performed by LSC and HPLC.

Two experiments were performed: PI and PII

Results
During the 24 hours study duration, no volatilization of ^{14}C-MCPP-P was measured. No radioactivity was measured from water frozen out of the air and no radioactivity was found in the CO_2 traps. At the walls of the volatilization chambers and the channels < 0.1% of the applied ^{14}C was measured.

Table B. 8.149. *Volatilization of MCPP-P formulated as Verigal D from plant surfaces. * Upper and lower air channels*

Experiment	Applied MCPP-P mg	Total air m³/h Upper* Lower	Air sample m³/h Upper Lower	Plants		
				extract mg eqv. (%)	NER (%)	Total (%)
PI	43.76	300.11 126.05	17.48 9.09	31.68 74.5%	9.26 21.8%	40.94 96.4%
PII	42.00	300.11 126.05	17.48 9.09	38.49 91.6%	4.00 9.5%	42.49 101.1%

1998 Evaluation Comments
The study was performed as the previous and the same comment applies.

Report:	**Jendrejczak *et al*.,1994a**
Title	Soil surface volatilization study of MCPP-P and Bifenox formulated as EXP30535 (official German reference No. RPA30535H). RPA Doc. 436989
Guidelines:	BBA IV, 6.1-2
GLP:	Yes
Deviations	None reported

Previous evaluations:	In DAR for original approval (1998). The original evaluation has been reproduced below.

Methods
The volatilization from the soil surface of ^{14}C-MCPP-P and ^{14}C-Bifenox formulated as RPA30535H was studied by direct determination using a volatilization chamber according to BBA IV, 6.1-2.

The SC formulation containing 292 g/l MCPP-P and 250 g/l Bifenox was added ^{14}C-MCPP-P (ring labelled, 99.5% pure) and ^{14}C-Bifenox. The soil was a sandy soil (German standard soil 2.1) and 230 g dry soil was placed in a container and moistured to 60% of maximal water capacity (MWC). The soil container area of 213.7 cm² was applied with 1.097 mg MCPP-P, corresponding to about 513 g MCPP-P/ha. The soil container was transferred to the volatilization chamber. The air was monitored after 1, 3, 6, and 24 hours and the soil after 24 hours.

Table B. 8.150. *Soil characteristics*

Soil	pH	Sand % 63-2000 µm	Silt % 2-63 µm	Clay % < 2 µm	OC%	FMC	CEC
Sand	5.9	87.4	9.1	3.5	0.7	26.1	4.9

Table B. 8.151. *Microclimatic conditions (measured) in the volatilization chamber*

Time	Air humidity	Air temperature	Air speed flow	Soil temperature
0 - 24 hours	32.7 ±2.1 %RH	23.3 ±0.6°C	1.45 ±0.12 m/s	22.6 ±0.6°C

Results

At sampling hours 1, 3 and 6, less than 0.2% of the estimated applied radioactivity was found in the air traps. About 0.5% of the estimated applied radioactivity was found in the air traps after 24 hours. In the soil, 103% of the estimated applied radioactivity were extracted and an additional 5.4% were found by combustion (non-extractable residues). MCPP-P represented about 41.3% of the radioactivity extracted from the soil.

Thus, it can be assumed that less than 1% of MCPP-P and Bifenox applied was volatilized from the soil surface within 24 hours when they were formulated as RPA30535.

Table B. 8.152. *Radioactivity and distribution after 24 hours. * Radioactivity applied: 200.164 kBq*

Compartment	Radioactivity (kBq)	% of applied radioactivity*
Air	1.088	0.543
Soil	217.09	108.457
Chamber	1.666	0.832
Total	219.845	109.832

1998 Evaluation Comments

The study was acceptable. MCPP-P had a low volatilization potential from soil in the study. The results represent the total ^{14}C activity from ^{14}C labelled MCPP-P and Bifenox.

Report:	Jendrejczak *et al*., 1994b
Title	Soil surface volatilization study of MCPP-P and Bifenox formulated as EXP04404 (official German reference No. RPA44040H). RPA Doc. 436793
Guidelines:	BBA IV, 6.1-2
GLP:	Yes
Deviations	None reported

Previous evaluations:	In DAR for original approval (1998). The original evaluation has been reproduced below.

Methods

The volatilization of ^{14}C-MCPP-P and ^{14}C-Bifenox from soil surface formulated as RPA44040H was studied by direct determination using a volatilization chamber according to BBA IV, 6.1-2.

The SC formulation containing 308 g/l MCPP-P and 250 g/l Bifenox was added ^{14}C-MCPP-P (ring labelled, 99.5% pure) and ^{14}C-Bifenox. The soil was a sandy soil (German standard soil 2.1) and 230 g dry soil was placed in a container and moistured to 60% of maximal water capacity (MWC). The soil container area of 213.7 cm^2 was applied with 1.453 mg MCPP-P, corresponding to about 680 g MCPP-P/ha. The soil container was transferred to the volatilization chamber. The air was monitored after 1, 3, 6 and 24 hours and the soil after 24 hours.

Table B. 8.153. *Soil characteristics*

Soil	pH	Sand % 63-2000 μm	Silt % 2-63 μm	Clay % < 2 μm	OC%	FMC	CEC
Sand	5.9	87.4	9.1	3.5	0.7	26.1	4.9

Table B. 8.154. *Microclimatic conditions (measured) in the volatilization chamber (mean ±S.D. values)*

Time	Air humidity	Air temperature	Air speed flow	Soil temperature
0 - 24 hours	32.1 ±1.8 %RH	22.1 ±0.3°C	1.24 ±0.11 m/s	18.2 ±0.2°C

Results
At sampling hours 1, 3 and 6 less than 0.2% of the estimated applied radioactivity was found in the air traps. About 0.7% of the estimated applied radioactivity was found in the air traps after 24 hours. In the soil 102% of the estimated applied radioactivity were extracted from the soil and an additional 6.5% were found by combustion (non-extractable residues). MCPP-P represented about 33.5% of the radioactivity extracted from the soil.

Thus, it can be assumed that less than 1% of MCPP and Bifenox applied was volatilized from the soil surface within 24 hours when they were formulated as RPA440440.

Table B. 8.155. *Radioactivity and distribution after 24 hours. * Radioactivity applied: 271.899 kBq.*

Compartment	Radioactivity (kBq)	% of applied radioactivity*
Air	1.901	0.699
Soil	294.706	108.380
Chamber	3.756	1.381
Total	300.363	110.468

1998 Evaluation Comments
The study was acceptable. MCPP-P had a low volatilization potential from soil in the study. The results represent the total ^{14}C activity from ^{14}C labelled MCPP-P and Bifenox.

Report:	**Hesse *et al.*, 1993**
Title	Evaluation of the volatilization of mecoprop-P and 2,4-D after application of BAS 076 10 H under field conditions. BASF Report No. 3585.
Guidelines:	BBA IV 6-1 (1990).
GLP:	Yes
Deviations	None reported

Previous evaluations:	In DAR for original approval (1998). The original evaluation has been reproduced below.

Methods
The volatilzation of mecoprop-P and 2,4-D was tested in two 24 hour field studies according to BBA IV 6-1 (1990).

The field location was located in Germany at Birkenheide, Rhineland-Palatinate and was 20 m long and 2 m wide. The test substance was Duplosan KV Combi, BAS 07610H, containing 338.08 g/l MCPP-P + 160.77 g/l 2,4-D formulated as dimethylammonium salt. The test substance was applied onto spring wheat at 4 l/ha, corresponding to 1.35 kg mecoprop-P/ha. The seeding density was 500 seeds/m^2. The plants were seeded at March 18 and sprayed on May 14 (Field I) and May 21 (Field II). Soil and plant samples were sampled and analyzed to determine the volatilization after 1, 3, 6, 10 and 24 hours. The quantity of volatilization was derived from the observed decrease in residues. The limit of determination was 0.01 mg/kg in soil and 0.05 mg/kg in plants.

Table B. 8.156. *Soil characteristics. OC: Organic carbon content. MWC: Maximum water capacity (g/100 g soil)*

Field: Soil type	pH	Sand % 63-2000 μm	Silt % 2-63 μm	Clay % < 2 μm	OC %	MWC %
I: clayey sand	4.6	81	6	13	1.2	30
II: clayey-loamy sand	4.6	80	8	12	0.7	30

Sunny, warm weather prevailed during the study with higher temperature especially in Field I. Neither extreme temperatures nor stormy or rainy conditions occurred during the trial.

Results

The observed decrease of mecoprop-P within 24 hours after application amounted to 51% and 42% in the soil and 47% and 44% in the plant samples.

Photodegradation on soil surfaces is known to take place.

The original results in μg were converted to the tested surface area of 181 cm^2 and given in $\mu g/cm^2$.

Table B. 8.157. *Field data*

Field: Soil type	MCPP-P kg/ha	Spray date	Soil temp*	Air temp	Rel.hum	Wind m/s
I: clayey sand	1.5	May 14, 11:40	32°C	28°C	36	0.5
II: clayey-loamy sand	1.35	May 21, 06:30	13°C	6°C	91	0.0

* temperature 5-10 cm below soil surface

Table B. 8.158. *Recovery*

Field: Soil type	Recovery at time after application (hours)					
	0.25	1	3	6	10	24
I: clayey sand 　　Soil, $\mu g/cm^2$ 　　Plants, mg/kg	4.66 64.8	4.19 88.6	2.68 52.2	2.83 35.2	1.52 38.0	2.15 38.0
II: clayey-loamy sand 　　Soil, $\mu g/cm^2$ 　　Plants, mg/kg	7.06 93.7	6.20 131.6	4.75 105.3	5.23 118.0	4.65 88.7	3.68 63.5

1998 Evaluation Comments

The different degradation processes can not be quantified in such a study. Both biotic and abiotic degradation (microbial and hydrolysis, photolysis) takes place as well as mobility and volatilisation.

However, assuming the degradation half-life to be 7-20 days and the photolytic half-life to be > 4 days, the study does indicate that volatilization does take place to some extent though even the laboratory studies have shown the opposite.

Report:	Maestracci, 1994
Title	Mecoprop-P estimation of the rate of photochemical transformation in the atmosphere under tropospheric conditions. Doc 436537.
Guidelines:	OECD Environment monograph No. 61 (1992).
GLP:	Yes
Deviations	None reported

Previous evaluations:	In DAR for original approval (1998) and Addendum II to DAR (2002). The original evaluation from Addendum II to DAR (2002) has been reproduced below.

Methods

The rate of photochemical transformation of mecoprop-P in the atmosphere under tropospheric conditions was estimated according to the method described in OECD Environment monograph No. 61 (1992).

The rate constant for the reaction of mecoprop with OH-radicals was calculated based on the structure formula. The diurnal and seasonally averaged concentration of hydroxyl radicals in the troposphere of the Northern hemisphere was set at 5×10^5 molecules/cm^3.

Results

Based on the reaction rate constant k calculated to be 18.28×10^{-12} cm^3/molecules/s and assuming first order reaction kinetics, the photochemical half-life in air was calculated to be 21 daylight hours.

Table B. 8.159. *Photochemical half-life in air.*

Method	Rate constant = k (cm^3/molecule/sec)	OH-concentration, (molecules/cm^3)	Half-life (hours)
Study calculation	18.28884×10^{-12}	5×10^5	21
AOP programme*	17.3954×10^{-12}	5×10^5	22

*AOP: ref.: Atmospheric Oxidation Program. AOPWIN. Syracuse Research Corporation, Syracuse 1995.

Model estimations, based on the AOP programme which is a computer model programme based on structure analysis, has been included in the table as its calculations supports the calculations performed in the document.

2002 Evaluation Comments

The study calculation is acceptable and according to Atkinson 1987 and 1988. The calculation uses 24-hour days and is in agreement with model estimations performed by the rapporteur.

Report:	**Sarafin, 1991**
Title	Photochemical oxidative degradation of mecoprop (Atkinson). BASF Report No 3157.
Guidelines:	Atkinson's method (1987), International Journal of Chemical Kinetics, vol 19, pg799-828
GLP:	No
Deviations	Not applicable

Previous evaluations:	In DAR for original approval (1998). The original evaluation has been reproduced below.

The photochemical oxidative degradation of mecoprop was calculated according to Atkinson's method (1987).

The rate constant for the reaction of mecoprop with OH-radicals was calculated based on the structure formula. The diurnal and seasonally averaged concentration of hydroxyl radicals in the troposphere of the Northern hemisphere was set at 5×10^5 molecules/cm^3.

Results

Based on the reaction rate constant k of 8.5×10^{-12} cm^3/s and assuming first order reaction kinetics, the photochemical half-life in air was calculated to be 45 hours.

1998 Evaluation Comments

The study calculation is performed according to Ref. IIA. 7.2.3 (Atkinson 1987). Recent changes in the calculation methods would have resulted in an estimated shorter half-life (c.f. below).

The US-EPA, previously, used a 24 hour day and a concentration of 5×10^5 OH-radicals/cm^3 which is a 24 hour average that includes night-time when OH concentration is zero. Today, US-EPA uses a 12 hour day because OH-radicals only exist during sunlight hours and the 12 hour period is an average daylight time for a whole year. Recent experimental observations (Leifer 1993, Mount & Eisele 1992) determined a concentration value of 1.5×10^6 for daylight hours.

Using 12 hour day and 1.5×10^6 OH-radicals/cm^3 would result in a half-life of 15 hours:

$T\frac{1}{2} = \ln 2 / (8.5 \times 10^{-12} * 1.5 \times 10^6) = 543535$ s = 15 h

Table B. 8.160. *Estimated photochemical oxidative degradation half-lives*

	Rate constant = k (cm^3/molecule/sec)	OH-concentration, (molecules/cm^3)	Half-life (hours)
Study calc	8.5×10^{-12}	5×10^5	45
12 hours	8.5×10^{-12}	1.5×10^6	15
AOP programme* 12h 24h	17.4×10^{-12}	1.5×10^6 5×10^5	7.4 22

AOP: ref.: Atmospheric Oxidation Program. AOPWIN. Syracuse Research Corporation, Syracuse 1995.

The difference between the documents by Sarafin 1991 and Maestracci 1994 lies in the interpretation of the articles by Atkinson. However, taking into account that these calculation are estimates and the large uncertainties in the understanding of the ambient atmospheric concentrations of the OH radical, the results are sufficient close and acceptable.

B.8.3.2. **Transport via air (CA 7.3.2)**

Physical-chemistry parameters for mecoprop-P reported in DRAR-Volume 3CA-B2:
  Vapour pressure: 1.4×10^{-3} Pa at 25°C
  Henry's Law Constant: 1.7×10^{-4} Pa m^3 mol^{-1}

For comparison with the trigger values, the applicant has calculated the vapour pressure at 20°C as 7.3×10^{-4} Pa using the Clausius-Clapeyron equation. This exceeds both regulatory triggers for plant (10^{-5} Pa at 20°C) and soil (10^{-4} Pa at 20°C).

Laboratory volatilisation studies demonstrate <1% and <0.1% volatilisation from soil and plant surfaces respectively in 24 hours (Kubiak 1994a and b, Jendrejczak 1994 a and b). However, a field study (Hesse, 1993) concluded volatilisation takes place to some extent.

The photochemical oxidative degradation of mecoprop-P in air is rapid (half-life 21 hours calculated using Atkinson method, 24 hour day, 5×10^6 OH cm^{-3}). Therefore, although volatilisation from soil and plant surfaces may occur, long-range transport is not considered likely.

B.8.3.3. **Local and global effects (CA 7.3.3)**

No data are provided on local and global effects. Due to the rapid photochemical oxidative degradation in air of mecoprop-P; local and global effects are expected to be negligible.

B.8.4. Monitoring data concerning fate and behaviour of the active substance, metabolites, degradation and reaction products

Previous Evaluations:	In DAR for original approval (1998) monitoring data was submitted by the RMS. The data was for mecoprop not mecoprop-P, therefore the data has not been reproduced.

	A survey of available monitoring data throughout Europe has been conducted (CA 7.5/01, Aldous, 2015). Five studies were identified by the applicant as potentially relevant during the literature search.

Report:	CA 7.5/01 Aldous, E., Johnson, I. & Keirle, R. (2015)
Title	Review of monitoring and occurrence of mecoprop-P in surface freshwater, groundwater and drinking water in Europe. WRc plc, UK Report No. UC10693.01
Guidelines:	Not applicable
GLP:	No – not applicable

Previous evaluations:	None: Submitted for the purpose of renewal under Regulation 844/2012

Review Method

Information on the monitoring and occurrence of mecoprop-P in groundwater, surface freshwater and drinking water was collected. This information was obtained from monitoring programmes in the 28 European Union Member States, plus Norway and Switzerland, and collected for the period 2009 to 2014, although if there were a lack of data, information prior to this period was included as reference material. No reason for the selection of this 5 year period is provided.

