Renewal Assessment Report

Diuron

Volume 3 – B.8 Environmental fate and behaviour

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Rapporteur Member State: Germany

Co-Rapporteur Member State: Denmark

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When	What
16 March 2018	First submission to EFSA

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B Summary of the data and information

B.8 Environmental fate and behaviour

B.8.1 Fate and behaviour in soil

The degradation route and rate of diuron in soil under aerobic conditions was investigated in three laboratory studies submitted for first EU approval:

- Hawkins et al, 1990
- Mackie and Hall, 1994
- De Vries, 1996

Besides, two laboratory soil study under aerobic conditions were performed with the diuron metabolites DCPMU and DCPU for first EU approval:

- Hennecke, 2005a
- Hennecke, 2005b

For first EU approval, a kinetic re-evaluation of the studies Mackie & Hall, 1994 and deVries, 1996 with diuron and the laboratory aerobic soil studies Hennecke, 2005a & b with the metabolites DCPMU and DCPU was performed by

- Schnoeder, 2006

For EU re-approval an additional kinetic re-evaluation of the study Hawkins et al, 1990 was submitted:

- Drechsler & Klein, 2016a & b

The degradation route and rate of diuron in soil under anaerobic conditions was investigated in the one laboratory studies submitted for first EU approval:

- Yu, 1988

Besides, a kinetic re-evaluation was also submitted for the anaerobic soil degradation study with diuron:

- Drechsler & Klein, 2016c & d

The soil photolysis of diuron was also investigated in two studies for first EU Annex I inclusion:

- Hennecke, 2005a

In addition to the laboratory studies, four field dissipation studies with diuron were submitted for first EU approval:

- Pogany (1993)
- Paetzold and Brümmer (1997)
- Tworkoski et al. (2000)
- Rouchard et al. (2000)
-

The storage stability of diuron was tested in one study for first EU approval:

- Sommer, 1993
-

The studies Tworkoski et al. (2000) and Rouchard et al. (2000) were not accepted for first EU approval and are thus not summarised here anymore.

A kinetic re-evaluation of the field dissipation studies Pogàny (1993), Pätzold and Brümmer (1996) and Rouchard et al. (2000) to derive persistence endpoints was also performed for first EU approval by:

- Schnoeder, 2006

A new kinetic re-evaluation to derive persistence endpoints of the field dissipation study Pogàny (1993)

was submitted for EU re-approval of diuron:

- Drechsler & Klein, 2016e & f

Besides, a new kinetic re-evaluation of the field dissipation study Pogàny (1993) to derive modelling endpoints according to EFSA (2014) was submitted for EU re-approval:

- Drechsler et al, 2016

The adsorption of diuron to soil was investigated in one laboratory study submitted for first EU approval:

- Bramble et al, 1998a

Besides, an additional study investigating the adsorption of diuron to soil was submitted for EU re-approval:

- Derz, 2009

The adsorption of the metabolites DCMPU, DCPU and mCPMU of diuron to soil was investigated in one laboratory study each submitted already for first EU approval:

- Brumhardt et al, 1998
- Heintze, 2002
- Bramble et al, 1998b

No column leaching study with diuron or its metabolites were submitted, however, a lysimeter study with diuron was performed already for first EU approval and is summarised under B.8.1.4.2:

- Bergstroem et al, 1996

The final results of all acceptable studies regarding the fate and behaviour of diuron and its metabolites in soil are summarised in Volume 1 under 2.8.1.

A search for open literature which included papers in peer-reviewed journals and reports from governments and other agencies in the EU and several other countries was performed by the applicant. The literature search strategy of the applicant and the evaluation of the RMS are described in detail in the Appendix to this document. Relevant studies found by the applicant and the RMS are discussed within the Appendix. No studies concerning the route and rate of diuron in soil, which have to be included in risk assessment, were found.

B.8.1.1 Route and rate of degradation in soil

B.8.1.1.1 Aerobic degradation

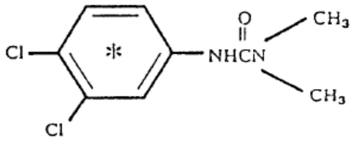
KCA 7.1.1.1/1 – Hawkins, et al, 1990 (study evaluated in the DAR, 2003)

Author:	Hawkins, D.R., Kirkpatrick, D., Shaw, D., Chan, S.C.
Title:	The Metabolism of [phenyl (U)-14C] diuron in Keyport silt loam soil under aerobic conditions
Date:	29.11.1990
Doc ID:	AMR-1202-88
Guidelines:	US EPA Guideline, Subdivision N, 162-1 (Oct 1982)
GLP:	Yes
Validity:	Acceptable

Material and Methods

In the study, the fate of ^{14}C-diuron in soil was investigated in the laboratory in sterile and non-sterile silt loam soil at 25 °C under aerobic conditions for up to one year. The properties of the test material is given in Table B.8.1-1.

Table B.8.1-1 Test material

Radiolabelled test item	
Test material:	[Phenyl (U)-^{14}C]Diuron
Lot/Batch #:	Radioactive file Number 235; Batch 3
Structure:	 *position of ^{14}C-label
Specific radioactivity:	44.1 µCi/mg
Radiochemical purity:	97 %
Non-radiolabelled test item	
Test material:	Diuron
IUPAC name:	3-(3,4-dichlorophenyl)-1,1-dimethylurea
Lot/Batch #:	14740-149
Purity:	100 %
Reference compounds	
DCPMU	N'-3,4-dichlorophenyl)-N-methylurea
DCPU	N-(3,4-dichlorophenyl)urea
DCA	3,4-dichloroaniline
TCAB	3,3'4,4'-tetrachloroazobenzene
TCAOB	3,3'4,4'-tetrachloroazoxybenzene

The soil characteristics are provided in Table B.8.1-2. Before use the soil was sieved through a 2 mm sieve. The microbial activity of the soil was determined prior to treatment, after 180 days and at the end of the experiment.

Table B.8.1-2 Soil characteristics

Soil Name	**Keyport soil**		
Soil location	Newark, Delaware (USA)		
Particle size distribution:			
Sand (2000 – 50 µm):	22 %		
Silt (50 – 2 µm):	59 %		
Clay (< 2 µm):	19 %		
Textural classification:	Silt loam		
Organic matter:	3.7 %		
pH:	4.6		
Cation exchange capacity:	8.9 meq/100 g		
Bulk density (disturbed soil):	0.96 g/cm^3		
Water holding capacity at 0.33 bar	26.5 %		
Microbial activity in non-sterile soil:	Day 0	Day 180	Day 365
Bacteria	2.8 x 10^7	6.2 x 10^6	1.52 x 10^6
Aerobic bacterial spores	4.3 x 10^5	7.00 x 10^5	1.07 x 10^6
Fungi	1.5 x 10^3	1.70 x 10^5	6.45 x 10^4
Actiomycetes	1.0 x 10^7	5.0 x 10^5	1.78 x 10^5

A volume of 380 µL of a stock solution of ^{14}C-diuron was added to 50 g (dry weight) sieved soil in 250 mL present biometer flasks to a final concentration of 19.5 µg/g soil (dry weight) to the non-sterile soil samples and 20.3 µg/g soil (dry weight) to the sterile soil samples. This is equivalent to an application rate of 14.625 kg as/ha and 15.225 kg as/ha, respectively (assuming a soil depth of 5 cm

and a soil density of 1.5 g/cm^3). Following application, sufficient distilled water was added to bring the soil water content to 75 % of the water content at 0.33 bar potential. Once the soil samples had been dispensed, the sterilised samples were prepared by autoclaving at 121 °C for 1 hour on three successive days. A total of 61 flasks were prepared, 32 for non-sterile application, 26 for sterile application and 3 control flasks for treatment with ^{14}C-cellulose. The soil flasks were kept in darkness, in a thermodynamically-controlled incubator with a mean temperature of 24.9 °C ± 0.2 °C, for up to one year prior to analysis. 0.5 M aqueous sodium hydroxide solution was added to the side tube of each flask (sterile and non-sterile) for trapping of CO_2. Trapping solution was taken for CO_2 analysis and replaced repeatedly.
Triplicate soil flasks of the non-sterile samples were taken for analysis 0, 7, 14, 30, 60, 120, 180, 240, 300 and 365 days after application of ^{14}C-diuron. Triplicate soil flasks of the sterile samples were taken for analysis 7, 14, 30, 60, 120, 180, 240 and 365 days after application of ^{14}C-diuron. The cellulose control samples were not sampled, but the trapping solutions in the side tubes were analysed repeatedly for CO_2 determination.

After incubation, the soil samples were first extracted 3 times with appr. 150 mL methanol : water (9:1 v/v) and subsequently 3 times with appr. 150 mL methanol. The extraction steps 1-6 were performed for one hour at room temperature each. In extraction step 7, the soil was extracted with appr. 250 mL methanol in a Soxhlet apparatus for 24 hours. Finally, in extraction step 8, the soil sampled were extracted with acetone/water/conc. phosphoric acid (85:13:2 v/v/v, appr. 100 mL) for 18 h at room temperature. In all cases the total soil sample was extracted, and extraction commenced the day the sample was taken. Extracts were separated from soil by centrifugation. Radioactivity in the extracts was measured using LSC. Additionally, extracts were analysed by HPLC and TLC. The radioactivity in the volatile traps were measured by LSC and the amount of CO_2 was determined by precipitation with barium chloride solution.

Results and Discussion

In the non-sterile soils treated with ^{14}C-cellulose, volatile radioactivity continued to evolve throughout the study reaching a cumulative total of 44.2 % after 365 d.

Total recoveries in the non-sterile and the sterile soil samples treated with diuron were between 99.1 to 103.6 % AR and between 95.2 and 100.4 % A, respectively. The material balance of the non-sterile soils is presented in Table B.8.1-3. Extractable radioactivity in the non-sterile samples after 365 d decreased to 81 %, while 14.9 % were formed. Mineralisation after 365 d amounted to 3.36 %. In the sterile soils, 90.3 % of the radioactivity still remained extractable after 365 d with 6.1 % non extractables. Mineralisation in the sterile samples remained < 0.07 %.
The distribution of the radioactivity in the non-sterile samples is presented in Table B.8.1-4. In the non-sterile samples diuron decreased from 97.8 % to 54.7 % after 365 d. One major metabolite DCPMU was formed with a maximum observed concentration of 21.7 % after 365 d. The additional identified metabolite DCPU remained below 5 % throughout the study. In the sterile samples, diuron decreased to 81.1 % after 365 d. No metabolite was formed in the sterile samples in concentrations above 5 %.

Table B.8.1-3 Material balance of radioactivity after incubation of ^{14}C-labelled diuron in a Keyport silt loam soil (non-sterile samples)

Time (days)	Extracts 1-6	Extract 7	Extract 8	Total extractable	Not extracted	Volatiles**	Total recovered
0	103.1	-	-	103.1	0.2	-	103.3
7	96.9	-	-	96.9	5.0	0.02	101.9
14	98.9	-	-	98.9	4.7	0.02	103.6
30	89.0	7.9	-	96.8	5.7	0.14	102.6
60	83.8	10.9	-	94.7	7.8	0.48	103.0
120	74.2	10.8	5.8	90.8	9.5	1.39	101.7
180	67.2	12.8	7.2	87.3	11.4	1.96	100.7

240	65.5	13.7	7.0	86.1	11.6	2.34	100.0
300	62.0	12.6	7.9	82.0	14.2	2.90	99.1
365	54.7	17.9	8.5	81.0	14.9	3.36	99.3

** CO_2

Table B.8.1-4 Distribution of the radioactivity after incubation of ^{14}C-labelled diuron in in a Keyport silt loam soil (non-sterile samples)

Time (days)	**Diuron**	**DCPMU**	**DCPU**	**Others***
0	97.7	-	-	-
0	97.9	-	-	-
7	92.4	1.8	0.3	0.9
7	95.5	1.6	0.3	1.0
14	94.8	1.8	0.3	1.6
14	95.1	2.1	0.5	1.5
30	86.0	4.7	0.9	4.7
30	86.8	4.7	0.8	4.9
60	83.8	8.1	0.6	3.2
60	82.0	8.4	0.6	2.8
120	68.3	14.2	0.6	5.8
120	71.9	13.0	0.5	4.2
180	62.6	17.6	0.6	5.0
180	64.1	16.2	0.6	4.2
240	60.5	17.4	0.7	6.0
240	58.5	18.0	0.6	6.1
300	54.6	16.9	0.7	5.9
300	55.3	18.1	0.6	6.5
365	46.9	22.5	0.7	7.0
365	51.0	20.9	0.6	7.1

* several individual compounds, none of which exceeded 3.5 % AR

Conclusion

The study was accepted for the first EU approval. When examining the study for re-approval of diuron several deviations from OECD 307 were found by the RMS: First, the history of pesticide application is missing, however an adaption of the microorganisms seems unlikely, since degradation of diuron in the Keyport soil was the slowest of all investigated soils. Details on sampling of the soil and of storage duration and conditions prior to use is missing and no pre-incubation of soil at test conditions was performed. However incubations with cellulose showed that the soil was still viable. The extraction procedure of the 7th step is considerably harsh - TLC and HPLC was performed with combined extracts from steps 1-7, thus no further separation of radioactive distribution is possible (diuron and DCPMU were found in extract 1-7 and in extract 8). However, no chemical alteration of diuron or its metabolites during the Soxhlet extraction are expected. The pH of the soil is more acidic then recommended in OECD 307.

Despite the deviations from OECD 309, the RMS is of the opinion, that the study is still acceptable to be used for exposure assessment of diuron.

After incubation at 25 °C with a moisture content of 75 % WHC (water holding capacity at 0.33 bar) for 365 days, diuron decreased in silt loam to 49 % while 14.9 % non-extractable residues and 3.36 % CO_2 were formed. One major metabolite DCPMU was found with maximum concentrations of 21.7 % on day 365 (mean of two measurements).

The DT_{50} and DT_{90} values of the study are not listed here anymore, since a new kinetic evaluation Drechsler and Klein, 2014a & b according to FOCUS kinetic guidance (2006, 2014) is available, which is described under B.8.1.1.6.

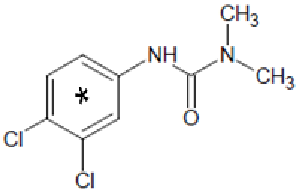
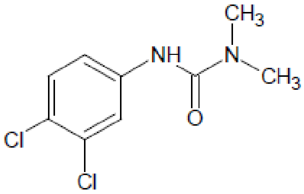
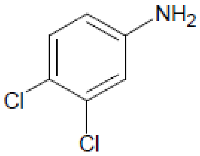
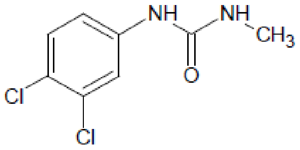
KCA 7.1.1.1/2 – Mackie and Hall, 1994 (study evaluated in the DAR 2003)

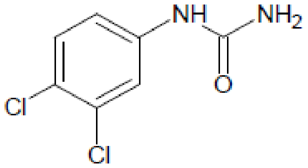
Author:	Mackie, J.A., Hall, B.E.
Title:	Degradation of [phenyl(U)-14C] diuron in soil under aerobic conditions
Date:	15.04.1994
Doc ID:	AMR 2603-93
Guidelines:	Danish Ministry of Environment Statuary Order on Chemical Pesticides (No. 791, 1987)
GLP:	Yes
Validity:	Acceptable

Material and Methods

The route and rate of degradation of diuron in aerobic soil were studied for maximal 100 days in 3 soils (sandy loam, loamy sand, sand) using radiolabelled test item, [^{14}C]diuron. The properties of the test material is given in Table B.8.1-5.

Table B.8.1-5 Test material

Radiolabelled test item	
Test material:	[Phenyl -^{14}C]Diuron
Lot/Batch #:	2760-221
Structure:	 * Position of radiolabel
Specific radioactivity:	50.2 µCi/mg
Radiochemical purity:	98.3 %
Reference items	
Test material:	Diuron
Structure:	
Lot/Batch #:	14740-149
Purity:	99.6 %
Test material:	DCA (3,4-dichloroaniline)
Structure:	
Lot/Batch #:	17239-10
Purity:	99.32 %
Test material:	DCPMU (N-(3,4-dichlorophenyl)-N'-methylurea)
Structure:	

Lot/Batch #:	15654-12
Purity:	99.88 %
Reference item:	DCPU (N-(3,4-dichlorophenyl)-urea)
Structure:	
Lot / Batch #:	R915-7
Chemical purity:	98.4 %

The soil characteristics are presented in Table B.8.1-6. Fresh soil samples were taken from areas where no pesticides were applied for the last 4-5 years. The soil samples were mixed and sieved to 2 mm and stored in the dark under moist and aerated conditions at 4 °C.

Table B.8.1-6 Soil characteristics

Origin	**Uppsala, S**		**Falkenberg, S**		**Mogenstrupvej, DK**	
Last pesticide use	1988		1988		1989	
pH value (KCl)	7.3		5.8		6.0	
Organic carbon [%] *	0.78		0.94		1.29	
Soil texture	Loamy sand		Sand		Sandy Loam	
% sand (63-2000 µm) **% silt (2 –63 µm)** **% clay (< 2 µm)**	84.2 5.7 10.1		90.0 7.8 2.1		58.2 24.1 17.7	
Cation exchange capacity [mEq/100 g]	4.32		2.45		9.05	
MWHC [%]	31.43		45.27		48.58	
Microbial activity:	Prior to dosing	At study termination	Prior to dosing	At study termination	Prior to dosing	At study termination**
Heterotrophic Bacteria Fungi Actiomycetes	11.9×10^6 5.1×10^4 39×10^5	32×10^6 10.7×10^4 9.1×10^5	9.9×10^6 8.7×10^4 8.5×10^5	5.5×10^6 7.2×10^4 19.5×10^5	38×10^6 51×10^4 35×10^5	35×10^6 20×10^4 37×10^5

* Organic carbon = organic matter/1.7
** soil incubations at 20 °C and 70 % MWHC

[^{14}C]diuron (17.6 mg) was dissolved in acetone:water (1:1, v/v; 50 mL). Liquid scintillation counting was applied to confirm homogeneity of radioactive content. The concentration of [^{14}C]diuron in the formulation was determined as 352 µg/mL.

The test solution (500 µL) was applied to 50 g soil (dry weight) to give a nominal concentration of 3.5 mg as/kg, which is equivalent to a field application rate of 2.625 kg active substance per ha (assuming a soil depth of 5 cm and a soil density of 1.5 g/cm^3). Soil samples from all three soil types were incubated aerobically in the dark at 20 °C and 70 % maximum water holding capacity (MWHC). In addition, the sandy loam soil samples were incubated at 10 °C and at 35 % MWHC to determine the effect of varying environmental conditions. The test systems were pre-incubated for 11 days under these conditions.

Following application, the soil samples in each incubation group were connected to a continuous air-flow system with moist carbon dioxide-free air. The gas mixture leaving the flasks was combined and then passed through a safety trap and traps containing ethanediol and ethanolamine to trap any liberated organic volatiles and carbon dioxide, respectively. The microbial counts of each soil used in this study was determined prior to initiation and in each incubation group at study termination. Soil

samples were taken for analysis in duplicate immediately after application, and after 8, 16, 32, 64 and 100 days of incubation.
Volatile traps were replenished at weekly intervals up to 4 weeks and thereafter at approximately 2 week intervals. In addition, traps were removed following the sampling of incubation units. Aliquots of ethanolamine trapping solutions from selected incubation periods were submitted to liquid scintillation counting to quantify the amount of radioactivity present.

Soil samples were extracted with methanol:water (9:1 v/v, approx. 100 mL) followed by one extraction step with methanol (approx. 100 mL). A further methanol extraction was performed on selected samples. Where the total radioactivity recovered from extraction was below 90 % AR, residues were Soxhlet extracted with methanol (approx. 24 hours). Radioactive concentrations in the extracts were determined by LSC. Extracted soil samples were combusted and analysed by LSC to determine the amount of non-extractable residues. The pattern of radiolabeled degradates was determined using thin layer chromatography (TLC) and high performance liquid chromatography (HPLC).
For TLC analysis, approx. 20 % by volume of the extracts of each soil sample was combined and concentrated to 10 mL under reduced pressure at ambient temperature. Aliquots (approx. 50 µL) of each concentrated extract were submitted to TLC. Non-radiolabelled diuron, DCPMU, DCPU and DCA were chromatographed with each extract. Following chromatography, quantification of radioactivity present on TLC plates was performed by linear analysis. Standards were visualised by irradiation with UV light. (254 nm). Co-chromatography of standard with radioactivity was used for the tentative identification of degradation products.
For HPLC analysis, an aliquot of each concentrated extract was mixed with an aliquot of standard mix (containing diuron and each of the reference standards) at a ratio of approx. 3:1 (v/v). Additionally aliquots of each individual standard (25 µL) and concentrated extract (100 µL) were subjected to HPLC. Quantification of radioactivity was performed by integrating the area under each peak.

Results and Discussion

The material balance of the soils incubated at 20 °C and 70 % MWHC is presented in Table B.8.1-7. The material balance of the sandy loam soil incubated at 10 °C and 70 % MWHC and at 20 °C and 35 % MWHC are presented in Table B.8.1-8 and Table B.8.1-9. Total recoveries were between 99.1 to 103.6 % AR and between 91 and 99 % AR.
Extractable residues in the loamy sand, the sand and the sandy loam after incubation at 20 °C and 70 %MWHC decreased to 51 %, 81 % and 65 %, respectively, after 100 d while 36 %, 14 % and 27 % non-extractable residues were formed. Extractable residues in the sandy loam after incubation for 100 d at 10 °C with 70 % MWHC and at 20 °C with 35 %MWHC decreased to 84 % and 44 %, respectively, while 12 % and 44 % non-extractable residues were formed. The volatile traps were only analysed in the loamy sand soil incubated at 20 °C and 70 % MWHC and in the sandy loam soil incubated at 20 °C and 35 % MWHC, since only neglible amounts of radioactivity were found in the traps of the remaining soils. In the loamy sand incubated at 20 °C and 70 % MWHC, 5 % CO_2 was formed after 100 d and 7 % CO_2 was formed in the sandy loam soil incubated at 20 °C and 35 % MWHC.

Table B.8.1-7 **Material balance of radioactivity after incubation of ^{14}C-labelled diuron in a loamy sand, a sand and a sandy loam, (at 20 °C and 70 % MWHC)**

loamy sand soil/ Uppsala				
Time (days)	**Extractables**	**Non-extractable residues**	**CO_2**	**Total recovery**
0	96	1	n.a.	97
8	92	4	<1	96
16	92	6	<1	97
32	84	11	1	97
64	68	25	3	96
100	51	36	5	92
Sand soil/ Falkenberg				
Time (days)	**Extractables**	**Non-extractable residues**	**CO_2**	**Total recovery**
0	94	1	n.a.	95
8	94	4	n.a.	98
16	92	7	n.a.	99
32	94	5	n.a.	98
64	90	8	n.a.	97
100	81	14	n.a.	95
Sandy loam soil/ Mogenstrupvej				
Time (days)	**Extractables**	**Non-extractable residues**	**CO_2**	**Total recovery**
0	93	2	n.a.	95
8	92	3	n.a.	95
16	92	6	n.a.	98
32	83	13	n.a.	96
64	72	23	n.a.	95
100	65	27	n.a.	91

n.a. not analysed

Table B.8.1-8 **Material balance of radioactivity after incubation of ^{14}C-labelled diuron in a sandy loam (at 10 °C and 70 % MWHC)**

Sandy loam soil/ Mogenstrupvej				
Time (days)	**Extractables**	**Non-extractable residues**	**CO_2**	**Total recovery**
0	93	2	n.a.	95
8	92	5	n.a.	97
16	91	7	n.a.	98
32	94	4	n.a.	98
64	89	8	n.a.	97
100	84	12	n.a.	96

n.a. not analysed

Table B.8.1-9 Material balance of radioactivity after incubation of ^{14}C-labelled diuron in a sandy loam (at 10 °C and 35 % MWHC)

Sandy loam soil/ Mogenstrupvej				
Time (days)	**Extractables**	**Non-extractable residues**	**CO_2**	**Total recovery**
0	94	1	n.a.	95
8	95	5	<1	99
16	91	7	1	99
32	81	15	1	97
64	65	25	4	93
100	44	44	7	94

n.a. not analysed

The distribution of the radioactivity of the soils incubated at 20 °C and 70 % MWHC is presented in Table B.8.1-10. The distribution of the radioactivity of the sandy loam soil incubated at 10 °C and 70 % MWHC and at 20 °C and 35 % MWHC are presented in Table B.8.1-11 and Table B.8.1-12. Diuron decreased in the loamy sand, the sand and the sandy loam after incubation at 20 °C and 70 %MWHC for 100 days to 3 %, 53 % and 24 %, respectively. Two major metabolites were formed: The metabolite DCPMU was found in in all three soils with maximum concentrations of 28 % after 32 days, 27 % after 64 d and 33 % after 100 d, respectively. The metabolite DCPU was only formed above 10 % in the loamy sand soil with a maximum concentration of 24.5 % after 64 d (mean of two measurements).

In the incubation of the sandy loam soil at 10 °C and 70 % MWHC, diuron decreased to 55 % after 100 d while the metabolite DCPMU was formed at a maximum concentration of 23 % at the end of the study. In the incubation of the sandy loam soil at 20 °C and 35 % MWHC, diuron decreased further than in the incubation at 70 % MWHC to 6 % after 100 d while the metabolites DCPMU and DCPU were formed in maximum concentrations of 33 % and 11 %, respectively, after 64 days.

Table B.8.1-10 Distribution of the radioactivity after incubation of ^{14}C-labelled diuron in a loamy sand, a sand and a sandy loam, (at 20 °C and 70 % MWHC)

loamy sand soil/ Uppsala				
Time (days)	**Diuron**	**DCPMU**	**DCPU**	**DCA**
0	93	1	n.d.	n.d.
0	93	1	n.d.	n.d.
8	75	11	3	n.d.
8	77	10	3	1
16	64	20	6	1
16	64	19	6	1
32	47	28	8	1
32	44	27	8	1
64	24	24	18	1
64	8	22	31	1
100	2	22	22	2
100	3	21	22	2
Sand soil/ Falkenberg				
Time (days)	**Diuron**	**DCPMU**	**DCPU**	**DCA**
0	92	<1	n.d.	n.d.
0	93	1	n.d.	n.d.
8	87	3	n.d.	n.d.
8	90	3	1	n.d.
16	83	5	1	n.d.
16	87	4	n.d.	n.d.
32	82	8	n.d.	2
32	82	9	n.d.	1
64	70	14	1	2
64	67	16	1	2
100	48	27	1	2
100	53	26	1	2
Sandy loam soil/ Mogenstrupvej				
Time (days)	**Diuron**	**DCPMU**	**DCPU**	**DCA**
0	90	1	n.d.	n.d.
0	92	1	n.d.	n.d.
8	82	7	1	1
8	84	6	1	1
16	77	9	1	1
16	77	10	1	2
32	62	16	1	3
32	61	16	1	3
64	36	29	4	2
64	34	29	4	1
100	25	34	3	2
100	24	32	4	2

n.d. not detected

Table B.8.1-11 **Distribution of the radioactivity after incubation of ^{14}C-labelled diuron in a a sandy loam, (at 10 °C and 70 % MWHC)**

Sandy loam soil/ Mogenstrupvej				
Time (days)	**Diuron**	**DCPMU**	**DCPU**	**DCA**
0	89	<1	n.d.	n.d.
0	91	1	n.d.	n.d.
8	87	3	n.d.	n.d.
8	86	4	n.d.	n.d.
16	84	4	1	n.d.
16	84	5	1	n.d.
32	80	8	1	2
32	79	10	1	2
64	65	15	2	2
64	67	16	2	2
100	56	23	2	2
100	55	23	2	2

n.d. not detected

Table B.8.1-12 **Distribution of the radioactivity after incubation of ^{14}C-labelled diuron in a a sandy loam, (at 20 °C and 35 % MWHC)**

Sandy loam soil/ Mogenstrupvej				
Time (days)	**Diuron**	**DCPMU**	**DCPU**	**DCA**
0	90	1	n.d.	n.d.
0	93	<1	n.d.	n.d.
8	79	11	2	1
8	80	10	3	1
16	70	15	3	1
16	68	15	2	2
32	51	24	3	2
32	52	25	2	2
64	16	33	11	2
64	16	32	11	2
100	10	21	9	2
100	6	22	11	2

Conclusion

The study was accepted for the first EU approval and is still considered acceptable by the RMS. Soxhlet extraction is considered harsh compared to natural environmental conditions, however, no chemical breakdown or change in chemical structure of the active substance or the metabolites is expected to occur.

The route and rate of degradation of [^{14}C]diuron under aerobic conditions were studied in a sandy loam soil, a loamy sand soil and a sand.
After incubation at 20 °C and 70 % MWHC for 100 days, diuron decreased in the loamy sand, the sand and the sandy loam to 3 %, 53 % and 24 %, respectively, while 36 %, 14 % and 27 % non-extractable residues were formed. The volatile traps were only analysed in the loamy sand soil incubated at 20 °C and 70 % where 5 % CO_2 was formed after 100 d. Two major metabolites were formed: The metabolite DCPMU was found in all three soils with maximum concentrations of 28 % after 32 days, 27 % after 100 d and 33 % after 100 d, respectively. The metabolite DCPU was only formed above 10 % in the loamy sand soil with a maximum concentration of 24.5 % after 64 d.

After incubation of diuron in the sandy loam soil at 10 °C and 70 % MWHC for 100 days, 12 % non-extractable residues were formed. Diuron decreased to 55 % after 100 d while the metabolite DCPMU was formed at a maximum concentration of 23 % at the end of the study. CO_2 was not analysed.
After incubation of diuron in the sandy loam soil at 20 °C and 35 % MWHC for 100 days, 44 % non-extractable residues were formed. Diuron decreased to 6 % after 100 d while the metabolites DCPMU and DCPU were formed in maximum concentrations after 64 days of 33 % and 11 %, respectively,.

The DT_{50} and DT_{90} values of the study are not listed here anymore, since a new kinetic evaluation Schnoeder, 2006 according to FOCUS kinetic guidance (2005) is available, which is described under B.8.1.1.6.

KCA 7.1.1.1/3 – de Vries, 1996 (study evaluated in the DAR, 2003)

Author:	de Vries, R.
Title:	Determination of the metabolism and degradation rate of diuron in soil
Date:	26.08.1996
Doc ID:	NOTOX project 157826
Guidelines:	BBA IV, 4-1 Fate of Plant Protectants in Soil-Degradation, Transformation and Metabolism (1986) College voor de Toelating van Bestrijdingsmiddelen, onderdeel G.1.1 (1991): Gedrag van het middel en zijn omzettingsprodukten in grond, water en lucht: Gegevens over de aard van de omzettingsprodukten en de snelheden waarmee deze worden gevorm
GLP:	Yes
Validity:	Yes

Material and Methods

In the study, the behaviour of ^{14}C-diuron in soil was investigated in the laboratory under aerobic conditions in a standard sandy soil Speyer soil 2.1 at 20 ± 2 °C under field capacity in the dark for a period of up to 101 days.

Table B.8.1-13: Test material

Radiolabelled test item	
Test material	[Ring-U-^{14}C]Diuron
Specific radioactivity	263 MBq/mmol
Radiochemical purity	100 %
IUPAC name:	3-(3,4-dichloro[ring-U-^{14}C]phenyl)-1,1-dimethylurea
CAS #:	330-54-1
Non-radiolabelled test item	
Test material:	Diuron
Purity:	>98 %
IUPAC name:	3-(3,4-dichlorophenyl)-1,1-dimethylurea
CAS #:	330-54-1
Reference compounds	
DCPMU	1-3,4-dichlorophenyl)-3-methylurea
DCPU	1-(3,4-dichlorophenyl)urea
DCA	3,4-dichloroaniline

The soil characteristics are provided in Table B.1.8-14. Before use the soil was sieved through a 2 mm sieve. The microbial biomass of the soil was determined prior to treatment and at the end of the experiment. For the incubations, 100 g soil (dry weight) was added to each flask, the moisture of the soil was adjusted to field capacity (pF2.5) and the flasks pre-incubated for 22 days at 20 ±5 °C.

Table B.8.1-14 Soil characteristics

Soil name		Speyer 2.1
Location		Rheinland-Pfalz Rheinzabern, Teufelskanzel
Horizon		20 cm
Chargenumber		F12095
Organic carbon content		0.62 %
Particles < 20 µm		6.5 %
Clay (< 2 µm)		1.9 %
Silt (2-63 µm)		9.8 %
Sand (63-2000 µm)		88.4 %
pH (0.01 M $CaCl_2$)		5.9
Maximum water capacity		31 %
Microbial biomass	**before treatment**	83 mg/100 g (dry weight)
	After the experiment	67 mg/ 100 g (dry weight)

After pre-incubation, the test solution was added to each flask at a concentration of 8 mg diuron/kg equivalent to a field application rate of 6 kg as/ha (assuming a soil depth of 5 cm and a soil density of 1.5 g/cm^3) and the flasks were incubated at 20 ± 2 °C under field capacity. Duplicate samples were taken after 0, 7, 13, 20, 28, 42, 54, 82 and 101 days.

The organic volatiles and $^{14}C-CO_2$ in the traps were analysed weekly by LCS.

Each soil sample was extracted 4 times for 30 minutes with 75 mL acetone. The acetone supernatants were combined and the acetone was evaporated using a rotary evaporator, The aqueous reside was then extracted three times for 1 min with 25 mL diethyl ether. The combined ether fractions were again evaporated. The residues were redissolved in 5 mL methanol.
Due to increasing amounts of non-extractable resiudes in the soil, an additional extraction step with dichlormethane (4 x 100 mL) was performed on all soil samples with the exception of the t=0 samples. Afterwards the fractions were evaporated to dryness and dissolved in 3 mL dichloromethane.
The extracts were analysed using LCS for quantification and radio-TLC for identification.
For determination of the non-extractable residues, 1 g of the dried extracted soils samples were combusted in an oxidiser and the resulting $^{14}C-CO_2$ was quantified by LCS.

Results and Discussion

The material balance and the distribution of the radioactivity after incubation of diuron in a sandy soil is presented in Table B.8.1-15 and Table B.8.1-16. Only mean values of the duplicate residue samples were available in the study report.