The information was obtained from publically available data from professional contacts (government departments and agencies and research organisations) in the above countries, WRc in-house data and literature and web searches. The literature search was conducted using Science Direct using the search terms given in Table B. 8.161.

Table B. 8.161. Search criteria used for the identification of relevant literature on the occurrence of mecoprop-P

Search terms for mecoprop-P	Descriptor terms
Mecoprop-P MCPP CAS No: 16484-77-8 (R)-2-(4-Chloro-2-methylphenoxy)propanoic acid (R)-Mecoprop 2M-4XP d-Mecoprop Duplosan KV EINECS 240-539-0 Mecoprop, D- UNII-455R9M917H (R)-2-(4-Chloro-2-methylphenoxy)propionic acid Propanoic acid, 2-(4-chloro-2-methylphenoxy)-, (2R)- Propanoic acid, 2-(4-chloro-2-methylphenoxy)-, (R)- (9CI) Propionic acid, 2-((4-chloro-o-tolyl)oxy)-, (+)-	Occurrence River Stream Upland Water Surface freshwater Fresh water Ground water Drinking water Tap water

Data were classified by the study authors in terms of their reliability according to the analytical method used and the degree of quality assurance applied. Three categories (I to III) were used, where III is the most reliable, with an additional category, X. being used where there was inadequate information to classify the data. Where information is provided on analytical methodologies and / or accredited quality control (AQC), the data are considered reasonably reliable, falling under Category II or III. However, many databases and spreadsheets were provided with no accompanying methodology and some reports which lacked sufficient detail on this subject were classified as Category X.

Category III; Reliable
Studies or data generated according to validated methods that are internationally recognised by laboratories that are accredited (e.g. ISO, GLP). The methodology and test parameters used are well documented and complete.

Category II; Reliable with restrictions
Studies or data generated in which the studies do not comply with national or international guidelines but are well documented and based on sound scientific principles. This may include data generated before the establishment of standardised guidelines or studies conducted in laboratories that are not accredited.

Category I; Unreliable
Studies or data generated using an unorthodox methodology that may introduce uncertainties and negate scientific precision and accuracy. This may also include inconsistent or biased methodologies or studies where insufficient controls were used.

Category X; Insufficient data
Studies where insufficient or limited data (including that on the analytical methodology) are provided and the data cannot be classified. This is not to say that the studies are considered reliable or unreliable. Studies include data located in secondary sources that are insufficiently referenced as to locate the original data.

Category III and II data were considered by the study authors to be of a standard that is reliable and suitable for use in the assessment. Data form category I and X were not considered to be suitable for use. However the authors note that data assigned category X may be used in a supporting manner to contribute towards a 'weight of evidence' approach.

The authors note that most studies did not distinguish between the limit of detection (LOD) and the limit of quantification (LOQ) and it is often not clear which limit is reported. In such cases, the given limits have been quoted as LOD, whereas LOQ are presented only where specific reference has been made to this limit in the reported studies.

Results

Table B. 8.162 summarises the information found on monitoring and occurrence of mecoprop-P in groundwater, surface freshwater and drinking water in the identified time period (2009-2014). The RMS notes that a number of Member States reported that mecoprop-P is not specifically monitored, although mecoprop is monitored but analytical methods do not discriminate between isomers. Both Finland and Sweden commented that mecoprop had not been authorised in their countries for a number of years and therefore any information on mecoprop would most likely be relevant for mecoprop-P. However, as the request for information was for mecoprop-P only, data on mecoprop has not been reported. The RMS considers that requesting information on mecoprop-P only was too restrictive. Obtaining data on both mecoprop and mecoprop-P with supporting information on when mecoprop was last authorised in each Member State would provide a more comprehensive data set.

Table B. 8.162. Monitoring and detections of mecoprop-P in groundwater, surface freshwater and drinking water (in the period 2009 – 2014)

Country	Groundwater	Surface freshwater	Drinking water†
Austria	Not monitored	Not monitored*	Not monitored*
Belgium	Not monitored*	-	-
Bulgaria	Not monitored	Not monitored	Not monitored
Croatia	Not monitored	Not monitored	Not monitored
Cyprus	Not monitored	Not monitored	Not monitored
Czech Republic	Not monitored*	Not monitored	-
Denmark	Not monitored	-	-
Estonia	-	-	-
Finland	Not monitored*	Not monitored	No information
France	Not monitored	Not monitored	Not monitored
Germany	-	-	-
Greece	-	-	-
Hungary	Not monitored	Not monitored	Not monitored
Ireland	Not monitored	Mecoprop-P monitored and detected >0.1 µg l^{-1}	Mecoprop-P monitored and detected <0.1 µg l^{-1}
Italy	-	Mecoprop-P monitored and detected <0.1 µg l^{-1}	-
Latvia	Not monitored	Not monitored	Not monitored
Lithuania	Not monitored	Not monitored	Not monitored
Luxembourg	Mecoprop-P monitored and detected >0.1 µg l^{-1}	Mecoprop-P monitored and detected >0.1 µg l^{-1}	Not monitored
Malta	Not monitored	Not monitored	Not monitored
Norway	Mecoprop-P monitored and detected <0.1 µg l^{-1}	Mecoprop-P monitored and detected >0.1 µg l^{-1}	Not monitored
Poland	-	-	-
Portugal	-	Not monitored	-
Romania	-	-	-
Slovakia	Not monitored	Mecoprop-P monitored and detected >0.1 µg l^{-1}	Not monitored
Slovenia	Not monitored*	Not monitored*	-
Spain	Not monitored	Not monitored	Not monitored
Sweden	Not monitored*	Not monitored*	Not monitored*
Switzerland	Not monitored*	Mecoprop-P monitored and detected >0.1 µg l^{-1}	-
The Netherlands	Mecoprop-P monitored and detected >0.1 µg l^{-1}	Mecoprop-P monitored and detected <0.1 µg l^{-1}	Mecoprop-P monitored and detected <0.1 µg l^{-1}
UK :			
England	Not monitored*	Not monitored*	Not monitored*
Wales	Not monitored*	Not monitored*	Not monitored*
Scotland	Not monitored*	Not monitored*	Not monitored*
Northern Ireland	Not monitored*	Not monitored*	Not monitored*

- No information obtained

*Mecoprop-P is not specifically monitored. Mecoprop is monitored but the analytical methods do not distinguish between isomers.

†the report does not specify whether the drinking water data refers to drinking water after treatment or water taken from abstraction points prior to treatment.

Table B. 8.163 provides information on all the available monitoring data for groundwater, surface freshwater and drinking water. The majority of the reported data came from national monitoring programmes and were

categorised as X due an absence of information on the analytical methods. In many cases LOD and LOQ were not reported, however, information on the analytical methods were not specifically requested when gathering the data.

Table B. 8.163. Summary of available mecoprop-P monitoring data in groundwater, surface freshwater and drinking water

Country	Year	No. of sites	No. of samples	Detected (samples)		Samples showing values* >0.1 µg L⁻¹		Max. conc. µg L⁻¹	LoD / LoQ µg L⁻¹	Quality Category[1]
				No.	% of total	No.	% of total			
Groundwater (GW)										
Austria	-	-	-	-	-	-	-	-	-	-
Belgium (Flanders)	-	-	-	-	-	-	-	-	-	-
Belgium (Wallonia)	-	-	-	-	-	-	-	-	-	-
Bulgaria	-	-	-	-	-	-	-	-	-	-
Croatia	-	-	-	-	-	-	-	-	-	-
Cyprus	-	-	-	-	-	-	-	-	-	-
Czech Republic	-	-	-	-	-	-	-	-	-	-
Denmark	-	-	-	-	-	-	-	-	-	-
Estonia	-	-	-	-	-	-	-	-	-	-
Finland	-	-	-	-	-	-	-	-	-	-
France	-	-	-	-	-	-	-	-	-	-
Germany	-	-	-	-	-	-	-	-	-	-
Greece	-	-	-	-	-	-	-	-	-	-
Hungary	-	-	-	-	-	-	-	-	-	-
Ireland	-	-	-	-	-	-	-	-	-	-
Italy	-	-	-	-	-	-	-	-	-	-
Latvia	-	-	-	-	-	-	-	-	-	-
Lithuania	-	-	-	-	-	-	-	-	-	-
Luxembourg	2013	168	717	1	0.14	1	0.14	1.438	0.025	X
Malta	-	-	-	-	-	-	-	-	-	-
Norway	2009-2012	≥3	≥36	-	-	0	0	-	-	X
Poland	-	-	-	-	-	-	-	-	-	-
Portugal	-	-	-	-	-	-	-	-	-	-
Romania	-	-	-	-	-	-	-	-	-	-
Slovakia	-	-	-	-	-	-	-	-	-	-
Slovenia	-	-	-	-	-	-	-	-	-	-
Spain	-	-	-	-	-	-	-	-	-	-
Sweden	-	-	-	-	-	-	-	-	-	-
Switzerland	-	-	-	-	-	-	-	-	-	-
The Netherlands	2013	96	294	61	20.75	≤10	≤3.4	0.11	0.01-0.05	X
United Kingdom:										
England	-	-	-	-	-	-	-	-	-	-
Wales	-	-	-	-	-	-	-	-	-	-
Scotland	-	-	-	-	-	-	-	-	-	-
Northern Ireland	-	-	-	-	-	-	-	-	-	-
Total GW	2009-2013	267	≥1,047	62[a]	5.92	≤11	1.05	0.11-1.438	0.01-0.05	X
Surface Water (FW)										
Austria	-	-	-	-	-	-	-	-	-	-
Belgium	-	-	-	-	-	-	-	-	-	-
Bulgaria	-	-	-	-	-	-	-	-	-	-
Croatia	-	-	-	-	-	-	-	-	-	-
Cyprus	-	-	-	-	-	-	-	-	-	-

Country	Year	No. of sites	No. of samples	Detected (samples)		Samples showing values* >0.1 µg L^{-1}		Max. conc. µg L^{-1}	LoD / LoQ µg L^{-1}	Quality Category[1]
				No.	% of total	No.	% of total			
Czech Republic	-	-	-	-	-	-	-	-	-	-
Denmark	-	-	-	-	-	-	-	-	-	-
Estonia	-	-	-	-	-	-	-	-	-	-
Finland	-	-	-	-	-	-	-	-	-	-
France	-	-	-	-	-	-	-	-	-	-
Germany	-	-	-	-	-	-	-	-	-	-
Greece	-	-	-	-	-	-	-	-	-	-
Hungary	-	-	-	-	-	-	-	-	-	-
Ireland	2009-2013	≥82	2,495	252	10.1	0	0	< 0.02 - >0.02	0.02	X
	2011	26	250	-	-	≤7	≤2.8	0.025-0.3	0.05-0.1	X
Italy	2012	175	878	-	-	0	0	0.005-0.06	0.01-0.1	X
Latvia	-	-	-	-	-	-	-	-	-	-
Lithuania	-	-	-	-	-	-	-	-	-	-
Luxembourg	2013	24	189	59	31.22	10	5.29	0.437	≤0.025	X
Malta	-	-	-	-	-	-	-	-	-	-
Norway	2009-2013	≥3	49	43	87.76	14	28.57	0.12-1.8	0.01	X
Poland	-	-	-	-	-	-	-	-	-	-
Romania	-	-	-	-	-	-	-	-	-	-
Slovakia	2011	16	172	NR	-	12	6.97	0.05-0.23	0.1	X
Slovenia	-	-	-	-	-	-	-	-	-	-
Spain	-	-	-	-	-	-	-	-	-	-
Sweden	-	-	-	-	-	-	-	-	-	-
Switzerland	2012	5	45	45	100	NR	-	0.47	0.001	II
The Netherlands	2013	10	91	39	42.86	0	0	0.06	0.01-0.05	X
United Kingdom										
England	-	-	-	-	-	-	-	-	-	-
Wales	-	-	-	-	-	-	-	-	-	-
Scotland	-	-	-	-	-	-	-	-	-	-
Northern Ireland	-	-	-	-	-	-	-	-	-	-
Total FW	**2009 – 2013**	**≥341**	**4,169**	**438[a]**	**10.51**	**≥43**	**≥1.03**	**0.005-1.8**	**0.01-0.05**	**II, X**
Drinking water (DW)										
Austria	-	-	-	-	-	-	-	-	-	-
Belgium	-	-	-	-	-	-	-	-	-	-
Bulgaria	-	-	-	-	-	-	-	-	-	-
Croatia	-	-	-	-	-	-	-	-	-	-
Cyprus	-	-	-	-	-	-	-	-	-	-
Czech Republic	-	-	-	-	-	-	-	-	-	-
Denmark	-	-	-	-	-	-	-	-	-	-
Estonia	-	-	-	-	-	-	-	-	-	-
Finland	-	-	-	-	-	-	-	-	-	-
France	-	-	-	-	-	-	-	-	-	-
Germany	-	-	-	-	-	-	-	-	-	-
Greece	-	-	-	-	-	-	-	-	-	-
Hungary	-	-	-	-	-	-	-	-	-	-
Ireland	2013	20	26	25	96.2	0	0	>0.001	0.001	X

Country	Year	No. of sites	No. of samples	Detected (samples)		Samples showing values* >0.1 µg L^{-1}		Max. conc. µg L^{-1}	LoD / LoQ µg L^{-1}	Quality Category[1]
				No.	% of total	No.	% of total			
Italy	-	-	-	-	-	-	-	-	-	-
Latvia	-	-	-	-	-	-	-	-	-	-
Lithuania	-	-	-	-	-	-	-	-	-	-
Luxembourg	-	-	-	-	-	-	-	-	-	-
Malta	-	-	-	-	-	-	-	-	-	-
Norway	-	-	-	-	-	-	-	-	-	-
Poland	-	-	-	-	-	-	-	-	-	-
Romania	-	-	-	-	-	-	-	-	-	-
Slovakia	-	-	-	-	-	-	-	-	-	-
Slovenia	-	-	-	-	-	-	-	-	-	-
Spain	-	-	-	-	-	-	-	-	-	-
Sweden	-	-	-	-	-	-	-	-	-	-
Switzerland	-	-	-	-	-	-	-	-	-	-
The Netherlands	2013	83	548	8	1.46	0	0	0	0.01-0.05	X
United Kingdom										
England	-	-	-	-	-	-	-	-	-	-
Wales	-	-	-	-	-	-	-	-	-	-
Scotland	-	-	-	-	-	-	-	-	-	-
Northern Ireland	-	-	-	-	-	-	-	-	-	-
Total DW	**2013**	103	574	33^a	5.75	0	0	0->0.001	0.001-0.05	X

Notes:

a = Not added as there may be overlap, i.e. monitoring sites are often the same but monitored over different years so maximum number of sites reported.

b = Some of the data do not report number of samples detected.

[1] = Quality category scale I to III, where III is the most reliable, with an additional category, X. being used where there was inadequate information to classify the data.

< = The term has been used when data taken from the original source has used a 'less than' sign (<), indicating that the value is less than the analytical method can measure. It has also been used in the totals column if it has been used in the section previously.

*detection at >0.1µg/l might not be relevant if the consideration is in relation to effects on aquatic organisms rather than in relation to the potential quality of water to be abstracted for drinking water

From the information collected:
- For all the water types (groundwater, surface freshwater and drinking water), data were reported for over 711 sites and >5,790 samples, of which ≥0.94% of the total (≥54 samples) were above the drinking water limit of 0.1 µg l^{-1}.
- Groundwater monitoring data showed that mecoprop-P was only monitored in groundwater in three countries (Luxembourg, Norway and the Netherlands). There were greater than 267 sites and over 1,047 samples. Mecoprop-P was detected and exceeded the 0.1 µg l^{-1} drinking water limit in ≤1.05% of groundwater samples (≤11 samples). Maximum concentrations in excess of 0.1 µg l^{-1} were reported in Luxembourg.
- Surface freshwater monitoring data showed that mecoprop-P was monitored in seven countries (Ireland, Italy, Luxembourg, Norway, Slovakia, Switzerland and the Netherlands). It was generally more frequently found and at higher concentrations than in groundwater. There were greater than 341 sites monitored and 4,169 samples analysed. Mecoprop-P was detected and exceeded 0.1 µg l^{-1} in ≥43 samples which represented ≤1.03% of all samples. Maximum concentrations in excess of the 0.1 µg l^{-1} drinking water limit were reported in Luxembourg, Norway and Slovakia.
- Drinking water monitoring data showed that mecoprop-P was only monitored in two countries (Ireland and the Netherlands). There were 103 sites and 574 samples analysed. Mecoprop-P did not exceed the 0.1 µg l^{-1} drinking water limit in any sample with a maximum concentration reported in the range 0 - >0.001 µg l^{-1}.