Table B.8.1-15 Material balance of radioactivity after incubation of ^{14}C-labelled diuron in the sandy soil Speyer 2.1

Time (days)	**Total $^{14}CO_2$**	**Volatiles**	**Extract 1**	**Extract 2**	**Bound residues**	**Total recovery**
0	-	-	97.1	-	1.3	98.4
7	0.1	< 0.01	86.5	2.2	3.8	92.6
13	0.4	< 0.01	85.5	2.6	4.4	92.9
20	0.9	< 0.01	83.8	2.0	6.0	92.6
28	1.3	0.01	83.0	1.4	5.1	90.7
42	1.6	< 0.01	78.3	9.5	2.8	92.1
54	2.1	0.01	74.6	10.8	3.5	91.1
82	9.8	< 0.01	73.9	12.1	4.1	99.8
101	31.8	< 0.01	48.0	10.3	3.6	93.7

Table B.8.1-16 Distribution of the radioactivity after incubation of ^{14}C-labelled diuron in the sandy soil Speyer 2.1

Time (days)	Diuron	Metabolite DCPU	Metabolite DCPMU
0	97.2	0	0
7	86.0	0	2.7
13	81.9	0	6.2
20	73.6	0.7	11.4
28	69.3	1.0	14.1
42	68.1	1.4	18.5
54	65.2	1.5	19.1
82	65.9	1.6	18.5
101	54.3	0.5	3.7

Conclusion

The study was accepted for the first EU approval and is still considered acceptable by the RMS.

After incubations of 101 d in the Speyer 2.1 sandy soil at 20 ± 2 °C and field capacity, diuron decreased in the soil samples to 54.3 %. Mineralisation amounted to 31.8 % CO_2 while 3.6 % non-extractable residues were formed. Two metabolites were identified in the soil. The metabolite DCPMU increased to a maximum of 19.1 % AR after 54 d with subsequent decrease. The metabolite DCPU remained <5 % throughout the study.

The DT_{50} and DT_{90} values of the study are not listed here anymore, since a new kinetic evaluation Schnoeder, 2005 according to FOCUS kinetic guidance (2005) is available, which is described under B.8.1.1.6.

B.8.1.1.2 Anaerobic degradation

KCA 7.1.1.2/ 1 –Yu, 1988 (study evaluated in the DAR, 2003)

Author:	Yu, W. C.
Title:	Anaerobic soil metabolism of [phenyl(U)-14C]diuron
Date:	30.03.1988
Doc ID:	AMR-552-86
Guidelines:	US EPA Guideline, Subdivision N, 162-1 (1982)
GLP:	Yes
Validity:	Acceptable

Material and Methods

The degradation route and rate of [phenyl (U)-^{14}C] diuron was investigated in a Keyport silt loam under anaerobic conditions.
The soil characteristics of the Keyport silt loam are presented in Table B.8.1-17.

Table B.8.1-17 Soil characteristics

Soil name	Keyport silt loam
Sand	14.0 %
Silt	59.2 %
Clay	26.8 %
Organic matter	1.3 %
pH	6.6
Cation exchange capacity (meq/100 g)	5.5
Bulk density (g/cc or g/cm^3)	1.07
Field capacity (g H_2O/100 g dry soil)	24.98

The ^{14}C-labelled diuron was applied to a 50 grams (dry weight) of keyport soil to a concentration of 8.27 ppm based on dry weight, equivalent to a field application rate of 10 lb as/acre, which corresponds to ca. 11.2 kg as/ha. The soil sample was mixed well and incubated in the dark at 25±1 °C and a soil moisture of 75 % of 0.33 bar under aerobic conditions for 30 days. Afterwards it was incubated at 25 °C under anaerobic conditions for 60 d. Two Traps with ethylene glycol for organic volatiles and sodium hydroxide for CO_2 determination were connected to the line of soil samples replaced after sampling of a soil flask.

During the aerobic period, air was slowly drawn through the test vessels and the two traps. During the anaerobic phase, the soil flasks were continuously purged with humidified nitrogen instead. Soil samples were collected at 0, 15 and 30 days of the aerobic period, and at 15, 30, 45 and 60 days of the anaerobic period after application of the test substance.
After sampling, 15 g aliquot of each soil sample was taken for extraction and chromatographic analysis. In addition, duplicate 1 g aliquots of day 0 and 30 samples of the aerobic period and day 30 and 60 samples of the anaerobic period were taken for microbiological testing. The radioactivity was determined with LSC after combustion of another gram of the sample and trapping the resulting CO_2. Radioactivity in the ethylene glycol and the sodium hydroxide traps were counted directly via LCS.
The aliquot of the soil sample for high performance liquid chromatography (HPLC) and thin layer chromatography (TLC) was first extracted 1 h in 30 mL methanol/water (9/1, v/v) and afterwards three times for 1 h each with 30 mL methanol. After each extraction step, the mixtures were centrifuged and the radioactivity in the supernatants was determined. Afterwards the pooled methanol/water methanol and methanol extracts were combined and concentrated at 35 °C. The methanol/water concentrates were extracted three times with dichloromethane until at least 99 % of the radioactivity was extracted into the dichloromethane. In the next extraction step the soil samples were subjected to a 24 h Soxhlet extraction with methanol. The radioactivity in duplicate aliquots were measured via LSC. In a final extraction step, the soil samples were extracted with acetone/water/concentrated phosphoric acid (85/13/2; v/v/v) for 24 h at 25 °C. The soils were washed twice with the extraction mixture and twice with acetone and the extract was again concentrated at 35 °C ad adjusted to a pH of 5 with 2N potassium hydroxide. The radioactivity of these concentrates was again determined via LSC. The remaining radioactivity in the extracted soils was determined via combustion and quantification of the resulting $^{14}CO_2$.
The extract were investigated using high performance liquid chromatography (HPLC) and thin layer chromatography (TLC) using analytical standards for diuron, DCPMU, DCPU, DCA. Additional the presence of TCAB and TCAOB was investigated via HPLC.

Results and Discussion

Microbiological tests showed, that the Keyport soil was viable throughout the study duration.
The distribution of the radioactivity is presented in Table B.8.1-18.

Table B.8.1-18 Recovery and distribution of the radioactivity after application of ^{14}C-labelled diuron to a Keyport loam soil

Component	aerobic conditions			anaerobic conditions			
	Time after application [days]						
	0	15	30	45	60	75	90
Extractables	96.2	105.3	101.7	93.1	95.0	88.6	99.2
Diuron	92.4	95.6	87.0	92.2	94.8	89.7	90.7
DCPMU	7.6	4.4	13.0	7.8	5.2	10.3	9.3
Total CO_2	<0.001	0.01	0.02	0.08	0.05	0.03	0.003
Organic volatiles	<0.001	0.08	0.09	0.03	0.02	0.04	0.02
Non-extractables	3.7	2.4	5.4	7.8	7.0	7.8	9.6
Mass balance	99.9	107.8	107.2	101.0	102.0	96.5	108.8

The total recovery ranged from 96.5 – 108 %. At least 90 % AR was extracted from the soil. Bound residues accounted for less than 10 % AR and volatile components were present in only insignificant quantities (< 0.09 % AR).
DCPMU was found as the only major metabolite under anaerobic conditions with a maximum occurrence of 10.3 % AR at 45 days in the anaerobic period.

Conclusion

The study was accepted for the first EU approval. After re-evaluation of the study to current guidelines, the following deviations were found by the RMS:
No information is available on the sampling of the soil, the storage prior to use and the pesticide applications on the field prior to sampling. Since the soil samples were not water-logged for the anaerobic incubation phase, probably only semi-anaerobic conditions were established during this incubation phase. No measurements were performed to establish, whether anaerobic conditions were established during this period. The extraction steps especially the Soxhlet extraction and the last extraction steps with acetone/water/concentrated phosphoric acid are considered very harsh.
However, no major changes in diuron and DCPMU concentrations were found during the anaerobic incubation phase indicating that diuron and its metabolite are stable under anaerobic conditions. Also no additional metabolites were formed that might have been formed due to the harsh extraction steps or during anaerobic degradation of diuron.
Thus, the study is still considered acceptable for EU re-approval of diuron. During the anaerobic phase a small decrease of diuron from 92.2 to 90.7 % was observed while DCPMU increased from 7.8 % to 13.0 % and afterwards decreased to 9.3 %. NER increased from 7.8 to 9.6 % while no additional CO_2 or volatile products were formed.

The DT_{50} and DT_{90} values of the study are not listed here anymore, since a new kinetic evaluation Drechsler and Klein, 2014c & d according to FOCUS kinetic guidance (20006, 2014) is available, which is described under B.8.1.1.8.

B.8.1.1.3 Soil photolysis

KCA 7.1.1.3/ 1 – Hennecke, 2005a (study evaluated in the Addendum, 2007)

Author:	Hennecke, D.
Title:	Soil Photolysis of Diuron
Date:	31.01.2005
Doc ID:	GAB-008/7-06 (994-07007)
Guidelines:	OECD draft 'Phototransformation of chemicals on soil surfaces' (2002) SETAC (1995)
GLP:	Yes
Validity:	Acceptable

Material and Methods

The soil photolysis of diuron on soil surfaces was tested on a sandy loam soil. The soil characteristics are summarised in Table B.8.1-19.

Table B.8.1-19 Soil characteristics

Designation	Laacherhof
pH value (H_2O)	6.76
pH value (KCl)	5.89
pH value ($CaCl_2$)	5.86
Organic carbon [%] *	2.29
Soil texture (USDA)	Sandy Loam
% clay (< 2 µm) **% silt (2 –50 µm)** **% sand (50-2000 µm)**	7.95 24.70 67.36
Soil texture (ISSS) **% clay (< 2 µm)** **% silt (2 –63 µm)** **% sand (63-2000 µm)**	 8.75 25.37 65.89
Cation exchange capacity [mEq/100 g]	92
MWHC [mL/kg dry mass]	56.1
Biomass (mg Cmic/100 g dry mass	24.8

Aliquots of soil (20 g based on dry mass) was placed as thin layers (approximate thickness: 2 mm) into a quartz glass trays (18 cm x 3.5 cm; height: 1 cm) which were covered gas-tight with a quartz glass plates. Diuron was applied onto the top of thin layers of air-dried soil as a mixture of ^{14}C-labelled and unlabelled diuron at a rate corresponding to 2.0 kg as/ha. The plates' outlet was connected gas-tight to a vacuum pump which continuously sucked CO_2 free synthetic air in order to ensure aerobic conditions during incubation. Volatile degradation products were trapped by means of wash bottles filled with ethylene glycol, 0.5 N H_2SO_4 and 1 N NaOH. The trays were transferred into a Heraeus Suntest apparatus and were irradiated continuously for up to 30 days in a Suntest apparatus which corresponds to 95.8 days exposure to natural summer sunlight at 50 °C northern latitude and normal day-night rhythm. Polychromatic visible and UV light (λmin = 290 nm; λmax = 800 nm) originated from a filtered xenon arc lamp was used for irradiation. The incubation temperature was maintained at 20 ± 5 °C.

Dark controls were prepared in the same way as the irradiated samples and stored in an incubator at 20 °C also connected to a flow through system with traps to collect volatile products.

Samples were taken at 0, 1, 3, 7, 11, 18 and 30 days. The extent of its photolytic degradation was determined under continuous conditions.

After sampling, the soil was transferred into a glass centrifuge tube and extracted on a horizontal shaker 3 times with an acetone/water mixture (2:1, v:v) for 30 minutes each. The extracted soil samples were air dried and combusted using a Harevy Oxidizer in order to quantify non-extractable radioactivity.

Total radioactivity in trapping solutions, soil extracts and extracted soil samples after combustion were analysed by LSC. Soil extracts were analysed by reversed-phase radio-HPLC with UV-detection for the test item and potential degradation products.

Results and Discussion

The distribution of the radioactivity is presented in Table B.8.1-20.

Table B.8.1-20 Distribution of applied radioactivity in irradiated and dark control samples (% of applied radioactivity)

Sample interval (days)	Organic extract	Diuron	DCPMU	Unknown	Non-extractable radioactivity	CO_2	Total[a]
Irradiation							
0	105.8	105.4	nd	nd	--	--	105.8
1	95.75	93.0	2.8	nd	2.58	0.12	98.45
3	90.13	87.0	3.1	nd	3.11	0.29	93.53
7	89.98	85.0	5.0	nd	3.90	2.17	96.05
11	89.30	82.0	5.3	2.0	3.85	3.01	96.17
18	76.78	70.2	4.2	2.4	5.03	2.31	84.15
30	88.19	79.0	6.6	2.5	6.39	5.61	100.29
Dark control							
0	105.8	105.4	nd	nd	--	--	105.8
1	97.92	97.9	nd	nd	1.28	0.00	99.20
3	99.65	99.7	nd	nd	2.08	0.01	101.74
7	96.61	96.6	nd	nd	2.71	0.00	99.32
11	93.55	93.5	nd	nd	1.7	0.00	95.26
18	92.83	92.8	nd	nd	4.23	0.01	97.06
30	98.47	98.5	nd	nd	5.34	0.05	103.86

-- … not performed
nd … not detected
[a] Total =organic extract, unknown and non-extractable radioactivity

Total recoveries of the samples ranged from 93.53 – 105.8 % except for day 18 of the irradiated samples were the total recovery was only 84.15 %.

In the irradiated samples, diuron decreased to 79.0 % after 30 d while 6.6 % of the metabolite DCPMU were formed. Other metabolites remained below 5 % throughout the study. At the end of the study, 5.61 % CO_2 and 6.39 % NER were formed. No volatiles other than CO_2 were detected in the traps.

In the dark samples, diuron remained almost stable throughout the study with 98.47 % of the radioactivity still present as diuron at the end of the study. In the dark controls, 0.05 % CO_2 and 5.34 % NER were formed.

The residues of diuron under irradiated and dark conditions are presented in Figure B.8.1-1.

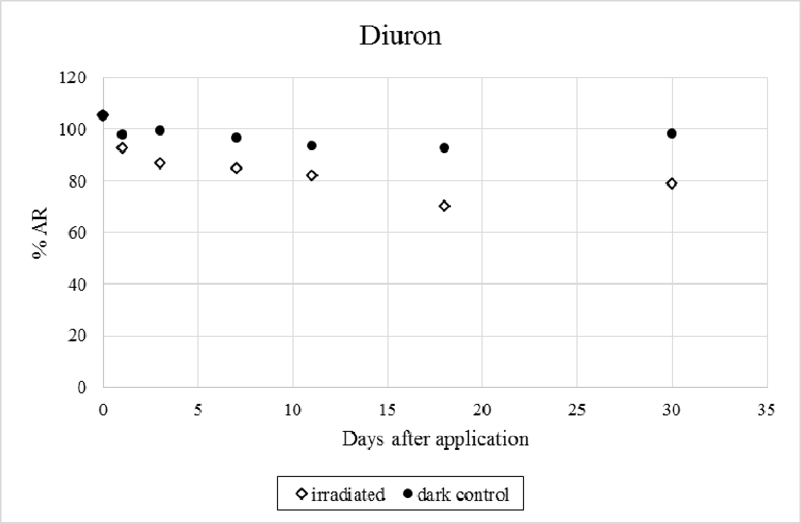


Figure B.8.1-1 **Residues of diuron on a sandy loam under irradiated and dark conditions**

Conclusion

The study was accepted for the first EU approval. After re-evaluation of the study for re-approval of diuron, the study is still considered acceptable by the RMS.
After irradiation on a sandy loam soil for 30 d, diuron decreased to 79.0 % after 30 d while 6.6 % of the metabolite DCPMU were formed. After irradiation, 5.61 % CO_2 and 6.39 % NER were formed. No volatiles other than CO_2 were detected in the traps.
In the dark samples, diuron remained almost stable throughout the study with 98.47 % of the radioactivity still present as diuron at the end of the study while 0.05 % CO_2 and 5.34 % NER were formed.

The DT_{50} and DT_{90} values of the study are not listed here anymore, since a new kinetic evaluation according to FOCUS kinetic guidance (20006, 2014) was performed by the RMS, which is described under B.8.1.1.9.

B.8.1.1.4 Rate of degradation in soil

B.8.1.1.5 Laboratory studies

B.8.1.1.6 Aerobic degradation of the active substance

KCA 7.1.2.1.1/1 – Schnoeder, 2006 (study evaluated in the Addendum, 2007)

Author:	Schnoeder, F.
Title:	Environmental fate endpoints for diuron and its metabolites – data review and kinetic calculations with model maker 4.0
Date:	23.03.2006
Doc ID:	DuPont-19861
Guidelines:	FOCUS Kinetic Guidance (2006)
GLP:	No, not applicable
Validity:	Acceptable

Material and Methods

In this study a kinetic re-evaluation was performed of the laboratory aerobic soil studies Mackie & Hall, 1994 and deVries, 1996 with diuron and the laboratory aerobic soil studies Hennecke, 2005a & b with the metabolites DCPMU and DCPU, respectively, the field dissipation studies Pogàny, 1993 and Rouchard et al, 2000 with diuron and the water/sediment study Sneikus, 2001 with diuron.
Here only the kinetic re-evaluation of the two laboratory studies Mackie & Hall, 1994 and deVries, 1996 with diuron are summarised. The summary of the kinetic re-evalution of laboratory studies Hennecke (2005a & b) with DCPMU and DCPU, respectively can be found under B.8.1.1.7. The summary of the kinetic re-evalution of the field dissipation studies Pogàny, 1993 and Rouchard et al, 2000 can be found under B.8.1.1.10 and the kinetic re-evaluation of the water/sediment study Sneikus, 2001 is described under B.8.2.2.3.

The kinetic re-evaluation of the experimental results from the studies Mackie & Hall, 1994 and deVries, 1996 excluding the degradation data derived from the sandy loam soil at 10 °C / 70 % MWHC and 20 °C / 35 % MWHC of Mackie and Hall, 1994, was performed according to FOCUS kinetic guidance (2005). Degradation rates for diuron and its metabolites DCPMU and DCPU were derived using the program ModelMaker version 4.0. The kinetic models SFO and FOMC were tested as recommended by FOCUS Kinetics Guidance (FOCUS, 2005).

Two models were used for kinetic evaluation. First the conceptual model presented in Figure B.8.1-2 was tested. If the degradation rate of flow F4 was not significant, the model was changed omitting flow F4 and Product 2. If only low levels of DCPU were observed in the respective soil study DCPU and flow F3 were also omitted from the model.

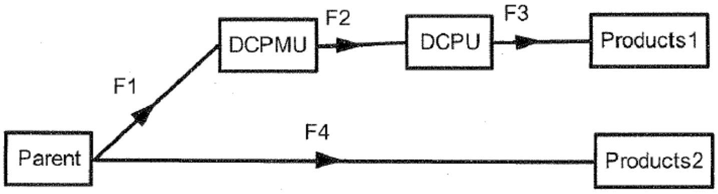


Figure B.8.1-2: **Conceptual model 1 used for kinetic re-evaluation of aerobic soil degradation studies with diuron**

The mean values of the residues presented in Table B.8.1-10 of the study Mackie & Hall, 1994 and the mean residue presented in Table B.8.1-16 of the study deVries, 1996 (no separate residue values of the two samples per time were presented in the study report of the latter) were used for kinetic re-evaluation. Values of metabolites at time point 0 were added to the parent. Non-detects were not modified because no suitable information on the LOD/LOQ were available from the study reports.

Results and Discussion

The degradation rates of diuron from the laboratory studies in soil under aerobic conditions are summarised in Table B.8.1-21.

Table B.8.1-21 Degradation rates of diuron in all investigated soils under aerobic conditions (not-normalised, persistence and modelling endpoints)

Soil	Soil type	T. (ºC)	Moisture	DT_{50} (d)	DT_{90} (d)	Kinetic model	Chi^2 error (%)	Ref.
Uppsala, S	Loamy sand	20	70 % MWHC	30	100	SFO	6	Mackie & Hall, 1994
Falkenberg, S	Sand	20	70 % MWHC	136	453	SFO	3	Mackie & Hall, 1994
Mogenstrupvej, DK	Sandy loam	20	70 % MWHC	57	189	SFO	4	Mackie & Hall, 1994
Speyer 2.1	Sand	20	FC	120	400	SFO	6	deVries, 1996

n.a. information on buffer solution not available

Table B.8.1-22 Degradation rates of DCPMU in all investigated soils under aerobic conditions (not-normalised, persistence and modelling endpoints)

Soil	Soil type	T. (ºC)	Moisture	DT_{50} (d)	DT_{90} (d)	Kinetic model	Chi^2 error (%)	Ref.
Uppsala, S	Loamy sand	20	70 % MWHC	25	84	SFO	14	Mackie & Hall, 1994
Falkenberg, S	Sand	20	70 % MWHC	80	266	SFO	22	Mackie & Hall, 1994
Mogenstrupvej, DK	Sandy loam	20	70 % MWHC	50	164	SFO	19	Mackie & Hall, 1994
Speyer 2.1	Sand	20	FC	62	206	SFO	15	deVries, 1996

n.a. information on buffer solution not available

Conclusion

The kinetic re-evaluation was considered acceptable for the previous EU-approval of diuron, however when re-assessing the study several deviations from FOCUS kinetic guidance were noted (2014): First, the average values of the residues were used instead of the replicates for the soils investigated in the study Mackie and Hall, 1994. No information on the replicates were available in the study deVries, 1996. Besides, no attempt was made to model formation fractions for the metabolites DCPMU and DCPU but formation fractions of 1 were assumed. For the Speyer 2.1, FOMC gave the better visual fit, however DFOP and HS were not tested for this soil. Finally, when the RMS repeated the modelling according to FOCUS (2014), the derived degradation rates for diuron and especially DCPMU were considerably different to the values derived from Schnoeder, 2006. Thus the kinetic re-evaluation of the laboratory aerobic soil studies Mackie and Hall, 1994 and de Vries, 1990 are not considered acceptable and the kinetic re-evaluation was repeated by the RMS as described below.

Since no new DT_{50} and DT_{90} values of diuron and its metabolites after degradation at 10 °C and 70 %

MWHC and at 20 °C and 35 % MWHC were performed by Schroeder, 2006, this was also included in the kinetic-re-evaluation of the RMS as described below.

Kinetic re-evaluation of the RMS of the laboratory aerobic soil studies Mackie and Hall, 1994 and de Vries, 1990

Material and Methods

The model CAKE, version 3.1 was used for kinetic evaluation. The measured residues of diuron, DPCMU and DCPU, which were used for the model, are presented in Table B.8.1-11, Table B.8.1-12 and Table B.8.1-16. Where metabolites were found at day 0, the respective amount was added to diuron and the respective concentration for the metabolite was set to zero. Since, no residues below LOD were found, no data processing of such values was required. The models SFO and FOMC were run using the diuron residues first. If FOMC resulted in a better fit than SFO, also DFOP and HS were tested. Afterwards, the best fit for diuron was used to extend the model to the metabolites DCPMU and DCPU using the degradation scheme shown in Figure B.8.1-3.

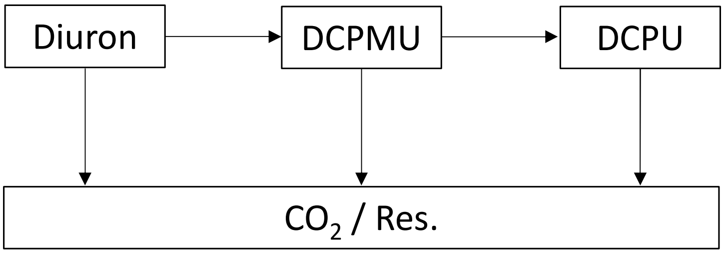


Figure B.8.1-3: **Degradation scheme used for kinetic re-evaluation of aerobic soil degradation studies Mackie and Hall, 1994 and de Vries, 1996 (kinetic re-evaluation of the RMS)**

Results and Discussion

In the loamy sand soil from Uppsala, SFO resulted in a better statistical fit than FOMC. The statistical results for both models are given in Table B.8.1-23.

Table B.8.1-23 **Statistical results of the kinetic models SFO and FOMC describing the degradation of diuron in the loamy sand soil from Uppsala (re-calculation of the RMS)**

Kinetic model	Parameter	Optimised value	Std. error	p-value (t-test)	% error χ^2 test	DT_{50} (d)	DT_{90} (d)	Visual assessment
SFO	M_0_parent	94.87	2.736	N/A	4.44	26.8	89.1	Very good
	k_ parent	0.02583	0.001866	3.76E-0084.44				
FOMC	M_0_parent	99.36	3.908	N/A	4.89	21.9	72.7	good
	α_parent	2.53E+003	nd	N/A				
	β_parent	7.99E+004	nd	N/A				

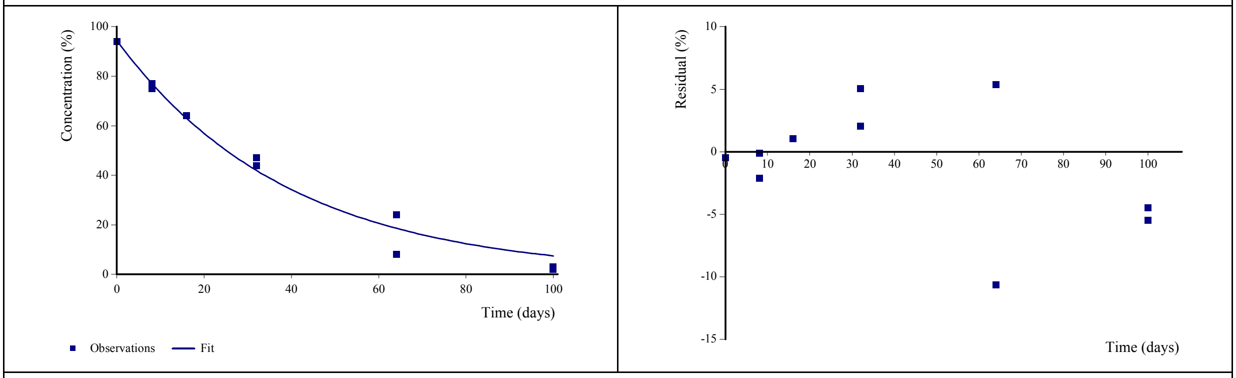
Since SFO resulted in a better visual and statistical fit than FOMC for diuron, it was also chosen for modelling the degradation of diuron together with its metabolites DCPMU and DCPU. For DCPU, a statistically reliable fit could only be obtained, when fixing the formation fraction to 1. When fixing the formation fraction to 1, the chi^2 error for the fit of DCPU was still slightly above 15 %, however the fit was still considered reliable by the RMS. Since, formation fraction and DT_{50} value of a metabolite should be regarded as a unit and a worst case formation fraction will lead to a smaller DT_{50} value for the metabolite, the derived formation fraction and degradation rate of DCPU should be only used for modelling, but not for persistence calculations. Additionally, it was also tested to fix the DT_{50} of

DCPU to 1000 d, however this approach also resulted in a less good fit for DCPU. The final statistical results of the SFO model for diuron and its metabolites DCPMU and DCPU is given in Table B.8.1-24. The visual fit is provided in Figure B.8.1-4.

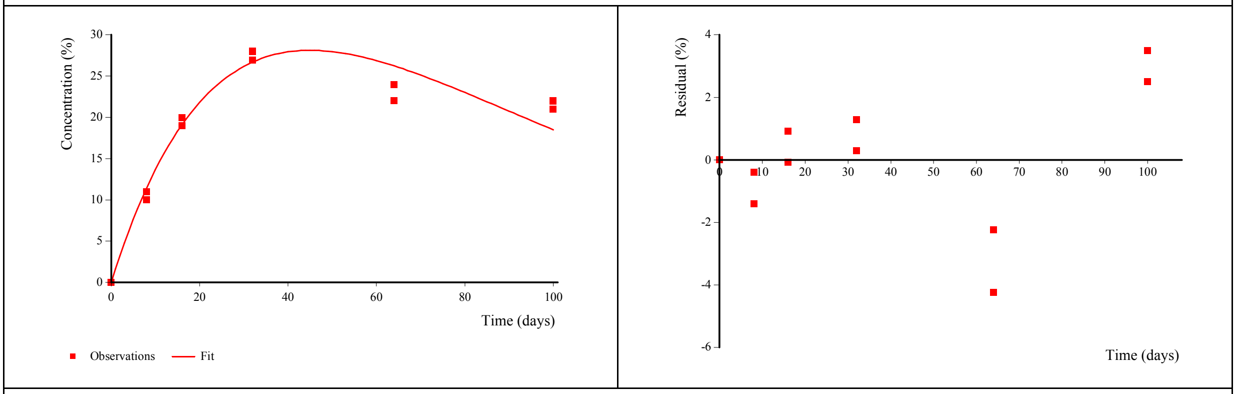
Table B.8.1-24 Statistical results of the kinetic models SFO describing the degradation of diuron and its metabolites DCPMU and DCPU in the loamy sand soil from Uppsala (re-calculation of the RMS)

Kinetic model	Parameter	Optimised value	Std. error	p-value (t-test)	% error χ^2 test	DT_{50} (d)	DT_{90} (d)
SFO (parent + met)	M0_parent	94.46	2.857	N/A	4.47	27.3	90.8
	k_parent	0.02536	0.001895	9.76E-014			
	k_met_DCPMU	0.7115	0.07388	N/A	8.06	35.8	119
	ff_met (is → DCPMU)	0.7115	0.07388	N/A			
	k_met_DCPU	0.01359	0.004589	0.003157	16.6	51	169
	ff_met_DCPU (DCPMU → DCPU)	1 (fixed)	N/A	N/A			

Diuron



DCPMU



DCPU (ff fixed to 1.0)

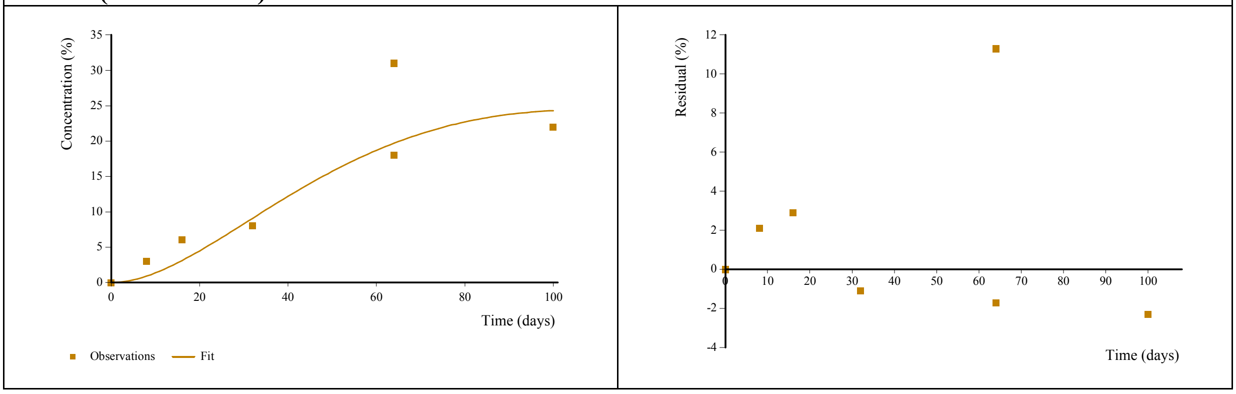


Figure B.8.1-4: Visual fit of the degradation of diuron and its metabolites DCPMU and

DCPU in the loamy sand soil from Uppsala using SFO as kinetic model (kinetic re-evaluation of the RMS)

In the sand soil from Falkenberg, SFO resulted in a better statistical fit than FOMC. The statistical results for both models are given in Table B.8.1-25.

Table B.8.1-25 Statistical results of the kinetic models SFO and FOMC describing the degradation of diuron in the sand soil from Falkenberg (re-calculation of the RMS)

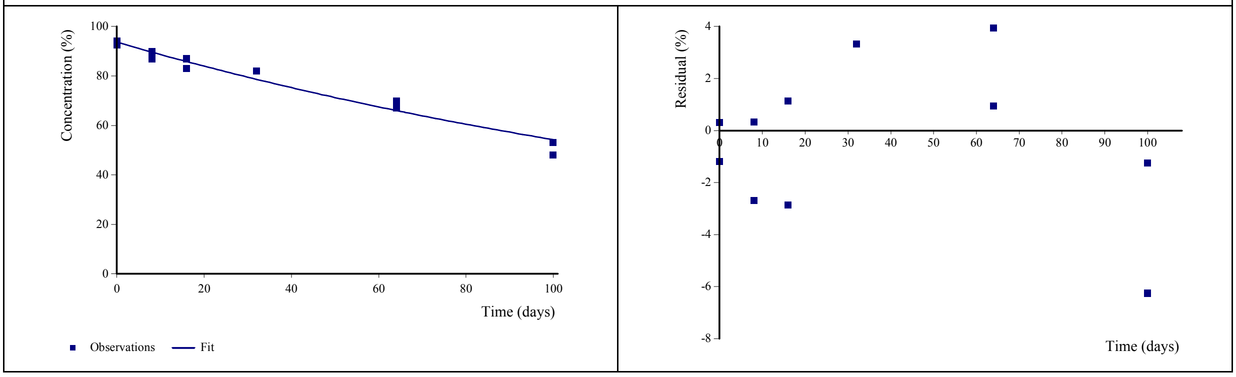
Kinetic model	Parameter	Optimised value	Std. error	p-value (t-test)	% error χ^2 test	DT_{50} (d)	DT_{90} (d)	Visual assessment
SFO	M_0_parent	93.65	1.425	N/A	2.45	126	417	Very good
	k_parent	0.00552	3.96E-004	3.51E-008				
FOMC	M_0_parent	95.26	1.714	N/A	2.72	112	377	Very good
	α_parent	52.53	nd	N/A				
	β_parent	8.42E+003	nd	N/A				

Since SFO resulted in a better visual and statistical fit than FOMC for diuron, it was also chosen for modelling the degradation of diuron together with its metabolite DCPMU. For DCPMU, a statistically reliable fit could only be obtained, when fixing the DT_{50} value to 1000 d. Since, formation fraction and DT_{50} value of a metabolite should be regarded as a unit, we believe that the derived DT_{50} value of the metabolite should only be used for modelling in analogy to the degradation rates with a fixed formation fraction, although the default DT_{50} value can be considered a worst case. The final statistical results of the SFO model for diuron and its metabolite DCPMU is given in Table. The visual fit is provided in Figure B.8.1-5.

Table B.8.1-26 Statistical results of the kinetic models SFO describing the degradation of diuron and its metabolite DCPMU in the sand soil from Falkenberg (re-calculation of the RMS)

Kinetic model	Parameter	Optimised value	Std. error	p-value (t-test)	% error χ^2 test	DT_{50} (d)	DT_{90} (d)
SFO (parent + met)	M0_parent	93.69	1.446	N/A	2.41	127	422
	k_parent	0.005463	3.99E-004	1.33E-011			
	k_met_DCPMU	6.9315E-04 (fixed)	N/A	N/A	9.56	1000	3320
	ff_met (as → DCPMU)	0.6419	0.05031	N/A			

Diuron



DCPMU (DT$_{50}$ fixed 1000 d)

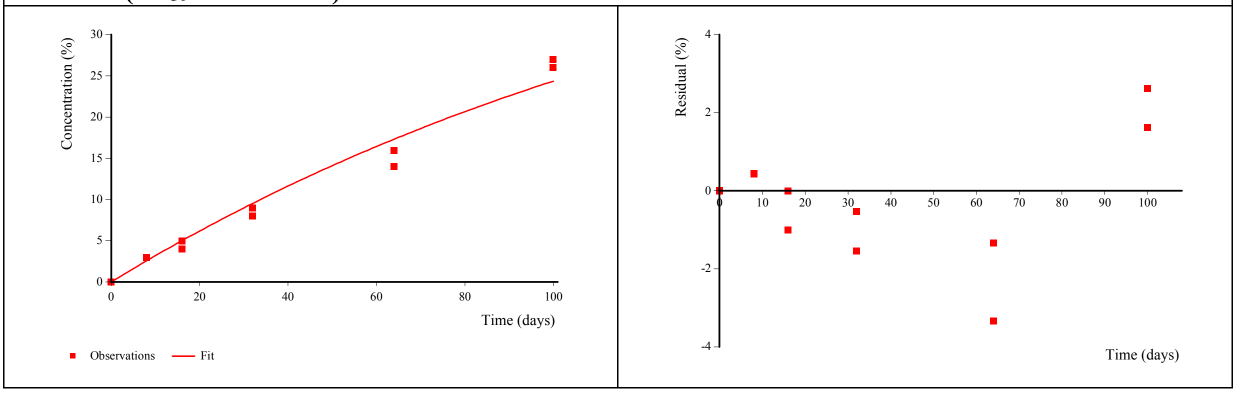


Figure B.8.1-5: Visual fit of the degradation of diuron and its metabolite DCPMU in the sand soil from Falkenberg using SFO as kinetic model (kinetic re-evaluation of RMS)

In the sandy loam soil from Mogenstrupvej at 20 °C and 70 % MWHC, SFO also resulted in a better statistical fit than FOMC. The statistical results for both models are given in Table B.8.1-27.

Table B.8.1-27 Statistical results of the kinetic models SFO and FOMC describing the degradation of diuron in the loamy sand soil from Mogenstrupvej at 20 °C and 70 % MWHC (re-calculation of the RMS)

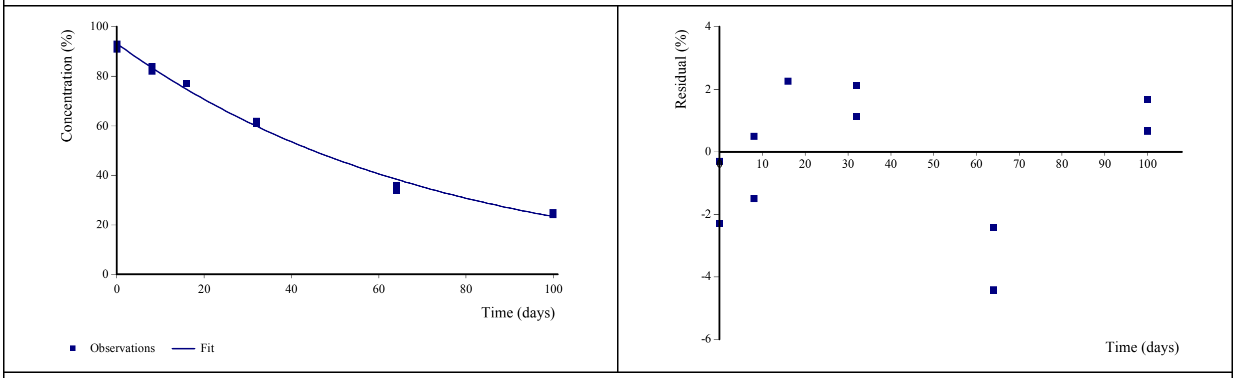
Kinetic model	**Parameter**	**Optimised value**	**Std. error**	**p-value (t-test)**	**% error χ^2 test**	**DT$_{50}$ (d)**	**DT$_{90}$ (d)**	**Visual assessment**
SFO	M$_0$_parent	93.32	1.158	N/A	2.49	49.9	166	Very good
	k_parent	0.01388	4.93E-004	3.74E-011				
FOMC	M$_0$_parent	94.93	1.51	N/A	2.76	46	154	Very good
	α_parent	136.5	nd	N/A				
	β_parent	9.04E+003	nd	N/A				

Since SFO resulted in a better visual and statistical fit than FOMC for diuron, it was also chosen for modelling the degradation of diuron together with its metabolite DCPMU. The final statistical results of the SFO model for diuron and its metabolite DCPMU is given in Table B.8.1-28. The visual fit is provided in Figure B.8.1-6.

Table B.8.1-28 Statistical results of the kinetic models SFO describing the degradation of diuron and its metabolite DCPMU in the sandy loam soil from Mogenstrupvej at 20 °C and 70 % MWHC (re-calculation of the RMS)

Kinetic model	**Parameter**	**Optimised value**	**Std. error**	**p-value (t-test)**	**% error χ^2 test**	**DT$_{50}$ (d)**	**DT$_{90}$ (d)**
SFO (parent + met)	M0_parent	93.29	1.221	N/A	2.49	50	166
	k_parent	0.01386	5.19E-004	3.16E-016			
	k_met_DCPMU	0.002038	N/A	0.001132	4.7	340	1130
	ff_met (is → DCPMU)	0.5413	0.03641	N/A			

Diuron



DCPMU

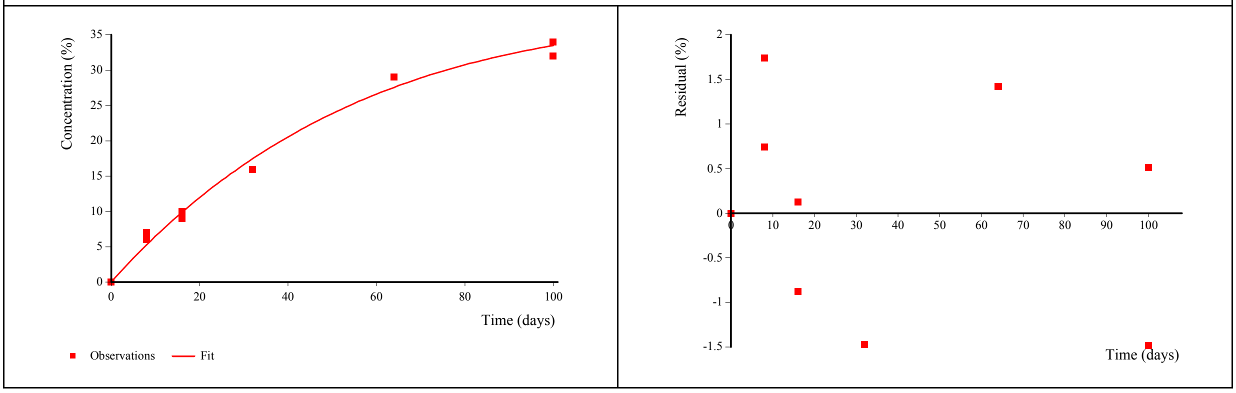


Figure B.8.1-6: **Visual fit of the degradation of diuron and its metabolite DCPMU in the sandy loam soil from Mogenstrupvej at 20 °C and 70 % MWHC using SFO as kinetic model (kinetic re-evaluation of the RMS)**

In the sandy loam soil from Mogenstrupvej at 10 °C and 70 % MWHC, SFO resulted in a better statistical fit than FOMC. The statistical results for both models are given in Table B.8.1-29.

Table B.8.1-29 **Statistical results of the kinetic models SFO and FOMC describing the degradation of diuron in the loamy sand soil from Mogenstrupvej at 10 °C and 70 % MWHC (re-calculation of the RMS)**

Kinetic model	Parameter	Optimised value	Std. error	p-value (t-test)	% error χ^2 test	DT_{50} (d)	DT_{90} (d)	Visual assessment
SFO	M_0_parent	90.55	0.5488	N/A	0.92	144	478	Very good
	k_parent	0.004821	1.52E-004	1.15E-011				
FOMC	M_0_parent	90.64	0.6045	N/A	1.01	146	527	Very good
	α_parent	9.713	38.49	N/A				
	β_parent	1970	260.4	N/A				

Since SFO resulted in a better visual and statistical fit than FOMC for diuron, it was also chosen for modelling the degradation of diuron together with its metabolite DCPMU. For DCPMU, a statistically reliable fit could only be obtained, when fixing the formation fraction to 1. However, since formation fraction and DT_{50} value of a metabolite should be regarded as a unit, we believe that a DT_{50} value of the metabolite with the fixed formation fraction should only be used for modelling but not for persistence calculations. Since the degradation rates at 10 °C and 70 % MWHC would only be used for persistence calculations anyway, no reliable degradation rates of DCPMU were found. DCPU was not included in the kinetic re-evaluation, since its concentration throughout the study remained below 3 %. The statistical results of the SFO model for diuron and its metabolite DCPMU is given in Table B.8.1-30. The visual fit is provided in Figure B.8.1-7.

Table B.8.1-30 **Statistical results of the kinetic models SFO describing the degradation of diuron and its metabolite DCPMU in the sandy loam soil from Mogenstrupvej at 10 °C and 70 % MWHC (re-calculation of the RMS)**

Kinetic model	Parameter	Optimised value	Std. error	p-value (t-test)	% error χ^2 test	DT_{50} (d)	DT_{90} (d)
SFO (parent + met)	M0_parent	90.18	0.5682	0.98	2.27	148	491
	k_parent	0.004686	1.54E-004	6.57E-018			
	k_met_DCPMU	0.008963	0.001321	8.81E-007	10.3	77.3	257
	ff_met (is → DCPMU)	1	fixed	N/A			

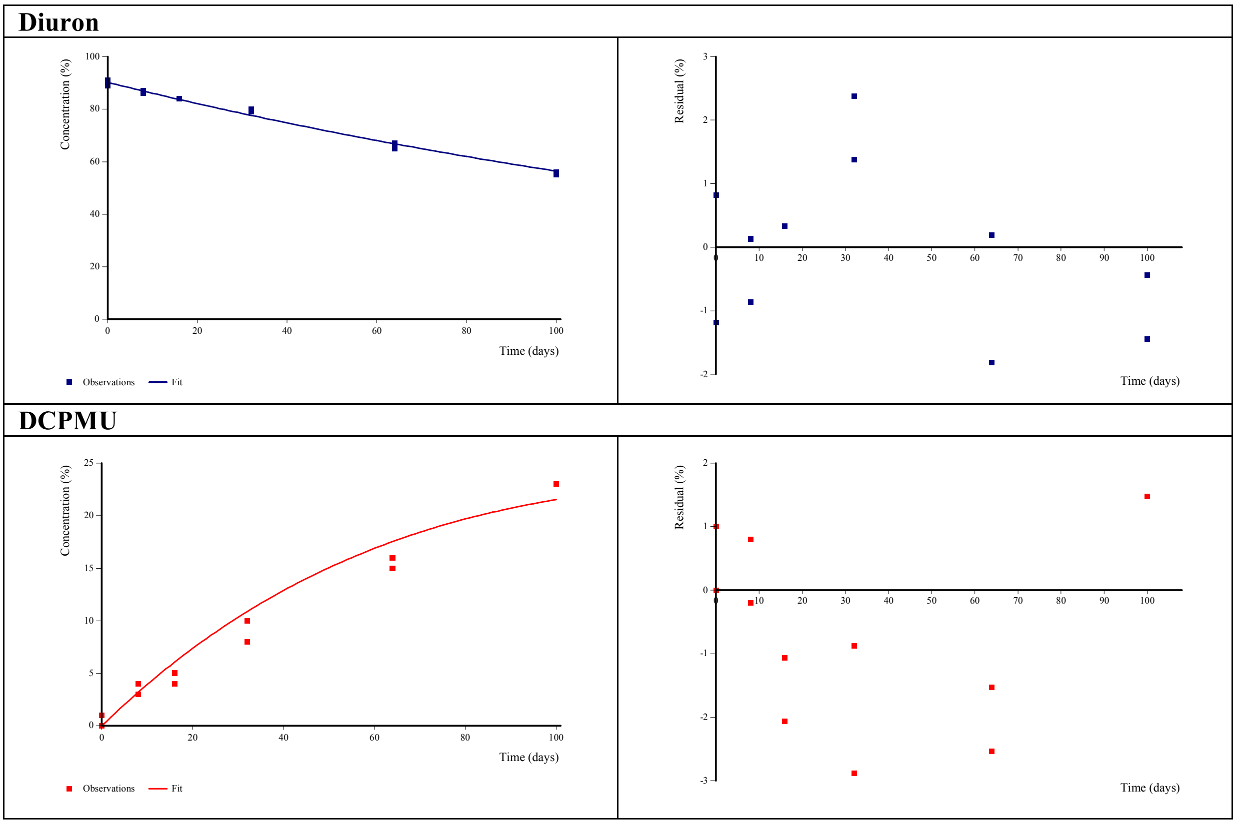


Figure B.8.1-7: **Visual fit of the degradation of diuron and its metabolite DCPMU in the sandy loam soil from Mogenstrupvej at 10 °C and 70 % MWHC using SFO as kinetic model (kinetic re-evaluation of the RMS)**

In the sandy loam soil from Mogenstrupvej at 20 °C and 35 % MWHC, SFO resulted in a better statistical fit than FOMC. The statistical results for both models are given in Table B.8.1-31.

Table B.8.1-31 **Statistical results of the kinetic models SFO and FOMC describing the degradation of diuron in the loamy sand soil from Mogenstrupvej at 20 °C and 35 % MWHC (re-calculation of the RMS)**

Kinetic model	Parameter	Optimised value	Std. error	p-value (t-test)	% error χ^2 test	DT_{50} (d)	DT_{90} (d)	Visual assessment
SFO	M_0_parent	94.72	2.505	N/A	5.97	30.8	102	Good
	k_parent	0.002249	0.00152	1.99E-008				
FOMC	M_0_parent	99.37	3.811	N/A	6.61	24.9	82.8	Good
	α_parent	347.1	Nd	N/A				

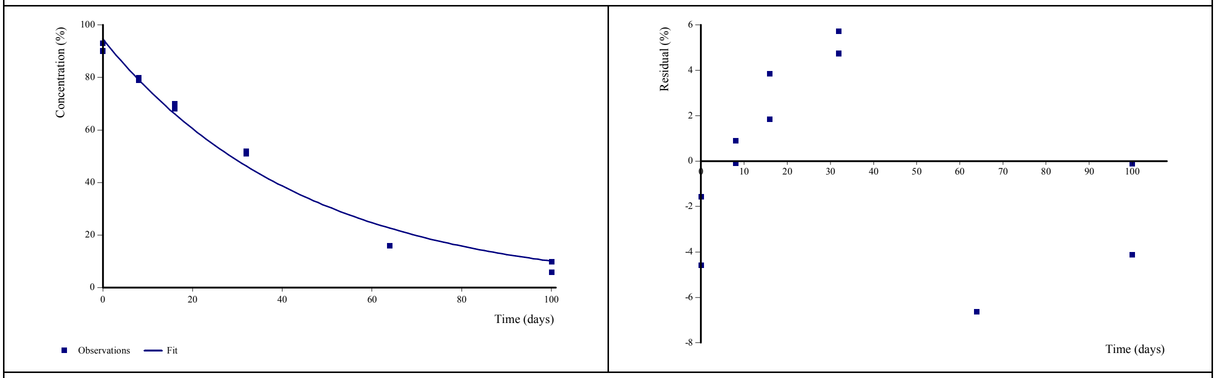
	β_parent	12400		N/A				

Since SFO resulted in a better visual and statistical fit than FOMC for diuron, it was also chosen for modelling the degradation of diuron together with its metabolites DCPMU and DCPU. The final statistical results of the SFO model for diuron and its metabolites DCPMU and DCPU is given in Table B.8.1-32. The visual fit is provided in Figure B.8.1-8. The visual fit of DCPU was not considered acceptable by the RMS, thus it was not included in the final list of degradation rates for this metabolite.

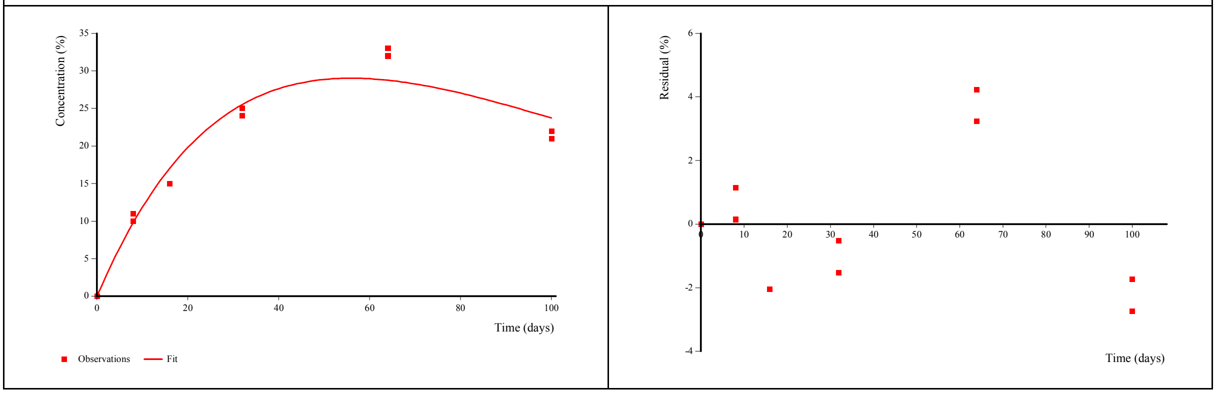
Table B.8.1-32 Statistical results of the kinetic models SFO describing the degradation of diuron and its metabolites DCPMU and DCPU in the sandy loam soil from Mogenstrupvej at 20 °C and 35 % MWHC (re-calculation of the RMS)

Kinetic model	Parameter	Optimised value	Std. error	p-value (t-test)	% error χ^2 test	DT_{50} (d)	DT_{90} (d)
SFO (parent + met)	M0_parent	94.57	2.687	N/A	5.98	31	103
	k_parent	0.002234	0.001623	9.43E-014			
	k_met_DCPMU	0.01407	0.002314	1.00E-006	8.53	49.3	164
	ff_met (as → DCPMU)	0.6741	0.007579	N/A			
	k_met_DCPU	0.03053	0.01492	0.02543	22.2	22.7	75.4
	ff_met (DCPMU → DCPU)	0.9349	0.3764	N/A			

Diuron



DCPMU



DCPU

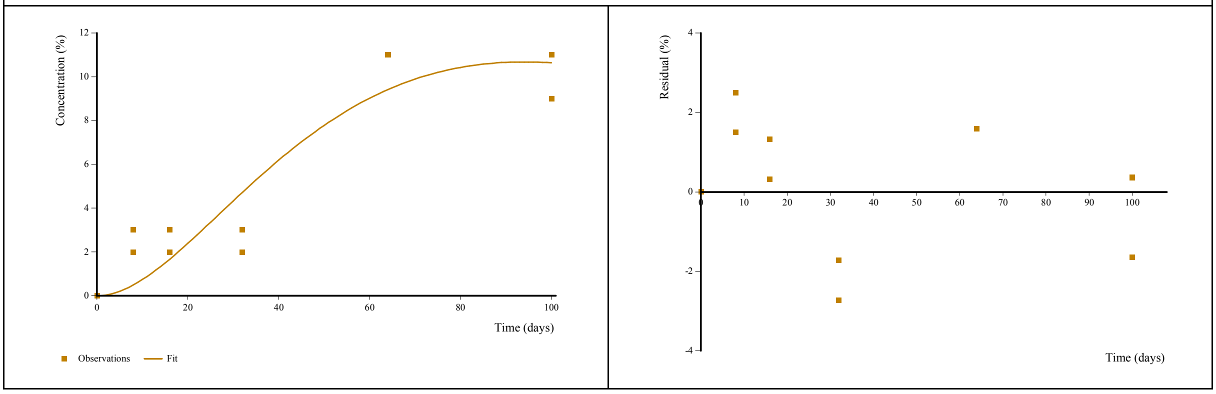


Figure B.8.1-8: **Visual fit of the degradation of diuron and its metabolites DCPMU and DCPU in the sandy loam soil from Mogenstrupvej at 20 °C and 35 % MWHC using SFO as kinetic model (kinetic re-evaluation of the RMS)**

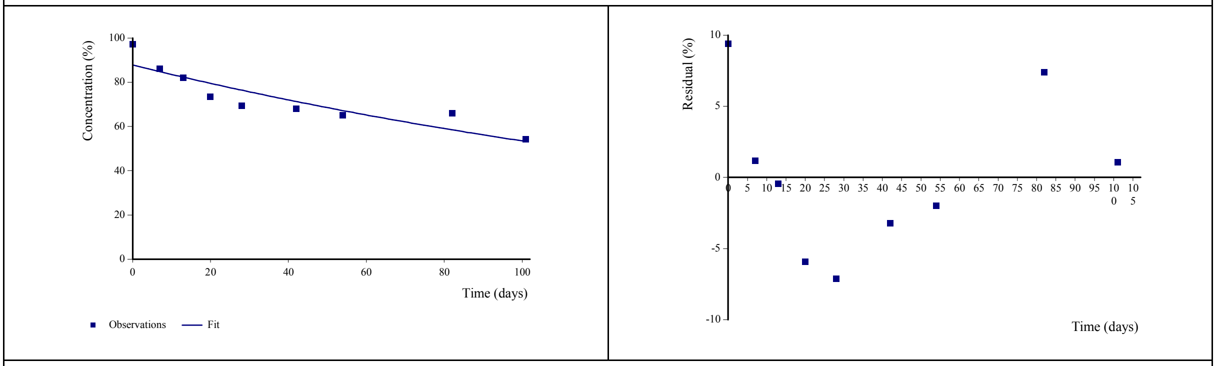
In the sand soil Speyer 2.1, FOMC resulted in a better statistically and visual fit than SFO. Thus, additionally to the DFOP and HS models were tested. The statistical results for all four models are given in Table B.8.1-33.

Table B.8.1-33 **Statistical results of the kinetic models SFO and FOMC describing the degradation of diuron in the sand soil Speyer 2.1 (re-calculation of the RMS)**

Kinetic model	Parameter	Optimised value	Std. error	p-value (t-test)	% error χ^2 test	DT$_{50}$ (d)	DT$_{90}$ (d)	Visual assessment
SFO	M$_0$_parent	87.81	3.349	N/A	5.69	140	465	poor
	k_parent	0.004956	9.35E-004	5.62E-004				
FOMC	M$_0$_parent	97.45	3.137	N/A	3	280	>10000	Very good
	α_parent	0.1847	0.04458	N/A				
	β_parent	6.714	4.376	N/A				
DFOP	M$_0$_parent	97.57	3.148	N/A	2.95	172	827	Very good
	k1_parent	0.08534	0.04805	0.06794				
	k2_parent	0.002455	0.00127	0.05545				
	g_parent	0.238	0.07266	N/A				
HS	M$_0$_parent	96.46	2.584	N/A	2.71	171	779	Very good
	k1_parent	0.01353	0.002387	0.001187				
	k2_parent	0.002646	7.90E-004	0.01014				
	tb_parent	22.18	4.666	N/A				

For the sand soil Speyer 2.1, the residual plot of the SFO model showed a clear trend and the model overestimated the degradation of diuron. From the biphasic kinetics, HS gave the best statistical fit and was thus also chosen for persistence calculations and modelling of diuron. However, according to FOCUS kinetic guidance (2014) using back-calculated SFO from biphasic kinetics for modelling will only be a worst case for the parent but not for the metabolites. Thus, SFO was chosen for modelling degradation rates of DCPM and DCPU. The visual fit and residual plot of diuron applying SFO and HS is provided in Figure B.8.1-9.

SFO



HS

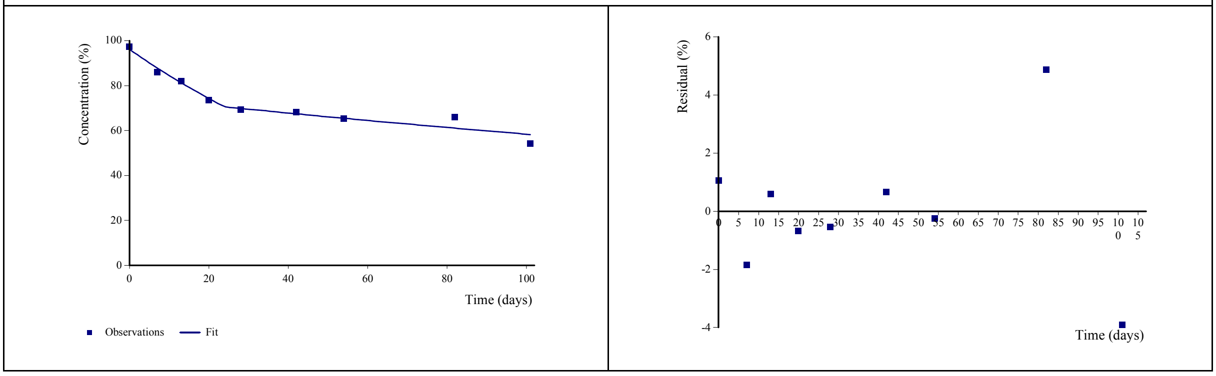


Figure B.8.1-9: **Visual fit of the degradation of diuron in the sand soil Speyer 2.1 using SFO and HS as kinetic models (kinetic re-evaluation of the RMS)**

An attempt was also made to derive degradation rates for DCPMU using both SFO and HS for diuron. However, no statistically and visually acceptable fit could be obtained. It was also tested to fix the formation fraction from diuron to DCPMU to 1 or to fix the DT_{50} value of DCPMU to 1000 d, however both measures didn't improve the fit of DCPMU. As an example, the statistical results of the SFO model for diuron together the metabolite DCPMU (without fixing formation fraction or DT_{50}) is presented in Table B.8.1-34. The visual fit is provided in Figure B.8.1-10.

Table B.8.1-34 **Statistical results of the kinetic models SFO for diuron and SFO for the metabolites DCPMU describing the degradation of the substances in the sand soil Speyer 2.1 (re-calculation of the RMS)**

Kinetic model	**Parameter**	**Optimised value**	**Std. error**	**p-value (t-test)**	**% error χ^2 test**	**DT_{50} (d)**	**DT_{90} (d)**	**Visual assessment**
SFO (parent +met)	M_0_parent	90.29	3.732	N/A	6.02	119	394	Poor
	k_parent	0.005838	0.001054	4.97E-005				
	k_ met_DCPMU	1	0.5502	N/A	35.7	31	103	poor
	ff_met (as → DCPMU)	0.02234	0.01912	0.1318				

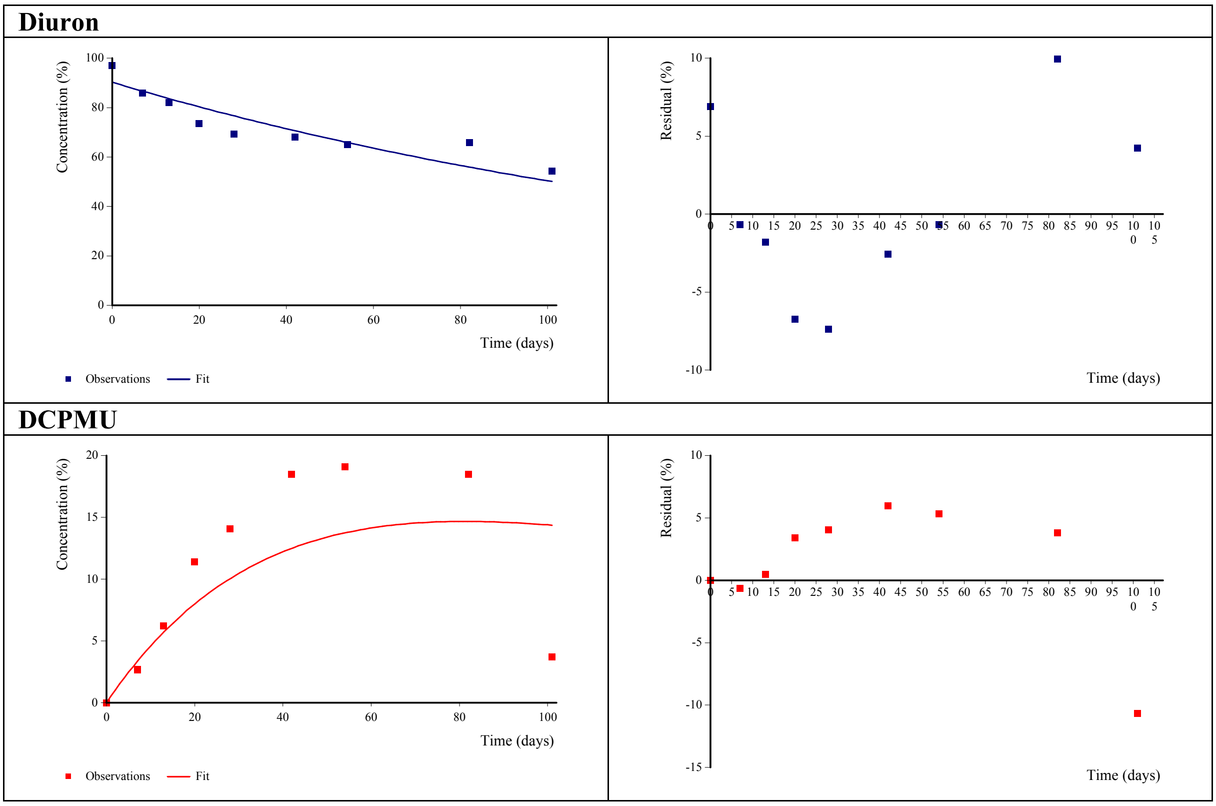


Figure B.8.1-10: **Visual fit of the degradation of diuron and DCPMU in the sand soil Speyer 2.1 using SFO as kinetic model (kinetic re-evaluation of the RMS)**

No normalisation of the derived degradation rates to the reference soil moisture of pF2 was required, since moisture corrections factor were equal or greater than one as shown in Table B.8.1-35.

Table B.8.1-35: **Moisture correction factors of the investigated soils**

Soil	Soil type	Study Moisture & Temp.-conditions	Moisture correction factor	Reference
Uppsala, S	Loamy sand	20°C, 70 % MWHC	1.372	Mackie & Hall, 1994
Falkenberg, S	Sand	20°C, 70 % MWHC	1.973	Mackie & Hall, 1994
Mogenstrupvej, DK	Sandy loam	20°C, 70 % MWHC	1.503	Mackie & Hall, 1994
Speyer 2.1	Sand	20°C, FC	1.0	De Vries, 1996

Conclusion

The final DT_{50} and DT_{90} values of diuron, DCPMU and DCPU to be used for persistence calculations are summarised in Table B.8.1-36, Table B.8.1-38 and Table B.8.1-40. The final DT_{50} values of diuron, DCPMU and DCPU to be used for modelling are summarised in Table B.8.1-37, Table B.8.1-39 and Table B.8.1-41.