- It must be noted that, whilst the presence of pesticides in drinking water indicates their presence in the source water, their concentrations or absence in drinking water do not necessarily reflect their concentration or absence in the source waters, as they may be removed during water treatment.
- The highest reported concentration of mecoprop-P was from a surface freshwater sample taken in Norway during 2011 with 1.8 μg l^{-1} and in a groundwater sample taken from a well situated in an alluvium in Luxembourg with 1.438 μg l^{-1}. There are no further details regarding these highest reported concentrations.

The study reports only one relevant paper identified from the literature searches for monitoring data – Idowu *et al* 2014. This paper was also identified in the literature review (McCondichie, 2014) and is therefore summarised and evaluated separately (CA7/06 Idowu, 2014 under data point CA 7.1.4.1.2).

RMS comments: The study reports a survey of monitoring data for mecoprop-P from national monitoring programmes between 2009 and 2014. A number of Member States reported that mecoprop-P is not specifically monitored although mecoprop is monitored but analytical methods do not discriminate between isomers. As the request for information was for mecoprop-P only, data on mecoprop has not been reported. Mecoprop has not been authorised in some Member States for a number of years and therefore data on racemic mecoprop is likely to be relevant to mecoprop-P. The RMS considers that requesting information on mecoprop-P only was too limited. Obtaining data on both mecoprop and mecoprop-P with supporting information on when mecoprop was last authorised in each Member State would provide a comprehensive data set. Additionally, requesting information on the analytical methods, sampling sites etc would aid in assessing the reliability of the data.

Report:	CA 7/09, Loos, R. *et al.*, 2010 Water Research, 44, pp2325-2335
Title	Occurrence of polar organic contaminants in the dissolved water phase of the Danube River and its major tributaries using SPE-LC-MS analysis
Guidelines:	None
GLP:	Not GLP
Deviations	Not applicable

Previous evaluations	None: Submitted for the purpose of renewal under Regulation 844/2012. This paper was identified by the applicant as potentially relevant during the literature review. The paper summary and relevance/reliability assessment provided by the applicant have been reproduced below. The RMS agrees with the applicant's assessment.

Executive Summary

The goal of the study was to analyse the occurrence and the possible presence of emerging organic contaminants in the Danube River basin and its tributaries in order to fulfil the monitoring requirements of the European Water Framework Directive.

Polar water-soluble organic contaminants were analysed in the dissolved liquid water phase of river water samples. The study was focused on pharmaceutical compounds, pesticides (including mecoprop) and their degradation products, perfluorinated acids and endocrine disrupting compounds etc. A total of 34 compounds were screened.

The water samples were taken just below the water surface at different points along the Danube River and its tributaries. Analyses were performed by solid-phase extraction (SPE) followed by a triple-quadrupole liquid chromatography mass spectrometry (LC-MS/MS). Compounds were identified by their retention time and their specific LC-MS-MRM transitions. An internal and an external quantification of the compounds was performed.

The detected concentration of pesticides was relatively low. The concentration of mecoprop was about 10 ng/L along the tributaries of Danube in Germany, Austria and Slovakia and <5 ng/L downstream the Danube River at the 1500 km point.

I.   MATERIALS AND METHODS

A.   MATERIALS

1.	**Test materials:**	Mecoprop and 33 others polar organic compounds
	CAS #:	7085-19-0 (for mecoprop)
	Purity:	Not stated

2.	**Water:**	Sampled from the Danube rivers and its tributaries. Details are provided below in the study design.

B.   STUDY DESIGN

1. Experimental conditions

The water was sampled along the Danube River and its tributaries, just below under the surface in the middle of the river. The study was launched in August 2007, in Regensburg, Germany. A total distance of 2600 km of the Danube River was assessed, through 10 countries, to the Danube Delta until late September. Samples were collected at 96 locations (73 samples from the Danube River and 23 tributary samples very close to Danube). Additional samples were also taken separately at 28 additional stations on the following tributaries: Morava, Drava, Tisza, Sava, Velika, Morava, Arges, Olt, Iskar, Rusenski Lom, Jantra, and Prut.

The river flow of the Danube was measured at several points. All the samples were stored in Methanol pre-cleaned PP plastic bottles of 0.5L at low temperature with freezing elements in styropor boxes. No chemical were used to help the preservation of the samples.

2. Method of analysis

Water samples were then extracted by a Solid Phase Extraction (SPE) with 200 mg cartridges. The extraction volume was 400 mL and was let to decant. After that sedimentation, the water was pouring slowly from the sample bottles into clean 1L glass bottles.

Prior to extraction the water samples were spiked with internal standard (Table B. 8.164).

Table B. 8.164. Composition of the internal standard for the quantification of each targeted compounds

Targeted compounds	Internal standards
Pesticides, pharmaceuticals + degradation products	Ibuprofen $^{13}C_3$, simazine $^{13}C_3$, atrazine $^{13}C_3$
Perfluorinated carboxylates, PFOS	PFOA $^{13}C_4$, PFOS $^{13}C_4$
Sulfamethoxazole, carbamazepine, caffeine, benzotriazoles	Carbamazepine d10
Alkylphenolics group	4-n-nonylphenol d8

The spiking level in the water samples was 10 ng/L for PFOA $^{13}C_4$ and PFOS $^{13}C_4$, and 100 ng/L for the other labelled compounds.

The elution was performed with 6 mL methanol, followed by evaporation to a volume of 500 μL, by using a TurboVap system.

After that, a reversed-phase liquid chromatography (RP-LC) was performed followed by electrospray ionization (ESI) mass spectrometry (MS) detection using atmospheric-pressure ionization (API) with a triple quadrupole MS/MS system.

Three separate LC-MS/MS runs (negative and positive ionization and specific run for alkyphenolic compounds on a different HPLC mobile phase) were performed to analyse all targeted compounds.

The analysis of mecoprop was performed with the positive ionization mode.

3. Identification, quantification and QA/QC

The compounds were identified by retention time match and their specific LC-MS/MS MRM transitions. Good performance of the developed analytical methods was demonstrated by successful participation in several inter-laboratory exercises. Quantification of the individual compounds was performed with similar internal standards (Table B. 8.164). Recoveries of different compounds were quite similar for all compounds and are lying in the range of 50–80% for the multi-compound method. The different recoveries are a major contribution to overall uncertainty of the method. The relative response factors of the compounds in relation to the IS were calculated in all cases. Thus, the reported concentrations are corrected with the recoveries of the compounds. A comparative check of internal quantification was always performed with external quantification. The limits of detection (LODs) for the SPE-LC-MS/MS procedure were calculated from the mean concentration of the blank of real water samples plus 3 times the standard deviation; 400 mL water was extracted and concentrated to 500 µL (enrichment factor 800). Ion suppression and matrix effects of the samples were not checked; they are relatively low for river water samples. Measurement uncertainty is estimated to be around 25–50%[14].

II.   RESULTS AND DISCUSSION

Thirty pesticides of polar water-soluble organic compound nature were triggered for this water monitoring along the Danube River, but the current summary is only focused on the results of mecoprop (Table B. 8.165). For each compound, the frequency of positive detection in [%], the average, the median and the percentile 90% were quantified by Excel Software.

Table B. 8.165. Analytical concentrations of mecoprop in the Danube River and its tributaries.

Chemical	LOD (ng/L)	Danube River					Tributary River				
Mecoprop	1	Freq. of positive detection [%]	Max [ng/L]	Average [ng/L]	Med [ng/L]	Per 90 [ng/L]	Freq. of positive detection [%]	Max [ng/L]	Average [ng/L]	Med [ng/L]	Per 90 [ng/L]
		63	17	4	3	9	30	25	3	0	8

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[14] Loos *et al*. (2009) EU-wide survey of polar organic persitent pollutants in European river waters. Environ. Poll. 157, 561-568
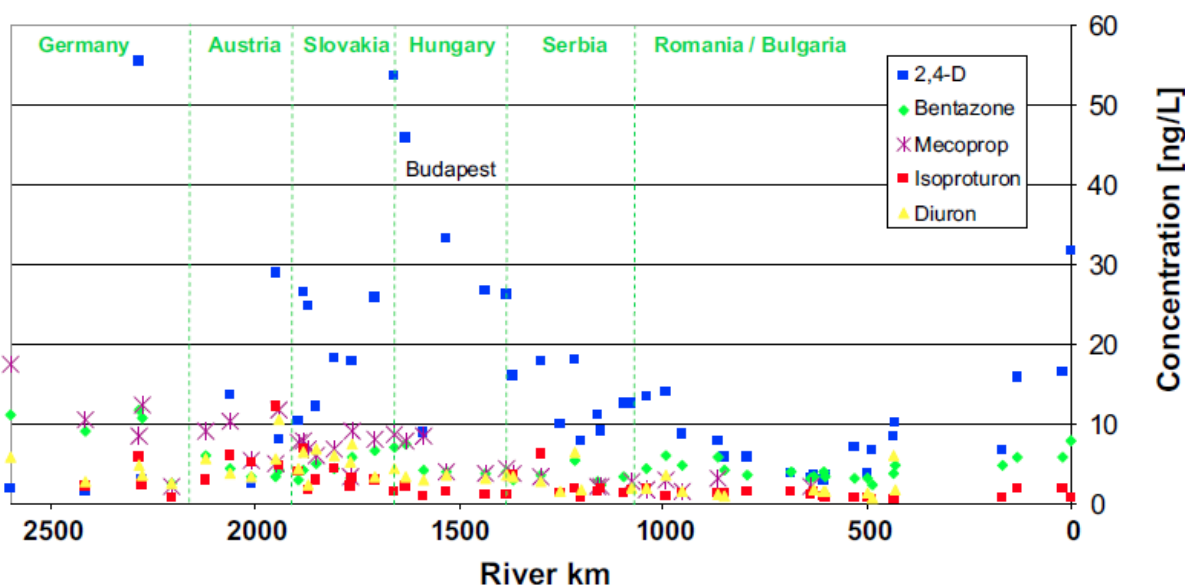
Figure B. 8.17.   Concentration of mecoprop in ng/L along the Danube River (pink crosses), Figure 5 in Loos R *et al*, 2010.

The mecoprop levels were about 10 ng/L in Germany, Austria and Slovakia and < 5 ng/L downstream the Danube River at the 1500 km point (Figure B. 8.17).

III.   CONCLUSION

Waste Water Treatment Plants remain the principal source of organic contaminant in the Danube River but the analytical results for the triggered compounds were in line with other European rivers (Rhine, Elbe or Po). Levels of mecoprop found were relatively low, potentially due to the time of year the study was conducted (August and September), when pesticide concentrations are expected to be lower.

Assessment of methodological quality

	Relevance	Reliability	Transparency and repeatability
Material	PFOA $^{13}C_4$, PFOS $^{13}C_4$: Wellington lab Ibuprofen $^{13}C_3$, simazine $^{13}C_3$, atrazine $^{13}C_3$: Cambridge Isotope Labs Carbamazepine d10: CDN Isotopes 4-n-nonylphenol d8: Dr. Ehrenstorfer	(seems correct)	Internal standard completely described in the original research report No information on the external standard of mecoprop.

	Relevance	Reliability	Transparency and repeatability
Method	SPE followed with HPLC-MS-MS is relevant method for pesticide monitoring in water.	The method relied on 13C internal standard in addition to external standards. The method was demonstrated performant by successful participation in several interlaboratory exercises [15] [16] [17].	Sampling points are well located on the map presented in the original report. Method used is accurately described in the original research report.
Results and interpretation	Relevant water monitoring results on the racemic mecoprop.	Reliable results since the method used was found reliable.	Results are fully presented in the article. Frequency of positive detection, the maximum, the average, the median and the Per90 are fully reported for each triggered compound.

Report:	CA 7/10, Nestorovska-Krsteska, A. *et al.*, 2008 Macedonian Journal Of Chemistry And Chemical Engineering, 27, pp25-33
Title	Determination of dimethoate, 2,4-Dichlorophenoxy acetic acid, mecoprop and linuron pesticides in environmental waters in Republic of Macedonia by High Performance Liquid Chromatography
Guidelines:	None
GLP:	No
Deviations	None

Previous evaluations	None: Submitted for the purpose of renewal under Regulation 844/2012. This paper was identified by the applicant as potentially relevant during the literature review. The paper summary and relevance/reliability assessment provided by the applicant have been reproduced below. The RMS agrees with the applicant's assessment.

Executive Summary

A HPLC-UV-DAD method for the determination of dimethoate, 2,4-Dichlorophenoxy acetic acid (2,4-D), mecoprop, and linuron in environmental waters was developed. The following parameters were determined in order to validate the method: retention factor, separation factor, LOD, LOQ, linearity, intraday precision and recovery.

Water samples were concentrated and extracted by a solid phase extraction method. Then, the investigated compounds were separated on Stability RP Pesticides chromatographic column using mobile phase composed of acetonitrile-water-acetic acid in volume fractions of 39:59:2 and flow rate of 0.7 mL/min. Ultraviolet absorption detection was carried out for dimethoate, 2,4-D, and mecoprop at 229 nm, and for linuron at 249 nm. Recoveries made from 500 mL of drinking waters using solid phase extraction ranged between 64.3-92.1%.

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[15] Farre *et al*. (2008) First interlaboratory exercise on non steroidal anti-inflammatory drugs analysis in environmental samples. Talanta 76. 580-590

[16] Van leewen *et al*. (2009) Significant improvements in the analysis of perfluorinated compounds in water and fish: results from an interlaboratory method evaluation study. J. Chromatogr. A 1216, 401-409

[17] Loos *et al*. (2008b) Laboratory intercomparison study for the analysis of nonyl- and octylphenol in river water. Trends Anal. Chem. 27 (1) 89-95

This method was then applied to environmental waters from 6 lakes of Macedonia that receive runoffs from agriculture land. The levels of pesticides under study ranged between 0.31 µg/L and 7.05 µg/L, depending on the compound and sampling period.

I.   MATERIALS AND METHODS

A.   MATERIALS

1.	**Test materials:**	Mecoprop
	CAS:	Not stated
	Purity:	Not stated
2.	**Water:**	Sampling of water from the waterfront of six lakes in the Republic of Macedonia

B.   STUDY DESIGN

1. Experimental conditions

Samples of water were taken from the waterfront of six lakes in the Republic of Macedonia. 500 mL of water was collected per sample in glass bottles. The collection of samples took place between October 2006 and July 2007 and water was stored in sterilised bottles. The sterilisation was undertaken with methanol and followed by combustion at 450°C in an oven for 24h. The samples were then stored at 4°C and filtered before the analysis.

Table B. 8.166.   Date and locations of samples taken from waters of 6 lakes of Macedonia

Sample	Date	Lake
1	08.06.06	Ohrid
2	08.07.06	Ohrid
3	09.07.06	Ohrid
4	09.07.06	Prespa
5	11.10.06	Ohrid
6	11.10.06	Ohrid
7	11.10.06	Ohrid
8	07.10.06	Mladost
9	19.06.07	Ohrid
10	19.06.07	Ohrid
11	19.06.07	Ohrid
12	19.06.07	Prespa
13	25.05.07	Dojran
14	25.05.07	Paljurci,Valandovo
15	25.06.07	Tikves

2. Method of analysis

Solid phase extraction: The conditioning of the cartridges was performed using 10 mL of methanol, followed by 10 mL of water at a flow rate of 2 mL/min. 500 mL of sample were passed through the cartridge at a flow rate of 10 mL/min. Following this concentration step, the cartridge was dried for 30 s with a gentle vacuum. A mixture of 4mL of acetonitrile/methanol 1:1 (v/v) was used for the elution step in order to desorb the pesticides from the cartridge. 50 µL of a mixture methanol/ammonia 4:1 was added to the eluent. The extract was then evaporated using a rotary evaporator to a volume of about 40-80 µL. After completion, a mixture of methanol/water 1:4 was added to this extract to obtain a total of 200 µL from which 50 µL were injected into the HPLC column. The procedure of extraction and concentration lasted around 2 hours.

HPLC determination: a Varian HPLC equipped with ternary gradient pump, 50 µL sample loop and with UV-DAD detector was used. The analytical column was a Stability RP Pesticides chromatographic column with the dimension 250 mm * 3 mm and particle size 5 µm. The optimum eluent flow rate was 0.7 mL/min and the UV detector wavelength was set at 229 nm mecoprop. In order to separate the pesticides, a mobile phase constituting a mixture of acetonitrile/water/acetic acid 36:59:2 (v/v/v) was used. Analysis were performed at room temperature and lasted 20 minutes.

II.   RESULTS AND DISCUSSION

A.   METHOD VALIDATION

The method validation was undertaken with four pesticides (dimethoate, 2,4-D, mecoprop, and linuron). Values obtained for mecoprop only are reported in this summary and presented in Table B. 8.167 to Table B. 8.169.

Table B. 8.167.   Limit of detection and limit of quantification for mecoprop

Compound	LOD (µg/L)	LOQ (µg/L)
Mecoprop	0.05	0.14

Table B. 8.168. Data for statistical assessment on calibration curves for mecoprop

Compound	Linearity concentration range (µg/L)	Regression equation	RSD (%)	R^2
Mecoprop	0.2 – 4.8	Y = 103.14x – 1780.6	6.0	0.9978

Table B. 8.169.   Recovery values of distilled water spiked with mecoprop

Compound	Recovery (%)	RSD (%)
Mecoprop	92	8

Identification of mecoprop in the extracted water samples was made by retention time match with an analytical standard of mecoprop. The identification of mecoprop was also confirmed by the comparison of the UV spectra of the pesticides standards and the UV spectra of the peaks of the substances detected in the samples.

B.   ANALYSIS OF WATER SAMPLES TAKEN FROM 6 LAKES OF MACEDONIA

The analysis was undertaken on water samples of 6 Macedonians lakes for which four pesticides were triggered (dimethoate, 2,4-D, mecoprop, and linuron). Values obtained for mecoprop only are reported in this summary.

Table B. 8.170. 7 Analytical concentrations of mecoprop in 7 samples* taken from Macedonian lakes

Sample	Mecoprop [µg/L]
1	0.57
2	0.70
4	0.45
6	0.31
7	2.85
8	1.04
13	2.45

*15 samples were analysed in the whole study, but mecoprop could be detected in only seven samples.

The   maximum   detected   concentration   of   mecoprop   occurred   in   October   (2.85µg/L).

III.   CONCLUSION

The method validation of SPE-HPLC-UV DAD showed reliable and relevant value for mecoprop and would be a useful tool to monitor this pesticide mecoprop was detected in 7 out of the 15 samples analysed, with a maximum of 2.85 µg/L (Ohrid Lake, sampled on 11.10.06).

Assessment of methodological quality

	Relevance	Reliability	Transparency and repeatability
Material	Pesticide analytical standard: provided by Riedel-de-Haen	(Seems correct)	Purity not stated
Method	SPE-HPLC-UV DAD is a relevant method for determination of pesticides in water.	Fully validated method: (separation factor, LOD, LOQ, linearity, intraday precision and recovery). However, concentration at which the accuracy test was conducted was not reported.	Sampling points are well located with GPS references in the original research report. The method requires 2h for the concentration and extraction step, and less than 30 min for the HPLC analyses. Method used is fully described in the original research report.
Results and interpretation	Relevant water monitoring results on the racemic mecoprop.	Results obtained for mecoprop are reliable since the method validation showed reliable parameters for mecoprop.	Concentration values correspond to the mean of three injections.

Report:	**CA 7/11, Rice, P. J. *et al.* (2010)**
	Environmental Toxicology and Chemistry, 29, pp1209-1214
Title	Pesticide transport with runoff from creeping bentgrass turf: relationship of pesticide properties to mass transport
Guidelines:	None stated
GLP:	Not stated, but assumed not GLP
Deviations	Not applicable

Previous evaluations	None: Submitted for the purpose of renewal under Regulation 844/2012.
	This paper was identified by the applicant as potentially relevant during the literature review.
	The paper summary and relevance/reliability assessment provided by the applicant have been reproduced below. The RMS agrees with the applicant's assessment. The study provides a measure of the amount of mecoprop-P likely to be found in run-off following application to turf. The study does not provide new endpoints and has not been used in the risk assessment.

Executive Summary

The off-site transport of pesticides with runoff is both an agronomic and environmental concern, resulting from reduced control of target pests in the area of application and contamination of surrounding ecosystems. Experiments were designed to measure the quantity of pesticides in runoff from creeping bentgrass (*Agrostis palustris*) turf managed as golf course fairway to gain a better understanding of factors that influence chemical availability and mass transport. Less than 1 to 23% of applied chloropyrifos, flutolanil, dimethylamine salt of mecoprop-P, dimethylamine salt of 2,4-Dichlorophenoxyacetic acid (2,4-D DMA), or dicamba was measured in edge-of-plot runoff when commercially available pesticide formulations were applied at label rates 23 ± 9h prior to simulated precipitation (62 ± 13 mm). Time differential between hollow tine core cultivation and runoff did not significantly influence runoff volumes or the percentage of applied chemicals transported in the runoff. With the exception of chlorpyrifos, all chemicals of interest were detected in the initial runoff samples and throughout the runoff events. Chemographs of the five pesticides followed trends in agreement with mobility classifications associated with their soil organic carbon partition coefficient (K_{OC}). Data collected from the present study provides information on the transport of chemicals with runoff from turf, which can be used in model simulations to predict nonpoint source pollution potentials and estimate ecological risks.

I.   MATERIALS AND METHODS

A.   MATERIALS

1.   Test materials: Several pesticides tested among which mecoprop-P was included.
Trimec® Bentgrass Formula herbicide (PBI Gordon) containing 9.92% mecoprop-P DMA was applied as test material for mecoprop-P.
Formulation containing other pesticides tested in the study are referenced in the article.

2.   Soils: The soil was characterized as Waukegan silt loam (fine-silty over sandy or sandy-skeletal, mixed superactive, mesic Typic Hapludolls) with 3% organic carbon, 29% sand, 55% silt, and 16% clay.

3.   Test site: The 976-m^2 study site was located in Saint Paul, Minnesota, USA, at the University of Minnesota Turfgrass Research, Outreach, and Education Center. A natural slope running east to west was graded to 4% with less than 1% slope from north to south and planted with L-93 creeping bentgrass sod a minimum of 14 months prior to initiation of the reported runoff studies. The study site was divided into six plots (24.4m x 6.1 m, length x width) prepared in an east-to-west direction, with runoff collection systems at the western edge of each plot.

B.   STUDY DESIGN

1. Experimental conditions

A runoff field study was undertaken on the test site after treatment with mecoprop-P and other pesticides.

Turf was regularly mowed, top-dressed with sand and irrigated as would be a golf fairway. In addition, plots were aerated twice during each season (June 21, 2005 and September 27, 2005; August 4, 2006 and September 19, 2006) with hollow tines [HT].

All plots were pre-wet beyond the soil saturation (volumetric water content: $68\pm3\%$) approximately 48 h prior to initiation of simulated precipitation, which ensured uniform water distribution throughout the plots and allow for collection of background samples.

Commercially available pesticide formulations including Trimec® Bentgrass Formula herbicide (PBI Gordon) containing 9.92% mecoprop-P (DMA salt) were applied to all plots perpendicular to runoff flow. Pesticide formulations were applied at label rates using a 4.6m spray boom fitted with TeeJet XR8004 nozzles spaced 50.8cm apart with a sprayer pressure of 138 kPa. The average measured application rates for all plots for the four events, were 17.5 ± 3.5 mg/m^2 mecoprop-P. Details on application of the other pesticides is provided in the article. Application was completed 24 h prior to initiation of each rainfall simulation. No irrigation or natural precipitation occurred between completion of the pesticide application and initiation of simulated precipitation. Petri dishes (glass, 14 cm) were distributed across the plots prior to pesticide application to verify chemical delivery and quantify actual application rates.

A rainfall simulator was built, which delivered precipitation at a rate of 33 ± 6 mm/h to two 24.4 m x 6.1 m plots simultaneously, in order to produce precipitation with droplet size spectrum, impact velocity, and spatial uniformity characteristic of natural rainfall. Simulated precipitation was initiated 22 ± 10 h following pesticide application and 63, 2, 11, and 15 d following HT core cultivation (i.e. August 23, 2005; September 30, 2005; August 15, 2006 and October 4, 2006). Precipitation was terminated 90 min after the onset of runoff totalling 59 ± 5 mm, 45 ± 8 mm, 71 ± 8 mm, and 75 ± 7 mm of precipitation, respectively. Rain gauges distributed throughout the plots measured rainfall rates of 24 ± 4 mm/h to 37 ± 2 mm/h.

2. Sampling

Stainless steel flashing guided the runoff from the turf into 6.1-m gutters, constructed of 15.2 cm schedule 40 polyvinyl chloride (PVC) pipe, which was cut in half lengthwise. Polyester landscape cloth covered the soil under the metal flashing to maintain soil structure. Large nails held the flashings in place, and paraffin wax provided a watertight seal between the turf edge and flashing. At the central point of the gutter, a PVC-T (15.2 cm x 15.2 cm x 15.2 cm) lead runoff to a stainless steel large 60° V trapezoidal flume (Plasti-Fab, Tualatin) equipped with a bubble-tube port and two sample-collection ports. The gutter system and trapezoidal flume were embedded in sand-filled trenches to provide support and maintain appropriate conditions for accurate measurement of runoff volume and flow rates. The alignment and integrity of the runoff collection systems were assessed each spring and prior to simulated precipitation events. Gutter covers and flume shields prevented precipitation from entering the runoff collection apparatus.

Automated runoff samplers (ISCO model 6700) equipped with flow meters (Isco model 730; Lincoln) recorded runoff flow rates every minute, calculated total runoff volumes, and collected time-paced (5 min) runoff samples into glass bottles. Water samples were removed from the samplers and stored at -20°C until laboratory analysis.

3. Description of analytical procedures

Water samples were processed by filtering 3ml through a 0.45 mm nylon syringe filter (Whatman) followed by methanol (0.5 ml) to rinse the filter. Each runoff sample was analyzed for pesticides. No samples were combined. Methanol rinsates of Petri dishes, containing pesticide residues for determination of actual application rates, were diluted with laboratory-grade organic-free water to 14% methanol to mimic the methanol and water content of the filtered runoff samples.

Concentrations of each pesticide were measured by direct injection (500µl) onto a high-performance liquid chromatograph (Waters model 717 plus autosampler and model 1525 binary pump) with a photodiode array detector (Waters model 2996) set at 230 nm. Analytes were eluted from an Agilent C-18 column (150mm long,

4.6mm diameter, 5-mm packing) using two solvents (solvent A: laboratory-grade organic-free water [0.17% trifluoroacetic acid]; solvent B: 82:18 methanol:acetonitrile) at a rate of 1 ml/min. Initial conditions, 60% B, were held for 2 min followed by a gradient ramped from 60 to 95% B in 23 min, a 3-min hold, then back to 60% B in 10 min with a 5-min hold.

Irrigation source water, background runoff water, and background runoff spiked with known quantities of pesticides served as blank and positive control samples.

4. Statistical analysis

Completely randomized analysis of variance was performed comparing the percent of applied precipitation resulting as runoff and the percent of applied chemicals transported in runoff for all runoff events. A significant F (at 0.01 or 0.05) implied a significant difference among means. Coefficients of determination were calculated to evaluate the association of runoff volume and chemical concentration with chemical load, and K_{OW}, K_{OC}, and water solubility with percentage of applied pesticides transported with runoff.

II.   RESULTS AND DISCUSSION

A.   DATA

The following results with regard to mecoprop-P were obtained during the study. Results on other tested pesticides are reported in the article.

Table B. 8.171.   Runoff volume and mecoprop-P transported in runoff

	August 23, 2005	September 30, 2005	August 15, 2006	October 4, 2006
Cumulative runoff volume				
Volume	3,149 + 932 L	1,856 + 139 L	3,964 + 168 L	3,843 + 130 L
As % of applied precipitation	36 + 11 %	28 + 2 %	33 + 8 %	35 + 1 %
Mecoprop-P mass transported in runoff				
As % of applied mecoprop-P*	22 %	12 %	11 %	19.5 %
Average % of applied mecoprop-P	16.2 + 5.3 %			
Average mass transported	2,717 + 991 µg/m²			
Average measured concentration in runoff	164.1 + 84.5 µg/L			

  * Data not provided, but extracted from figure 2 in the article.

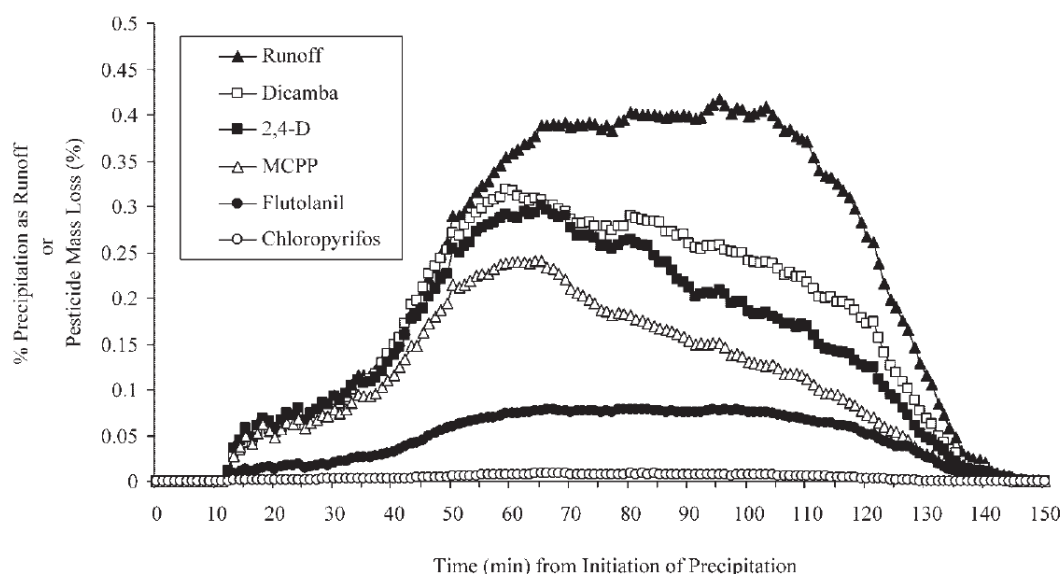The mobility and transport of the evaluated pesticides with runoff is depicted in Figure B. 8.18.

Figure B. 8.18.   Runoff hydrograph and pesticide (dicamba, 2,4-D DMA, mecoprop-P DMA, flutolanil, and chlorpyrifos) chemographs representing the average of all replicates from the four runoff events (August 23, 2005; September 30, 2005; August 15, 2006; October 4, 2006). Runoff quantities are reported as a mean percentage of total simulated precipitation. Pesticide mass loss in runoff is reported as the mean percentage of applied active ingredient. Figure 3 in Rice PJ *et al*, 2010.

B.   RUNOFF

Runoff was first observed 22 ± 3 min following the initiation of precipitation. Steady-state runoff rates were measured for 54 ± 9 min beginning approximately 64 min after the initiation of precipitation with average flow rates of 27 ± 8 L/min and maximum flow rates of 43 ± 10 L/min.

C.   ANALYTICAL METHOD PERFORMANCE

Analysis of the source water applied as simulated precipitation and maintenance irrigation contained no residues of mecoprop-P.

Reported recovery for mecoprop-P was $104\pm7\%$. Limit of detection ranged from 2.5 to 3.7 µg L^{-1} (article does not specify LOD per pesticide). Limit of quantification for mecoprop-P was 5.3 µg L^{-1}.

D.   STATISTICAL ANALYSIS

Although the time differential between aeration and runoff varied from one rain event to another (63, 2, 11, and 15 d), the following measures were statistically similar at each dates (August 23, 2005; September 30, 2005; August 15, 2006 and October 4, 2006):

- mean percentage of applied precipitation resulting as runoff;

- mean percentage of applied mecoprop-P transported in each runoff event;

Statistical analysis of chemical loads with runoff volumes and chemical concentrations revealed loads were more associated with runoff volume than chemical concentrations mecoprop-P, volume $r^2 = 0.60$, concentration $r^2 = 0.14$).

Similar statistical conclusions were drawn for the other tested pesticides.

Analysis of percentage of applied pesticides recovered in the runoff (dicamba [22.8%], 2,4-D [21.1%], mecoprop-P [16.2%], flutolanil [5.8%], chlorpyrifos [0.9%]) with the water solubility, K_{OC}, and K_{OW} of the

active ingredients suggests K_{OC} ($r^2 = 0.60$), K_{OW} ($r^2 = 0.55$), and water solubility ($r^2 = 0.37$) describe only a portion of the difference in the observed chemical transport, with K_{OC} and K_{OW} somewhat better predictors of chemical availability than water solubility for the experimental conditions of the present study.

III.   CONCLUSIONS

A runoff field study was undertaken on mecoprop-P and other pesticides on golf turf. The results are consistent with other publication and assumption of existing model (i.e. correlation with K_{OC}, K_{OW} and with runoff volumes). Soil aeration was found to have no influence on runoff.

With regard to mecoprop-P, an average of 16.2 % of the applied active substance was transported by runoff through an entire rainfall event. The chemograph indicates a peak at 0.25% of applied rate for mecoprop-P around 60 min. after initiation of the rain fall event.

Applicants conclusions: The data collected in this study could be used in conjunction with other similar studies in order to develop, refine and/or validate models intended to determine PEC_{SW} resulting from runoff entry in the managed turf situation.