Table B.8.1-36 **Degradation rates of diuron in the soils of the studies Mackie and Hall, 1994 and de Vries, 1996 under aerobic conditions (persistence endpoints)**

Soil	Soil type	pH	T. (°C)	Moisture	DT_{50} (d)	DT_{90} (d)	Kinetic model	Chi^2 error (%)	Reference
Uppsala, S	Loamy sand	7.3^a	20	70 % MWHC	27.3	90.8	SFO	4.47	Mackie & Hall, 1994

Falkenberg, S	Sand	5.8 [a]	20	70 % MWHC	127	422	SFO	2.41	Mackie & Hall, 1994
Mogenstrupvej, DK	Sandy loam	6.0 [a]	20	70 % MWHC	50	166	SFO	2.49	Mackie & Hall, 1994
Mogenstrupvej, DK	Sandy loam	6.0 [a]	10	70 % MWHC	148	491	SFO	2.27	Mackie & Hall, 1994
Mogenstrupvej, DK	Sandy loam	6.0 [a]	20	35 % MWHC	31	103	SFO	5.98	Mackie & Hall, 1994
Speyer 2.1	Sand	5.9 [b]	20	FC	171	779	HS	2.71	De Vries, 1996

a measured in KCl
b measured in CaCl$_2$

Table B.8.1-37 DT$_{50}$ values of diuron in the soils of the studies Mackie and Hall, 1994 and de Vries, 1996 under aerobic conditions (modelling endpoints)

Soil	**Soil type**	**pH**	**T. (°C)**	**Moisture**	**DT$_{50}$ at 20 °C and pF2 (d)**	**Kinetic model**	**Chi^2 error (%)**	**Reference**
DT$_{50}$ values of diuron for modelling diuron								
Uppsala, S	Loamy sand	7.3 [a]	20	70 % MWHC	27.3	SFO	4.47	Mackie & Hall, 1994
Falkenberg, S	Sand	5.8 [a]	20	70 % MWHC	127	SFO	2.41	Mackie & Hall, 1994
Mogenstrupvej, DK	Sandy loam	6.0 [a]	20	70 % MWHC	50	SFO	2.49	Mackie & Hall, 1994
Speyer 2.1	Sand	5.9 [b]	20	FC	262	HS, slow phase	2.71	De Vries, 1996
DT$_{50}$ values of diuron for modelling DCPMU and DCPU								
Uppsala, S	Loamy sand	7.3a	20	70 % MWHC	27.3	SFO	4.47	Mackie & Hall, 1994
Falkenberg, S	Sand	5.8 a	20	70 % MWHC	127	SFO	2.41	Mackie & Hall, 1994
Mogenstrupvej, DK	Sandy loam	6.0 a	20	70 % MWHC	50	SFO	2.49	Mackie & Hall, 1994
Speyer 2.1	Sand	5.9 [b]	20	FC	140	SFO	5.69	De Vries, 1996

a measured in KCl
b measured in CaCl$_2$

Table B.8.1-38 Degradation rates of the metabolite DCPMU in the soils of the studies Mackie and Hall, 1994 and de Vries, 1996 under aerobic conditions (persistence endpoints)

Soil	**Soil type**	**pH**	**T. (°C)**	**Moisture**	**DT$_{50}$ (d)**	**DT$_{90}$ (d)**	**Kinetic model**	**Chi^2 error (%)**	**Reference**
Uppsala, S	Loamy sand	7.3 [a]	20	70 % MWHC	35.8	119	SFO	8.06	Mackie & Hall, 1994
Falkenberg, S	Sand	5.8 [a]	20	70 % MWHC	-$^{1)}$	-$^{1)}$	-$^{1)}$	-$^{1)}$	Mackie & Hall, 1994
Mogenstrupvej, DK	Sandy loam	6.0 [a]	20	70 % MWHC	340	1130	SFO	4.7	Mackie & Hall, 1994
Mogenstrupvej, DK	Sandy loam	6.0 [a]	10	70 % MWHC	-$^{2)}$	-$^{2)}$	-$^{2)}$	-$^{2)}$	Mackie & Hall, 1994
Mogenstrupvej, DK	Sandy loam	6.0 [a]	20	35 % MWHC	49.3	164	SFO	8.53	Mackie & Hall, 1994

Speyer 2.1	Sand	5.9 [b]	20	FC	-3)	-3)	-3)	-3)	De Vries, 1996

a measured in KCl

1) a statistically reliable fit could only be found fixing the DT_{50} to 1000 d, the derived degradation rate should to our opinion not be used for persistence calculations

2) a statistically reliable fit could only be found fixing the ff to 1, the derived degradation rate should to our opinion not be used for persistence calculations

3) no statistically reliable fit could only be found

Table B.8.1-39 **DT_{50} values and formation fractions of the metabolite DCPMU in the soils of the studies Mackie and Hall, 1994 and de Vries, 1996 under aerobic conditions (modelling endpoints)**

Soil	**Soil type**	**pH**	**T. (°C)**	**Moisture**	**f.f.***	**DT_{50} at 20 °C and pF2 (d)**	**Kinetic model**	**Chi² error (%)**	**Reference**
Uppsala, S	Loamy sand	7.3[a]	20	70 % MWHC	0.712	35.8	SFO	8.06	Mackie & Hall, 1994
Falkenberg, S	Sand	5.8 [a]	20	70 % MWHC	0.642	1000§	SFO	9.6	Mackie & Hall, 1994
Mogenstrupvej, DK	Sandy loam	6.0 [a]	20	70 % MWHC	0.541	340	SFO	4.7	Mackie & Hall, 1994
Speyer 2.1	Sand	5.9 [b]	20	FC	-1)	-1)	-1)	-1)	De Vries, 1996

a measured in KCl

1) no statistically and visually reliable fit could be obtained

* diuron → DCPMU

§ fixed default value

Table B.8.1-40 **Degradation rates of the metabolite DCPU in the soils of the studies Mackie and Hall, 1994 and de Vries, 1996 under aerobic conditions (persistence endpoints)**

Soil	**Soil type**	**pH**	**T. (°C)**	**Moisture**	**DT_{50} (d)**	**DT_{90} (d)**	**Kinetic model**	**Chi² error (%)**	**Reference**
Uppsala, S	Loamy sand	7.3[a]	20	70 % MWHC	-2)	-2)	-2)	-2)	Mackie & Hall, 1994
Falkenberg, S	Sand	5.8 [a]	20	70 % MWHC	n.a.	n.a.	n.a.	n.a.	Mackie & Hall, 1994
Mogenstrupvej, DK	Sandy loam	6.0 [a]	20	70 % MWHC	n.a.	n.a.	n.a.	n.a.	Mackie & Hall, 1994
Speyer 2.1	Sand	5.9 [b]	20	FC	n.a.	n.a.	n.a.	n.a.	De Vries, 1996

a measured in KCl

n.a. not applicable, no or only very low conc. <5 % of DCPU were found

2) a statistically reliable fit could only be found fixing the formation fraction to 1, the derived degradation rates should thus not be used for persistence calculations

Table B.8.1-41 **DT_{50} values and formation fractions of the metabolite DCPU in the soils of the studies Mackie and Hall, 1994 and de Vries, 1996 under aerobic conditions (modelling endpoints)**

Soil	**Soil type**	**pH**	**T. (°C)**	**Moisture**	**f.f.***	**DT_{50} at 20 °C and pF2 (d)**	**Kinetic model**	**Chi² error (%)**	**Reference**
Uppsala, S	Loamy sand	7.3[a]	20	70 % MWHC	1§	51	SFO	16.6	Mackie & Hall, 1994

Falkenberg, S	Sand	5.8[a]	20	70 % MWHC	n.a.	n.a.	n.a.	n.a.	Mackie & Hall, 1994
Mogenstrupvej, DK	Sandy loam	6.0[a]	20	70 % MWHC	n.a.	n.a.	n.a.	n.a.	Mackie & Hall, 1994
Speyer 2.1	Sand	5.9[b]	20	FC	n.a.	n.a.	n.a.	n.a.	De Vries, 1996

a measured in KCl
* DCPMU → DCPU
n.a. not applicable, no or only very low conc. <5 % of DCPU were found
§ fixed default value

KCA 7.1.2.1.1/2 – Drechsler & Klein, 2016a & b (new studies)

Author:	Drechsler, S. Klein, C.
Title:	Assessment of the degradation kinetics of diuron in soil under laboratory conditions according to the recommendations of the FOCUS report on degradation kinetics (2006, 2014)
Date:	01.03.2016
Doc ID:	782-002
Guidelines:	FOCUS degradation kinetics guidance (2006, 2014)
GLP:	No, not applicable
Validity:	Acceptable

Author:	Drechsler, S. Klein, C.
Title:	Raw data to assessment of degradation kinetics of diuron in soil under laboratory conditions according to the recommendations of the FOCUS Report on degradation kinetics (2006, 2014)
Date:	01.03.2016
Doc ID:	782-007
Guidelines:	FOCUS degradation kinetics guidance (2006, 2014)
GLP:	No, not applicable
Validity:	Acceptable

Material and Methods

In this study a kinetic re-evaluation was performed of the laboratory aerobic soil study Hawkins, 1990 with diuron according to FOCUS degradation kinetics guidance (2006, 2014).
The model KinGUI version 2.1 was used for modelling applying SFO and FOMC. The residues of diuron presented in Table B.8.1-4 were used for kinetic evaluation after day-length correction of the residues to obtain DT_{50} and DT_{90} values at 20 °C and pF 2. The residues after day length correction are presented in Table B.8.1-42.
No additional processing of the residues were required.
No attempt was made to derive degradation rates for the metabolite DCPMU.

Table B.8.1-42 Resiudes of diuron in the Keyport silt loam soil after day length correction of the sampling days

Corrected Time (days)	Diuron
0	97.7
0	97.9
9	92.4

9	95.5
19	94.8
19	95.1
40	86.0
40	86.8
80	83.8
80	82.0
160	68.3
160	71.9
240	62.6
240	64.1
319	60.5
319	58.5
399	54.6
399	55.3
486	46.9
486	51.0

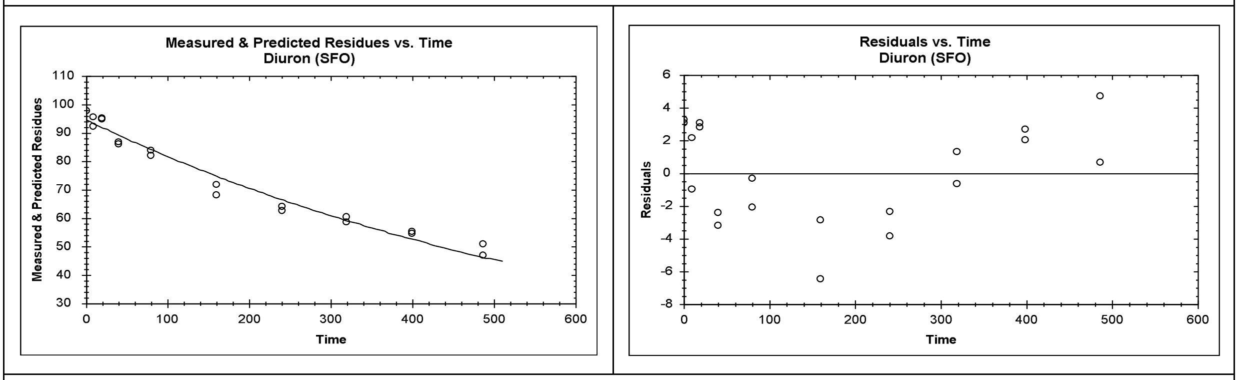
Results and Discussion

In the Keyport silt loam, FOMC resulted in a better statistical and visual fit than SFO. However, SFO was still considered sufficient to be used for modelling. The statistical results for both models are given in Table B.8.1-43. The visual fits and residual plots of both fits are presented in

Table B.8.1-43 Statistical results of the kinetic models SFO and FOMC describing the degradation of diuron in the Keyport silt loam

Kinetic model	Parameter	Optimised value	Std. error	p-value (t-test)	% error χ^2 test	DT_{50} (d)	DT_{90} (d)
SFO	M_0_parent	9.46	1.074	<2E-16	2.877	470.8	1564
	k_parent	1.472E-03	6.603E-05	7.31E-15			
FOMC	M_0_parent	97.46	0.8937	<2E-16	1.473	522.7	13314
	α_parent	0.5515	0.1033	2.72E-05			
	β_parent	207.8851	62.5621	0.00201			

SFO:



FOMC:

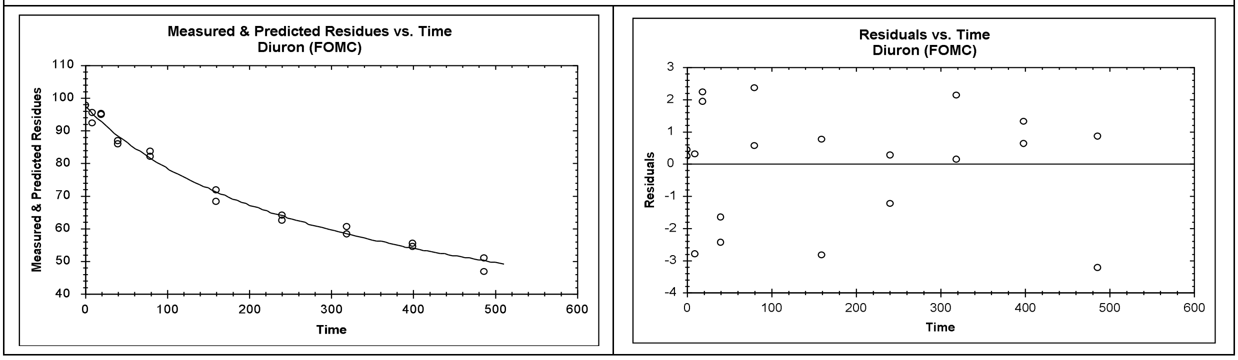


Figure B.8.1-11: Visual fit of the degradation of diuron in the Keyport silt loam using SFO and FOMC as kinetic model

The final degradation rate of diuron in a silt loam normalised to 20 °C and pF2 from the laboratory study Hawkins et al, 1990 under aerobic conditions is presented in Table B.8.1-44.

Table B.8.1-44 Degradation rates of diuron in the Keyport silt loam under aerobic conditions normalised to 20 °C and pF2

Soil	Soil type	DT_{50} (d)	DT_{90} (d)	Kinetic model	Chi^2 error (%)	Ref.
Keyport	Silt loam	470.8	>1000	SFO	2.88	Hawkins et al, 1990

Conclusion

The kinetic re-evaluation and the time-step normalisation of the degradation of diuron in the Keyport silt loam is considered acceptable by the RMS. However, no attempt was made by the applicant to derived degradation rates and formation fractions for DCPMU as was done by Schnoeder, 2006 for the other soils. Thus, an additional attempt was made by the RMS to also derive formation fractions and degradation rates for DCPMU.

Additonal kinetic re-evaluation of the RMS of the laboratory aerobic soil study Hawkins et al, 1990

Material and Methods

The model CAKE, version 3.1 was used for kinetic evaluation. The residues of diuron, DCPMU presented in Table B.8.1-4 were used together with the day-length corrected sampling days given in in

Table B.8.1-42. The residues of DCPMU on day 0 were set to zero.

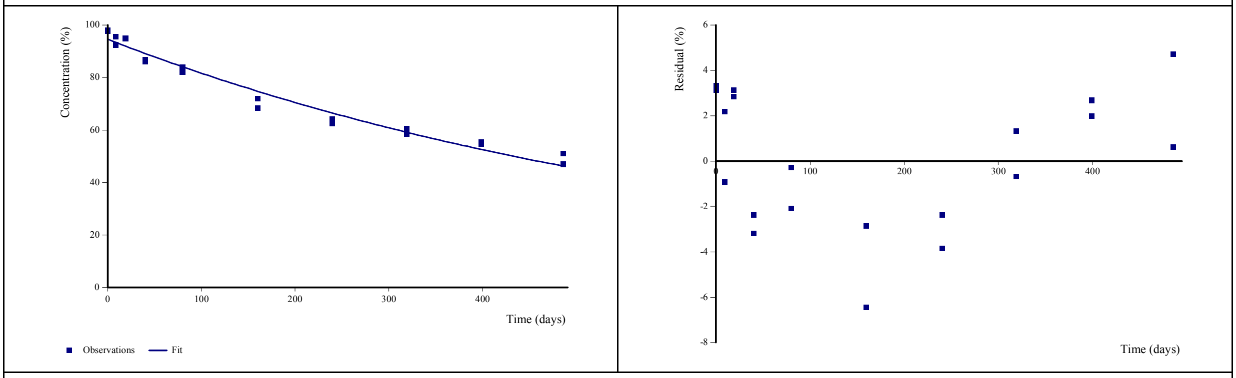
Results and Discussion

The final statistical results of the SFO model for diuron and its metabolite DCPMU is given in Table B.8.1-45. The visual fit is provided in Figure B.8.1-12.

Table B.8.1-45 Statistical results of the kinetic models SFO describing the degradation of diuron and its metabolite DCPMU in the Keyport silt loam (re-calculaton of RMS)

Kinetic model	Parameter	Optimised value	Std. error	p-value (t-test)	% error χ^2 test	DT_{50} (d)	DT_{90} (d)
SFO (parent + met)	M0_parent	94.57	1.077	N/A	2.88	472	1570
	k_parent	0.00147	6.62E-005	4.06E-022			
	k_met_DCPMU	0.8399	0.07125	N/A	7.22	234	778
	ff_met (as → DCPMU)	0.00296	4.17E-004	1.67E-008			

Diuron



DCPMU

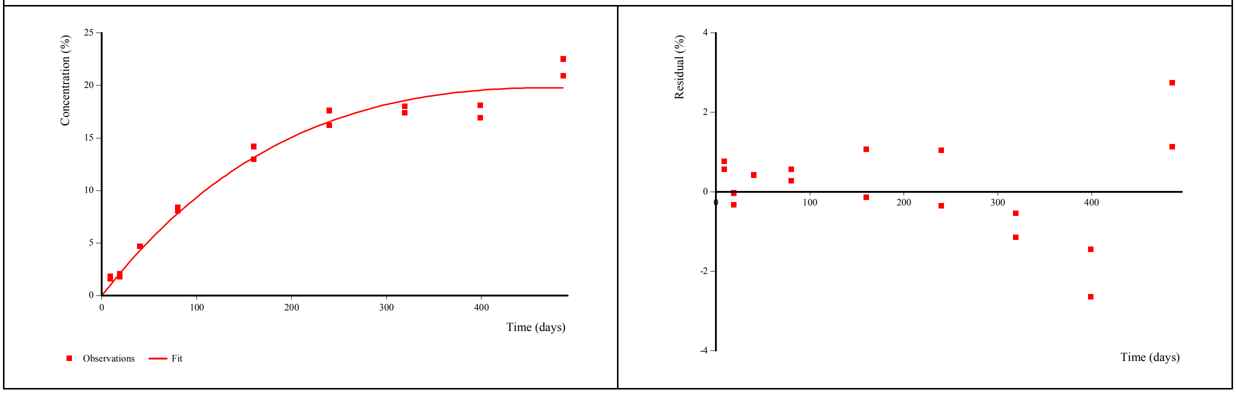


Figure B.8.1-12: Visual fit of the degradation of diuron and its metabolite DCPMU in the Keyport silt loam using SFO as kinetic model (kinetic re-evaluation of the RMS)

Conclusion

The final DT_{50} and DT_{90} values at 20 °C and pF2 of diuron and DCPMU in the Keyport silt loam to be used for persistence calculations and modelling are summarised in Table B.8.1-46 and Table B.8.1-47.

Table B.8.1-46 Degradation rates of diuron in the soils of the study Hawkins et al, 1990 under aerobic conditions (persistence and modelling endpoints)

Soil	Soil type	pH	T. (°C)	Moisture	DT_{50} (d)	DT_{90} (d)	Kinetic model	Chi^2 error (%)	Reference
Keyport	Silt loam	4.6^a	20^*	$pF2^*$	472	1570	SFO	2.9	Hawkins et al, 1990

a buffer solution not known
* normalised from 25 °C and 75 % of the water content at 0.33 bar potential using time-step normalisation

Table B.8.1-47 Degradation rates and formation fractions of the metabolite DCPMU in the soils of the study Hawkins et al, 1990 under aerobic conditions (persistence and modelling endpoints)

Soil	Soil type	pH	T. (°C)	Moisture	$f.f.^{**}$	DT_{50} (d)	DT_{90} (d)	Kinetic model	Chi^2 error (%)	Reference
Keyport	Silt loam	4.6^a	20^*	$pF2^*$	0.840	234	778	SFO	7.22	Hawkins et al, 1990

a buffer solution not known
* normalised from 25 °C and 75 % of the water content at 0.33 bar potential using time-step normalisation
** diuron → DCPMU

B.8.1.1.7 Aerobic degradation of metabolites

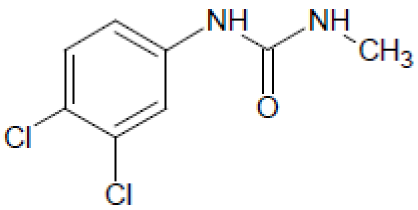
KCA 7.1.2.1.2/1 – Hennecke, 2005b (study evaluated in the Addendum, 2007)

Author:	Hennecke, D.
Title:	Aerobic soil degradation of 3,4-dichlorophenyl methylurea (DCPMU)
Date:	02.03.2005
Doc ID:	GAB-010/7-90
Guidelines:	OECD No. 307 (2002), SETAC-Europe, Part 1, Section 1.1: aerobic degradation (1995)
GLP:	Yes
Validity:	Acceptable

Material and Methods

The aerobic degradation of DCPMU, a metabolite of diuron, in aerobic soil was studied for up to 120 days in 3 German soils (a loam, a silt loam and a sandy loam) at 20 +/- 2 °C and 50 % MWHC.

Table B.8.1-48 Test material

Test item:	**DCPMU (N-(3,4-dichlorophenyl)-N'-methylurea)**
Structure:	
Lot / Batch #:	90112ELB02
Chemical purity:	99.7 %
Stability of test compound:	Dry storage at < 5 °C, in the dark

Reference item:	**DCA (3,4-dichloroaniline)**
Lot / Batch #:	31028
Chemical purity:	99.0 %
Stability of test compound:	Dry storage at < 5 °C, in the dark
Reference item:	**DCPU (N-(3,4-dichlorophenyl)-urea)**
Lot / Batch #:	E1926
Chemical purity:	99.5 %
Stability of test compound:	Dry storage at < 5 °C, in the dark

The soil characteristics are presented in Table B.8.1-49. Prior to use, the soil samples were sieved to 2 mm and stored in the dark under moist and aerated conditions at 20 °C.

Table B.8.1-49 Soil characteristics

Designation	Höfchen	Wurmwiese	Laacherhof
pH value (KCl)	5.93	4.72	5.89
pH value (H_2O)	6.72	5.81	6.76
Organic carbon [%] *	2.41	1.50	2.29
Soil texture (USDA)	Silt Loam	Loam	Sandy Loam
% clay (< 2 µm)	18.15	13.68	7.95
% silt (2 –50 µm)	75.01	40.96	24.70
% sand (50-2000 µm)	6.84	45.36	67.36
Soil texture (ISSS)			
% clay (< 2 µm)	15.58	15.29	8.75
% silt (2 –63 µm)	79.14	42.85	25.37
% sand (63-2000 µm)	5.28	41.86	65.89
Cation exchange capacity [mEq/100 g]	164	76	92
WHC_{max} [mL/kg dry mass]	68.5	55.3	56.1
Microbial biomass [mg C/100g dry mass]			
Start of incubation	44.8	16.0	24.8
End of incubation	52.2	9.1	15.4

* Organic carbon = organic matter/1.7

An application rate of ~0.8 mg as/kg soil dry weight for DCPMU was used since the predicted environmental concentration of DCPMU in soil following an application of diuron at a rate of 2.0 kg/ha is 0.76 mg/kg. DCPMU was dissolved in acetonitrile to give a test solution concentration of 83.9 µg/mL. 500 µL of the test solution (500 µL) was applied to each of the 50 g soil (dry weight) to give a test concentration of 0.839 mg as/kg.

Viable soil samples from all three soil types were incubated aerobically in the dark at 20 °C and 50 % WHC_{max}. The dishes were covered loosely with aluminium. Sterile soil samples were treated the same way but were locked gas tight after application. The soils were analysed for their microbial biomass using the SIR method just before application and at the end of the study.

Soil samples were taken for analysis in duplicate immediately after application and after 1, 3, 7, 14, 28, 50, 80 and 120 days of incubation. Sterile soil samples were only taken at day 28 and 120.

After incubation, soil samples were extracted three times with acetone/water (2:1 v/v, 80 mL) by shaking for 30 minutes. The combined extracts were filtered, concentrated and soaked up by Extrelut columns. The columns were subsequently partitioned and extracted with dichloromethane. After removal of all remaining eluents under a gentle stream of nitrogen the residue was redissolved in acetonitrile/water (1:1, v/v) and analysed by reversed-phase HPLC/UV. The limit of detection by HPLC/UV was found to be 0.014 mg/L and the limit of determination was 0.046 mg/L.

In order to validate the extraction procedure, recovery experiments were performed by applying the test tiem to the soils and applying the extraction method after having stored the soil samples under a fume hood for 1 hour.

Identification was performed by means of the simultaneous recorded UV-spectrum and by regular analysis of DCPMU standard solutions.

Results and Discussion

The recovery of DCPMU in the tests to validate the extraction procedure were 74.1 %, 73.4 % and 75.9 % for the soils Wurmwiese, Höfchen and Laacherhof, respectively.

The residues of DCPMU extracted from soil are shown in Table B.8.1-50. All percent values in the table are mean values of duplicates since the single values were not stated in the report.

Table B.8.1-50 Residue values of DCPMU in different soils under aerobic conditions (in % of nominal)

Time after application [d]	Wurmwiese (Loam)	Höfchen (Silt loam)	Laacherhof (Sandy loam)
0	77.1	71.1	80.1
1	66.6	71.3	73.1
3	66.9	68.7	69.8
7	55.7	52.3	57.0
14	52.3	52.2	45.0
28	45.6	45.2	43.1
50	38.9	44.0	35.4
80	36.5	37.5	41.7
120	34.9	33.1	35.7
28 d sterilised	72.6	72.9	75.3
120 d sterilised	41.0	45.0	44.8

Residue values of DCPMU in viable soil continuously decreased from initially 77.1 %, 71.1 % and 80.1 % to 34.9 %, 33.1 % and 35.7 % at study end, respectively for the loam, silt loam and sandy loam soil. In sterile soil the recovery values of DCPMU accounted for 72.6 %, 72.9 % and 75.3 % at day 28 and 41.0 %, 45.0 % and 44.8 % at study end, respectively for the loam, silt loam and sandy loam soil. No known diuron metabolite other than the test item could be detected.

Conclusion

The study was already validated for first EU approval and considered acceptable. During first EU approval some minor deviations from the OECD guidance are found which are described in the Addendum, 2007. The two deviations that according to the current RMS might have some influence on the results of the study is listed below:
Detailed description of the collection site and especially the history of pesticide use at the site and the procedure of sampling are not reported. The pH range of the three soil was with pH 5.81 to 6.76 very similar, although both the SETAC and the OECD guideline suggest the use of soil with different pH values.

The metabolite DCPMU was incubated in a loam, silt loam and sandy loam soil at 50 % WHC_{max} and 20 °C for 120 days. During incubation, residues of DCPMU decreased from initially 77.1 %, 71.1 % and 80.1 % to 34.9 %, 33.1 % and 35.7 % at study end for the loam, silt loam and sandy loam soil, respectively.

Despite these deviations, the study is still considered acceptable by the RMS.

The DT_{50} and DT_{90} values of the study are not listed here anymore, since a new kinetic evaluation Schnoeder, 2005 according to FOCUS kinetic guidance (2005) is available, which is also described below.

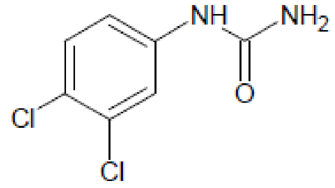
KCA 7.1.2.1.2/2 – Hennecke, 2005c (study evaluated in the Addendum, 2007)

Author:	Hennecke, D.
Title:	Aerobic soil degradation of 3,4-dichlorphenyl urea (DCPU)
Date:	02.03.2005
Doc ID:	GAB-009/7-90
Guidelines:	OECD No. 307 (2002), SETAC-Europe, Part 1, Section 1.1: aerobic degradation (1995)
GLP:	Yes
Validity:	Acceptable

Material and Methods

The aerobic degradation of DCPU, a metabolite of diuron, in aerobic soil was studied for up to 120 days in 3 German soils (a loam, a silt loam and a sandy loam) at 20 +/- 2 °C and 50 % MWHC.

Table B.8.1-51 Test material

Test item	**DCPU (N-(3,4-dichlorophenyl)-urea)**
Structure:	
Lot / Batch #:	E1926
Chemical purity:	99.5 %
Stability of test compound:	Dry storage at < 5 °C, in the dark
Reference item	**DCA (3,4-dichloroaniline)**
Lot / Batch #:	31028
Chemical purity:	99.0 %
Stability of test compound:	Dry storage at < 5 °C, in the dark
Reference item:	**DCPU (N-(3,4-dichlorophenyl)-urea)**
Lot / Batch #:	E1926
Chemical purity:	99.5 %
Stability of test compound:	Dry storage at < 5 °C, in the dark

The soil characteristics are presented in Table B.8.1-6. Prior to use, the soil samples were sieved to 2 mm and stored in the dark under moist and aerated conditions at 20 °C.

Table B.8.1-52 Soil characteristics

Designation	Höfchen	Wurmwiese	Laacherhof
pH value (KCl)	5.93	4.72	5.89
pH value (H_2O)	6.72	5.81	6.76
Organic carbon [%] *	2.41	1.50	2.29
Soil texture (USDA)	Silt loam	Loam	Sandy Loam
% clay (< 2 µm)	18.15	13.68	7.95
% silt (2 –50 µm)	75.01	40.96	24.70
% sand (50-2000 µm)	6.84	45.36	67.36
Soil texture (ISSS)			
% clay (< 2 µm)	15.58	15.29	8.75
% silt (2 –63 µm)	79.14	42.85	25.37
% sand (63-2000 µm)	5.28	41.86	65.89
Cation exchange capacity [mEq/100 g]	164	76	92
WHC_{max} [mL/kg dry mass]	68.5	55.3	56.1
Microbial biomass [mg C/100g dry mass]			
Start of incubation	44.8	16.0	24.8
End of incubation	52.2	9.1	15.4

* Organic carbon = organic matter/1.7

An application rate of ~0.6 mg as/kg soil dry weight for DCPU was used since the predicted environmental concentration of DCPU in soil following an application of diuron at a rate of 2.0 kg/ha is 0.56 mg/kg. DCPU was dissolved in acetonitrile to give a test solution concentration of 55.95 µg/mL. 500 µL of the test solution was applied to each of 50 g soil (dry weight) to give a test concentration of 0.56 mg as/kg.

Viable soil samples from all three soil types were incubated aerobically in the dark at 20 °C and 50 % maximum water holding capacity (MWHC). The dishes were covered loosely with aluminium. Sterile soil samples were treated the same way but were locked gas tight after application. The soils were analysed for their microbial biomass using the SIR method just before application and at the end of the study.

Soil samples were taken for analysis in duplicate immediately after application and after 1, 3, 7, 14, 28, 50, 80 and 120 days of incubation. Sterile soil samples were only taken at day 28 and 120.

After incubation, soil samples were extracted three times with acetone/water (2:1 v/v, 80 mL) by shaking for 30 minutes. The combined extracts were filtered, concentrated and soaked up by Extrelut columns. The columns were subsequently partitioned and extracted with dichloromethane. After removal of all remaining eluents under a gentle stream of nitrogen the residue was redissolved in acetonitrile/water (1:1, v/v) and analysed by reversed-phase HPLC/UV. The limit of detection by HPLC/UV was found to be 0.011 mg/L and the limit of determination was 0.037 mg/L.

In order to validate the extraction procedure, recovery experiments were performed by applying the test tiem to the soils and applying the extraction method after having stored the soil samples under a fume hood for 1 hour.

Identification was performed by means of the simultaneous recorded UV-spectrum and by regular analysis of DCPU standard solutions.

Results and Discussion

The recovery of DCPU in the tests to validate the extraction procedure were 75.9 %, 72.8 % and 80.79 % for the soils Wurmwiese, Höfchen and Laacherhof, respectively.

The residues of DCPU extracted from soil are shown in Table B.8.1-53. All percent values in the table are mean values of duplicates since the single values were not stated in the report.

Table B.8.1-53 Residue values of DCPU in different soils under aerobic conditions (in % of nominal)

Time after application [d]	Wurmwiese (Loam)	Höfchen (Silt loam)	Laacherhof (Sandy loam)
0	80.5	77.3	82.9
1	68.4	65.8	69.2
3	62.1	57.4	60.0
7	43.3	45.1	44.6
14	29.3	21.4	31.7
28	12.9	5.5	18.9
50	7.3	< LOD	7.4
80	5.4	< LOD	5.4
120	4.6	< LOD	< LOD
28 d sterilised	67.4	69.2	77.3
120 d sterilised	27.3	34.2	33.3

LOD: Limit of Detection.

Residue values of DCPU in viable soil continuously decreased from initially 80.5 %, 77.3 % and 82.9 % to 4.6 % and below LOD at study end, respectively, for the loam, silt loam and sandy loam soil.
In sterile soil the recovery values of DCPU accounted for 67.4 %, 69.2 % and 77.3 % at day 28 and 27.3 %, 34.2 % and 33.3 % at study end, respectively for the loam, silt loam and sandy loam soil.
In all soils the amount of applied DCPU decreased continuously during incubation. No 3,4-DCA metabolite other than the test item could be detected.

Conclusion

The study was already validated for first EU approval and considered acceptable. During first EU approval some minor deviations from the OECD guidance are found which are described in the Addendum, 2007. The two deviations that according to the current RMS might have some influence on the results of the study is listed below:
Detailed description of the collection site and especially the history of pesticide use at the site and the procedure of sampling are not reported. Besides, the pH range of the three soil was with pH 5.81 to 6.76 very similar, although both the SETAC and the OECD guideline suggest the use of soil with different pH values.

Despite this deviation, the study is still considered acceptable by the RMS.

The metabolite DCPU was incubated in a loam, silt loam and sandy loam soil at 50 % WHC_{max} and 20 °C for 120 days. During incubation, residues of DCPU decreased from initially 80.5 %, 77.3 % and 82.9 % to 4.6 % and below LOD at study end for the loam, silt loam and sandy loam soil, respectively.

The DT_{50} and DT_{90} values of the study are not listed here anymore, since a new kinetic evaluation Schnoeder, 2005 according to FOCUS kinetic guidance (2005) is available, which is also described below.

KCA 7.1.2.1.2/3 – Schnoeder, 2006 (study evaluated in the Addendum, October 2007)

Author:	Schnoeder, F.
Title:	Environmental fate endpoints for diuron and its metabolites – data review amd kinetic calculations with model maker 4.0
Date:	23.03.2006
Doc ID:	DuPont-19861 (994-07008)
Guidelines:	FOCUS Kinetic Guidance (2006)
GLP:	No, not applicable
Validity:	acceptable

Material and Methods

In this study a kinetic re-evaluation was performed of the laboratory aerobic soil studies Mackie & Hall, 1994 and deVries, 1996 with diuron and the laboratory aerobic soil studies Hennecke, 2005a & b with the metabolites DCPMU and DCPU, respectively, the field dissipation studies Pogàny, 1993 and Rouchard et al, 2000 with diuron and the water/sediment study Sneikus, 2001 with diuron.
Here only the kinetic re-evaluation of the studies Hennecke, 2005a & b with the metabolites DCPMU and DCPU, respectively, is summarised. The summary of the kinetic re-evalution of laboratory studies Mackie & Hall, 1994 and deVries, 1996 with diuron can be found under B.8.1.1.6. The summary of the kinetic re-evalution of the field dissipation studies Pogàny, 1993 and Rouchard et al, 2000 can be found under B.8.1.1.10 and the kinetic re-evaluation of the water/sediment study Sneikus, 2001 is described under B.8.2.2.3.

The kinetic re-evaluation of the experimental results from the studies Hennecke, 2005a & b was performed according to FOCUS kinetic guidance (2005). Degradation rates for DCPMU and DCPU were derived using the program ModelMaker version 4.0. The kinetic models SFO, FOMC, DFOP and HS were tested.

The residues of DCPMU presented in Table B.8.1-50 of the study Hennecke, 2005c and the residues of DCPU presented in Table B.8.1-53 of the study Hennecke, 2005b were used for kinetic re-evaluation. Non-detects of DCPU were not modified because no suitable information on the LOD/LOQ were available from the study reports.

Results and Discussion

The statistical results of all models describing the degradation of DCPMU in the loam soil Wurmwiese, the silt loam Höfchen and the sandy loam Laacher Hof are given in Table B.8.1-54, Table B.8.1-55 and Table B.8.1-56, respectively. The visual fits and residual plots are provided in Figure B.8.1-13, Figure B.8.1-14 and Figure B.8.1-15.