Assessment of methodological quality

	Relevance	Reliability	Transparency & repeatability
Material	Commercial formulation of mecoprop-P used. 4% slope golf turf test site.	Nominal purity of formulation stated. No GLP certificate of analysis. Soil characterised.	Commercial formulation reference and test site fully described.
Method	Experimental condition found relevant for the purpose of the study (runoff field study). Analytical method relevant for pesticide analysis in water.	No GLP statement. Care was taken to eliminate sources of varialibity on runoff (e.g. prewetting of soil, sand filled tranched in runoff collection system, …). Analytical method was tested for lack of interference and accuracy/repeatability.	Method and experimental condition were described transparently with many technical details. Experiment was conducted on 4 replicates (different date and different differential with last core cultivation).
Results & interpretation	Results expressed in amount of pesticide transported in runoff, % of applied pesticide transported in runoff and chemographs were found relevant information for developing or validating models.	The results are similar to those found by other authors on the same pesticides, and are in correlation with the known primary parameters influencing runoff in validated models (K_{OC}).	No raw result presented. Only final figures are mentioned in the article. In certain cases, only average over the 4 tested rain event is provided.

Report:	**CA 7/12, Zhao, Y.Q. *et al.* (2012)**
	International Journal of Environmental Studies, 70, pp59-72
Title	Current status of pesticides application and their residue in the water environment in Ireland
Guidelines:	None
GLP:	Not applicable
Deviations	Not applicable

Previous evaluations	None: Submitted for the purpose of renewal under Regulation 844/2012.
	This paper was identified by the applicant as potentially relevant during the literature review.
	The paper summary and relevance/reliability assessment provided by the applicant have been reproduced below. The RMS agrees with the applicant's assessment

Executive Summary

Pesticides have been listed by the Irish Environmental Protection Agency as potentially dangerous pollutants that may pose a significant risk to the water environment in the Republic of Ireland (ROI). Although this analysis of pesticides data was based on the existing pesticides application survey in ROI, this study aims to produce a geographical information system profile for the amount of pesticides used in agriculture and the distribution of their use in different parts of the country. The study identifies and reports on the six most widely used pesticides in ROI, they are MCPA, glyphosate, chlorothalonil, mecoprop-P, chlormequat and mancozeb. More significantly, the study discusses the application of pesticides and their potential impact on the Irish water environment by examining the status of pesticide residue in the Irish water environment. Finally, the study surveys possible strategies for the removal of pesticides residues, with attention to some of the studies done worldwide.

I.   MATERIALS AND METHODS

A.   MATERIALS

1.   Test materials: None. This study reviews existing information. No experiment was conducted. However, the review undertaken by Zhao Y.Q. *et al.* (2012) focusses on the 6 active substances which are the most widely used in ROI: MCPA, glyphosate, chlorothalonil, mecoprop-P, chlormequat and mancozeb

B.   STUDY DESIGN

The main aim of this study was to produce a Geographical Information System (GIS) survey of the current status of pesticide use in ROI. Information was collected from the following data base:

- A data base from Pesticide Registration & Control Division of The Department of Agriculture, Food and the Marine (DAFM), which provides a national survey of PPPs usage for forage crops and grassland areas as well as for arable crops. The DAFM database provides details of the quantities of active substances/pesticides used; the reasons for their application; regions (but not the precise counties) where used; and the most widely used active substances. The database gives the amounts of each active substance or active substance combination applied to each crop.

- Data on the amount of each crop grown in each county from the Central Statistics Office (CSO).

Combining the information from both databases allowed the authors to develop a GIS profiles using ArcGIS software. To give an accurate representation of the amounts of pesticide used in each county, the units used were kilograms per square kilometre (kg/km^2).

This study also reviewed the results from the Irish EPA pesticide water monitoring program. However, no methodology was set up in order to relate the determined GIS profile to the results of the water monitoring program.

Zhao Y.Q. *et al.* also discuss the possible entry routes of pesticide in water, the existing EU relevant Regulations, and the potential of available water purification techniques to remove pesticide from drinking water.

II.   RESULTS AND DISCUSSION

A.   TOTAL PESTICIDES USAGE IN ROI

The pesticide usage survey from DAFM revealed the following information:

- 2,089,287 kg of active substance are applied each year in ROI over 4.4 million hectares;

- 60% of which being fungicides and 26% being herbicides;

- The 6 active substances which are the most widely used in ROI are MCPA, glyphosate, chlorothalonil, mecoprop-P, chlormequat and mancozeb

B.   GIS PROFILES

A geographical profile of the total quantity of pesticides used in each county in ROI was produced. The GIS profile indicates that County Louth is the highest consumer of pesticides in ROI with an average active substance application rate of 146.7 kg/km^2. One reason is that due to an abundance of good farm land, the growth of crops needs a relatively high amount of treatment with PPPs. County Dublin is the second highest user of pesticides in ROI. Despite Dublin's high levels of urbanisation, there is a large amount of high quality farmland in County Dublin area as a whole, resulting in high pesticide usage. In addition to this, North county Dublin is known for its very concentrated vegetable producing areas, crops which tend to require higher PPP input. In contrast, County Mayo is the lowest contributor with an average application rate of just 3.7 kg/km^2 probably due to its peat land nature. It is clear that the main areas of pesticide use are along the east coast of the country. This is due to better quality land, the growth of crops dependent on greater PPP usage and greater demand for food products in densely populated regions.

Computed data show that MCPA, glyphosate, chlorothalonil, mecoprop-P, chlormequat and mancozeb are the six most widely used pesticides in agriculture in ROI. Information on each of these is given by a GIS profile with geographical distribution in each county. MCPA is the most widely used pesticide in ROI. There appears to be a gradual change in use from the largest user in County Monaghan (3.9 kg/km^2) to the smallest user in County Dublin (1.4 kg/km^2). But, the change does not seem to be significant, showing that MCPA is a general, widely used pesticide.

Information on the distribution of all of the top six most widely used pesticides is included in the paper (Zhao Y.Q. *et al*, 2012), however for the purposes of this submission only information on mecoprop-P is summarised here. Mecoprop-P is mainly used for grass treatment as well as weed control in cereal crops. County Wexford is the largest user of mecoprop-P (9.5 kg/km^2) by a wide margin and as can be seen from the geographical representation of the data in the report and its use is heavily concentrated in the South-East, which is the ROI's primary spring barley growing region.

C.   PESTICIDES WATER MONITORING

Individual pesticides have long been detected in drinking water throughout ROI. According to the Irish EPA's report on drinking water quality, in recent years, the number of samples exceeding the 0.1 µg/L value is very low. Table B. 8.172 summarises the overall results of the total pesticides in Irish drinking water samples.

Table B. 8.172. Pesticides monitoring in Irish drinking water samples

Year	Total samples analysed	Samples of pesticides detected	No of pesticide exceeded 0.1 µg/L	No of pesticide exceeded 0.5 µg/L	Reference
2006	1342	190	11	2	Irish EPA, 2007
2007	1481	224	13	4	Irish EPA, 2008
2008	1445	n/a	n/a	3	Irish EPA, 2010
2009	1372	n/a	10	2	Irish EPA, 2010
2010	1335	n/a	5	1	Irish EPA, 2011

This suggests that a relatively small number of pesticides are being detected and the trend seems to be a reduction in pesticides found at concentrations > 0.1 µg/L.

The Irish EPA published a Dangerous Substances Regulations National Implementation Report in 2005. The EPA tested a large number of rivers, lakes and tidal waters for the presence of a wide range of dangerous substances, Atrazine being one of these. According to the EPA report, out of 299 test sites, 12 exceeded the drinking water limit (Irish EPA, 2006).

C.   REMOVAL AND REMEDIATION

Zhao Y.Q. *et al.* made a scientific literature review in order to assess the potential of water treatment process to remove pesticide. They reported the following information:

- Studies have shown that conventional drinking water treatment processes are not effective in removing certain types of pesticides. This is mainly due to the fact that various families of pesticides would request different treatment process. Some of the methods currently being employed throughout Europe include preoxidation by chlorine, preoxidation by ozone, coagulation with aluminium sulphate, activation carbon filtration, nanofiltration and combinations of these techniques;

- Coagulation-flocculation using aluminium sulphate as coagulant removed below 50% of the pesticides in jar test experiments;

- Nanofiltration process has a good capacity to remove some pesticides from water, and the membrane material used in the filtration process greatly influences the percentage of pesticides removed;

- Oxidation by chlorine removes 60% of pesticides, although combining oxidation with a coagulation–flocculation–decantation process is more effective. Oxidation by ozone removes 70% of the pesticides. Although combination with a subsequent coagulation–flocculation–decantation process does not improve the efficiency of the process, combination with an activated-carbon absorption process gives rise to 90% removal of pesticides;

- Advanced oxidation process using TiO_2-containing composites have been developed and trials have been conducted for MCPA and 2, 4-D removal in the presence of UV light. Results show that the pesticides can be successfully removed mainly by the integrated adsorption and the enhanced superior photocatalyst;

- Aluminium containing water treatment residual (Al-WTR) holds great promise of adsorption affinity with phosphorus and was advocated to be reuse as pesticide pre-treatment to prevent their entry to water bodies in various runoffs.

III.   CONCLUSIONS

Mecoprop-P is one of the 6 most widely used pesticides in ROI. A GIS profile was developed for the total use of pesticide in ROI and for mecoprop-P in particular. It could be used as a tool for correlating future water

monitoring program to the actual uses of pesticide in ROI. However, the reported results from the Irish water monitoring program undertaken so far does not allow to establish such relationship. Whilst pesticides where found in water above 0.1 μg/L on limited occasions, the identity of these active substances were not reported.

Assessment of methodological quality

	Relevance	Reliability	Transparency & repeatability
Material	Mecoprop-P is one of the pesticides for which a GIS profile was established in this publication.	Not applicable.	Not applicable.
Method	The method was found relevant for the establishment of GIS profile. However, no relationship between the GIS and the water monitoring program could be made since the identity of the active substances recovered in water was not reported.	The data bases used for the development of GIS profile are maintained by official services (DAFM and CSO) and should be reliable.	The method use for the GIS development is transparently explained and should be repeatable.
Results & interpretation	The GIS profile of mecoprop-P could be useful for future water monitoring program. However, the lack of detailed information from the existing water monitoring results does not allow any correlation with the GIS profiles established.	The combination of the data from the 2 databases involve simple arithmetic and should be reliable.	The raw data from the d-bases combined in the GIS development were not reported (too much information), which induces a lack of transparency.

Report:	**Kot-Wasik, A., Dębska, J. & Namieśnik, J. (2004)**
Title	Monitoring of organic pollutants in coastal waters of the Gulf of Gdańsk, Sourthern Baltic Marine Pollution Bulletin 49, p264-276
Guidelines:	None
GLP:	No, literature data

Previous evaluations;	None: Submitted for the purpose of renewal under Regulation 844/2012.
	This paper was identified by the applicant as relevant during the literature review.
	The paper monitored organic pollution in the Gulf of Gdansk. Mecoprop was detected, however the analytical method did not distinguish between isomers. Results are reported as summaries and graphs only. Seasonal variation in phenoxyacids (which includes mecoprop) and chlorophenols was noted to correspond with agricultural use timing.
	The study does not provide new endpoints and has not been relied on for the risk assessment.

Executive Summary

This paper provides an overview of changes in organic pollution of coastal waters in the Gulf of Gdańsk over the period 1996 to 2001. Levels of a wide range of pollutants were determined, including volatile organic compounds (VOC), volatile organohalogen compounds (VOX), chlorophenols, phenoxyacids, polychlorinated biphenyls (PCBs) and polycyclic aromatic hydrocarbons (PAHs). However only the information concerning chlorophenols are phenoxyacids is relevant to this submission and therefore only those have been reported in this summary.

The average concentrations of chlorophenols and phenoxyacids detected in the samples collected were between 0.1 and 6.0 and 0.05 and 2.2 µg dm^{-3}, respectively. However, remarkably high concentrations of 2,4-dichlorophenol (6 µg dm^{-3}) were obtained in samples collected from the Vistula River.

Seasonal variation was observed in the data collected, with higher levels of both phenoxyacids and chlorophenols being detected in spring, corresponding with the application timing of phenoxyacids in agriculture.

I.   MATERIALS AND METHODS

A.   STUDY DESIGN

1. Sampling

Seven sampling sites were selected along the Polish coastline: Hel, Władysławowo, Gdynia beach, Gdynia-Orłowo cliff, Gdańsk-Brzeźno jetty, Vistula mouth and Kiezmark.   Sampling sites are situated (a) in the open sea, where most recreation sites are set and (b) in the sea shore area of the Gulf of Gdansk where the industry and big cities with their infrastructure are located. Figure B. 8.19 gives an overview of the location of the sampling sites, with Table B. 8.173 describing the sites. The seawater was collected episodically from a location 50m from the shore of each test site. pH determinations were made immediately after delivery of samples to the laboratory. Toxicity measurements of water samples were performed using the ToxAlert 100 test which is based on measurement of decreasing luminescence of *Vibrio fischeri* bacterium added to a water sample.
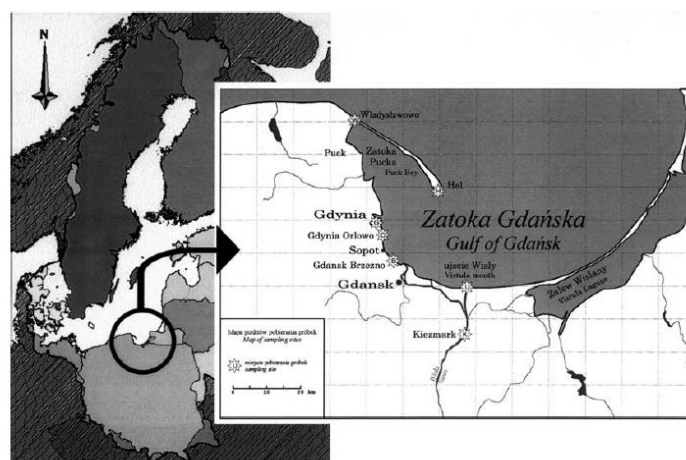

Figure B. 8.19. Sampling sites along the coastal line of the Gulf of Gdańsk

Table B. 8.173. Description of sampling sites

Sampling site	Abbreviation	Description
Hel	(H)	Situated at the top end of the Hel Peninsula; one side adjacent to the open sea, the other is laying within the Gulf of Gdańsk, its port and beaches
Władysławowo	(W)	Situated in Hel Peninsula; fish industry, fish port and bathing places on the open sea
Gdynia beach	(G)	Typical recreation area situated in the centre of the town; neighbourhood of shipyard and port, with commercial or tourist passenger vessels

Sampling site	Abbreviation	Description
Gdynia-Orłowo cliff	(O)	Typical recreation area surrounded by trees, beaches and sea
Gdańsk-Brzeźno jetty	(B)	Typical recreation area in the neighbourhood of park; further neighbourhood of shipyard; north port, petroleum refinery, phosphates fertilised, close to the entrance of the biggest port in the Gulf of Gdańsk
Vistula mouth	(U)	Vistula mouth, no direct point source of pollution
Kiezmark	(K)	Situated 40 km upstream from Vistula mouth; river carrying waters from catchment area

2. Description of analytical procedures for determination of pollutants in seawater

Only methods for phenols and phenoxyacids are summarised here.

Phenols were analysed according to the method described previously. Briefly, water samples were collected in amber glass bottles and were acidified with orthophosphoric acid to pH <2. The analytes were pre-concentrated using a solid phase extraction (SPE) method with EN200 mg (Merck) columns. Before usage, each column was conditioned with acetonitrile (2 x 2.5 ml), methanol (2 x2.5 ml), HPLC grade water (2 x 2.5 ml) and water acidified to pH 2 by orthophosphoric acid (2 x 2.5 ml). Then 300 ml of the seawater sample was passed through the column. Afterwards, columns were washed with HPLC grade water and dried in a stream of nitrogen. Elution into glass vials was performed with acetonitrile (2 x 2.5 ml). Then 1 ml of acidified water was added and solvent was evaporated to 1 ml. Immediately before chromatographic analysis each extract was diluted with water acidified with phosphoric acid (1:1) and a sample volume of 100 µl was injected. The conditions of the chromatographic system used for the final determination, with HPLC-DAD, are presented in Table 2. The detection limits were different for each analyte and are included in Table B. 8.174. Recoveries are not reported.