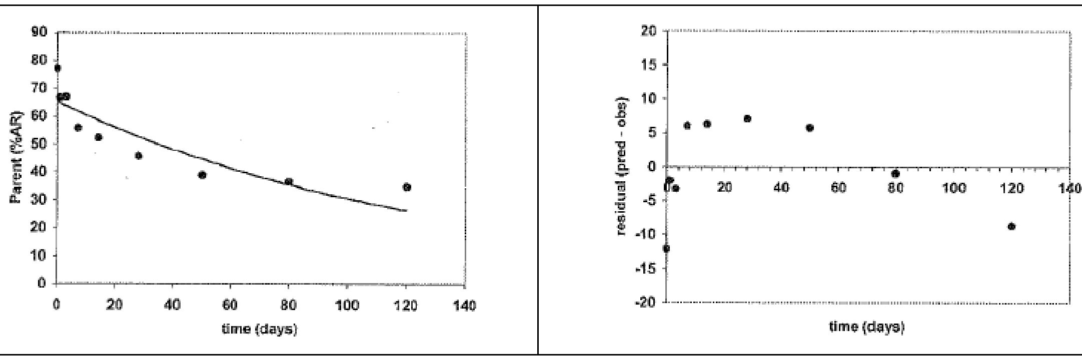
The statistical results of all models describing the degradation of DCPU in the loam soil Wurmwiese, the silt loam Höfchen and the sandy loam Laacher Hof are given in Table B.8.1-57, Table B.8.1-58 and Table B.8.1-59. The visual fits and residual plots are provided in Figure B.8.1-16, Figure B.8.1-17 and Figure B.8.1-18.

Table B.8.1-54 Statistical results of the kinetic models SFO, FOMC, DFOP and HS describing the degradation of DCPMU in the soil Wurmwiese

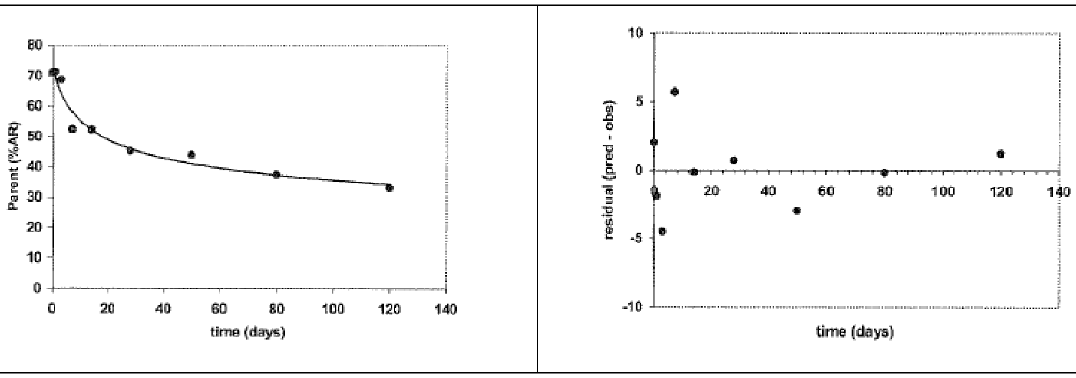
Kinetic model	Parameter	Optimised value	Std. error	p-value (t-test)	% error χ^2 test	DT_{50} (d)	DT_{90} (d)	Visual assessment
SFO	M_0	65.122	3.5749	0.0000	10.02	91.8	304.9	poor
	k	0.00755	0.00174	0.0025				
FOMC	M_0	75.612	2.0841	0.0000	3.01	72	244608	Good
	α	0.19869	0.030114	0.0003				
	β	2.2673	1.1341	0.0463				
DFOP	M_0	74.01	2.3608	0.0000	3.88	101	565	Very good
	k_1	0.12046	0.04753	0.0261				
	k_2	0.00276	0.00133	0.0463				

	g	0.36515	0.06394	0.0011				
HS	M_0	74.091	2.6733	0.0000	4.58	85	489	good
	k_1	0.04101	0.01092	0.0066				
	k_2	0.00399	0.00111	0.0078				
	t_b	9.5655	2.6932	0.0082				

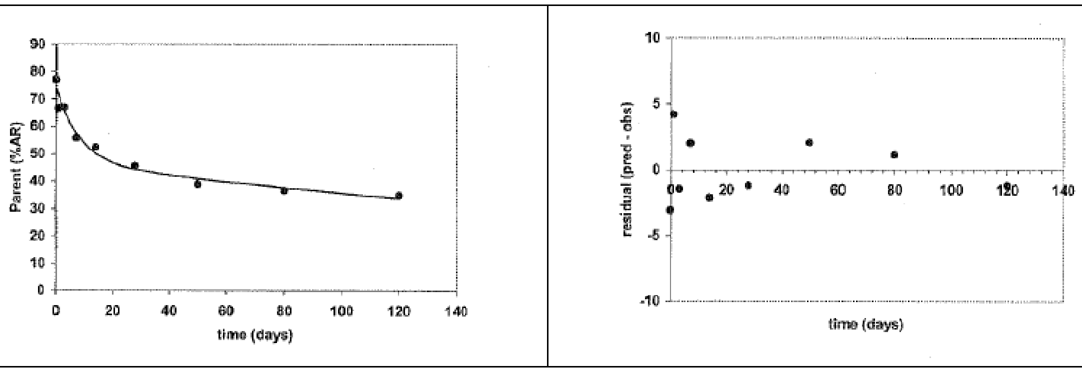
SFO



FOMC



DFOP



HS

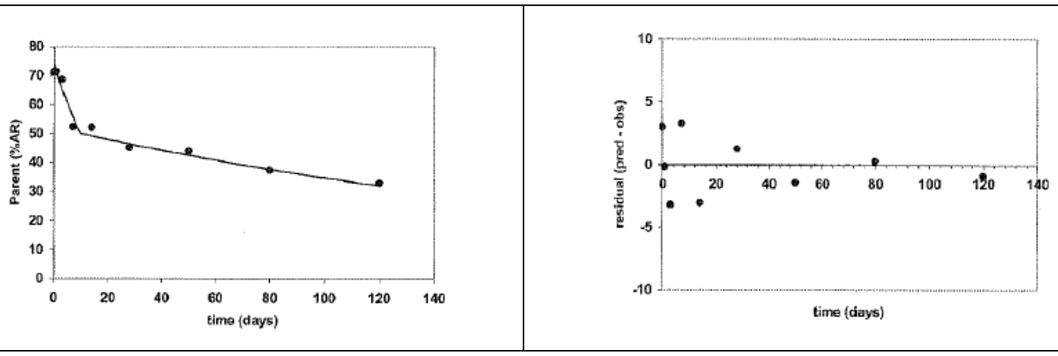
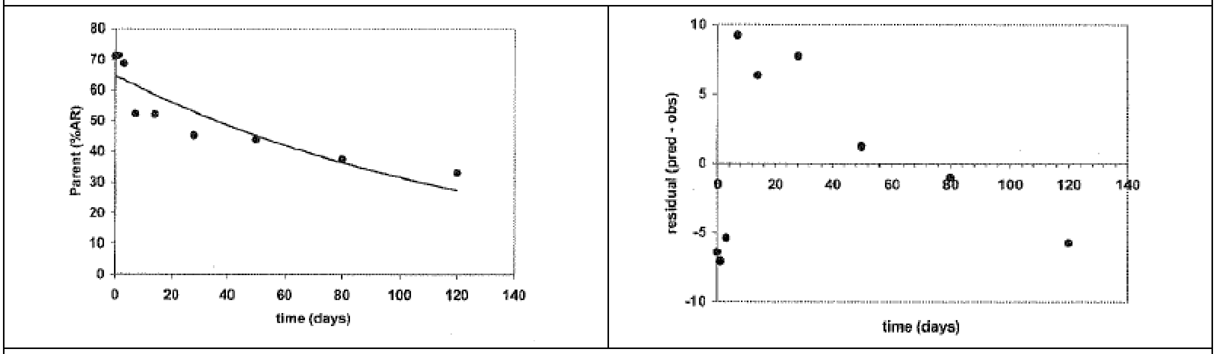


Figure B.8.1-13: **Visual fits and residual plots of the degradation of DCPMU in the soil Wurmwiese using SFO, FOMC, DFOP and HS as kinetic models**

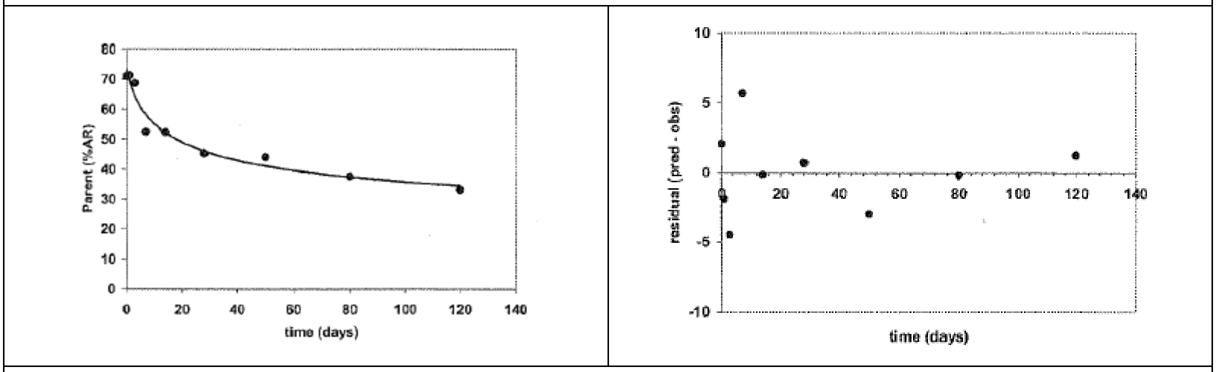
Table B.8.1-55 Statistical results of the kinetic models SFO, FOMC, DFOP and HS describing the degradation of DCPMU in the soil Höfchen

Kinetic model	Parameter	Optimised value	Std. error	p-value (t-test)	% error χ^2 test	DT_{50} (d)	DT_{90} (d)	Visual assessment
SFO	M_0	64.702	3.317	0.0000	9.31	96.8	321.6	poor
	K	0.00716	0.00159	0.0020				
FOMC	M_0	73.161	2.894	0.0000	4.51	89	176674	good
	A	0.21304	0.043244	0.0013				
	B	3.5746	2.3839	0.0922				
DFOP	M_0	73.45	2.6669	0.0000	4.19	101	565	Very good
	k_1	0.31242	0.06235	0.0020				
	k_2	0.15372	0.07496	0.0478				
	G	0.00347	0.00128	0.0213				
HS	M_0	73.688	2.0513	0.0000	3.50	89	475	Very good
	k_1	0.04316	0.0085	0.0019				
	k_2	0.00417	0.00083	0.0020				
	t_b	8.2167	1.6716	0.0022				

SFO



FOMC



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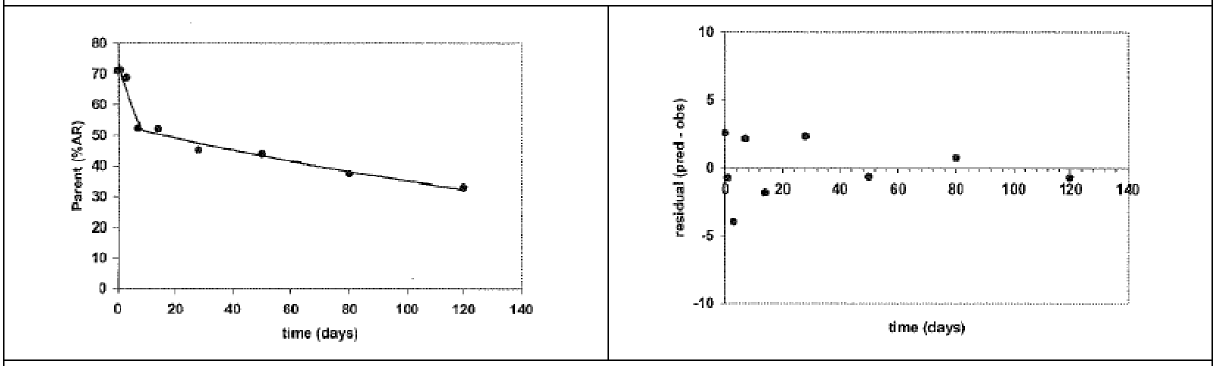


HS

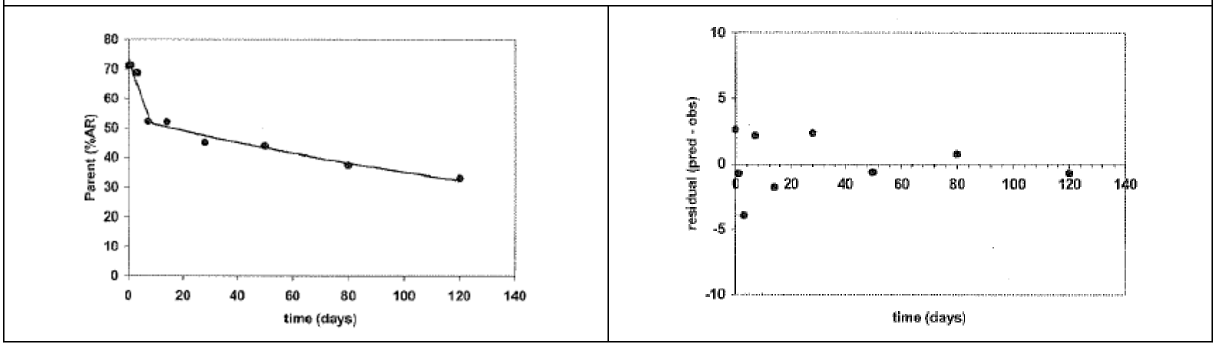
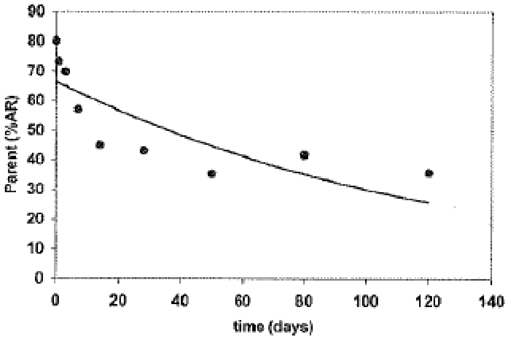


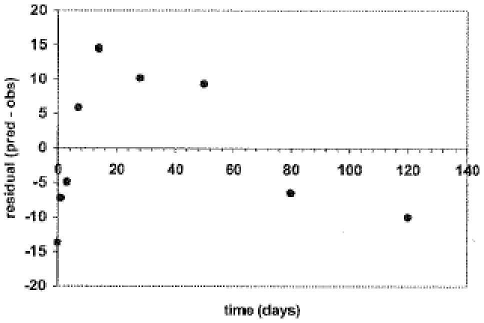
Figure B.8.1-14: Visual fits and residual plots of the degradation of DCPMU in the soil Höfchen using SFO, FOMC, DFOP and HS as kinetic models

Table B.8.1-56 Statistical results of the kinetic models SFO, FOMC, DFOP and HS describing the degradation of DCPMU in the soil Laacherhof

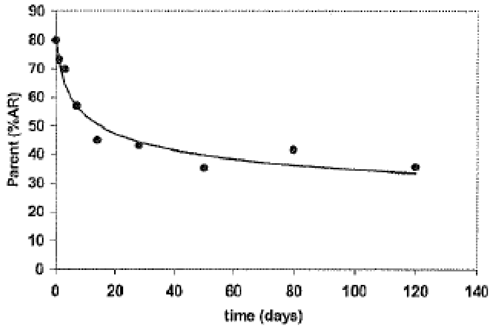
Kinetic model	Parameter	Optimised value	Std. error	p-value (t-test)	% error χ^2 test	DT$_{50}$ (d)	DT$_{90}$ (d)	Visual assessment
SFO	M_0	66.431	5.2422	0.0000	14.44	87.7	291.4	poor
	K	0.00790	0.00257	0.0089				
FOMC	M_0	81.018	4.0517	0.0000	5.57	46	153562	good
	A	0.19923	0.042139	0.0016				
	B	1.4688	1.1342	0.1215				
DFOP	M_0	79.642	2.3681	0.0000	3.84	33	2469	Very good
	k_1	0.12107	0.031	0.0057				
	k_2	0.00065	0.00132	0.3207				
	G	0.49496	0.052	0.0001				
HS	M_0	78.842	2.3346	0.0000	3.93	68	964	Very good
	k_1	0.04589	0.00914	0.0020				
	k_2	0.0018	0.00095	0.0580				
	t_b	12.936	2.5255	0.0019				

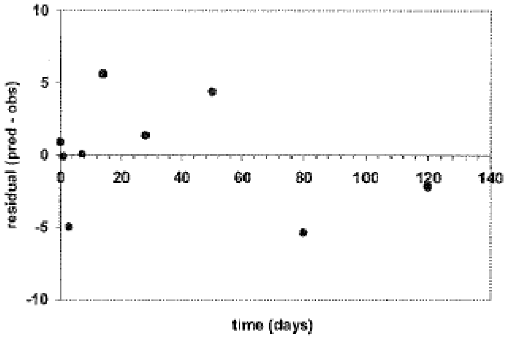
SFO





FOMC





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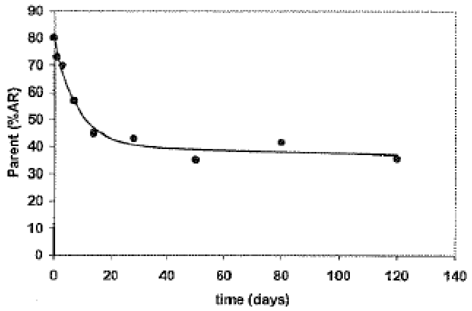

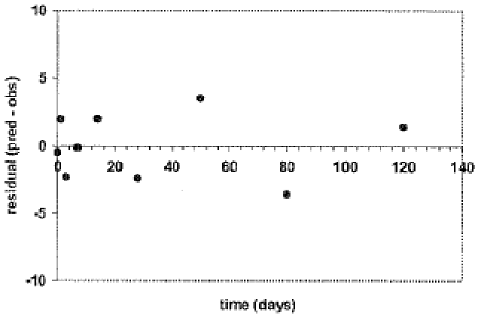

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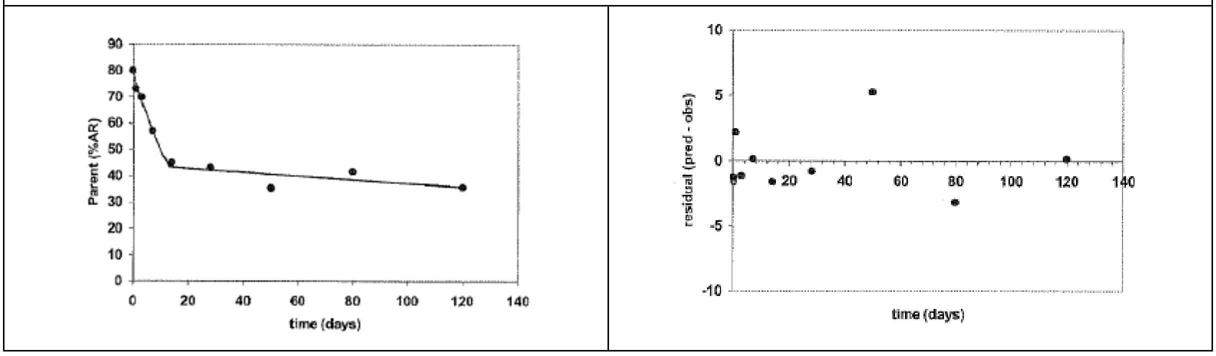
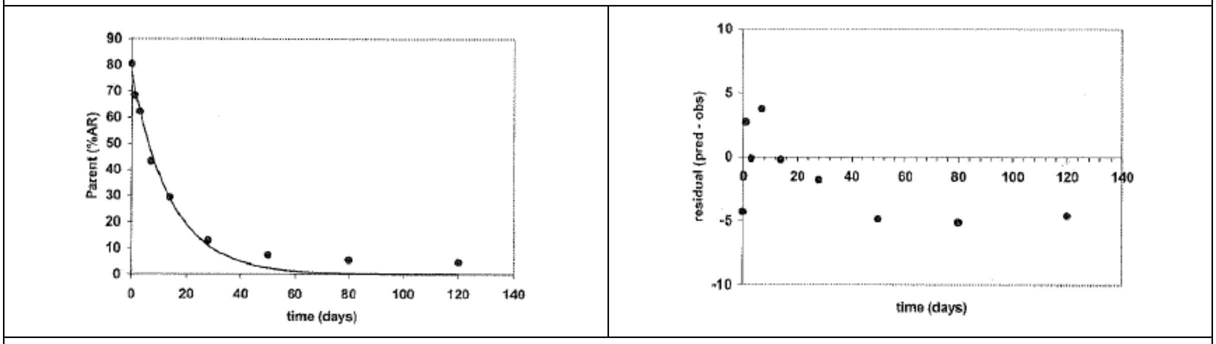


Figure B.8.1-15: Visual fits and residual plots of the degradation of DCPMU in the soil Laacher Hof using SFO, FOMC, DFOP and HS as kinetic models

Table B.8.1-57 Statistical results of the kinetic models SFO, FOMC, DFOP and HS describing the degradation of DCPU in the soil Wurmwiese

Kinetic model	Parameter	Optimised value	Std. error	p-value (t-test)	% error χ^2 test	DT_{50} (d)	DT_{90} (d)	Visual assessment
SFO	M_0	76.205	2.7525	0.0000	8.71	10.1	33.5	poor
	K	0.06871	0.00743	0.0000				
FOMC	M_0	79.158	1.8372	0.0000	4.48	8.5	50.2	very good
	A	1.5961	0.40518	0.0038				
	B	15.54	5.707	0.0173				
DFOP	M_0	77.9	1.6911	0.0000	5.56	8.9	49.8	very good
	k_1	0.09382	0.01384	0.0005				
	k_2	0.00741	0.008	0.1982				
	G	0.86712	0.07833	0.0001				
HS	M_0	76.711	1.9913	0.0000	5.56	9.7	40.6	very good
	k_1	0.07148	0.0058	0.0000				
	k_2	0.00694	0.01102	0.2784				
	t_b	31.311	8.0717	0.0058				

SFO



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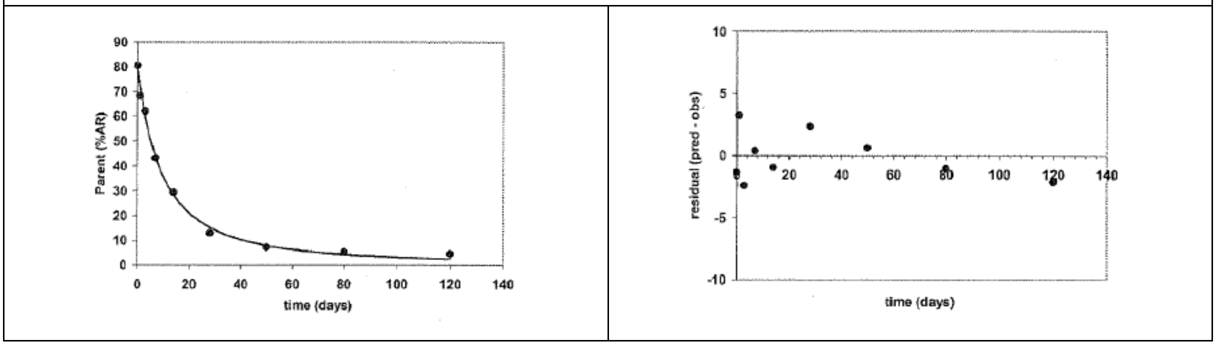

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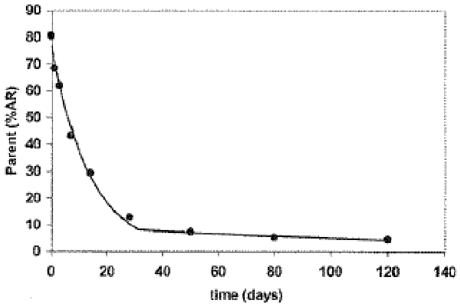

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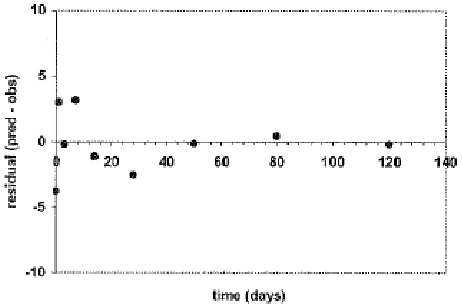

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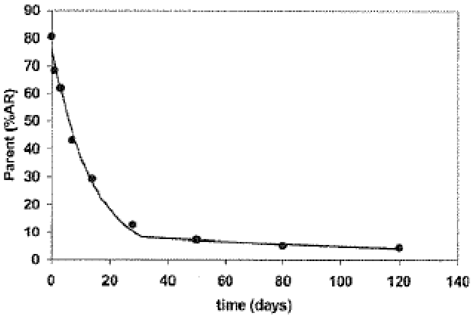

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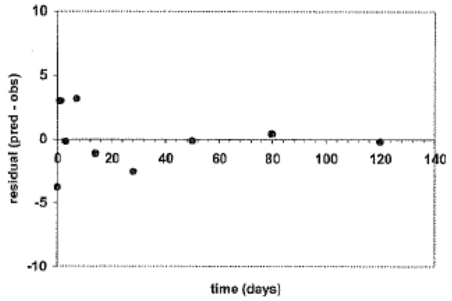

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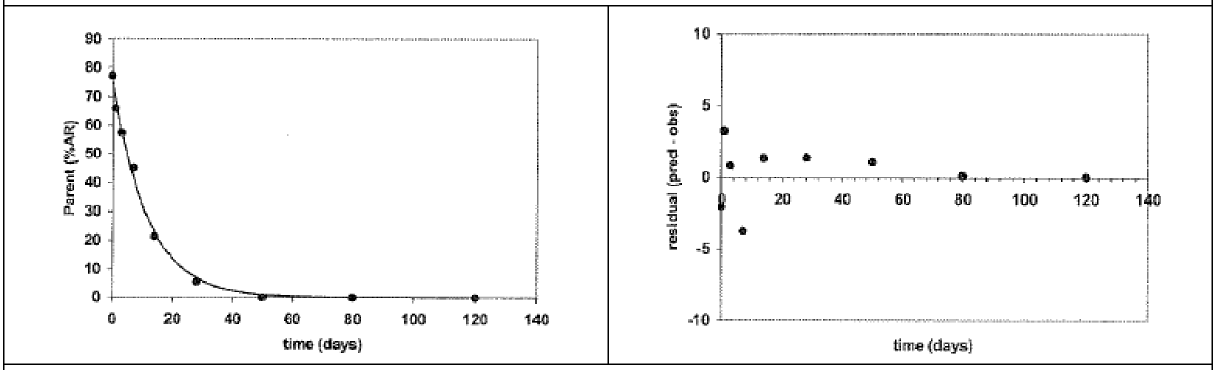
Figure B.8.1-16: **Visual fits and residual plots of the degradation of DCPU in the soil Wurmwiese using SFO, FOMC, DFOP and HS as kinetic models**

Table B.8.1-58 **Statistical results of the kinetic models SFO, FOMC, DFOP and HS describing the degradation of DCPU in the soil Höfchen**

Kinetic model	Parameter	Optimised value	Std. error	p-value (t-test)	% error χ^2 test	DT_{50} (d)	DT_{90} (d)	Visual assessment
SFO	M_0	75.211	1.5759	0.0000	5.16	8.1	27.0	Very good
	K	0.08530	0.00528	0.0000				
FOMC	M_0	75.212	1.8875	0.0000	5.46	8.1	27.0	Very good
	A	916.58	3528.2	0.4019				
	B	10737	40626	0.40002				

SFO



FOMC

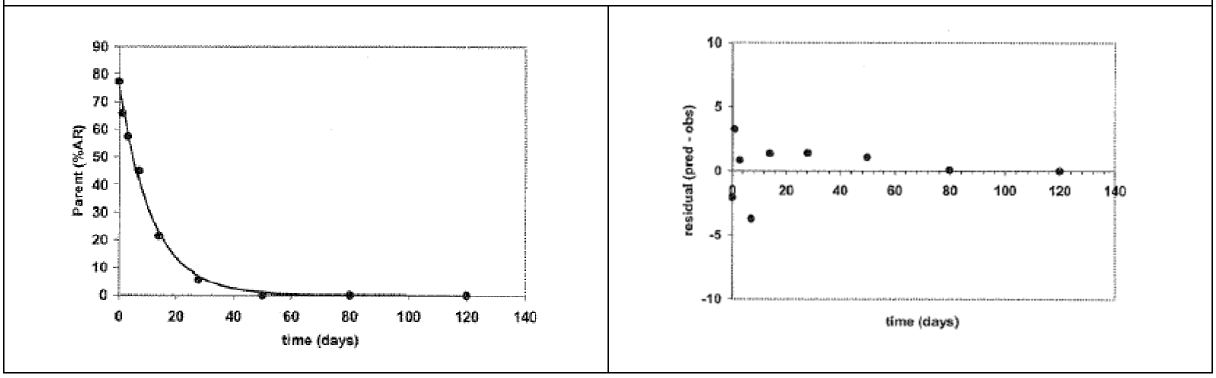
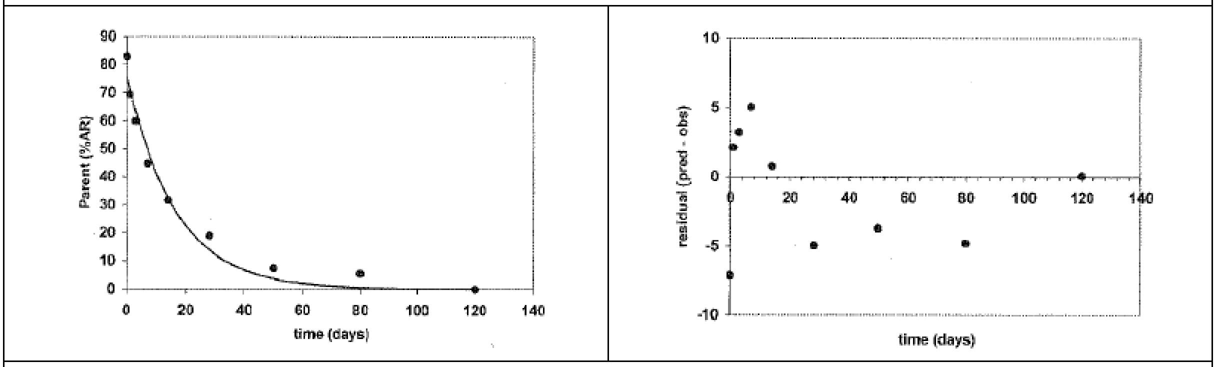


Figure B.8.1-17: **Visual fits and residual plots of the degradation of DCPU in the soil Höfchen using SFO, FOMC, DFOP and HS as kinetic models**

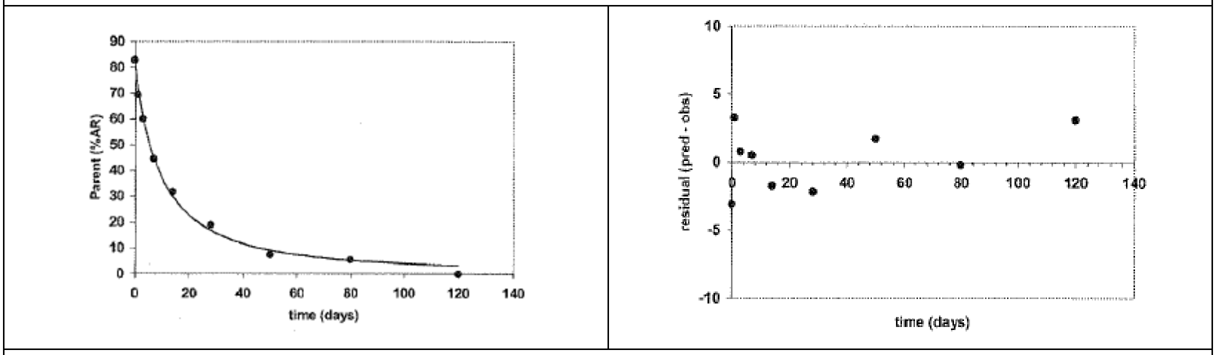
Table B.8.1-59 **Statistical results of the kinetic models SFO, FOMC, DFOP and HS describing the degradation of DCPU in the soil Laacher Hof**

Kinetic model	Parameter	Optimised value	Std. error	p-value (t-test)	% error χ^2 test	DT_{50} (d)	DT_{90} (d)	Visual assessment
SFO	M_0	75.778	3.1109	0.0000	9.27	11.5	38.1	poor
	K	0.06042	0.00753	0.0000				
FOMC	M_0	79.825	2.1326	0.0000	5.11	8.9	56.3	good
	A	1.4622	0.4075	0.0058				
	B	14.703	6.0828	0.0260				
DFOP	M_0	81.584	1.8356	0.0000	3.76	8.6	50.8	Very good
	k_1	0.33321	0.10868	0.00140				
	k_2	0.03724	0.00462	0.0002				
	G	0.3364	0.006679	0.0020				
HS	M_0	79.521	2.0992	0.0000	5.11	7.9	52.6	Very good
	k_1	0.08749	0.00962	0.0001				
	k_2	0.03569	0.00671	0.0016				
	t_b	8.226	2.3909	0.0092				

SFO



FOMC



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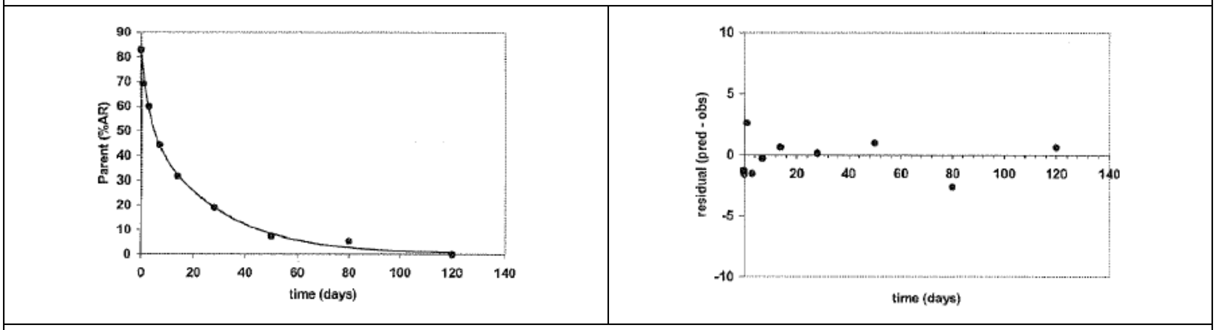

HS

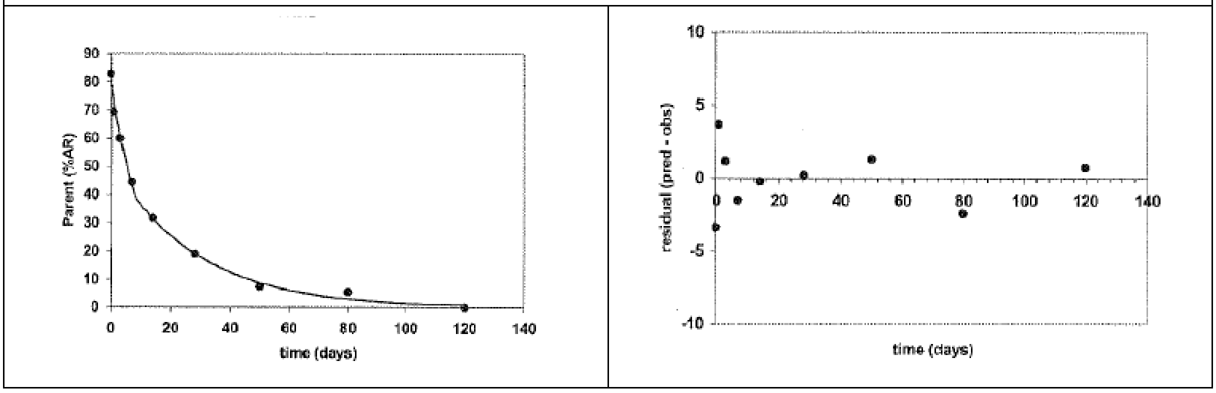

Figure B.8.1-18: Visual fits and residual plots of the degradation of DCPU in the soil Laacher Hof using SFO, FOMC, DFOP and HS as kinetic models

In the study Schnoeder, 2006, SFO kinetics was chosen for modelling endpoints of DCPMU and DCPU for all soils. However, the RMS does not agree with this decision. Thus, only the final DT_{50} and DT_{90} of the study Schnoeder, 2006 to be used for persistence calculations are not summarised here. For modelling, the endpoints chosen by the RMS are described and summarised below.