Table B. 8.174.   Working parameters of HPLC-DAD system used for the final determination of chlorophenols and phenoxyacids

Parameters	Details	
Chromatograph	Chromatograph Merck Hitachi 7000 series	
Mobile phase	A: H_2O+0.1% v/v CH_3COOH	
	B: ACN:MeOH (1:1, v/v)+0.01% v/v CH_3COOH	
Gradient	At time 0–75% A, then gradient in 15 min 43% A, then in 22 min 35% A and at 30 min 0% A kept for 10 min	
Flow rate	0.7 ml min^{-1}	
Temperature	25 ºC	
Injection volume	100 µl	
Detection parameters		
Compound	**Wavelengths of detection**	**Limit of detection**
Phenol	270 nm	0.15
2-chlorophenol	280 nm	0.05
2,4-dichlorophenol	280 nm	0.05
4-chloro-3-methylphenol	280 nm	0.05
Pentachlorophenol	305 nm	0.20
2,4-D	230 nm	0.06
MCPA	230 nm	0.06
Dichlorprop	230 nm	0.09
Mecoprop	230 nm	0.09
Dinoseb	305 nm	0.03

II.   RESULTS AND DISCUSSION

A. Temperature, pH, Toxicity and Salinity

The pH of seawater from the coastal zone varied from 8 to 8.5 with the more alkaline values associated with samples from the Vistula River, probably because of the discharge of untreated wastewaters. The toxicity varied from 10 units for seawater samples collected from Hel and Władysławowo up to 65 for water sampled in the Vistula River. Seawater samples from Gdynia and Gdańsk exhibit toxicity in between 25 and 32 units. The only exception was observed for Gdynia-Orłowo, where toxicity was relatively low (always between 1–5 units). Within sampling period the salinity of surface waters of Gdańsk Bay varied from 7.3 to 8.4 but was lower in the vicinity of Vistula River 5.5–6.5.

B.   Phenoxyacids and chlorophenols

Within the monitoring period no chlorophenols were detected in seawater samples obtained up to 2001. In autumn and spring of the last two years, chlorophenols and phenoxyacids were observed in waters at low $\mu g \ dm^{-3}$ concentrations. The average concentrations of the chlorophenols and phenoxyacids ranged between 0.1 and 6.0 and 0.05 and 2.2 $\mu g \ dm^{-3}$, respectively (Results are presented in graphical form only). Typical seasonal changes in concentration of phenoxyacids and chlorophenols have been observed, as shown in Figure B. 8.20. High concentrations of 2,4-dichlorophenol (6 $\mu g \ dm^{-3}$) were observed in samples collected from the Vistula River, which carry pollutants from the catchment area. This result compares to a relatively high content of chlorophenols and phenoxyacids found in samples collected from the pier in Gdańsk, where recreation areas and beaches are located.

In general five times higher concentrations of phenoxyacids were detected in the spring period when these herbicides are applied in agriculture. Significantly higher concentrations of chlorophenols are also evident in spring compared with autumn, which suggests that degradation processes are the sources of phenol derivates rather that human activity.
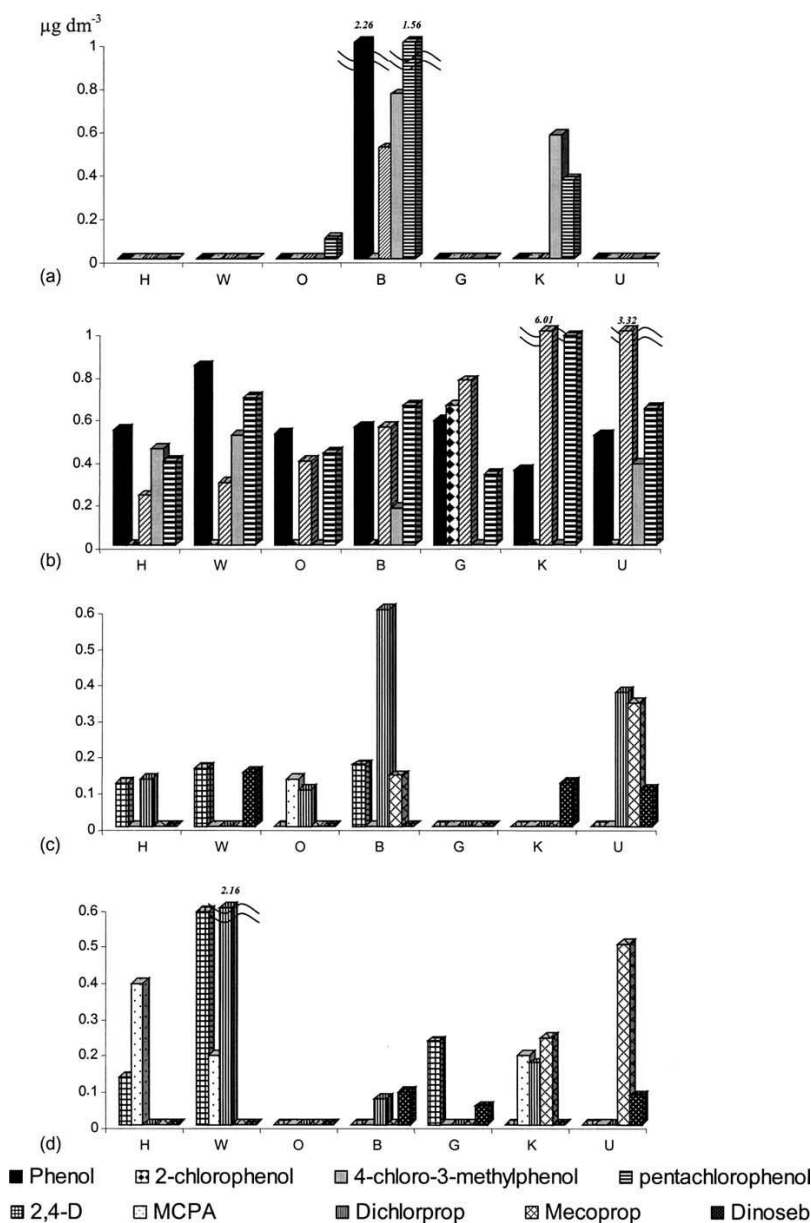
Figure B. 8.20 Seasonal changes in the concentration ($\mu g\ dm^{-3}$) of chlorophenols (a and b) and phenoxyacids (c and d).   Data for seawater samples collected in spring period are followed by data collected for autumn period (reproduced from Kot-Wasik, 2004)

III.   CONCLUSIONS

Chlorophenols and phenoxyacids were detected in the samples collected in the Gulf of Gdańsk at concentrations between 0.1 and 6.0 and 0.05 and 2.2 $\mu g\ dm^{-3}$, respectively. However, remarkably high concentrations of 2,4-dichlorophenol (6 $\mu g\ dm^{-3}$) were obtained in samples collected from the Vistula River.

Seasonal variation was observed in the data collected, with higher levels of both phenoxyacids and chlorophenols being detected in spring, corresponding with the application timing of phenoxyacids in agriculture.

Persistence criteria for classification of a compound as a persistent organic pollutant (POP)

Mecoprop-P fulfils the persistence criteria of a persistent organic pollutant (POP) as laid out in Regulation 1107/2009.

Mecoprop-P data that meet the definitions for persistence are highlighted in bold in the table below.

Criterion	Definition	Mecoprop-P data	Criteria met?
Persistence	**DT50 (water) > 2 months** DT50 (soil) > 6 months DT50 (sediment) > 6 months	<u>Soil</u> DT50 10.12d (longest non-normalised laboratory DT50, FOMC DT90/3.32) <u>Water</u> From aerobic water-sediment studies: From aerobic mineralisation in surface water study: fresh water without suspended sediment – **no degradation observed after 58 days (DT50 >1000 days default value)** <u>Sediment</u> No half-life in marine water or sediment available.	Yes Mecoprop-P meets the criterion for 'Persistence' in water

Table within "Mecoprop-P data" cell:

Water/sediment system	DegT50 Whole system (best fit model) (days)
Manningtree	58.9 (SFO)
Ongar	8.31 (HS DT90/3.32)
Calwich Abbey	29.1 (HS DT90/3.32)
Swiss Lake	**244 (SFO)**

Persistence criteria for classification of a compound as a persistent, bioaccumulative and toxic substance (PBT)

Mecoprop-P fulfils the persistence criteria of a persistent, bioaccumulative and toxic substance (PBT) as laid out in Regulation 1107/2009.

Mecoprop-P data that meet the definitions for persistence are highlighted in bold in the table below.

Criterion	Definition	Mecoprop-P data	Criteria met?
Persistence	— the half-life in marine water is higher than 60 days, **— the half-life in fresh or estuarine water is higher than 40 days,** — the half-life in marine sediment is higher than 180 days, — the half-life in fresh or estuarine water sediment is higher than 120 days, or — the half-life in soil is higher than 120 days. Assessment of persistency in the environment shall be based on available half-life data collected under appropriate conditions, which shall be described by the applicant.	<u>Soil</u> DT50 10.12d (longest non-normalised laboratory DT50, FOMC DT90/3.32) <u>Water</u> From aerobic water-sediment studies: <table><tr><td>Water/sediment system</td><td>DegT50 Whole system (best fit model) (days)</td></tr><tr><td>**Manningtree**</td><td>**58.9 (SFO)**</td></tr><tr><td>Ongar</td><td>8.31 (HS DT90/3.32)</td></tr><tr><td>Calwich Abbey</td><td>29.1 (HS DT90/3.32)</td></tr><tr><td>**Swiss Lake**</td><td>**244 (SFO)**</td></tr></table> From aerobic mineralisation in surface water study: fresh water without suspended sediment – **no degradation observed after 58 days (DT50 >1000 days default value)** <u>Sediment</u> No half-life in marine water or sediment available.	Yes Mecoprop-P meets the criterion for 'Persistence' in water

Persistence criteria for classification of a compound as a very persistent and very bioaccumulative substance (vPvB)

Mecoprop-P fulfils the persistence criteria of a very persistent and very bioaccumulative substance (vPvB) as laid out in Regulation 1107/2009.

Mecoprop-P data that meet the definitions for persistence are highlighted in bold in the table below.

Criterion	Definition	Mecoprop-P data	Criteria met?
Persistence	**— the half-life in marine, fresh- or estuarine water is higher than 60 days,** — the half-life in marine, fresh- or estuarine water sediment is higher than 180 days, or — the half-life in soil is higher than 180 days.	<u>Soil</u> DT50 10.12d (longest non-normalised laboratory DT50, FOMC DT90/3.32) <u>Water</u> From aerobic water-sediment studies: <table><tr><td>Water/sediment system</td><td>DegT50 Whole system (best fit model) (days)</td></tr><tr><td>Manningtree</td><td>58.9 (SFO)</td></tr><tr><td>Ongar</td><td>8.31 (HS DT90/3.32)</td></tr><tr><td>Calwich Abbey</td><td>29.1 (HS DT90/3.32)</td></tr><tr><td>**Swiss Lake**</td><td>**244 (SFO)**</td></tr></table> From aerobic mineralisation in surface water study: fresh water without suspended sediment – **no degradation observed after 58 days (DT50 >1000 days default value)** <u>Sediment</u> No half-life in marine water or sediment available.	Yes Mecoprop-P meets the criterion for 'Persistence' in water

B.8.5. REFERENCES RELIED ON

LITERATURE SEARCH

RMS comments:	Two literature searches have been conducted: - McCondichie, 2014a searched for mecoprop-P and synonyms only - Exponent International Ltd, 2015 & McCondichie, 2014b widened the search to include mecoprop The literature review reports are evaluated below. Any studies identified as relevant or of potential relevance are summarised and evaluated under the appropriate data point.

Report:	**McCondichie A, 2014a**
Title	Mecoprop-P – Literature search for renewal of active substance under reg. 1107/2009
Guidelines:	None
GLP:	No
Deviations	None

Previous evaluations:	None: Submitted for the purpose of renewal under Regulation 844/2012 The literature search was conducted for the active substance, mecoprop-P only. The aqueous photodegradation product, *o*-cresol, was not included in the search. The RMS considers the literature search acceptable from an Environmental Fate and Behaviour perspective for the active substance, mecoprop-P, only.

A literature search was conducted to identify scientific peer-reviewed open literature on the active substance mecoprop-P (CAS 16484-77-8) and its synonyms, along with its 2-ethyl hexyl ester (CAS 861229-15-4), and its potassium (CAS 66423-05-0) and dimethylamine (DMA) salts (CAS 66423-09-4). The relevance criteria were based on the data requirements under Regulation (EU) No 283/2013 and Regulation (EU) No 284/2013.

PROQUEST ® DIALOG was selected as the research tool which searches the following databases:
- AGRICOLA Professional
- AGRIS
- Aquatic Science and Fisheries Abstracts (ASFA)
- BIOSIS Previews®
- British Library Inside Conferences
- CAB Abstracts
- Chemical Safety NewsBase
- Current Contents Search®
- Embase®
- Embase® Alert
- Foodline®: Science2
- HSELINE: Health and Safety
- Incidence & Prevalence Database
- International Pharmaceutical Abstracts
- Lancet Titles
- MEDLINE®

- New England Journal of Medicine
- Oceanic Abstracts
- PASCAL
- Pollution Abstracts
- ProQuest Biological & Health Science Professional
- ProQuest Environmental Science Professional
- Registry of Toxic Effects of Chemical Substances (RTECS®)
- SciSearch®: a Cited Reference Science Database
- Toxfile®
- Water Resources Abstracts

Proquest Dialog was chosen a way to search multiple databases simultaneously allowing large coverage to be obtained cost effectively. Patent databases were omitted and most duplicates were automatically removed by the software. The search was restricted to the last 10 years (2004-2014).

The search was initially conducted for mecoprop-P using the following terms:

- Mecoprop-P
- CAS 16484-77-8
- (+)-MCPP
- (R)-2-(4-Chloro-2-methylphenoxy)propanoic acid
- (R)-Mecoprop
- 2M-4XP
- Duplosan KV
- EINECS 240-539-0
- Mecoprop, D-
- d-Mecoprop
- (R)-2(4-Chloro-2-methylphenoxy)propionic acid
- Propanoic acid, 2-(4-chloro-2-methylphenoxy)-, (2R)-
- Propanoic acid, 2-(4-chloro-2-methylphenoxy)-, (R)- (9CI)
- Propanoic acid, 2-(4-chloro-o-tolyl)oxy)-, (+)-
- (r)-2-(4-chloro-o-tolyloxy)-propionic acid
- MCPP-P
- CMPP-p
- Optica

The applicant reports that Optica alone produced 205,362 hits and (+)-MCPP alone produced 7,528 hits. Many of these hits were irrelevant to mecoprop-P, therefore the search string was refined to items in which both Optica and mecoprop-P or both (+)-MCPP and mecoprop-P were mentioned. The final search string for mecoprop-P and its synonyms is reported in Table B. 8.175. Further searches were conducted for 2-ethyl hexyl ester, potassium salt and dimethylamine (DMA) salt all were conducted in relation to mecoprop-P and its synonyms (see Table B. 8.175).

Table B. 8.175.   Search strategy

Database	PROQUEST ® DIALOG: 26 databases
Justification for choosing the source	Extensive and efficient, covered fields are well suited to the data requirements
Date of the search	20/05/2014
Date span of the search	2004-2014

Database	PROQUEST ® DIALOG: 26 databases
Date of the latest database update included in the search	20/05/2014
Search strategies — Mecoprop-P and its synonyms	Patents excluded Mecoprop-P **OR** 16484-77 **OR** (Mcpp **AND** Mecoprop-P) **OR** (R)-2-(4-Chloro-2-Methylphenoxy)propanoic acid **OR** (R)-Mecoprop **OR** 2M-4XP **OR** Duplosan KV **OR** 240-539-0 **OR** Mecoprop, D- **OR** d-Mecoprop **OR** (R)-2-(4-Chloro-2-methylphenoxy)propionic acid **OR** Propanoic acid, 2-(4-chloro-2-methylphenoxy)-, (2R)- **OR** Propanoic acid, 2-4(4-chloro-2-methylphenoxy)-, (R)- (9CI) **OR** Propionic acid, 2-((4-chloro-o-tolyl)oxy)-, (+)- **OR** (R)-2-(4-Chloro-o-tolyloxy)-propionic acid **OR** MCPP-P **OR** CMPP-p **OR** (Optica **AND** Mecoprop-P)
2-ethyl hexyl ester in relation to mecoprop-P	Patents excluded 2-ethyl hexyl ester (2-EHE) **AND** (Mecoprop-P and its synonyms) **OR** CAS861229-15-4
potassium salt in relation to mecoprop-P	Patents excluded Potassium **AND** (Mecoprop-P and its synonyms) **OR** CAS 66423-05-0 **OR** Zolaprofos
dimethylamine (DMA) salt in relation to mecoprop-P	Patents excluded Dimethylamine (DMA) salt **AND** (Mecoprop-P and its synonyms) **OR** CAS 66423-09-4
Total number of records retrieved after search	120

In total the searches retrieved 120 titles (Table B. 8.176), a number that could be manually checked for relevance. No further restrictions on the search terms were required. The titles were manually filtered to select any relevant or potentially relevant records based on their title. This reduced the number to 36 titles for which abstracts were obtained. Following assessment of the abstracts a total of 12 studies were identified covering all data requirements, 11 of which were identified as potentially relevant to Environmental Fate and Behaviour. Full texts of the potentially relevant studies were obtained (Table B. 8.177 lists the relevant studies ordered by data requirement and Table B. 8.178 lists the relevant studies ordered by author).