Since degradation of DCPMU shows a clear biphasic trend in all three soils, biphasic kinetics are chosen for persistence calculations and from biphasic kinetics back-calculated SFO kinetics are chosen as modelling endpoints. However, since according to FOCUS kinetics guidance (2014), from biphasic kinetics back-calculated SFO will only be a worst case for DCPMU as primary metabolite but not for DCPU, which is formed as secondary metabolite from DCPMU, additionally the SFO kinetics of DCPMU are chosen to be used in a separate modelling for DCPU.

FOMC was chosen as best fit kinetic for persistence calculations of DCPMU in the soil Wurmwiese. Since 10 % of initial applied DCPMU was not reached at the end of the study in this soil, the slow phase of the DFOP kinetic is chosen as kinetic for modelling of DCPMU. HS is chosen as best fit kinetic for persistence calculations of DCPMU in the soil Höfchen. The slow phase of the HS kinetic is also chosen for modelling of DCPMU in the soil Höfchen. For the soil Laacher Hof, HS is also chosen for persistence calculations of DCPMU. The slow phase of the HS kinetic is chosen as kinetic for modelling of DCPMU in the soil Laacherhof.

FOMC is chosen as best fit kinetic for persistence calculations of DCPU in the soil Wurmwiese. For modelling FOMC $DT_{90}/3.32$ should be used for DCPU in the soil Wurmwiese. For the soil Höfchen, SFO is acceptable to be used both for modelling and persistence calculations of DCPU. For the soil Laacher Hof, DFOP is chosen for persistence calculations of DCPU. FOMC $DT_{90}/3.32$ should be used for modelling of DCPU in this soil.

No moisture normalisation of the DT_{50} values of DCPMU and DCPU was performed for the studies Hennecke, 2005b and c. Thus, the moisture normalisation was done by the RMS using default values for the maximum water holding capacity. The moisture correction factors are listed in Table B.8.1-60.

Table B.8.1-60 Moisture correction factors of the investigated soils

Soil	Soil type	Default MWHC (1 kPa)	Moisture correction factor
Wurmwiese	Loam	31	0.716
Höfchen	Silt loam	32	0.712
Laacherhof	Sandy Loam	27	0.787

Conclusion

The kinetic re-evaluation was considered acceptable for the previous EU-approval of diuron. When re-assessing the study two deviations from FOCUS kinetic guidance were noted (2014): For the degradation of DCPU in the soil Höfchen all three sampling points where no DCPU residues could be detected anymore were included in the kinetic models. Besides, the first residue values below LOD was not set to ½ LOD as recommended in FOCUS (2006, 2014). However, when the RMS repeated the kinetic evaluation according to FOCUS (2006, 2014), a good agreement with the degradation rates derived by Schnoeder, 2006 was found for all soils and both metabolites. Thus, the kinetic evaluation of the two soil studies Hennecke, 2005b and c is considered acceptable by the RMS except for the fact, that back-calculated SFO from biphasic kinetics should be used for DCPMU for all soils and for DCPU for two soils and not SFO as was chosen by the applicant.

The final DT_{50} and DT_{90} of DCPMU to be used for persistence calculations are summariaed in Table B.8.1-61 and Table B.8.1-63. The DT_{50} values of DCPMU and DCPU to be used for modelling are summarised in Table B.8.1-62 and Table B.8.1-64.

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Table B.8.1-61 Degradation rates of DCPMU in the soils investigated by Hennecke, 2005b under aerobic conditions (persistence endpoints)

Soil	Soil type	pH H_2O	T. (ºC)	Moisture	DT_{50} (d)	DT_{90} (d)	Kinetic model	Chi^2 error (%)	Reference
Wurmwiese	loam	5.81	20	50 % MWHC	72	>10,000	FOMC	3.01	Hennecke, 2005b
Höfchen	Silt loam	6.72	20	50 % MWHC	89	475	HS	3.50	Hennecke, 2005b
Laacherhof	Sandy Loam	6.76	20	50 % MWHC	68	964	HS	3.93	Hennecke, 2005b

Table B.8.1-62 DT_{50} values of DCPMU in the soils investigated by Hennecke, 2005b under aerobic conditions (modelling endpoints)

Soil	Soil type	pH H_2O	T. (ºC)	Moisture	DT_{50} – not normalised	DT_{50} at 20°C and pF2 (d)	Kinetic model	Chi^2 error (%)	Reference
Modelling endpoints of DCPMU to be used when modelling DCPMU									
Wurmwiese	loam	5.81	20	50 % MWHC	251	179.8	DFOP, slow phase	3.88	Hennecke, 2005b
Höfchen	Silt loam	6.72	20	50 % MWHC	166	118.3	HS, slow phase	3.50	Hennecke, 2005b
Laacherhof	Sandy Loam	6.76	20	50 % MWHC	385	303.1	HS, slow phase	3.93	Hennecke, 2005b
Modelling endpoints of DCPMU to be used when modelling DCPU									
Wurmwiese	loam	5.81	20	50 % MWHC	91.8	65.7	SFO	10.02	Hennecke, 2005b
Höfchen	Silt loam	6.72	20	50 % MWHC	96.8	68.9	SFO	9.31	Hennecke, 2005b
Laacherhof	Sandy Loam	6.76	20	50 % MWHC	87.7	69.0	SFO	14.44	Hennecke, 2005b

Table B.8.1-63 Degradation rates of DCPU in the soils investigated by Hennecke, 2005c under aerobic conditions (persistence endpoints)

Soil	Soil type	pH H_2O	T. (ºC)	Moisture	DT_{50} (d)	DT_{90} (d)	Kinetic model	Chi^2 error (%)	Reference
Wurmwiese	loam	5.81	20	50 % MWHC	8.5	50.2	FOMC	4.48	Hennecke, 2005c
Höfchen	Silt loam	6.72	20	50 % MWHC	8.1	27.0	SFO	5.16	Hennecke, 2005c
Laacherhof	Sandy Loam	6.76	20	50 % MWHC	8.6	50.8	DFOP	3.76	Hennecke, 2005c

Table B.8.1-64 **DT_{50} values of DCPU in the soils investigated by Hennecke, 2005c under aerobic conditions (modelling endpoints)**

Soil	**Soil type**	**pH H_2O**	**T. (°C)**	**Moisture**	**DT_{50} – not normalised**	**DT_{50} at 20 °C and pF2 (d)**	**Kinetic model**	**Chi^2 error (%)**	**Reference**
Wurmwiese	loam	5.81	20	50 % MWHC	15.12	10.8	FOMC DT_{90}/ 3.32	4.48	Hennecke, 2005c
Höfchen	Silt loam	6.72	20	50 % MWHC	8.1	5.8	SFO	5.16	Hennecke, 2005c
Laacherhof	Sandy Loam	6.76	20	50 % MWHC	17.0	13.4	FOMC DT_{90}/ 3.32	5.11	Hennecke, 2005c

B.8.1.1.8 Anaerobic degradation of the active substance and metabolites

KCA 7.1.2.1.3/1 and KCA 7.1.2.1.4/1 – Drechsler & Klein, 2016c & d (new studies)

Author:	Drechsler, S. Klein, C.
Title:	Assessment of the degradation kinetics of diuron in soil under anaerobic laboratory conditions according to the recommendations of the FOCUS report on degradation kinetics (2006, 2014)
Date:	01.03.2016
Doc ID:	782-010
Guidelines:	FOCUS degradation kinetics guidance (2006, 2014)
GLP:	No, not applicable
Validity:	Not acceptable

Author:	Drechsler, S. Klein, C.
Title:	Raw data to assessment of degradation kinetics of diuron in soil under anaerobic laboratory conditions according to the recommendations of the FOCUS Report on degradation kinetics (2006, 2014)
Date:	01.03.2016
Doc ID:	782-011
Guidelines:	FOCUS degradation kinetics guidance (2006, 2014)
GLP:	No, not applicable
Validity:	Not acceptable

Material and Methods

In this study a kinetic re-evaluation was performed of the laboratory anaerobic soil study Yu, 1988 with diuron according to FOCUS degradation kinetics guidance (2006, 2014).
The model KinGUI version 2.1 was used for modelling applying SFO and FOMC for diuron and SFO for its metabolite DCPMU. The residues of diuron and metabolite DCPMU presented in Table B.8.1-65 were used for kinetic evaluation.
For the kinetic evaluation results of both the aerobic and the anaerobic phase were considered. As only four data points were available after change to the anaerobic phase, not enough data points for an adequate kinetic evaluation of just the anaerobic phase are available.

Table B.8.1-65 Processed residues of diuron and its soil metabolite DCPMU after incubation in a Keyport loam soil

Time after application [days]	Diuron	DCPMU	phase
0	103.7	0.0	Aerobic
15	95.6	4.4	
30	87.0	13.0	
45	92.2	7.8	Anaerobic
60	94.8	5.2	
75	89.7	10.3	
90	90.7	9.3	

Results and Discussion

The estimated kinetic parameters for diuron applying SFO and FOMC kinetics are summarised in Table B.8.1-66.

Table B.8.1-66 Estimated kinetic parameters and the resulting DT_{50} and DT_{90} values of Diuron from the study by Yu (1988) using SFO and FOMC models

Kinetic parameter	SFO	FOMC
M(0)	98.16	103.70
k_1 or alpha	0.001	0.016
k_2 or beta	-	0.020
Ch^2 error	3.36	2.39
P	0.068 (k)	0.281 (alpha) 0.470 (beta)
Standard deviation	3.239 (M(0)) 0.001 (k)	3.444 (M(0)) 0.025 (alpha) 0.249 (beta)
Lower / upper confidence interval (zero included?)	k: -1.13 x 10-4 / 0.002 (yes)	alpha: -0.034 / 0.066 (yes) beta: -0.468 / 0.508 (yes)
Visual fit	intermediate	intermediate
DT_{50} (d)	618.2	>1000
$DT_9$0 (d)	>1000	>1000

SFO was chosen as suitable fit for diuron and was used to further model the degradation rate of DCPMU. The estimated kinetic parameters for diuron and DCPMU applying SFO are presented in Table B.8.1-67.

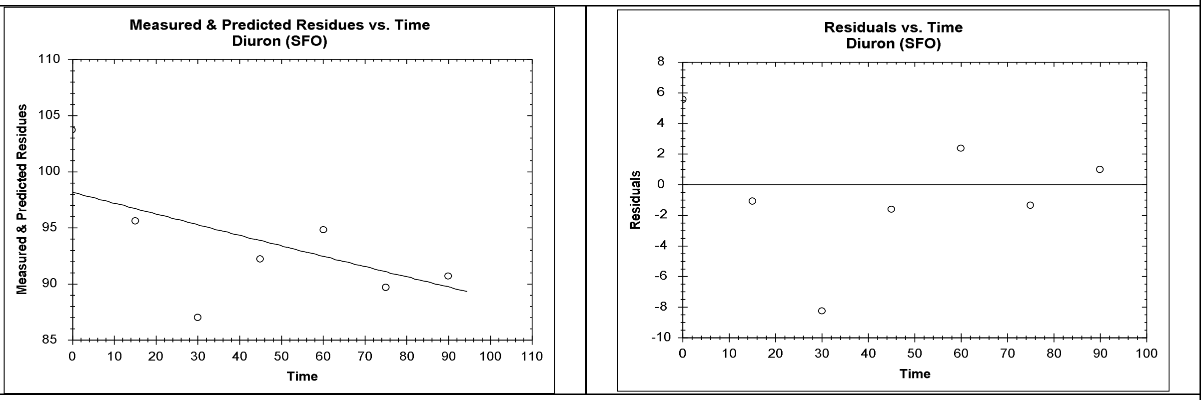
Table B.8.1-67 Estimated kinetic parameters and the resulting DT_{50} and DT_{90} values of Diuron and DCPMU from the study by Yu (1988) using SFO model

Kinetic parameter	Diuron	DCPMU
M(0)	100.5	-
k_1	0.002	0.006
Ch^2 error	3.59	36.85
P	0.020 (k)	0.403 (k)
Standard deviation	3.632 (M(0)) 0.001 (k)	0.026 (k)
Lower / upper confidence interval (zero included?)	k: 2.88 x 10-4 / 0.003 (no)	k: -0.044 / 0.057 (yes)
Visual fit	intermediate	intermediate
DT_{50} (d)	417.1	106.9
DT_{90} (d)	>1000	355
Formation fraction	-	1

Visual fits were presented in the Appendix of the study. For the metabolite visual plots were labelled as SFO and as SFO fixed. No further explanation was given in the study, however the RMS assumes from the estimated kinetic parameters that the formation fraction of DCPMU was fixed in the final plot.

The visual fits and residual plots using SFO for diuron and SFO with the formation fraction fixed to 1 for DCPMU are presented in Figure B.8.1-19.

Diuron



DCPMU

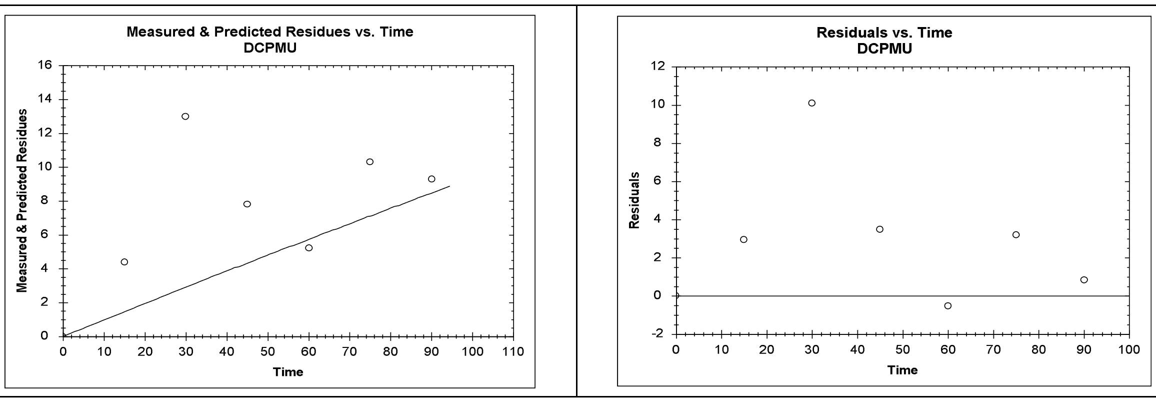


Figure B.8.1-19: Visual fit of the anaerobic degradation of diuron and its metabolite DCPMU in the Keyport silt loam using SFO as kinetic model

The resulting DT_{50} and DT_{90} values of diuron and DCPMU chosen by the applicant were then normalised to a temperature of 20 °C since the study was performed at 25 °C. The resulting DT_{50} and DT_{90} values are listed in Table B.8.1-68.

Table B.8.1-68 Normalised DT_{50} and DT_{90} values of Diuron and DCPMU

Substance	DT_{50} at 20 °C (d)	DT_{90} at 20 °C (d)
Diuron	670	>1000
DCPMU	171.7	570

Conclusion

The study was evaluated by the RMS and was considered unacceptable for various reasons listed below:

The study report was very poor. It was not stated how the data were processed nor when parameters were fixed during kinetic evaluation. The first time point of diuron was set to 103.7 %. It is not clear how this time point was derived since total mass balance at day 0 was only 99.9 % (see Table B.8.1-18). Without this processed time point, degradation of diuron would be considerably lower as already

modelled. The first time point of the metabolite DCPMU was set from 7.6 % AR to zero, which is according to kinetic guidance (2014) but was not mentioned in the study report. Also the visual plot for diuron is not very good and could be considered as poor.
The aerobic phase was considered together with the anaerobic phase to derive kinetic parameters which is not considered acceptable to derive kinetic parameters describing the anaerobic degradation. Only four data points are available for the anaerobic phase, thus no kinetic evaluation is possible for both diuron and DCPMU.
The visual fit of DCPMU using SFO with the formation fraction fixed to 1 is not intermediate but poor and the chi2 error is far beyond 15 %.
Thus, neither the DT_{50} and DT_{90} values of diuron nor of DCPMU are acceptable.

B.8.1.1.9 Soil photolysis of the active substance

Kinetic re-evaluation of the RMS of the soil photolyis study Hawkins et al, 1990

Material and Methods

The kinetic evaluation of the residues in the soil photolysis study Hennecke, 2005a were performed before current kinetic guidance were available. When the RMS repeated the evaluation, different degradation rates were obtained for diuron under irradiated conditions. Thus the new evaluation performed by the RMS is presented here. The residues of diuron under irradiated conditions presented in Table B.8.1-20 were used for kinetic evaluation. The model CAKE v.3.1 was used applying the models SFO, FOMC, DFOP and HS.

Results and Discussion

The estimated kinetic parameters for diuron applying SFO and FOMC kinetics are summarised in Table B.8.1-69.

Table B.8.1-69 Estimated kinetic parameters and the resulting DT_{50} and DT_{90} values of Diuron from the study by Hennecke, 2005a using SFO, FOMC, DFOP and HS models

Kinetic parameter	SFO	FOMC
M(0)	94.31	105.4
k or alpha	0.00979	0.06704
Beta	-	0.1923
Ch^2 error	6.21	3.38
P	0.02544 (k)	-
Standard deviation	M0: 4.42	M0: 4.463
	k: 0.00383	Alpha: 0.0.243
		Beta: -0.3099
Lower / upper confidence interval (zero included?)	M0: 5.41 – 103.2 (no)	M0: 95.87 – 114.9 (no)
	k: 0.002072 – 0.01751 (no)	Alpha: 0.01524 – 0.1188
		Beta: -0.4681 – 0.8531 (yes)
Visual fit	acceptable	Good
DT_{50} (d)	70.8	5950
DT_{90} (d)	235	>10,000
Kinetic parameter	**DFOP**	**HS**
M(0)	102.3	99.65
k_1	0.2445	0.0277
k_2	0.33E-022	8.32E -004
g or t_b	0.2503	8.957
Ch^2 error	4.28	5.16
P	k1: 0.2213	k1: 0.0831
	k2: 0.5	k2: 0.4555
Standard deviation	M0: 5.3	M0: 5.262
	k1: 0.008189	k1:0.01522
	k2: 0.145	k2:0.006847
	g: 0.145	tb: 5.218
Lower / upper confidence interval (zero included?)	M0: 89.87 – 114.8 (no)	M0: 87.27 – 112 (no)
	k1: -0.4077 – 0.8967 (yes)	k1: -0.008105 – 0.06351 (yes)
	k2: -0.09105 – 0.5916 (yes)	k2: -0.01528 – 0.001694 (yes)
	g: -0.09105 – 0.5916 (yes)	tb: -3.322 – 21.24 (yes)
Visual fit	good	Acceptable
DT_{50} (d)	>10,000	544
DT_{90} (d)	>10,000	2480

The biphasic kinetic model gave the better visual fits, however, the derived statistical parameter were not considered reliable. Besides, according photodegradation is generally expected to follow SFO kinetics. Thus, the SFO was accepted here, since the chi2 error remained below 15 % and also the remaining statistical parameter are sufficiently robust. The resulting visual fit and the residual plot are presented in Figure B.8.1-20.

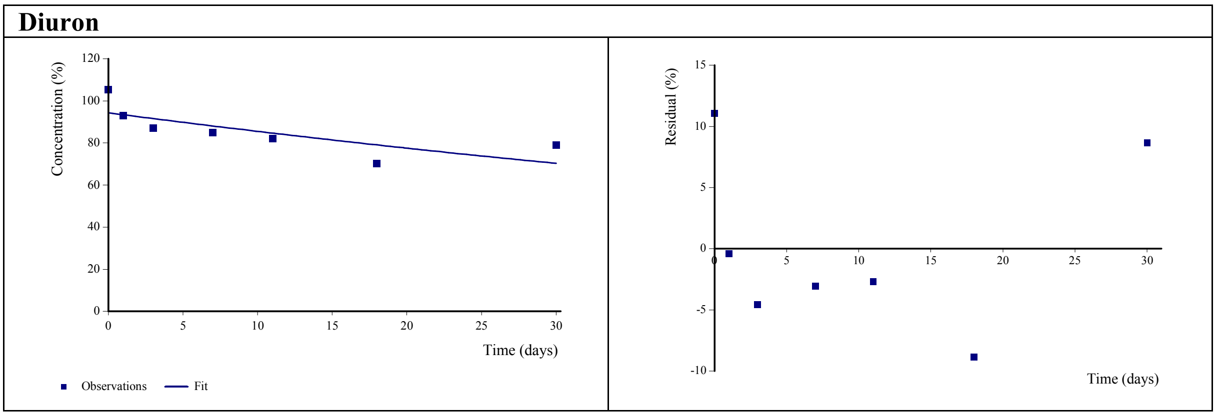


Figure B.8.1-20: **Visual fit of the soil photolysis of diuron on a sandy loam using SFO as kinetic model**

Conclusion

A new kinetic evaluation of the soil photolysis study Hennecke, 2005a according to FOCUS kinetic guidance (2014) was performed by the RMS. Under irradiated conditions diuron degraded on a sandy loam soil with a DT_{50} of 70.8 d and a DT_{90} of 235 d.

B.8.1.1.10 Field studies

KCA 7.1.2.2.1/1– Paetzold & Bruemmer, 1997 (study evaluated in the DAR, 2003)

Author:	Paetzold, S. Bruemmer, G.W.
Title:	Abbau-, Sorptions- und Verlagerungsverhalten des Herbizides Diuron in einer obstbaulich genutzten Parabraunerde aus Loess
Date:	26.10.1997
Doc ID:	Pflanzenernähr. Bodenk., 160, 165-170
Guidelines:	Not stated
GLP:	None stated
Validity:	Not acceptable

Material and Methods

The investigation was carried out in three consecutive years following a dosage of 2 kg/ha diuron, which was applied on 5. May 1992 and 11. May 1993 and 3 kg/ha diuron on 16. May 1994, each in the formulation KARMEX, in the apple orchard Klein-Altendorf near Bonn, Germany. Diuron had also been used on the test sites prior to the current study in October 1990, which is why a pre-adaptation of soil microorganisms must be assumed. Samples were taken in depths 0-5, 5-10, 10-15, 15-30, 30-60 and 60-90 cm at 6 to 9 time intervals, the first being immediately after application and the latest 12 months after application. Extraction of soil samples was performed with a 4:1 methanol/water solution. Identification and quantitation was done with HPLC and UV detection. The diuron residues dependent on soil depth and time as well as the distribution coefficient K_d were determined.

Results and Discussion

An accumulation of biologically effective residues of diuron was not observed, although a carry-over of diuron residues in a range of 46-77 µg/kg dry soil in the 0-5 cm layer occurred between different years. $DisT_{50}$ values were derived for the residue; data from four applications within the years 1990-1994 in the upper layer (0-5 cm) of Orthic Luvisol soil in Klein-Altendorf. Diuron disappearance was described by kinetics of first and higher orders, DT_{50} values ranged between 14 and 30 days. K_d values immediately following application were found in the range 4-8 L/kg, after 3 months 21-47 L/kg and after 6 months 105-155 L/kg, respectively. One year after application Kd was approximately 200 L/kg.

Conclusion

The study was evaluated for the first EU approval of diuron and was considered acceptable by the previous RMS.
However, after re-assessment of the study for EU re-approval, we do not consider this study to be acceptable anymore, since according to the authors' own statement all sites used were treated with diuron for several years before the actual field trials were started. Therefore, a pre-adaptation of soil organisms to diuron has to be assumed. Degradation rates derived from this study were indeed significantly lower than those from studies with no expected pre-adaptation. Thus, the results were not considered as realistic worst case condition and will not be used for exposure and risk assessment of diuron.

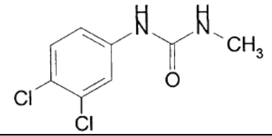
KCA 7.1.2.2.1/2– Pogány, 1993 (study evaluated in the DAR, 2003)

Author:	Pogány, E.
Title:	Dissipation of diuron in soils under field conditions
Date:	15.01.1993
Doc ID:	2138/91
Guidelines:	BBA Guidelines for Official Testing of Plant Protectants, Part IV, 4-1, Fate of Plant Protectants in Soil-Degradation, Transformation and Metabolism, December 1986
GLP:	Yes
Validity:	Partly acceptable

Material and Methods

The dissipation of diuron in soil under field conditions without vegetation was determined at six locations in Germany. The applied formulation and the reference substances used for analysis of the residues are presented in Table B.8.1-70.

Table B.8.1-70 Test items

Non-radiolabelled test item	
Trade name:	Diuron Bayer
Type of Formulation:	80 WP
Content of active substance:	Diuron 80.20 % (certified by analysis)
IUPAC name of active substance:	3-(3,4-dichloro-phenyl)-1-methyl-urea
Structure active substance:	
CAS # active substance:	330-54-1
Batch #:	232071107
Reference substances	
Test material:	**Diuron**
IUPAC name:	3-(3,4-dichlorophenyl)-1,1-dimethylurea
Purity:	99.7 %
Test material:	**DCPMU**
IUPAC name:	N'-3,4-dichlorophenyl)-N-methylurea
Purity:	99.7 %

The field dissipation studies were carried out in six different typical agricultural regions of Germany according to the requirements in the BBA guidelines. Average temperature and precipitation data from the sites and soil characteristics of the field plots are summarised in Table B.8.1-71.

Table B.8.1-71 Weather conditions and soil characteristics of the field trials

Location	Burscheid (Höfchen)	Albig	Maasen	Kirch-lauter	Swisttal Hohn	Monheim (Laacher Hof)
Temperature and precipitation						
Mean temperature (°C)	10.7	11.2	10.7	8.7	11.8	11.9
Total precipitation during the study period (mm)	919	359	544	400	548	661
Soil characteristics						
pH (in 0.01 ml $CaCl_2$ solution)	6.8	7.6	5.6	6.5	6.8	6.7
Organic C (%)	1.11	1.16	2.22	0.79	1.00	1.27
Organic matter (%)	1.91	2.00	3.82	1.36	1.72	2.18
Moisture capacity (g/100 g dry soil)	41.1	45.8	34.3	37.3	38.5	36.6
Nitrogen content (mg/100 g dry soil)	140	270	200	130	110	140
Clay (< 0.002 mm) (%)	19.4	35.9	4.6	4.5	13.1	13.0
Silt (0.002-0.060 mm) (%)	72.8	51.4	31.6	24.2	63.6	29.8
Sand (0.060-2.000 mm) (%)	7.8	12.7	63.8	71.3	23.3	57.2
Soil classification (USDA)	Silt loam	Silty clay loam	Sandy loam	Sandy loam	Silt loam	Sandy loam

The test substance was applied from April to May 1991 to the different field sites at an application rate of 10 kg/ha of the formulated product (*Diuron Bayer*) which is equal to 8 kg diuron/ha. Application was conducted using spray equipment. The total test duration was nine month for every site (April/May 1991 to February/March 1992). Before and during the experimental period, mechanical weed control was performed. Samples were taken immediately after application (immediately after drying of the spray film and after 30, 60, 90, 120, 150, 180, 210 and 300 days (± 2 days) after application. At each sampling time, 20 cores were taken using a pushing sampling system (Wacker Hammer) down to a depth of 30 cm per sampling. Samples were transported in a cooler box and stored at -20 °C until sample preparation and analysis in the laboratory. Detailed information on air temperature, sunshine and rainfall were recorded during the field trials and can be found in the original study report.
For analysis, frozen samples (whole cores) were cut into 10 cm segments. Samples of the 20 cores of one segment were milled and homogenised. A part of these homogenised soil samples were taken for analysis. Samples were extracted with acetone : water (2 : 1, v : v) (frequency and duration not specified). After concentration via evaporation samples were cleaned up by liquid-liquid-partition on Ex-tube-columns, eluting diuron and its metabolites with 150 mL dichloromethane. The solvent was evaporated to dryness and residues were re-dissolved in acetonitrile : water (1 : 1, v : v). Measurement of the extracts was done by HPLC with UV-detection. LOD of the analytical method was 0.01 mg/kg for diuron and its metabolites.

Results and Discussion

The entire method including soil extraction, combustion and volatile trapping was validated via mass balancing, which was separately performed with diuron and DCPMU test substances (Table B.8.1-72). Mean recovery rates of Diuron and DCPMU were determined to be 97.5 and 93.9 % with a range of 88.2 to 95.0 % for diuron and 86.1 and 94.0 % for DCPMU, respectively.

Table B.8.1-72 Mean recovery of mass balances during method validation with soil samples from all sites included in the trials

Field site	Mean recovery	
	Diuron [%]	DCPMU [%]
Burscheid	92.6	90.2
Albig	88.2	86.1
Maasen	99.3	97.2
Kirchlauter	91.5	87.6
Swisttal	95.0	94.0
Monheim	92.5	89.0
Overall mean recovery	93.5	89.8

The residues of diuron are given in Table B.8.1-73 and Table B.8.1-74. The residues of DCPMU are given in Table B.8.1-75 and Table B.8.1-76.

The main part of the diuron and DCPMU residues were encountered in the uppermost soil layer. For most of the samples, no Diuron or DCPMU was detected above the LOD in in the deepest 20-30 cm soil layer. However, in five samples diuron was detected in the 20-30 cm soil layer with a maximum concentration of 0.025 mg/kg at time zero at the field site Kirchlauter. The metabolite DCPMU was also detected in five samples with a maximum concentration of 0.032 mg/kg immediately after application and after 60 days at the field site Kirchlauter. During the field trials, diuron deceased from 4.0 to 0.2 mg/kg after 300 days in the upper layer of the field site Burscheid, from 4.8 to 2.0 mg/kg in Albig, from 3.7 to 1.4 mg/kg in Kirchlauter, from 3.5 to 0.4 mg/kg in Swisttal and from 4.2 to 0.3 mg/kg in Monheim. A maximum concentration of 0.83 mg/kg DCPMU was observed at the Kirchlauter field trial 302 days after application.