The RMS considers that from an Environmental Fate and Behaviour perspective the search strategy used is comprehensive for mecoprop-P and that the 36 potentially relevant studies were correctly identified following the initial filter of results based on the title.

Table B. 8.176. Results of the study selection process

Data requirements(s) captured in the search:	all
Total number of titles retrieved after all searches of peer-reviewed literature	120
Number of titles excluded from the search results after rapid assessment for relevance	84
Total number of abstracts assessed in detail	36
Number of studies excluded from further consideration after detailed assessment of abstract for relevance	24

Number of studies not excluded for relevance after detailed assessment of abstracts (full-texts obtained)	12

Table B. 8.177.   Report of all relevant studies and studies of unclear relevance (ordered by data requirement)

EU Point	OECD Point	Author(s)	Year	Title	Source
CA 7.1.2.2.1	IIA 7.3.1.1	Rodriguez-Cruz, MS, Baelum, Jacob , Shaw, Liz J , Sorensen, Sebastian R , Shi, Shengjing , Aspray, Thomas , Jacobsen, Carsten S , Bending, Gary D	2010	Biodegradation of the herbicide mecoprop-P with soil depth and its relationship with class III tfdA genes	Soil biology & biochemistry.
CA 7.1.2.2.1	IIA 7.3.1.1	Buss , Thrasher, J , Morgan, P , Smith, JWN	2006	A review of mecoprop attenuation in the subsurface	Quarterly Journal Of Engineering Geology And Hydrogeology
CA 7.1.3.1.1	IIA 7.4.1	Nolan, B T , Dubus, I G , Surdyk, N , Gautier, A , Crouzet, C , Flehoc, C	2007	Sorption of 7 weak-acid pesticides in 41 European soils: controlling factors and empirical modelling.	Environmental fate and ecological effects of pesticides
CA 7.1.3.1.1	IIA 7.4.1	Piwowarczyk, Agnieszka A. , Holden, Nicholas M.	2013	Phenoxyalkanoic acid herbicide sorption and the effect of co-application in a Haplic Cambisol with contrasting management	Chemosphere
CA 7.1.4.2	IIA 7.4.7	Idowu, I A , Alkhaddar, R M , Atherton, W	2014	Possible source term of high concentrations of mecoprop-P in leachate and water quality: impact of climate change, public use and disposal.	Environmental Technology
CA 7.1.4.2	IIA 7.4.7	Beinum, W van , Beulke, S , Sinclair, C J , Smart, R , Brown, C D	2007	The effect of soil type on pesticide leaching.	Environmental fate and ecological effects of pesticides
CA 7.2.2.3	IIA 7.8.3	Degenhardt, Dani , Cessna, Allan J. , Raina, Renata , Farenhorst, Annemieke , Pennock, Dan J.	2011	Dissipation of six acid herbicides in water and sediment of two canadian prairie wetlands	Environmental Toxicology and Chemistry

EU Point	OECD Point	Author(s)	Year	Title	Source
CA 7.5	IIA 7.12	Rice, P J , Horgan, B P , Rittenhouse, J L	2010	Pesticide transport with runoff from creeping bentgrass turf: relationship of pesticide properties to mass transport.	Environmental Toxicology and Chemistry
CA 7.5	IIA 7.12	Zhao, Y Q , Singleton, P , Meredith, S , Rennick, G W	2013	Current status of pesticides application and their residue in the water environment in Ireland.	International Journal of Environmental Studies
CA 7.5	IIA 7.12	Nestorovska-Krsteska, Aleksandra , Mirceska, Meri , Aaron, Jean-Jacques , Zdravkovski, Zoran	2008	Determination of dimethoate, 2,4-dichlorophenoxy acetic acid, mecoprop and linuron pesticides in environmental waters in republic of Macedonia by high performance liquid chromatography	Macedonian Journal Of Chemistry And Chemical Engineering
CA 7.5	IIA 7.12	Loos, Robert , Locoro, Giovanni , Contini, Serafino	2010	Occurrence of polar organic contaminants in the dissolved water phase of the Danube River and its major tributaries using SPE-LC-MS2 analysis	WATER RESEARCH

Table B. 8.178. Report of all relevant studies and studies of unclear relevance (ordered by author)

Author(s)	OECD Point	Year	Title	Source
Beinum, W van , Beulke, S , Sinclair, C J , Smart, R , Brown, C D	IIA 7.4.7	2007	The effect of soil type on pesticide leaching.	Environmental fate and ecological effects of pesticides
Buss , Thrasher, J , Morgan, P , Smith, JWN	IIA 7.3.1.1	2006	A review of mecoprop attenuation in the subsurface	QUARTERLY JOURNAL OF ENGINEERING GEOLOGY AND HYDROGEOLOGY
Degenhardt, Dani , Cessna, Allan J. , Raina, Renata , Farenhorst, Annemieke , Pennock, Dan J.	IIA 7.8.3	2011	DISSIPATION OF SIX ACID HERBICIDES IN WATER AND SEDIMENT OF TWO CANADIAN PRAIRIE WETLANDS	Environmental Toxicology and Chemistry

Author(s)	OECD Point	Year	Title	Source
Idowu, I A , Alkhaddar, R M , Atherton, W	IIA 7.4.7	2014	Possible source term of high concentrations of mecoprop-P in leachate and water quality: impact of climate change, public use and disposal.	Environmental Technology
Loos, Robert , Locoro, Giovanni , Contini, Serafino	IIA 7.12	2010	Occurrence of polar organic contaminants in the dissolved water phase of the Danube River and its major tributaries using SPE-LC-MS2 analysis	WATER RESEARCH
Nestorovska-Krsteska, Aleksandra , Mirceska, Meri , Aaron, Jean-Jacques , Zdravkovski, Zoran	IIA 7.12	2008	Determination of dimethoate, 2,4-dichlorophenoxy acetic acid, mecoprop and linuron pesticides in environmental waters in republic of Macedonia by high performance liquid chromatography	MACEDONIAN JOURNAL OF CHEMISTRY AND CHEMICAL ENGINEERING
Nolan, B T , Dubus, I G , Surdyk, N , Gautier, A , Crouzet, C , Flehoc, C	IIA 7.4.1	2007	Sorption of 7 weak-acid pesticides in 41 European soils: controlling factors and empirical modelling.	Environmental fate and ecological effects of pesticides
Piwowarczyk, Agnieszka A. , Holden, Nicholas M.	IIA 7.4.1	2013	Phenoxyalkanoic acid herbicide sorption and the effect of co-application in a Haplic Cambisol with contrasting management	Chemosphere

Author(s)	OECD Point	Year	Title	Source
Rice, P J , Horgan, B P , Rittenhouse, J L	IIA 7.12	2010	Pesticide transport with runoff from creeping bentgrass turf: relationship of pesticide properties to mass transport.	Environmental Toxicology and Chemistry
Rodriguez-Cruz MS, Baelum, Jacob , Shaw, Liz J , Sorensen, Sebastian R , Shi, Shengjing , Aspray, Thomas , Jacobsen, Carsten S , Bending, Gary D	IIA 7.3.1.1	2010	Biodegradation of the herbicide mecoprop-P with soil depth and its relationship with class III tfdA genes	Soil biology & biochemistry.
Zhao, Y Q , Singleton, P , Meredith, S , Rennick, G W	IIA 7.12	2013	Current status of pesticides application and their residue in the water environment in Ireland.	International Journal of Environmental Studies

The full text studies were assessed for relevance, reliability, repeatability and transparency (Table B. 8.179). Of the 11 studies identified as relevant to Environmental Fate and Behaviour all were considered of some potential relevance by the applicant:

- 3 studies are considered most likely to be taken into account for the risk assessment without major doubt on reliability, need for additional confirmatory data or further interpretation (Rodrigez-Cruz *et al.*, 2010; Piwowarczyk *et al.*, 2013; Loos *et al.*, 2010)

- 4 studies are at least partially relevant for the risk assessment and should be taken into account but do not provide final endpoints (Rice *et al.*, 2010; Degenhardt *et al.,* 2011; Zhao *et al.*, 2012; Nestorovska-Krsteska *et al.*, 2008)

- 1 study gives important background information on the properties, uses and environmental fate of mecoprop-P (Buss *et al.* 2006)

- 1 study should be taken into account even if it does not provide accurate conclusions (Idowu *et al*, 2014)

- 2 studies are relevant to some extent but which were not fully peer-reviewed and should be considered with care due to significant reliability issues (Nolan *et al.*, 2007; van Beinum *et al.*, 2007).

The identified studies are summarised and evaluated under the relevant data point in this document.

Table B. 8.179. Data from open literature that may be considered for the renewal dossier

EU point	OECD point	Authors	Type of study	Applicants comments/reliability
CA 7.1.2.2.1	IIA 7.3.1.1	Buss *et al.*, 2006	Literature review	-

EU point	OECD point	Authors	Type of study	Applicants comments/reliability
CA 7.1.2.2.1	IIA 7.3.1.1	Rodriguez-Cruz S *et al.*, 2010	Sorption	The methods are reported in another reference, but the results are reported transparently
CA 7.1.3.1.1	IIA 7.4.1	Nolan BT *et al.*, 2007	Sorption	Not fully peer-reviewed Some issues in the reporting of the method and results
CA 7.1.3.1.1	IIA 7.4.1	Piwowarczyk A *et al.*, 2013	Sorption	A standard Koc study
CA 7.1.4.2	IIA. 7.4.7	Idowu *et al.*, 2014	Scientific literature review	Conclusions not considered to be particularly reliable. Some of the information in the paper is sketchy.
CA 7.1.4.2	IIA. 7.4.7	Van Beinum W et al., 2007	Lysimeter	Not fully peer-reviewed. Reliability is questionable mainly due to the size of the lysimeters, preferential flow, the experimental conditions, the date of application and the application rate
CA 7.2.2.3	IIA 7.8.3	Degenhardt D et al., 2011	Surface water dissipation	Application rate is out of range of what can be expected in the EU waters Homogeneity issue, approximate results Good transparency
CA 7.5	IIA 7.12	Loos *et al.*, 2010	Water monitoring	Reliable water monitoring study Data obtained could be useful as comparison values with possible results from modelling
CA 7.5	IIA 7.12	Nestorovska-Krsteska A *et al.,* 2008	Water monitoring	Data obtained could be useful as comparison values with possible results from modelling. Seven dectections out of the 15 samples analysed
CA 7.5	IIA 7.12	Rice P.J *et al.,* 2010	Runoff field study	Representative rainfall event on representative golf fairway turf
CA 7.5	IIA 7.12	Zhao Y.Q *et al.,* 2012	Monitoring of usage	Method used in transparent and should be repeatable

Report:	Exponent International Ltd, 2015
Title	Literature Review Report: Exponent Project Number 1500401.UK0 - 3688
Guidelines:	None
GLP:	No
Deviations	None

Report:	McCondichie, A, 2014b
Title	MCPP and CMPP – Literature Search for Renewal of Active Substance under Reg. 1107/2009 RSA/NUF014_4018
Guidelines:	None
GLP:	No
Deviations	None

Previous evaluations:	None: Submitted for the purpose of renewal under Regulation 844/2012 This literature review was submitted to expand the search to include mecoprop. Papers already identified in McCondichie, 2014a were excluded from consideration. Four additional papers were identified as relevant for consideration in the risk assessment. The RMS considers the literature search acceptable from an Environmental Fate and Behaviour perspective.

The literature search was conducted in two parts; the development of the search strategy and initial literature search were conducted in McCondichie, 2104b, then the relevance and reliability assessment of the identified literature was conducted by Exponent International Ltd, 2015.

McCondichie, 2014b

The search aimed to identify literature for the racemic form of mecoprop (CMPP, MCPP, CAS 93-65-2). The search was carried out using the Proquest Dialog which includes the following databases;

- AGRICOLA Professional
- AGRIS
- Aquatic Science and Fisheries Abstracts (ASFA)
- BIOSIS Previews®
- British Library Inside Conferences
- CAB Abstracts
- Chemical Safety NewsBase
- Current Contents Search®
- Embase®
- Embase® Alert
- Foodline®: SCIENCE
- HSELINE: Health and Safety
- Incidence & Prevalence Database
- International Pharmaceutical Abstracts
- Lancet Titles
- MEDLINE®
- New England Journal of Medicine
- Oceanic Abstracts
- PASCAL

- Pollution Abstracts
- ProQuest Biological & Health Science Professional
- ProQuest Environmental Science Professional
- Registry of Toxic Effects of Chemical Substances (RTECS®)
- SciSearch®: a Cited Reference Science Database
- Toxfile®
- Water Resources Abstracts

Patent databases were omitted from the search and most duplicates were automatically removed by the software.

Synonyms were initially searched individually to spot any which would cause issue with the search process and those which produced large numbers of results individually were considered for deletion. 'CMPP' produced 2174 results and 'MCPP' produced 7600 results. This was due to these abbreviations having other meanings, totally unrelated to mecoprop. It was decided that any reliable paper would define the meaning of these abbreviations, most likely using a chemical name and/or CAS number. The search string already covers the IUPAC chemical name and synonyms, common and trade names. On this basis it was considered appropriate to remove CMPP and MCPP from the search string. The final search string became:

("36147_RIEDEL" **OR** "37107-00-9" **OR** "4-Chloro-2-methylphenoxy-alpha-propionic acid" **OR** "(4-Chloro-2-methylphenoxy)propionic acid" **OR** "7085-19-0" **OR** "93-65-2" **OR** "AJ-087/41885651" **OR** "alpha-(2-Methyl-4-chlorophenoxy)propionic acid" **OR** "(+)-alpha-(4-Chloro-2-methylphenoxy) propionic acid" **OR** "Anicon B" **OR** "Anicon P" **OR** "BRN 2212752" **OR** "Caswell No. 559" **OR** "CCRIS 1464" **OR** "Celatox CMPP" **OR** "Chipco turf herbicide mcpp" **OR** "CID7153" **OR** "Compitox" **OR** "202-264-4" **OR** "230-386-8" **OR** "EPA Pesticide Chemical Code 031501" **OR** "FBC CMPP" **OR** "Hedonal" **OR** "HSDB 1738" **OR** "Isocarnox" **OR** "Iso-Cornox" **OR** "Kilprop" **OR** "Liranox" **OR** "LS-124601" **OR** "LS-190737" **OR** "Mechlorprop" **OR** "Mecomec" **OR** "Mecopar" **OR** "Mecopeop" **OR** "Mecoper" **OR** "Mecopex" **OR** "Mecoprop" **OR** "Mecoturf" **OR** "Mecprop" **OR** "Mepro" **OR** "Methoxone" **OR** "MLS000084910" **OR** "Morogal" **OR** "Mwcoprop" **OR** "N.b. mecoprop" **OR** "NCGC00163831-01" **OR** "NSC60282" **OR** "NSC 60282" **OR** "Okultin MP" **OR** "PDSP1_001803" **OR** "PDSP2_001786" **OR** "Propanoic acid, 2-(4-chloro-2-methylphenoxy)-" **OR** "Propionic acid, 2-(2-methyl-4-chlorophenoxy)-" **OR** "Propionic acid, 2-(4-chloro-2-methylphenoxy)" **OR** "Propionic acid, 2-((4-chloro-o-tolyl)oxy)-" **OR** "Propionic acid, 2-[(4-chloro-o-tolyl)oxy]-, (.+/-.)-" **OR** "Proponex-plus" **OR** "PS324_SUPELCO" **OR** "Rankotex" **OR** "RD 4593" **OR** "Runcatex" **OR** "SMR000019256" **OR** "ST5407022" **OR** "SYS 67 Mecmin" **OR** "U 46 KV fluid" **OR** "Vi-Par" **OR** "Vi-Pex" **OR** "WLN: QVY1&OR DG B1" **OR** "19095-88-6" **OR** "1929-86-8" **OR** "2-(2-Methyl-4-chlorophenoxy)propanoic acid" **OR** "2-(2-Methyl-4-chlorophenoxy)propionic acid" **OR** "2-(2'-Methyl-4'-chlorophenoxy)propionic acid" **OR** "2-(4-chloro-2-methyl-phenoxy)propanoic acid" **OR** "2-(4-chloro-2-methylphenoxy)propanoic acid" **OR** "2-(4-chloro-2-methyl-phenoxy)propionic acid" **OR** "2-(4-Chloro-2-methylphenoxy)propionic acid" **OR** "2-(4-Chloro-2-tolyloxy)propionic acid" **OR** "2-(4-Chloro-o-tolyl)oxylpropionic acid" **OR** "(+-)-2-((4-Chloro-o-tolyl)oxy)propionic acid" **OR** "2-(4-Chlorophenoxy-2-methyl)propionic acid" **OR** "2M-4CP" **OR** "2M4KhP" **OR** "2M 4KhP" **OR** "2-Mcpp" **OR** "2-Methyl-4-chlorophenoxy-.alpha.-propionic acid" **OR** "3-06-00-01266")

The RMS considers this search string acceptable and the removal of MCPP and CMPP reasonable.