Table B.8.1-73 Residue of diuron in the field trials Burscheid (Höfchen), Albig and Maasen (mean of duplicate analysis)

Soil layer (cm)	**Burscheid (Höfchen)**		**Albig**		**Maasen**	
	Days after application	**Diuron (mg/kg soil)**	**Days after application**	**Diuron (mg/kg soil)**	**Days after application**	**Diuron (mg/kg soil)**
0-10	0	3.959	0	4.731	0	4.486
10-20		0.039		0.045		0.074
20-30		< 0.01		**0.016**		**0.020**
0-10	30	3.406	30	4.465	30	2.901
10-20		< 0.01		< 0.01		0.026
20-30		< 0.01		< 0.01		0.012
0-10	60	2.962	60	3.570	61	4.043
10-20		0.038		< 0.01		< 0.01
20-30		< 0.01		< 0.01		< 0.01
0-10	92	1.182	90	3.124	90	2.456
10-20		0.015		0.016		< 0.01
20-30		0.01		< 0.01		< 0.01
0-10	118	0.387	120	4.330	120	2.662
10-20		0.019		< 0.01		< 0.01
20-30		< 0.01		< 0.01		< 0.01
0-10	150	0.185	150	2.782	150	2.969
10-20		< 0.01		< 0.01		< 0.01
20-30		< 0.01		< 0.01		< 0.01
0-10	180	0.232	180	2.866	180	2.893
10-20		0.016		< 0.01		< 0.01
20-30		< 0.01		< 0.01		< 0.01
0-10	212	0.182	210	2.304	210	2.585
10-20		< 0.01		< 0.01		< 0.01
20-30		< 0.01		< 0.01		< 0.01
0-10	300	0.210	300	1.959	300	2.765
10-20		< 0.01		< 0.01		< 0.01
20-30		< 0.01		< 0.01		< 0.01

TableB.8.1-74 Residue of diuron in the field trials Kirchlauter, Swisttal Hohn and Monheim (Laacher Hof) (mean of duplicate analysis)

Soil layer (cm)	Kirchlauter		Swisttal Hohn		Monheim (Laacher Hof)	
	Days after application	Diuron (mg/kg soil)	Days after application	Diuron (mg/kg soil)	Days after application	Diuron (mg/kg soil)
0-10	0	3.553	0	3.502	0	4.136
10-20		0.099		0.032		0.018
20-30		**0.025**		< 0.01		< 0.01
0-10	30	2.734	30	3.454	30	2.925
10-20		< 0.01		< 0.01		< 0.01
20-30		< 0.01		< 0.01		< 0.01
0-10	60	2.374	60	3.136	61	2.871
10-20		< 0.01		< 0.01		0.010
20-30		< 0.01		< 0.01		< 0.01
0-10	92	1.739	90	2.229	90	1.432
10-20		0.042		< 0.01		0.025
20-30		**0.014**		< 0.01		**0.012**
0-10	118	1.721	120	0.945	120	0.687
10-20		0.038		0.017		0.033
20-30		**0.013**		< 0.01		< 0.01
0-10	150	1.655	150	0.739	152	0.615
10-20		< 0.01		< 0.01		< 0.01
20-30		< 0.01		< 0.01		< 0.01
0-10	182	1.625	181	0.489	181	0.301
10-20		< 0.01		< 0.01		< 0.01
20-30		< 0.01		< 0.01		< 0.01
0-10	210	1.163	210	0.390	210	0.320
10-20		< 0.01		< 0.01		< 0.01
20-30		< 0.01		< 0.01		< 0.01
0-10	302	1.053	300	0.356	300	0.296
10-20		0.340		< 0.01		< 0.01
20-30		< 0.01		< 0.01		< 0.01

Table B.8.1-75 Residue of DCPMU in the field trials Burscheid (Höfchen), Albig and Maasen (mean of duplicate analysis)

Soil layer (cm)	Burscheid (Höfchen)		Albig		Maasen	
	Days after application	DCPMU (mg/kg soil)	Days after application	DCPMU (mg/kg soil)	Days after application	DCPMU (mg/kg soil)
0-10	0	0.028	0	< 0.01	0	0.012
10-20		0.013		< 0.01		< 0.01
20-30		< 0.01		< 0.01		< 0.01
0-10	30	0.233	30	0.258	30	0.179
10-20		< 0.01		< 0.01		< 0.01
20-30		< 0.01		< 0.01		< 0.01
0-10	60	0.471	60	0.363	61	0.390
10-20		0.025		< 0.01		< 0.01
20-30		< 0.01		< 0.01		< 0.01
0-10	92	0.205	90	0.418	90	0.280
10-20		0.014		< 0.01		< 0.01
20-30		< 0.01		< 0.01		< 0.01
0-10	118	0.066	120	0.669	120	0.374
10-20		< 0.01		< 0.01		< 0.01
20-30		< 0.01		< 0.01		< 0.01
0-10	150	0.037	150	0.466	150	0.439
10-20		< 0.01		< 0.01		< 0.01
20-30		< 0.01		< 0.01		< 0.01
0-10	180	0.041	180	0.551	180	0.493
10-20		< 0.01		< 0.01		< 0.01
20-30		< 0.01		< 0.01		< 0.01
0-10	212	0.036	210	0.470	210	0.447
10-20		< 0.01		< 0.01		< 0.01
20-30		< 0.01		< 0.01		< 0.01
0-10	300	0.047	300	0.405	300	0.445
10-20		< 0.01		< 0.01		< 0.01
20-30		< 0.01		< 0.01		< 0.01

Table B.8.1-76 Residue of DCPMU in the field trials Kirchlauter, Swisttal Hohn and Monheim (Laacher Hof) (mean of duplicate analysis)

Soil layer (cm)	Kirchlauter		Swisttal Hohn		Monheim (Laacher Hof)	
	Days after application	DCPMU (mg/kg soil)	Days after application	DCPMU (mg/kg soil)	Days after application	DCPMU (mg/kg soil)
0-10 10-20 20-30	0	0.041 < 0.01 0.032	0	0.042 < 0.01 < 0.01	0	0.027 < 0.01 < 0.01
0-10 10-20 20-30	30	0.247 < 0.01 0.029	30	0.220 < 0.01 < 0.01	30	0.192 < 0.01 < 0.01
0-10 10-20 20-30	60	0.486 < 0.01 0.032	60	0.411 < 0.01 < 0.01	61	0.363 < 0.01 < 0.01
0-10 10-20 20-30	92	0.599 0.013 0.026	90	0.547 < 0.01 < 0.01	90	0.325 < 0.01 < 0.01
0-10 10-20 20-30	118	0.652 0.012 0.023	120	0.345 < 0.01 < 0.01	120	0.237 < 0.01 < 0.01
0-10 10-20 20-30	150	0.674 < 0.01 < 0.01	150	0.295 < 0.01 < 0.01	152	0.190 < 0.01 < 0.01
0-10 10-20 20-30	182	0.799 < 0.01 < 0.01	181	0.156 < 0.01 < 0.01	181	0.086 < 0.01 < 0.01
0-10 10-20 20-30	210	0.602 < 0.01 < 0.01	210	0.131 < 0.01 < 0.01	210	0.089 < 0.01 < 0.01
0-10 10-20 20-30	302	0.778 0.033 0.019	300	0.086 < 0.01 < 0.01	300	0.073 < 0.01 < 0.01

Conclusion

In the first EU approval this study was considered acceptable. It was re-evaluated here within the scope of the renewal of approval and only considered acceptable for persistence calculations. At four of the six locations, Albig, Maasen, Kirchlauter and Monheim, significant amounts of diuron were detected in the lowest sampling depth (20-30 cm). Therefore leaching could not be excluded in these trials. Leaching itself might bias the kinetic evaluation of degradation, because the amount leached might be regarded as degraded substance. Furthermore, just the soils with low degradation rates tend to leaching, because the probability to reach groundwater is higher when degradation takes longer.

High sand contents generally increases hydraulic permeability. At the same time sandy soils have lower water retention capacity, which tends to decrease microbial degradation. Both factors enhance the leaching potential. The trials with by far highest sand content Maasen (64 %), Kirchlauter (71 %) and Monheim (57 %) are among the four soils showing leaching indications, in Kirchlauter at six of nine sampling points. The four soils are either characterised by low organic carbon (Albig, Kirchlauter, Monheim) or lowest pH value (Maasen), which in addition to high sand content generally decelerate microbial degradation. The characteristics of the four soils promote leaching, which bias the kinetic evaluation of degradation. That is why the soils could not be used for kinetic evaluation in preparation for modelling. This applies for the active substance diuron as well as for its metabolite DCPMU, as we cannot exclude formation of this metabolite after the parent leached into deeper soil layers.

In contrast, the two field trials with no substance detects in the deepest sampled layer, Burscheid and Swisttal, are both classified as silt loam. This soil class is remarkably less permeable and tendentially

characterised by higher microbial degradation than soils with high sand content (e.g. sandy loams). Particular soil characteristics thereby prevent the substance from leaching here. Furthermore pH is the same in both soils and organic carbon content is very similar. All factors prove that the two soils alone do only represent this small part of agricultural soils, which is advantageous to microbial degradation. The similar and exceptionally low DT_{50} values calculated by Drechler & Klein (2016) are rather a direct consequence of this best case particularity than representative degradation rates for agriculturally used soils in the EU. Taking only these two soils into account would bias an average degradation value (e.g. geomean) to a best case situation due to an unproportionally high fraction of high degrading soils. Therefore, the entire study cannot be used for calculating a representative geomean value and for modelling purposes. For persistence endpoints all field trials can be considered since the longest degradation rate and not an average value is used.
The DT_{50} and DT_{90} values of the study are not listed here anymore, since two new kinetic evaluations Schnöder (2006) and Drechsler & Klein (2016) according to FOCUS (2005) and FOCUS (2006, 2014), respectively, are available. These studies are described below. The kinetic evaluation by Drechsler & Klein (2016) was accepted for persistence endpoints of the parent diuron. For the metabolite DCPMU a new kinetic evaluation was performed by the RMS.

KCA 7.1.2.2.1/3– Sommer, 1993 (study evaluated in the DAR, 2003)

Author:	Sommer, H.
Title:	Storage Stability of Diuron in Soil
Date:	08.03.1993
Doc ID:	RA-112/93
Guidelines:	BBA Guidelines for Official Testing of Plant Protectants, Part IV, 4-1, Fate of Plant Protectants in Soil-Degradation, Transformation and Metabolism, December 1986
GLP:	Yes
Validity:	Yes

Material and Methods

The purpose of this study was to determine the stability of diuron and DCPMU in soil under the storage conditions of the institute of product information and residue analysis. Previous studies with diuron have shown that the compound formed a major metabolite DCPMU. Therefore, the active ingredient and its metabolite represent the total residue. In addition the results of the metabolism studies showed that under laboratory conditions the DT_{90} values in soil are above 100 days. According to BBA field dissipation studies are required in this case. To show that the residues in the stored soil samples are stable, this study was conducted. The soil samples comprised of a mixture of three standard soils from LUFA-Speyer (Table B.8.1-77). This mixture was used rather than the single soils to register possible influences of all three different soils. The soil samples of the standard soils were classified according to USDA specifications.

Table B.8.1-77 Soil characteristics

	Standard soil 2.1 LUFA Speyer	Standard soil 2.2 LUFA Speyer	Standard soil 2.3 LUFA Speyer
pH (in 0.01 ml $CaCl_2$ solution)	5.4	5.5	5.7
Organic C (%)	0.54	2.15	0.75
Organic matter (%)	0.93	3.71	1.29
Soil density (g/mL)	2.55	2.5	1.5
Fe-content (dithionit soluble) (mg/kg soil)	2675	3025	3025
Nitrogen content (%)	0.06	0.14	0.5
Clay (< 0.002 mm) (%)	5.3	4.0	6.5
Silt (0.002-0.063 mm) (%)	8.8	13.0	27.7
Sand (0.063-2.0 mm) (%)	85.9	83.0	65.8
Soil classification according to USDA	loamy sand	sandy loam	sandy loam

Untreated mixed soil samples were fortified with diuron and desmethyldiuron (DCPMU) at a concentration of 2.0 mg/kg. The concentration is about half of the maximum residues that could be expected for field samples. Soil samples were analysed at day 0 and after 28, 54, 86, 1245, 180, 238 and 363 days of storage. Soil samples were analysed for the active ingredient diuron and the metabolite desmethyldiuron according to the liquid chromatographic method of Pogány (1990) (Pogány, E. (1990). Method for high performance liquid chromatographic determination of residues of the herbicides diuron and bromacil in soil. Method 00231. Unpublished report of BAYER AG, Leverkusen, PF-F/UF-RA). Soil samples were extracted with 2 : 1 (v:v) acetone/water (duration and frequency not reported). After a liquid-liquid partition on Extube-columns the active ingredient and the metabolite were eluted with dichloromethane. The identification and quantification of the residue was done by high pressure liquid chromatography and UV-detection.

Results and Discussion

Table B.8.1-78 and Table B.8.1-79 summarise the percentages of diuron and DCPMU, respectively, recovered in the method validation test.

Table B.8.1-78 Recovered amounts of diuron in percent of added amount

Day	**Recovered amounts, single values (%)**	**Recovered amounts, mean values (%)**	**Standard deviations (%)**	**Relative standard deviations**
0	101/97.3/92.5/94.7	96.3	3.3	0.03
28	95.6/93.5/97.5	95.5	1.8	0.02
54	94.5/73.2/56.0*⁾	83.8	12.3	0.15
86	82.2/90.1/99.4	90.6	7.7	0.08
124	98.3/89.8/47.0*⁾	94.0	5.0	0.05
180	91.5/87.3/89.7	89.5	1.9	0.02
238	92.2/98.8/95.9	95.6	3.0	0.03
363	97.1/96.8/91.7	95.2	2.7	0.03
Overall single values		93.1	6.1	0.07

*⁾ Outliers that were rejected at the 95 % confidence level. Additionally detected as outlier by Box- and Whisker plot (data points more than three interquartile ranges below the first quartile). Regression analysis of the data including and excluding the outliers showed that the result of the storage stability study is not significantly influenced by rejection of the outliers.

Table B.8.1-79 Recovered amounts of DCPMU in percent of added amount

Day	Recovered amounts, single values (%)	Recovered amounts, mean values (%)	Standard deviations (%)	Relative standard deviations
0	97.3/94.0/89.5/89.2	92.5	3.6	0.04
28	95.2/93.2/97.1	95.2	1.7	0.02
54	93.9/72.7/56.0*)	83.3	12.2	0.15
86	82.1/90.2/98.9	90.4	7.5	0.08
124	97.3/89.5/47.6*)	93.4	4.5	0.05
180	91.8/87.5/89.8	89.7	1.9	0.02
238	91.6/98.6/96.0	95.4	3.2	0.03
363	97.1/97.0/92.0	95.3	2.6	0.03
Overall single values		92.2	5.9	0.06

*) Outliers that were rejected at the 95 % confidence level. Additionally detected as outlier by Box- and Whisker plot (data points more than three interquartile ranges below the first quartile). Regression analysis of the data including and excluding the outliers showed that the result of the storage stability study is not significantly influenced by rejection of the outliers.

The mean recovery during method validation was 98 % for diuron with a relative standard deviation of 0.11 and 94 % for DCPMU with a relative standard deviation of 0.10. The lower limit of the practical working range of the analytical method for soil was 0.01 mg/kg. The mean recovery during analyses of samples of the storage stability study was 98.8 % for diuron with a relative standard deviation of 0.07 and 97.0 % for DCPMU with a relative standard deviation of 0.06. No residues > 0.01 mg/kg were detected in any of the control samples. The recovery of diuron and DCPMU at day 0 was 96.3 % and 92.5 %, at day 363 it was 95.2 % and 95.3 %, respectively.

Considering different concentrations added of 0.01, 0.1 and 1 mg/kg (see study by Sommer 1993), single recovery values for diuron range from 76 to 112 %, whereby the lowest fortification level underlid highest fluctuations, probably due to lower limit of practical working range being equal to this value. Higher concentrated samples range from 91 to 102 %, which can be considered acceptable. Same applies for DCPMU.

Conclusion

The study was considered acceptable at first EU approval of diuron. After re-evaluation of the study for re-approval of diuron, the RMS still considers the study to be acceptable.

The study followed BBA guideline (1986). Recoveries are generally 90-102 %, which is considered acceptable by the guideline, except for the lowest concentrated samples which exhibited concentrations levels close to the detection limit. Thus, the higher concentrated samples tested (0.1 and 1 mg/kg) can be regarded as stable under the applied preparation methods. This concentration range matches the residue contents in the actual samples of the field study. Diuron and DCPMU are thus considered as stable during transport and sample preparation.

KCA 7.1.2.2.1/4– Schnoeder, 2006 (study evaluated in the Addendum, 2007)

Author:	Schnoeder, F.
Title:	Environmental fate endpoints for diuron and its metabolites – data review and kinetic calculations with model maker 4.0
Date:	23.03.2006
Doc ID:	duPont-19861
Guidelines:	FOCUS (2005)
GLP:	No, not applicable
Validity:	Partly acceptable

Material and Methods

In this study, a kinetic re-evaluation was performed of the laboratory aerobic soil studies Mackie & Hall, 1994 and deVries, 1996 with diuron and the laboratory aerobic soil studies Hennecke, 2005a & b with the metabolites DCPMU and DCPU, respectively, the field dissipation studies Pogàny (1993), Pätzold and Brümmer (1996) and Rouchard et al. (2000) with diuron and the water/sediment study Sneikus (2001) with diuron.

Here only the kinetic re-evaluation of the field dissipation studies Pogàny (1993), Pätzold and Brümmer (2000) and Rouchard et al. (2000) are summarised. The summary of the kinetic re-evalution of laboratory studies Mackie & Hall, 1994 and deVries, 1996 with diuron and Hennecke (2005a & b) with DCPMU and DCPU, respectively, can be found under B.8.1.1.6 and B.8.1.1.7. The kinetic re-evaluation of the water/sediment study Sneikus, 2001 is described under B.8.2.2.3.

The degradation of diuron and its primary metabolite DCPMU was investigated at 6 German sites (Pogany 1993). The results from one site (Maasen) were excluded from the kinetic re-evaluation due to decreased degradation of diuron.

The residues of diuron and its metabolite DCPMU listed in Table B.8.1-73 to Table B.8.1-76 were used for kinetic re-evaluation. Therefore the residues of all sampled soil depths were summed up and soil samples with residues <LOD were counted as zero. Normalisation to the reference temperature of 20 °C was performed according to FOCUS (2005) via time step normalisation. Soil temperature was estimated from measured daily air temperatures at the field sites (please refer to Pogany 1993). No normalisation of the residues to a reference soil moisture of pF 2 was performed. Residues with corrected day lengths were used to derive modelling endpoints, residues without the actual sampling days were used to derive endpoints for persistence calculations.

The results are only presented as short summary, because they were not used for the further risk assessment.

Results and Discussion

The endpoints for diuron and DCPMU in soil obtained under field conditions for modelling and persistence are summarised in Table B.8.1-80 and Table B.8.1-8, respectively.

Table B.8.1-80 **DT_{50} and DT_{90} values of diuron from field dissipation studies that were used for modelling and for persistence calculations within this study (all SFO)**

Field trial	**Modelling endpoints**			**Persistence endpoints**			**Reference**
	DT_{50} at 20 °C (Days)	**DT_{90} at 20 °C (Days)**	**Chi^2 (%)**	**DT_{50} Not norm. (Days)**	**DT_{90} Not norm. (Days)**	**Chi^2 (%)**	
Albig (DE)	177	588	12	236	783	10	Pogány (1993)
Burscheid	36	119	19	55	182	25	Pogány (1993)
Swisstal Hohn (DE)	58	193	16	80	266	19	Pogány (1993)
Kirchlauter (DE)	84	280	10	151	503	10	Pogány (1993)
Monheim (DE)	42	141	13	61	202	16	Pogány (1993)
Klein-Altendorf (DE)	22	72	16	30	100	16	Pätzold & Brümmer (1997)
Gorsem* (BE)	-	-	-	72	239	8	Rouchaud et al. (2000)

* Gorsem lacks weather data (normalisation not possible) and is thus only used for comparison with persistence triggers

Table B.8.1-81 DT_{50} and DT_{90} values of DCPMU from field dissipation studies that were used for modelling and for persistence calculations within this study (all SFO)

Field trial	Modelling endpoints			Persistence endpoints			Reference
	DT_{50} (Days)	DT_{90} (Days)	Chi^2 (%)	DT_{50} Not norm. (Days)	DT_{90} Not norm. (Days)	Chi^2 (%)	
Albig (DE)	32	107	13	42	140	13	Pogány (1993)
Burscheid	24	81	12	27	88	17	Pogány (1993)
Swisstal Hohn (DE)	44	145	9	63	208	8	Pogány (1993)
Kirchlauter (DE)	41	137	12	76	251	15	Pogány (1993)
Monheim (DE)	21	69	12	83	277	10	Pogány (1993)
Klein-Altendorf (DE)	60	196	11	77	256	12	Pätzold & Brümmer (1997)

Conclusion

The field dissipation study of Pätzold & Brümmer (1997) is not considered acceptable by us due to possible pre-adaption of the microorganisms, as outlined in more detail in the conclusion of the respective study (please refer to KCA 7.1.2.2.1/1). The results of the study Pogány 1993 are only considered acceptable for persistence calculations, since diuron was found in the deepest sampled soil layer of four of the six field trials (please refer to KCA 7.1.2.2.1/4 for more details). Thus, the normalised DT_{50} values derived from this study are not considered acceptable for modelling purposes.

The results by Schnöder (2006) were not used for further risk assessment. For diuron, the results by Drechsler & Klein (2016) were used instead, because the evaluation was performed according to the most current FOCUS guidance (2014). Nevertheless the results were very similar to those by Schnöder 2006. For DCPMU the RMS did own calculations in line with FOCUS (2014), which are presented in KCA 7.1.2.2.1/5.

KCA 7.1.2.2.1/5– Drechsler & Klein, 2016e & f (new study)

Author:	Drechsler, S. Klein, C.
Title:	Assessment of the degradation kinetics of diuron in soil under field conditions according to the recommendations of the FOCUS report on degradation kinetics (2006, 2014)
Date:	01.03.2016
Doc ID:	782-006
Guidelines:	
GLP:	No, not applicable
Validity:	Partly acceptable

Author:	Drechsler, S. Klein, C.
Title:	Raw data to Assessment of the degradation kinetics of diuron in soil under field conditions according to the recommendations of the FOCUS report on degradation kinetics (2006, 2014)
Date:	01.03.2016
Doc ID:	782-008
Guidelines:	
GLP:	No, not applicable
Validity:	Partly acceptable

Material and Methods

In this study, a kinetic re-evaluation according to FOCUS (2006, 2011) was performed of the field

dissipation study by Pogány (1993) to derive persistence endpoints for diuron.
The diuron residues of the field sites Burscheid, Albig, Kirchlauter, Swisttal and Monheim listed Table B.8.1-73 and Table B.8.1-74 were used for the kinetic-re-evaluaton. The residues among soil layers were summed up, values <LOD were considered using 0.5*LOD according to FOCUS (2006, 2014). The assessment was conducted according to the FOCUS degradation kinetics guidance (2006, 2014) using the model KinGUI 2.1. Four kinetic models, SFO, FOMC, DFOP and HS, were tested and best fit analysis was conducted to derive DT_{50} and DT_{90} for persistence endpoint.

Results and Discussion

The resulting DT_{50} and DT_{90} values of diuron are listed in Table B.8.1-82. The dissipation of diuron in all field trials followed SFO with DT_{50} values between 54.3 and 233.3 d. DT_{90} values were in the range of 180 to 775 days. Best fit analysis resulted in a worst case based on SFO kinetics for diuron of the field site Albig with a DT_{50} value of 233.3 days and a DT_{90} value of 775.1 days.

Table B.8.1-82 Statistical results of the kinetic evaluation of diuron (all SFO)

Field trial	Parameter	Optimised value	Std. error	p-value (t-test)	% error χ^2 test	DT_{50} (d)	DT_{90} (d)	Visual assessment
Albig	M0_diuron	7.11	0.486	n/a	9.92	233.3	775	good
	k_ diuron	0.003	0.001	8.09E-4				
Burscheid	M0_diuron	6.65	0.688	n/a	25.34	54.3	180	acceptable
	k_ diuron	0.013	0.002	1.34E-5				
Kirchlauter	M0_diuron	4.90	0.351	n/a	11.19	157.0	522	good
	k_ diuron	0.004	0.001	2.52E-4				
Monheim	M0_diuron	6.45	0.444	n/a	15.62	59.9	199	acceptable
	k_ diuron	0.012	0.001	3.54E-5				
Swisttal	M0_diuron	6.11	0.594	n/a	19.7	78.4	260	acceptable
	k_ diuron	0.009	0.002	3.5E-4				

Figure B.8.1-21, Figure B.8.1-22, Figure B.8.1-23, Figure B.8.1-24 and Figure B.8.1-25 show the visual fits and residual plots of the field trials Albig, Burscheid, Kirchlauter, Monheim and Swisttal, which were used for kinetic evaluation.

Diuron (Albig)

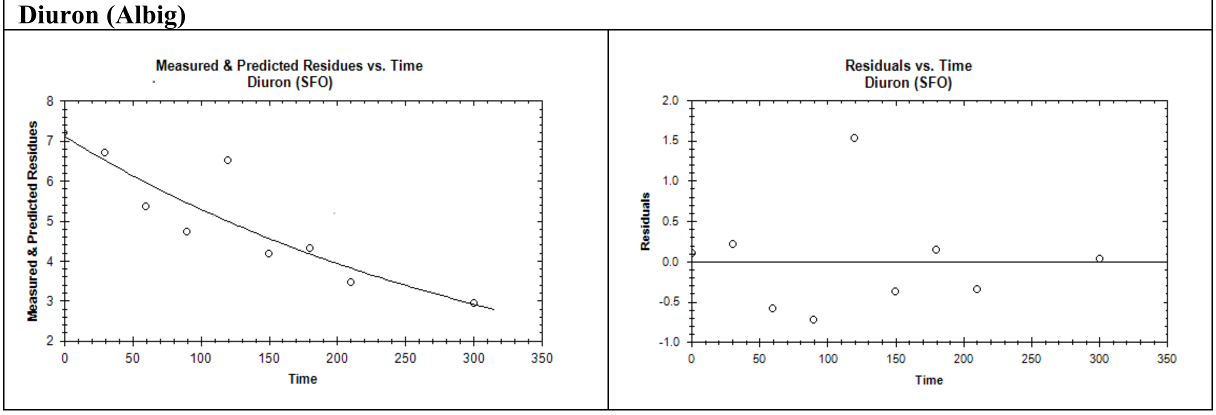


Figure B.8.1-21: Visual fit of the degradation of diuron at the field trial Albig (SFO, Drechsler & Klein 2016)

Diuron (Burscheid)

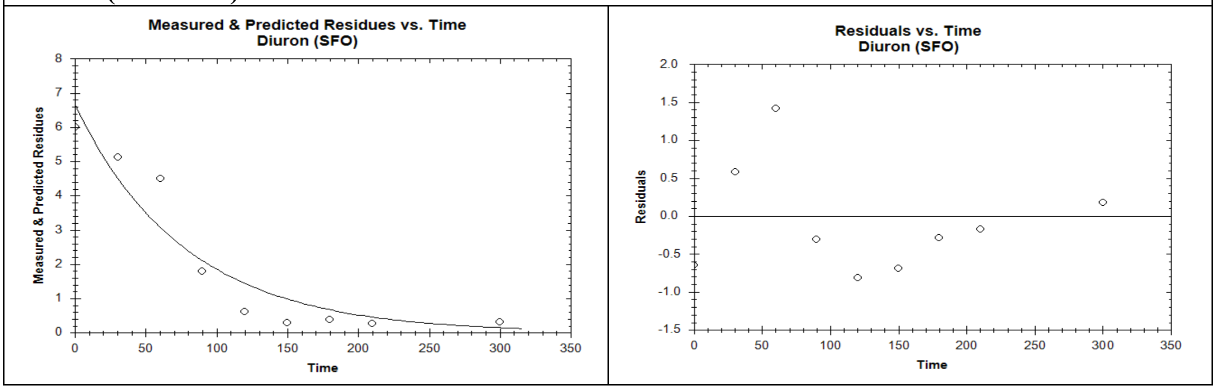


Figure B.8.1-22: Visual fit of the degradation of diuron at the field trial Burscheid (SFO, Drechsler & Klein 2016)

Diuron (Kirchlauter)

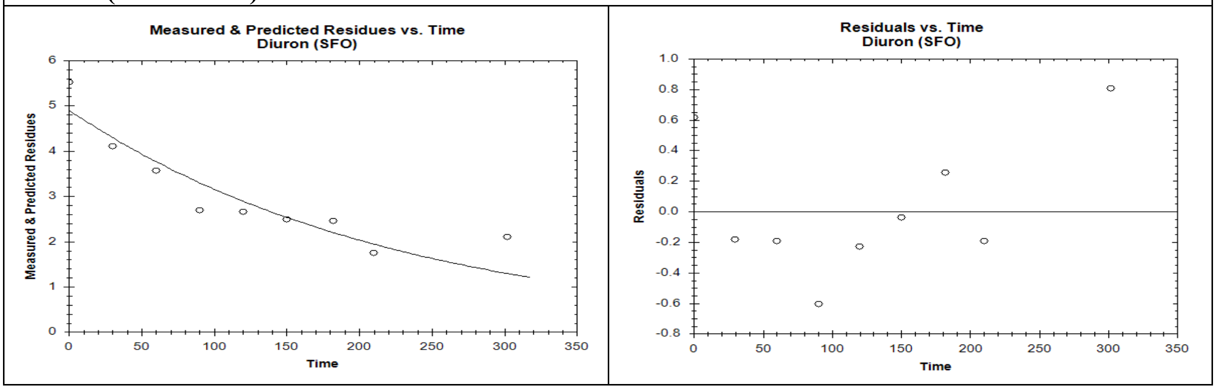


Figure B.8.1-23: Visual fit of the degradation of diuron at the field trial Kirchlauter (SFO, Drechsler & Klein 2016)

Diuron (Monheim)

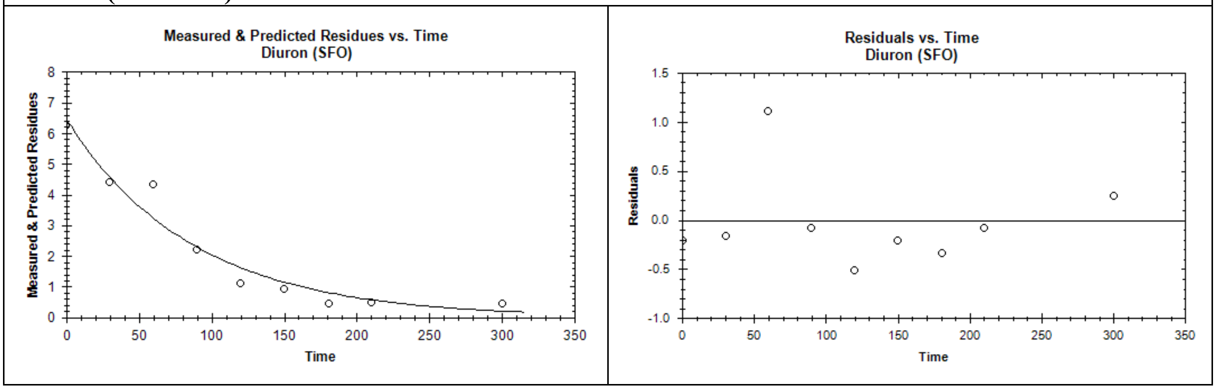


Figure B.8.1-24: Visual fit of the degradation of diuron at the field trial Monheim (SFO, Drechsler & Klein 2016)

Diuron (Swisttal)

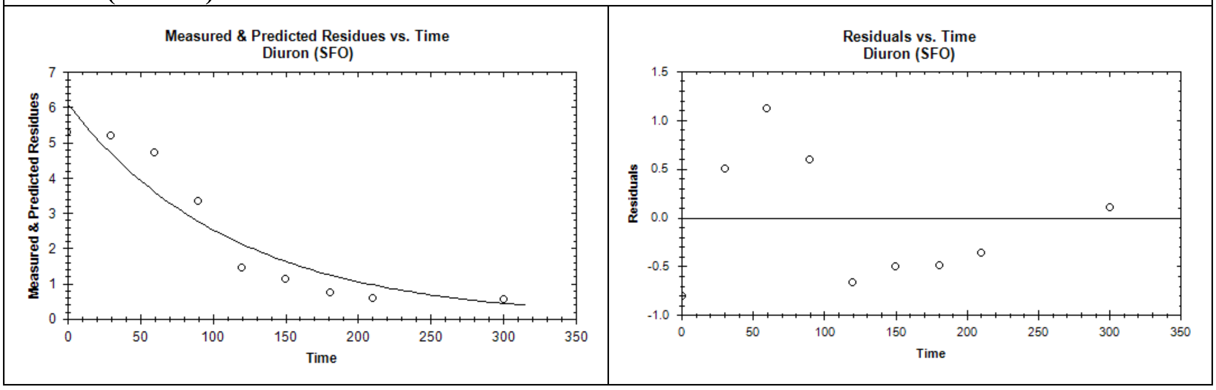


Figure B.8.1-25: **Visual fit of the degradation of diuron at the field trial Swisttal (SFO, Drechsler & Klein 2016)**

Conclusion

The kinetic evaluation was done according to FOCUS (2006, 2014) guidance. Values are very similar to those of Schnöder (2006) and the ones re-calculated by the RMS. In accordance with Schnöder (2006), the results of Drechsler & Klein (2016g) are applicable for Albig, Burscheid (Höfchen), Swisstal-Hohn, Monheim (Laacher Hof) and Kirchlauter. However, we believe, that the results of the Maasen soil cannot be neglected. Thus kinetic re-evaluation of the trial Maasen was performed below. A kinetic evaluation of the degradation of metabolite DCPMU was not performed for any of the soils and was thus also performed by the RMS below.

Kinetic evaluation by the RMS of the field trial Maasen in the dissipation study Pogany (1993) regarding diuron

The model CAKE, version 3.1, was used for kinetic evaluation of DCPMU. The data derived from Pogany (1993) and are available in Table B.8.1-75 and Table B.8.1-76.
The sum concentration among all soil layers was used. Residues below LOD were set to ½ * LOD according to FOCUS (2014). The model SFO was run for all field trials, results were assessed according to statistical parameters and the quality of visual fit. The applied degradation scheme is given in Figure B.8.1-3.

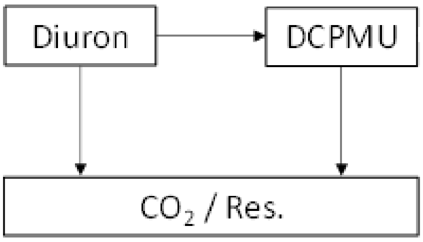


Figure 8.1-26: **Degradation scheme used for kinetic re-evaluation by the RMS of the field dissipation study Pogany 1993 regarding the metabolite DCPMU**

Kinetic evaluation was not performed for the field trial Maasen by Drechsler & Klein 2016, although there is no indication for invalidity of this field trial. Therefore the RMS performed own kinetic evaluation based on the raw data from Pogany 1993 in analogy to KCA 7.1.2.2.1/4 (kinetic re-evaluation by the RMS). Methodical details are provided in the respective chapter. Table B.8.1-83 summarises the statistical parameters and DT_{50} and DT_{90} value of diuron determined in Maasen field trial. Figure B.8.1-27 shows the kinetic fit and residuals for Maasen trial.

Table B.8.1-83 Statistical results of the kinetic evaluation of diuron for Maasen field trial (kinetic evaluation by the RMS, parameters from best fit FOMC model)

Field trial	Parameter	Optimised value	Std. error	p-value (t-test)	% error χ^2 test	DT_{50} (d)	DT_{90} (d)	Visual assessment
Maasen	M_0_diuron	4.424	0.3986	n/a	11.3	792	>10,000	acceptable
	α diuron	0.1521	7.94E-4	0.02042				
	β diuron	8.392						

Diuron (Maasen)

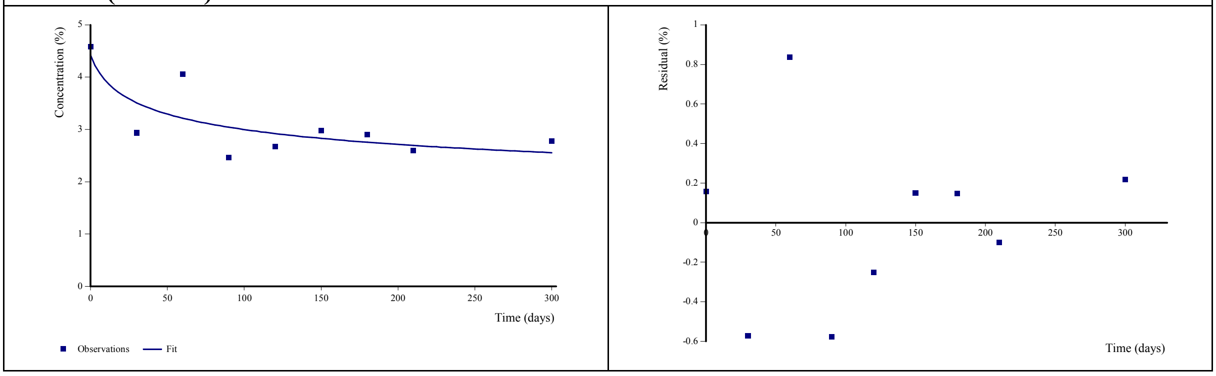


Figure B.8.1-27: Visual fit of the degradation of diuron at the field trial Maassen (FOMC, kinetic evaluation by the RMS)

Table B.8.1-84 summarises all DT_{50} and DT_{90} values accepted and used as persistence endpoints. These values are included in the LoEP.