This search string produced 6864 hits and the date range 2004-2014 was applied to reduce the number to 671. These were manually sifted in order to identify any potentially relevant papers and 166 were selected. Abstracts for these were retrieved for review. A further manual sift was carried out to remove any duplicates not caught by the search programme and also to remove any papers that would already have been considered in the mecoprop-P search (McCondichie, 2014a). This reduced numbers to 143 potentially relevant references.

Exponent International Ltd, 2015

Articles of potential relevance to the regulatory data package for the active substance were investigated in further detail by examining the abstract and/or the full article text. Relevancy criteria for Environmental Fate are given

in Table B. 8.180. Where articles were considered to meet the criteria for relevance, an assessment of the reliability of the study was carried out using the following reliability categories:

1: Reliable without restriction

Studies/data which were carried out or generated according to generally valid and/or internationally accepted testing guidelines (preferably performed to GLP) or in which the test parameters documented are based on a specific (national) testing guideline or in which all parameters described are closely related/comparable to a guideline method.

2: Reliable with restriction

Studies/data (mostly not performed according to GLP), in which the test parameters documented to not totally comply with the specific testing guideline, but are sufficient to accept the data or in which investigations are described which cannot be subsumed under a testing guideline, but which are nevertheless well documented and scientifically acceptable.

3: Not reliable

Studies/data in which there are interferences between the measuring system and the test substance or in which organisms/test systems were used which are not relevant in relation to the exposure or which were carried out or generated according to a method which is not acceptable, the documentation of which is not sufficient for an assessment and which is not convincing for an expert judgement.

4: Not assignable

Studies/data which do not give sufficient experimental details and which are only listed in short abstracts or secondary literature (books, reviews etc.)

Table B. 8.180. Relevancy criteria – Environmental fate

Data requirement (data point)	Relevancy criteria considered
Fate and behaviour in soil (KCA 7.1)	1. Well-defined test material applied as active substance or plant protection product (not as a by-product or ingredient of a soil amendment) 2. Substrate is a representative soil for agricultural uses with well-defined soil properties (e.g. pH, organic carbon content, microbial biomass etc). This is also relevant for field studies. 3. No previous contamination of the soil. 4. Active substance is not applied as a mixture with other active substances
Fate and behaviour in water and sediment (KCA 7.2)	1. Well-defined test material applied as active substance or plant protection product. 2. Test samples used are samples from representative European aquatic resources with no contamination 3. Active substance is not applied as a mixture with other active substances
Fate and behaviour in air (KCA 7.3)	1. Well-defined test material. 2. Areas investigated are relevant for Europe.

A summary of the selection process is given in Table B. 8.181. The RMS notes that 143 records were identified in the initial search, however, the summary table only lists 142. It is unclear why one study was excluded and the RMS was unable to identify which study was excluded from the information available. After detailed assessment 20 of these studies were retained of which 5 were considered both relevant and reliable (category 1 + 2). The RMS considers that papers relevant to Environmental Fate and Behaviour have been identified and

agrees with the reliability categories assigned.   Table B. 8.182 lists the studies considered both relevant and reliable.

Table B. 8.181. Summary of the study selection process

Summary of the review	n
Total number or summary records retrieved after removing duplicates from all database searches	142
Number of summary records excluded after rapid assessment for relevance (by title/abstract)	98
Number of summary records of potential/unclear relevance assessed in further detail (by abstract/full-text)	44
Number or studies excluded from further consideration after detailed assessment for relevance (by abstract/full-text)	24
Number of studies not excluded for relevance after detailed assessment (i.e. relevant studies and studies of unclear relevance)	20
Number of relevant but not reliable studies (reliability categories 3+4) identified by the literature search and appraisal process	15
Number of relevant and reliable studies (reliability categories 1+2) identified by the literature search and appraisal process	5

Table B. 8.182. Relevant and reliable studies (categories 1+2) ordered by data point

Data point	Author	Year	Reference	Title
KCA 7.1.2.1.1	Rodriguez-Cruz *et al*	2006	Soil Biology & Biochemistry (2006) Vol. 38(9), pp. 2910-2918	Field-scale study of the variability in pesticide biodegradation with soil depth and its relationship with soil characteristics
KCA 7.2.3	Barth *et al*.	2007	Science of the Total Environment (2007), Vol 376, pp40-50	Deposition, persistence and turnover of pollutants: first results from the EU project AquaTerra for selected river basins and aquifers
KCA 7.2.2.3	Bromilow *et al.*	2006	Journal of Evironmental Science and Healt, Part B, Pesticides, Food Contaminants and Agricultural Wasttes (2006), Vol 41(1) pp1-16	Behaviour of pesticides in sediment/water systems in outdoor mesocosms
KCA 7.5	Kot-Wasik *et al*	2004	Marine Pollution Bulletin (2004) Vol. 49(3), pp. 264-276	Monitoring of organic pollutants in coastal waters of the Gulf of Gdan´sk, Southern Baltic.: Special issue: Estuaries and Brackish Waters: Pollution Barriers or Sources to the Sea?
KCA 8.2.6/8.2.7	Cedergreen & Streiberg	2005	Pest Management Science (2005) Vol. 61(12), pp. 1152-1160	The toxicity of herbicides to non-target aquatic plants and algae: assessment of predictive factors and hazard

The references relied on list has been updated to include the newly submitted data relied on as well as those original submitted tests and studies (in *italics*) that are still considered relevant to support the application for renewal.

Data Point	Author(s)	Year	Title Company Report No. Source (where different from company) GLP or GEP status Published or not	Vertebrate study Y/N	Data protection claimed Y/N	Justification if data protection is claimed	Owner	Previous evaluation
CA 7.1.1.1 (IIA 7.1.1)	*Schocken, M*	*1997*	*MCPP-P Aerobic Soil Metabolism 96-4-6482 Springborn Laboratories Inc, USA GLP Not published*	*N*	*N*	-	*MCPP-P Task Force*	*In Addendum 1 to DAR (May 2000)*
CA 7.1.1.3/01	Connor, S.R.	1996a	MCPP-P – soil photolysis study 96-1-6346 Springborn Laboratories Inc, USA GLP Not published	N	N	-	MCPP-P Task Force	None: submitted for the purpose of renewal
CA 7.1.2.1.1 /CA 7.1.1.3 /CA 7.2.1.1	Hazlerigg, C & Garratt, J	2015	A kinetic analysis of the degradation of mecoprop-P and its metabolites in aerobic soils as well as via photolysis in soil and water E2015-11 Enviresearch Not GLP Not published	N	Y	New data submitted	Nufarm	None: submitted for the purpose of renewal
CA 7.1.3.1.1 (IIA 7.1.2)	*Matla YA & Vonk JW*	*1993*	*Adsorption of mecoprop-P to soil particles in three soil types. TNO report IMW-R 93/035. Task Force KII 7.8: Reg. Doc. No. BASF 93/10223 Task Force KIII 9.5: Reg. Doc.*	*N*	*N*	-	*MCPP-P Task Force*	*In DAR (1998)*

Data Point	Author(s)	Year	Title Company Report No. Source (where different from company) GLP or GEP status Published or not	Vertebrate study Y/N	Data protection claimed Y/N	Justification if data protection is claimed	Owner	Previous evaluation
			No. BASF 93/10223 GLP Not published					
CA 7.1.3.1.1 (IIA 7.1.2)	*Obrist JJ,*	*1986e*	*Adsorption/desorption of mecoprop on representative agricultural soils. Hazleton Laboratories America, Study No. HLA 6015-324, Aug 14, 1986 Nufarm Task Force KII: 7.1.2/01 GLP Not published*	*N*	*N*	*-*	*MCPP-P Task Force*	*In DAR (1998)*
CA 7.1.3.1.1/ 01	Simmonds, M	2010	[^{14}C]-Mecoprop-P: adsorption to and desorption from four soils QC/09/001 Battelle UK Ltd GLP Not published	N	Y	New data submitted	Nufarm	None: submitted for the purpose of renewal
CA 7.2.1.1 (IIA 7.2.1.1)	*Anonymous*	*1982*	*Behaviour of pesticides in water. Hydrolytical stability. Jan. 4, 1982 Nufarm Task Force KII: 7.2.1.1/01 Task Force KII 7.12: Reg. Doc. No. BASF 82/10060 Not published*	*N*	*N*	*-*	*MCPP-P Task Force*	*In DAR (1998)*
CA 7.2.1.1 (IIA 7.2.1.2)	*Obrist JJ*	*1986a*	*Photodegradation and hydrolysis of mecoprop in aqueous buffer.*	*N*	*N*	*-*	*MCPP-P Task Force*	*In DAR (1998)*

Data Point	Author(s)	Year	Title Company Report No. Source (where different from company) GLP or GEP status Published or not	Vertebrate study Y/N	Data protection claimed Y/N	Justification if data protection is claimed	Owner	Previous evaluation
			Hazleton Lab. America, Study 6015-320, Sept 8, 1986. *Nufarm Task Force KII: 7.2.1.2/01* *Task Force KII 7.14: Reg. Doc. No. BASF 86/0484 GLP* *Not published*					
CA 7.2.1.1 (IIA 7.2.1.2)	*Obrist JJ*	*1988*	*Amendment to: Photodegradation and hydrolysis of mecoprop in aqueous buffer. Hazleton Lab. America* *Nufarm Task Force KII: 7.2.1.2/01* *Task Force KII 7.15: Reg. Doc. No. BASF 88/0620 GLP* *Not published*	*N*	*N*	*-*	*MCPP-P Task Force*	*In DAR (1998)*
CA 7.2.1.1 (IIA 7.2.1.2)	*Obrist JJ*	*1990*	*Supplement No. 1 to the final report: Photodegradation and hydrolysis of mecoprop in aqueous buffer. Hazleton Lab. America, Study 6015-320. April 17, 1990* *Task Force KII 7.16: Reg. Doc. No. BASF 90/0205 GLP* *Not published*	*N*	*N*	*-*	*MCPP-P Task Force*	*In DAR (1998)*
CA 7.2.1.2/01	Connor, S.R	1996b	MCPP-P – Aqueous photolysis study	N	Y	New data submitted	MCPP-P Task Force	None: submitted for the purpose of renewal

Data Point	Author(s)	Year	Title Company Report No. Source (where different from company) GLP or GEP status Published or not	Vertebrate study Y/N	Data protection claimed Y/N	Justification if data protection is claimed	Owner	Previous evaluation
			96-1-6341 Springborn Laboratories Inc, USA GLP Not published					
CA 7.2.2.1/01	Feil, N	2010	Ready biodegradability of mecoprop-P in a manometric respirometry test 55481163 IBACON GLP Not published	N	Y	New data submitted	Nufarm	None: submitted for the purpose of renewal
CA 7.2.2.2/01	Traub, M	2014	Aerobic mineralisation of [^{14}C]Mecoprop-P in surface water S13-00242 Eurofins Agroscience Services GLP Not published	N	Y	New data submitted	Nufarm	None: submitted for the purpose of renewal
CA 7.2.2.3 (IIA 7.2.1.3.2)	*Cooper, J L D & Unsworth, R H*	*1996*	*Mecoprop-P: Degradation in Two Water/Sediment Systems Rhone-Poulenc Ltd, UK P 95/123 (BASF Reg Doc # 96/100348) GLP Not published*	*N*	*Y (but expired)*	*NA*	*MCPP-P Task Force*	*In Addendum II to DAR (July 2002)*
CA 7.2.2.3/01	Hazlerigg, C. and Garratt, J.	2014	Kinetic analysis of mecoprop-P degradation in water-sediment studies E2014-25	N	N	New guidance	Nufarm	None: submitted for the purpose of renewal

Data Point	Author(s)	Year	Title Company Report No. Source (where different from company) GLP or GEP status Published or not	Vertebrate study Y/N	Data protection claimed Y/N	Justification if data protection is claimed	Owner	Previous evaluation
			Enviresearch Not GLP Not published					
CA 7.2.2.3/02	Roohi, A	2015	[^{14}C]-Mecoprop-P: Route and Rate of Degradation in Two Water/Sediment Systems at 20 ± 2°C Laboratory: Battelle UK Ltd. Report No. WU/14/004 GLP Not published	N	Y	New data submitted	Nufarm	None: submitted for the purpose of renewal
CA 7.3.1 (IIA 7.2.2.1)	Kubiak, R.	1994a	Investigation of the volatilization of $_{14}$C-MCPP-P and $_{14}$C-Bifenox formulated according to Foxtril super (RPA30535H) from plant surfaces under laboratory conditions. SLFA, FB Phytomedizin. Study No. RPA15. Sept 19, 1994. Task Force KII 7.20: Reg. Doc. No. BASF 94/11248. GLP Not published	N	N	-	MCPP-P Task Force	In DAR (1998)
CA 7.3.1 (IIA 7.2.2.1)	Kubiak, R.	1994b	Investigation of the volatilization of $_{14}$C-MCPP-P and $_{14}$C-Bifenox formulated according to Verigal D (RPA44040H)	N	N	-	MCPP-P Task Force	In DAR (1998)

Data Point	Author(s)	Year	Title Company Report No. Source (where different from company) GLP or GEP status Published or not	Vertebrate study Y/N	Data protection claimed Y/N	Justification if data protection is claimed	Owner	Previous evaluation
			from plant surfaces under laboratory conditions. SLFA, FB Phytomedizin. Study No.: RPA14. Aug.25, 1994. Task Force KII 7.21: Reg. Doc. No. BASF 94/11252. GLP Not published					
CA 7.3.1 (IIA 7.2.2.2)	*Jendrejczak N, Turier G, Maestracci M*	*1994a*	*Soil surface volatilization study of MCPP-P and Bifenox formulated as EXP30535 (official German reference No. RPA30535H). GLP Not published*	*N*	*N*	*-*	*MCPP-P Task Force*	*In DAR (1998)*
CA 7.3.1 (IIA 7.2.2.2)	*Jendrejczak N, Turier G, Maestracci M,*	*1994b*	*Soil surface volatilization study of MCPP-P and Bifenox formulated as EXP04404 (official German reference No. RPA44040H). GLP Not published*	*N*	*N*	*-*	*MCPP-P Task Force*	*In DAR (1998)*
CA 7.3.1 (IIA 7.2.2.3)	*Hesse B, Fegert A & Sarafin R,*	*1993*	*Evaluation of the volatilization of mecoprop-P and 2,4-D after application of BASF 076 10 H under field conditions. BASF Report No. 3585. April*	*N*	*N*	*-*	*MCPP-P Task Force*	*In DAR (1998)*

Data Point	Author(s)	Year	Title Company Report No. Source (where different from company) GLP or GEP status Published or not	Vertebrate study Y/N	Data protection claimed Y/N	Justification if data protection is claimed	Owner	Previous evaluation
			19, 1993. *Task Force KII 7.22: Reg. Doc. No. BASF 93/11516.* *GLP* *Not published*					
CA 7.3.1 (IIA 7.2.3)	*Maestracci M*	*1994*	*Mecoprop-P estimation of the rate of photochemical transformation in the atmosphere under tropospheric conditions. Rhône-Poulenc study 94-28, Apr.14, 1994. Doc. 436537 Task Force KII 7.27: Reg. Doc. No. BASF 94/11249 GLP Not published*	*N*	*Y but expired*	*N/A*	*MCPP-P Task Force*	*In DAR (1998) and Addendum II to DAR (July 2002).*
CA 7.3.1 (IIA 7.2.3)	*Sarafin R*	*1991*	*Sarafin R, 1991 Photochemical oxidative degradation of mecoprop (Atkinson). BASF Report No. 3157 June 1991. Task Force KII 7.25: Reg. Doc. No. BASF 91/10327. Non-GLP Not published*	*N*	*N*	*-*	*MCPP-P Task Force*	*In DAR (1998)*
CA 7.3.2	Comb, A	2000a	Mecoprop-P (Pure Grade) Physico-Chemical Properties,	N	Y	New data submitted	Nufarm	None: submitted for the purpose of renewal

Data Point	Author(s)	Year	Title Company Report No. Source (where different from company) GLP or GEP status Published or not	Vertebrate study Y/N	Data protection claimed Y/N	Justification if data protection is claimed	Owner	Previous evaluation
			Amended Final Report NUF004/99523 Huntingdon Life Sciences, UK GLP Not published ⇨ CA 2.1/01					