Table B.8.1-84 Summary of all DT_{50} and DT_{90} values of diuron used as persistence end-points / triggers

	Albig	Burscheid	Kirchlauter	Maasen	Monheim	Swisttal
Kinetic model	SFO	SFO	SFO	FOMC	SFO	SFO
DT_{50} [d]	233.3	54.3	157.0	792	59.9	78.4
DT_{90} [d]	775	180	522	>10,000	199	260

Kinetic re-evaluation by the RMS of the field dissipation study Pogany (1993) regarding the primary metabolite DCPMU of diuron

The degradation of the metabolite DCPMU was kinetically re-evaluated by the RMS according to FOCUS 2014 guidance. The methodical details are in analogy to the re-calculation of the parent diuron in Maasen field trial (see above). The statistical results are provided in Table B.8.1-85. The kinetic model used was SFO for all field trials except Maasen, for which FOMC was used. Figure B.8.1-28, Figure B.8.1-29, Figure B.8.1-30, Figure B.8.1-31, Figure B.8.1-32 and Figure B.8.1-33 illustrate the visual fits of DCPMU degradation and residuals in the field trials Albig, Burscheid, Kirchlauter, Maasen, Monheim and Swisttal, respectively.

Table B.8.1-85 Statistical results of the kinetic re-evaluation of DCPMU (re-calculation of the RMS)

Field trial	**Parameter**	**Optimised value**	**Std. error**	**p-value (t-test)**	**% error χ^2 test**	**DT_{50} (d)**	**DT_{90} (d)**	**Visual assessment DCPMU**
Albig$^{a)}$	M_0_diuron	4.748	0.3347	n/a	9.93 $^{c)}$	231$^{c)}$	769 $^{c)}$	acceptable
	k_diuron	0.002994	6.13E-4	1.50E-4				
	f_diuron>DCPMU	0.7574	0.259	n/a	11.2 $^{d)}$	54.1 $^{d)}$	180 $^{d)}$	
	k_DCPMU	0.01281	0.003453	0.001307				
Burscheid $^{a)}$	M_0_diuron	4.493	0.4773	n/a	25.4 $^{c)}$	52.2 $^{c)}$	173 $^{c)}$	poor *
	k_diuron	0.01329	0.002438	5.54E-5				
	f_diuron>DCPMU	0.4137	0.2703	n/a	43.5 $^{d)}$	16.4 $^{d)}$	54.6 $^{d)}$	
	k_DCPMU	0.04221	0.02646	0.06731				
Kirchlauter $^{a)}$	M_0_diuron	3.268	0.2394	n/a	11 $^{c)}$	157 $^{c)}$	522 $^{c)}$	acceptable
	k_diuron	0.004409	7.44E-4	2.50E-5				
	f_diuron>DCPMU	0.7073	0.1883	n/a	10 $^{d)}$	132 $^{d)}$	439 $^{d)}$	
	k_DCPMU	0.005249	0.001708	0.004448				
Maasen $^{b)}$	M_0_diuron	4.424	0.3986	n/a	11.3 $^{c)}$	792 $^{c)}$	>10,000 $^{c)}$	acceptable
	α / β diuron	0.1521 / 8.392	7.94E-4	0.02042				
	f_diuron>DCPMU	0.2644	0.5921	n/a	10.5 $^{d)}$	>10,000 $^{d)}$	>10,000 $^{d)}$	
	k_DCPMU	6.47E-5	0.003313	0.004415				
Monheim $^{a)}$	M_0_diuron	4.314	0.3071	n/a	15.6 $^{c)}$	59.3 $^{c)}$	197 $^{c)}$	poor *
	k_diuron	0.01169	0.001443	9.75E-7				
	f_diuron>DCPMU	0.2827	0.07569	n/a	15.1 $^{d)}$	33 $^{d)}$	110 $^{d)}$	
	k_DCPMU	0.02104	0.005108	6.05E-4				
Swisttal $^{a)}$	M_0_diuron	4.128	0.4147	n/a	19.8 $^{c)}$	75.7 $^{c)}$	251 $^{c)}$	poor *
	k_diuron	0.009162	0.001619	9.91E-5				
	f_diuron>DCPMU	0.4465	0.1721	n/a	19.6 $^{d)}$	33.2 $^{d)}$	110 $^{d)}$	
	k_DCPMU	0.02088	0.007041	0.005463				

$^{a)}$ Diuron and DCPMU calculated with SFO $^{b)}$ Diuron calculated with FOMC, DCPMU calculated with SFO
$^{c)}$ value for diuron $^{d)}$ value for DCPMU
* By the end of the study phases with constant concentrations are clearly visible, which indicate a stagnation in degradation. Although very important for exposure assessment, this stagnation cannot be considered by the fits. That is why they are characterised as "poor".

DCPMU (Albig)

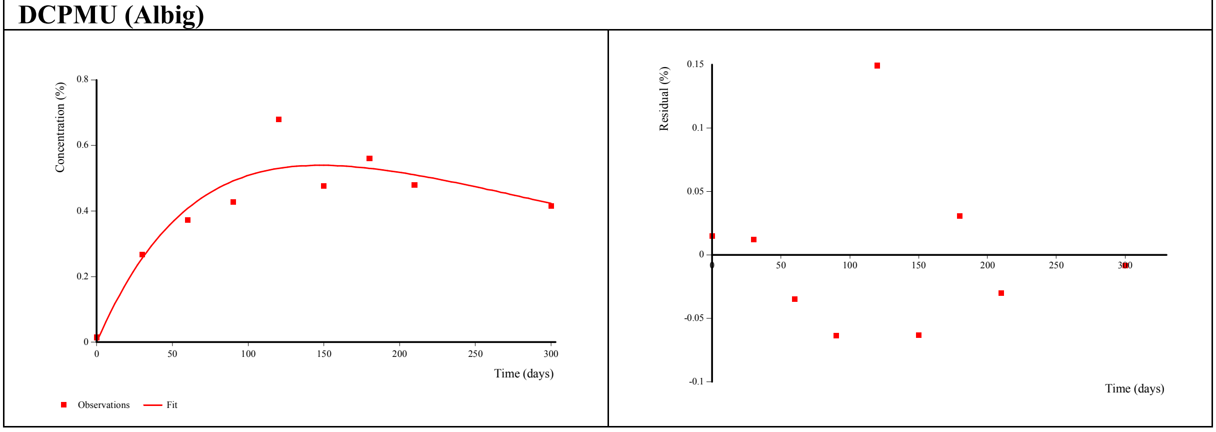


Figure B.8.1-28: Visual fit of the degradation of DCPMU at the field trial Albig (SFO, kinetic re-evaluation by the RMS)

DCPMU (Burscheid)

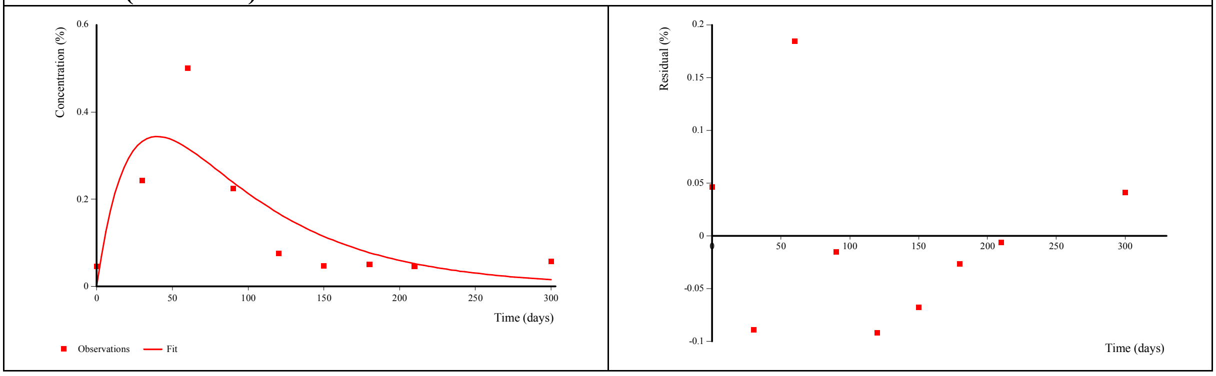


Figure B.8.1-29: Visual fit of the degradation of DCPMU at the field trial Burscheid (SFO, kinetic re-evaluation by the RMS)

DCPMU (Kirchlauter)

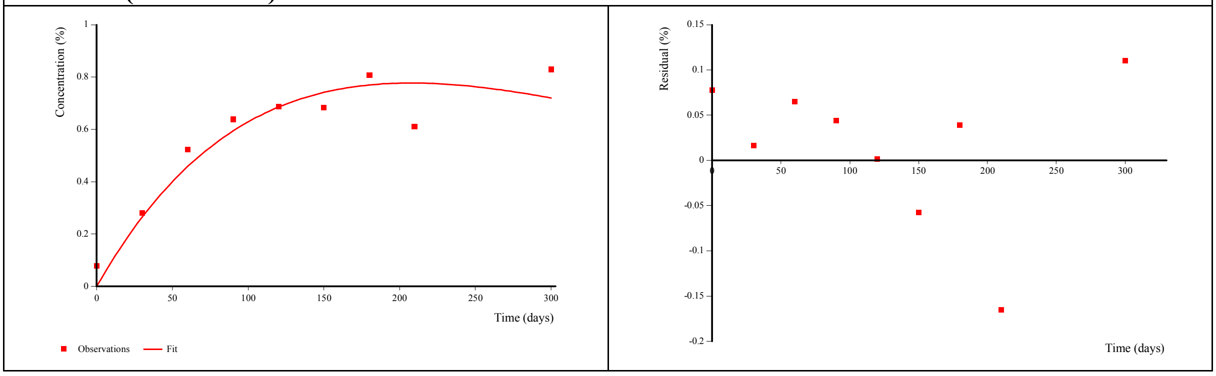


Figure B.8.1-30: Visual fit of the degradation of DCPMU at the field trial Kirchlauter (SFO, kinetic re-evaluation by the RMS)

DCPMU (Maassen)

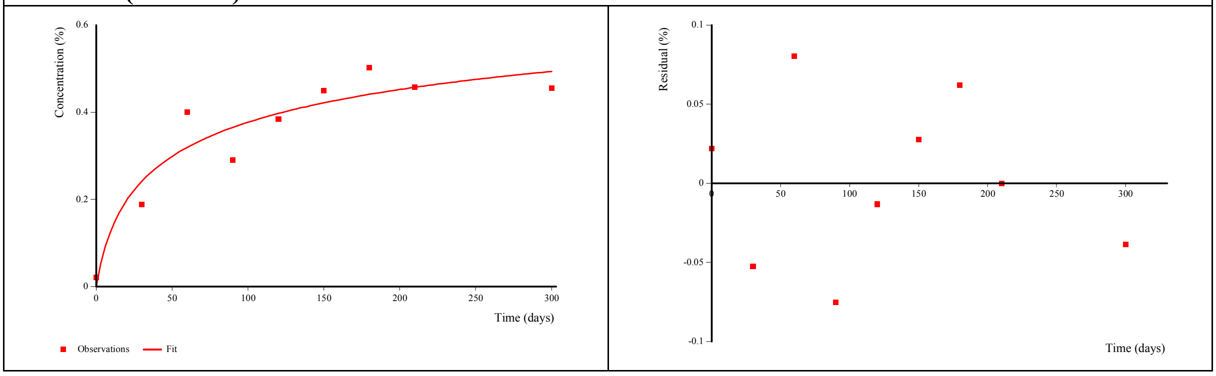


Figure B.8.1-31: Visual fit of the degradation of DCPMU at the field trial Maassen (FOMC, kinetic re-evaluation by the RMS)

DCPMU (Monheim)

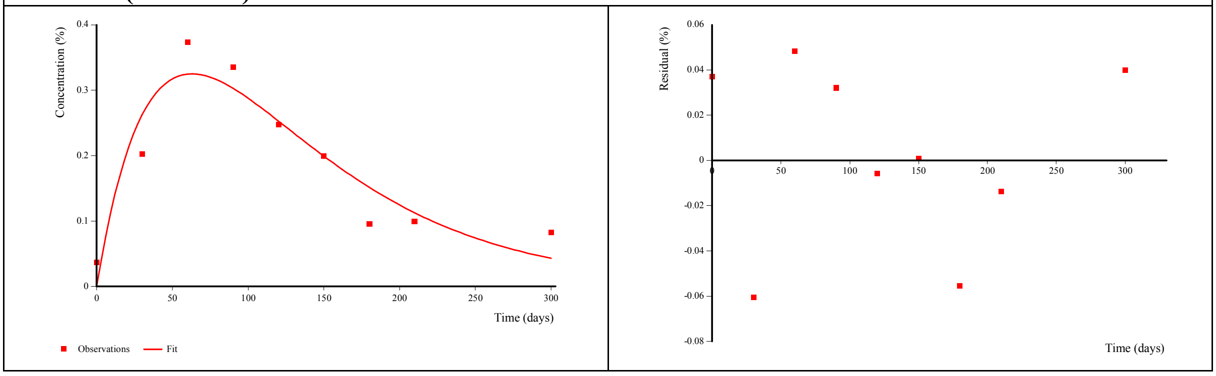


Figure B.8.1-32: **Visual fit of the degradation of DCPMU at the field trial Monheim (SFO, kinetic re-evaluation by the RMS)**

DCPMU (Swisttal)

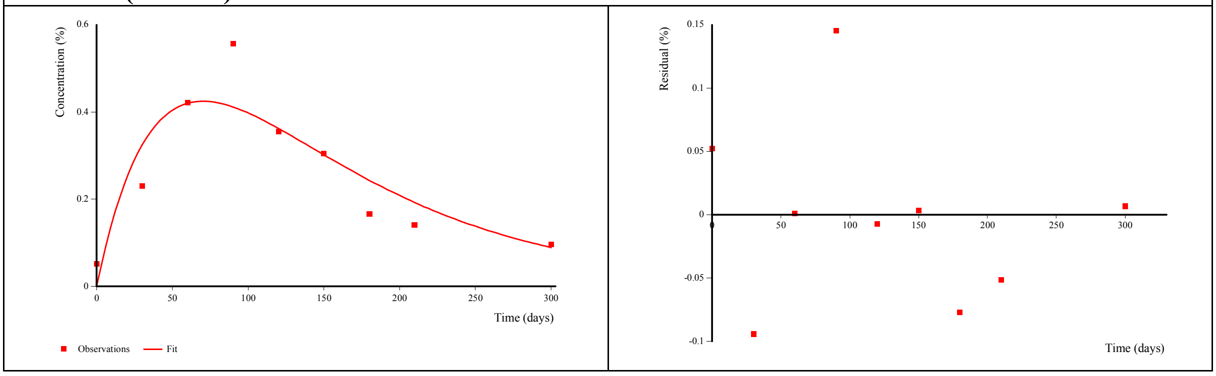


Figure B.8.1-33: **Visual fit of the degradation of DCPMU at the field trial Swisttal (SFO, kinetic re-evaluation by the RMS)**

The kinetic evaluation resulted in three field trials with acceptable visual fits and sufficiently low X^2 values (<15 %), namely Albig, Kirchlauter and Maasen (Table B.8.1-85, Figure B.8.1-28, Figure B.8.1-30, Figure B.8.1-31). However, these evaluations are critical, because no significant decrease in concentration of DCPMU can be observed by the end of the studies. The degradation rates modelled are therefore only derived from that degradation, which occurs simultaneously to formation. This procedure contains high inaccuracies. Particularly at Maasen field trial, degradation of the parent diuron stagnates from day 90 on at >50 % of the initial concentration. Therefore, it cannot be predicted how much DCPMU will be formed after the end of the study. The DT_{50} values of DCPMU from these studies, 54.1 days (Albig), 132 days (Kirchlauter) and >10,000 days (Maasen), are only acceptable as persistence trigger and to fulfil the data requirements for metabolites with DT_{50} >60 days in laboratory studies (EU regulation No. 283/2013, 7.1.2.2.1. (a)). For PEC modelling of DCPMU, data from laboratory studies were used.

The kinetic evaluation of the field trials Burscheid, Monheim and Swisttal are not acceptable at all because of high X^2 values (>15 %) and poor visual fits (Table B.8.1-85, Figure B.8.1-29, Figure B.8.1-32, Figure B.8.1-33). In all of the three cases phases with stagnating degradation are recognisable by the end of the studies, but not considered by the visual fits, which could yield too short DT_{50} values. Data derived from these kinetic evaluations confirmed this assumption, as DT_{50} values were 16.4 days (Burscheid), 33.0 days (Monheim) and 33.2 days (Swisttal) and therefore significantly lower than those from the field trials Albig, Kirchlauter and Maasen.

As a consequence, the results from the field trials Burscheid, Monheim and Swisttal for DCPMU are not listed in the LoEP.

KCA 7.1.2.2.1/6– Drechsler et al, 2016 (new studies)

Author:	Drechsler, S. Klein, C. Lobe, I.
Title:	Assessment of the normalisation of the dissipation rate of diuron determined in a field dissipation study to reference FOCUS conditions and its relevance on environmental fate modelling
Date:	01.03.2016
Doc ID:	782-001
Guidelines:	FOCUS (2011, 2006), EFSA (2014)
GLP:	No, not applicable
Validity:	Not acceptable

Author:	Drechsler, S. Klein, C.
Title:	Raw data to assessment of the normalisation of the dissipation rate of diuron determined in a field dissipation study to reference FOCUS conditions and its relevance on environmental fate modelling
Date:	01.03.2016
Doc ID:	782-009
Guidelines:	-
GLP:	No, not applicable
Validity:	Not acceptable

Material and Methods

In this assessment, temperature and moisture normalised $\mathrm{DegT}_{50,\mathrm{matrix}}$ values of diuron from the field dissipation study Pogány, 1993 were derived according to EFSA 2014 (EFSA Journal 2014;12(5):3662). For the kinetic evaluation of non-normalised values for persistence assessment and $\mathrm{PEC}_{\mathrm{soil}}$ calculations please refer to KCA 7.1.2.2.1/5.

The normalisation procedure followed the recommendations of the FOCUS kinetic guidance (2006/2011) using the time-step normalisation approach. Five of the six field sites, Burscheid, Albig, Kirchlauter, Swisttal and Monheim, were included in the normalisation. Soil moisture and soil temperature had not been measured in any of the field trials. Therefore daily values of these parameters were modelled by PEARL 4.4.4 using the Makkink approach. Weather data from the nearest weather station of the DWD (Deutscher Wetterdienst) were ordered and used as input parameter for the PEARL 4.4.4 model. Additionally, PEARL 4.4.4 requires the input of the Van Genuchten-Mualem parameters like saturated water content $\mathrm{Theta}_{\mathrm{SAT}}$ (θs), residual water content $\mathrm{Theta}_{\mathrm{RES}}$ (θr), saturated conductivity $\mathrm{K}_{\mathrm{SAT}}$ (Ks), reciprocal of air entry value under dry conditions $\mathrm{Alpha}_{\mathrm{Dry}}$ (αd), reciprocal of air entry value under wet conditions $\mathrm{Alpha}_{\mathrm{WET}}$ (αw), empirical parameter in hydraulic conductivity function Lambda (λ) and empirical parameter in Van Genuchten equation n (-). These parameters were estimated based on the soil characteristic data with the program Rosetta 1.2. Rosetta is a software package implementing pedotransfer functions. The parameters $\mathrm{Alpha}_{\mathrm{DRY}}$ (applies to the main drying curve of the retention curve) and $\mathrm{Alpha}_{\mathrm{WET}}$ (applies to the main wetting curve) were set to be equal as hysteresis was not simulated in agreement with conditions recommended by FOCUS scenarios.

The normalisation was performed via correction factors based on differences between modelled soil moisture and soil temperature values and reference soil moisture of 10 kPa (pF 2) and soil temperature of 20 °C conditions on a daily basis, as recommended by FOCUS.

To obtain $\mathrm{DegT}_{50,\mathrm{matrix}}$ values according to the EFSA (2014) guidance, residues sampled before the first 10 mm rain had fallen, were eliminated from the normalised data set. With this new data set, kinetic calculations were conducted with SFO using the normalised residue values of the study. SFO was considered appropriate for all field trials included (see KCA 7.1.2.2.1/5).

Results and Discussion

The derived $\mathrm{DegT}_{50,\mathrm{matrix}}$ values of diuron are presented in Table B.8.1-86. Furthermore it was tested if the field $\mathrm{DegT}_{50,\mathrm{matrix}}$ values are significantly shorter than the laboratory $\mathrm{DegT}_{50,\mathrm{matrix}}$ values using the EFSA Endpoint Selector (EFSA, 2014). As the field $\mathrm{DegT}_{50,\ \mathrm{matrix}}$ values were significantly shorter and five field $DegT_{50,matrix}$ values of Diuron are available, the geometric mean of 46.5 days was considered to be the adequate DT_{50} for modelling purposes.

Table B.8.1-86 Summary of $DegT_{50,matrix}$ values of diuron for modelling purposes

Field trial	**Burscheid**	**Albig**	**Kirchlauter**	**Swisttal**	**Monheim**
Kinetic model	SFO	SFO	SFO	SFO	SFO
$DegT_{50,matrix}$ [d]	27.7	99.4	74.5	27.1	39.1
X^2	24.4	21.7	6.8	15.9	20.0

In a next step it was tested if the field $DegT_{50,matrix}$ values were significantly shorter than the laboratory $DegT_{50,matrix}$ values using the EFSA Endpoint Selector (EFSA, 2014). According to the Student’s t-test, the five field $DegT_{50,\ matrix}$ values were significantly shorter than the laboratory studies. Thus, a geometric mean of the five field $DegT_{50,matrix}$ values was calculated to be 46.5 days and considered as the adequate DT_{50} for modelling purposes.

Conclusion

This newly submitted study was not considered acceptable by the RMS. As described in KCA 7.1.2.2.1/4 and KCA 7.1.2.2.1/5 the raw data used (Pogany 1993) were only considered acceptable for persistence calculations, since diuron was found in the deepest sampled soil layer of four of the six field trials. Thus, no valid $DegT_{50,matrix}$ values could be derived from these data. As a consequence, the RMS cannot accept the kinetic re-evaluation performed in this study and the use of the derived normalised DT_{50} values for modelling purposes. For PEC_{gw} and $PEC_{sw/sed}$ modelling laboratory data was used (please refer to KCA 7.1.2.1.1).

B.8.1.2 Adsorption and desorption in soil

B.8.1.2.1 Adsorption and desorption of the active substance

KCA 7.1.3.1.1/1 – Bramble et al, 1998a (study evaluated in the DAR, 2003)

Author:	Bramble Jr., F.Q. Behmke, F.D. Norwood, G.I.
Title:	Batch equilibrium (adsorption/desorption) of ^{14}C-diuron, fenuron, and N’-(3’chlorophenyl)-N,N-dimethylurea on soil
Date:	06.02.1998
Doc ID:	AMR 4584-97
Guidelines:	U. S. Environmental Protection Agency, Pesticide Assessment Guidelines, Subdivision N, Chemistry; Environmental Fate 163-1;Leaching and Adsorption/Desorption Studies
GLP:	Yes
Validity:	Not acceptable

Material and Methods

In this study the adsorption and desorption characteristics of diuron, fenuron and N’-(3’chlorophenyl)-N,N-dimethylurea (mCPDMU) were studied in various soil types yielding the re-registration of diuron in the USA. The diuron test substance was ^{14}C radiolabelled, whereas the metabolites fenuron and mCPDMU were not labelled. The study was conducted with duplicate samples at ambient room temperature (22 ±3 °C) and concentrations ranging from 0.1 to 5 µg/L. The five test soils used are characterised in Table B.8.1-87. Results of fenuron are not shown, because it was not shown to be a major metabolite of diuron.

Table B.8.1-87 Soil characteristics

	Type	Origin	Texture (%)				pH	CEC
			sand	silt	clay	O.M.		
Myaka	Sand	Bradenton, FL	91.2	4.0	4.8	0.5	6.7	2.9
Donna	Sandy clay loam	Donna, TX	46.0	25.6	28.4	0.8	8.0	17.3
Chino	Loam	Madera, CA	43.2	46.0	10.8	1.4	8.2	20.5
Barclay	Silty clay loam	Newark, DE	10.0	60.0	30.0	2.9	7.1	8.9
Keyport	Silt loam	Chesapeake, MD	20.0	66.0	14.0	7.7	4.1	1.5

Three soil/solution ratio (1:15, 1:6 and 1:1) were tested to find the optimal soil-to-solution ratio for diuron and mCPDMU. The most appropriate soil/solution ratio turned out to be 1:15 for diuron and 1:6 for mCPDMU, respectively. The equilibration time for both test substances was determined and yielded 12 hours. The prepared test solutions were analysed with LSC for actual concentrations. HPLC with UV and radiochemical detection were used to analyse test solutions and aqueous test sample fractions in order to examine the purity of the test substance and to monitor degradation in the test sample solution. Soil combustion and subsequent analyses were performed after the desorption step for mass balancing.

Screening experiments were performed at a single concentration (2 ± 0.5 µg/L) to establish the percentage adsorbed and determine adsorption and desorption distribution coefficients (K_d, K_{OC}, K_{OM}) (OECD 106, Tier 2). Isotherm experiments were performed for each test substance with Chino, Barclay and Keyport soils only. Four concentrations (0.1, 0.5, 1 and 5 µg/mL) were tested to provide data for adsorption and desorption Freundlich isotherms. Freundlich distribution coefficients (K_F, K_{FOC}, K_{FOM}) and regression constants (1/n) were derived from these data according to OECD 106 (Tier 3).

Results and Discussion

Table B.8.1-88 and Table B.8.1-89 summarise the results of the screening and isotherm sorption experiments for diuron. For results from tests with the metabolite mCPDMU please refer to KCA 7.1.3.1.2/3.

Table B.8.1-88 Results from screening experiments of adsorption/desorption with diuron

Test soil		% OM	Screening (1 conc. 2 ± 0.5 µg/mL)					
			Adsorption			Desorption		
			K_d	K_{OC}	K_{OM}	K_d	K_{OC}	K_{OM}
Myaka	Sand	0.5	1.7	578	335	nc	nc	nc
Donna	Sandy clay loam	0.8	1.7	366	212	nc	nc	nc
Chino	Loam	1.4	14	1750	1015	5.5	681	395
Barclay	Silty clay loam	2.9	6.9	410	238	2.4	145	84
Keyport	Silt loam	7.7	27	607	352	14	315	183

nc: not calculated; -: not tested

Table B.8.1-89 Results from Freundlich isotherm experiments of adsorption/desorption with diuron

Test soil		% OM	Freundlich Isotherm (0.1-5.0 µg/mL)							
			Adsorption				Desorption			
			K_F	1/n	K_{FOC}	K_{FOM}	K_F	1/n	K_{FOC}	K_{FOM}
Myaka	Sand	0.5	-	-	-	-	-	-	-	-
Donna	Sandy clay loam	0.8	-	-	-	-	-	-	-	-
Chino	Loam	1.4	14	0.85	1666	967	6.2	0.8	769	446
Barclay	Silty clay loam	2.9	7.9	0.85	468	271	3.9	0.83	230	134
Keyport	Silt loam	7.7	28	0.93	626	363	16	0.88	354	206

nc: not calculated; -: not tested

The total recovery range for diuron was 99-102 % in the five test soils. Screening tests revealed that the adsorption was not significant (<10 %) on Myaka and Donna soils and no Freundlich isotherm experiments were conducted with these soils. However, the K_{OC} values were rather low, but in the same range as the other test soils. The results of the Freundlich isotherm tests (K_{FOC} = 468-1666) indicate moderate to strong soil adsorption and, consequently, medium to low potential for mobility. Regression constants (1/n) of the Freundlich isotherms were less than 1, indicating that the sorption coefficient (K_d) varied inversely with concentration along the isotherms.

Conclusions

The study followed EFA guideline and is in principle in line with OECD 106 and was considered acceptable in the previous EU evaluation. However, this study was not considered acceptable in the renewal of the approval due to the following issues.

The two soils Myaka and Donna had to be excluded in the study, because the adsorption to soil was < 10 % in the screening test, while OECD 106 requires a minimum adsorption of 20 % to derive valid Freundlich isotherms. Among other factors like low organic carbon and high sand content, the soil/solution ratio was chosen too low. Inaccurate results could have been avoided by increasing the soil/solution ratio or applying the direct method, which includes the analysis of water and soil to determine the adsorption percentage. However, the soil characteristics of Myaka and Donna correspond with natural soils under agricultural use. Excluding these soils would bias the study results to a best case situation since only the higher adsorption characteristics of the remaining three soils would be considered. To avoid this the RMS decided to exclude the entire study. The newly submitted adsorption study by Derz (2009) (KCA 7.1.3.1.1/2) contains a sufficient number of data points characterising the adsorption behaviour of diuron. The study was considered acceptable and covers a sufficiently wide range of soil properties regarding pH value, OC and sand content.

KCA 7.1.3.1.1/2 – Derz, 2009 (new study)

Author:	Derz, K.
Title:	Determination of the adsorption/ desorption of preventol A6
Date:	01.10.2009
Doc ID:	LAN-001/7-13 (731-001)
Guidelines:	OECD No. 106
GLP:	Yes
Validity:	Acceptable

Material and Methods

The adsorption and desorption behaviour of diuron was studied according to OECD 106 with five top soils. A summary of characteristics of the soils used is presented in Table B.8.1-90.

Table B.8.1-90 Soil characteristics

Soil	Soil type (USDA)	Sand [%]	Silt [%]	Clay [%]	OC [%]	pH ($CaCl_2$)	CEC [meq/100 g]
RefeSol 01-A	Loamy sand	67	27	6	0.99	5.5	3.7
RefeSol 03-G	Silt loam	16	54	30	3.52	5.6	12.6
RefeSol 05-G	Silt loam	16	62	22	2.79	4.7	10.0
RefeSol 06-A	Silty clay loam	11	45	44	2.10	7.2	24.5
LUFA 2.3	Loamy sand	59	32	9	0.98	6.4	8.0

Due to the fact that diuron is comparatively poorly soluble in aqueous solutions, all stock or application solutions were prepared in the organic solvent acetonitrile, which content did not exceed 0.1 %. Soil aliquots were mixed with 0.01 N $CaCl_2$-solution spiked with a variable diuron concentration in a certain soil:solution ratio and agitated for 12, 24, 72 or 96 hours at 20 °C. The aqueous supernatents were analysed on diuron and mCPDMU concentrations with HPLC (indirect method). Blank (without diuron) and control samples (without soil) were included in the test. Mass balances were calculated by additional soil combustion after desorption. In order to determine the optimal soil to solution ratio, ratios of 1:25, 1:16.7 and 1:10 were tested using soils RefeSol 03 (high OC content) and RefeSol 06-A (high clay content) at a nominal start concentration of 200 µg/L. For the screening test, an optimal soil:solution ratio of 1:10 was chosen and all soils were tested with a fixed concentration of approximately 200 µg/L. For the Freundlich isotherm experiments, all soils with each five concentrations of 0.2 mg/L, 0.44 mg/L, 0.97 mg/L, 2.13 mg/L and 4.69 mg/L in the optimum soil:solution ratio of 1:10 were tested. Adsorption and desorption isotherms were determined in the five soils via linear regression analysis using the logarithms of concentration dependent sorption data (empirical Freundlich Isotherms). Sorption coefficients (K_F) were normalised according to the organic carbon content (K_{FOC}) to address the key role of organic matter for adsorption affinity.

Results and Discussion

The detected amount of diuron in the control samples remained stable in the range of 97.0 % to 105.5 % for the entire test period. This indicates that there was hardly any adsorption to the test vessels' surface after 48 h, 72 h and 96 h of agitation, respectively. According to the mass balance test in the two soils the recovery of diuron after 48 hours of equilibration was 93.7 % for soil RefeSol 03-G and 90.5 % for the soil RefeSol 06-A (mean values). It can be concluded that diuron is mainly stable under the applied test conditions.

In the screening test, adsorption equilibrium was achieved after 24 h to 48 h with an adsorbed diuron fraction ranging between 43.1 % and 66.5 %. About 25.6 % to 41.2 % of the adsorbed diuron was desorbed after 48 hours. Desorption rates were almost independent from agitation time. The results of the screening test of five soils are summarised in Table B.8.1-91.

Table B.8.1-91 Fractions adsorbed/desorbed and results of the screening test after 48 h

Soil	Soil type (DIN)	Adsorption			Desorption		
		A [%]	$K_{d(ads)}$ [cm³/g]	$K_{oc(ads)}$ [cm³/g]	D [%]	$K_{d(des)}$ [cm³/g]	$K_{oc(des)}$ [cm³/g]
RefeSol 01-A	Loamy sand	43.1	7.7	774	41.2	9.3	943
RefeSol 03-G	Silt loam	66.5	20.4	579	25.6	23.9	678
RefeSol 05-G	Silt loam	59.5	15.1	543	34.3	13.8	493
RefeSol 06-A	Silty clay loam	52.6	11.5	548	36.2	13.9	660
LUFA 2.3	Loamy sand	46.9	9.4	959	29.5	14.7	1497

The Freundlich isotherm parameters for adsorption and desorption are listed in Table B.8.1-92. The adsorption coefficients (K_f) for diuron ranged from 4.48 to 12.52 mL/g, corresponding to a factor of about 3, in the five tested soils. K_{foc} values ranged from 293 to 504 mL/g. A significant correlation between adsorption and organic carbon content (OC) of the soils was observed (R^2 =0.9348).

Desorption coefficients (K_f) between 7.8 and 15.5 mL/g were determined in the tested soils, K_{foc} values ranged between 370 and 934 mL/g. For the calculation of modelling endpoints LUFA 2.3 was excluded by the applicant, because 1/n was < 0.7.

Table B.8.1-92 Freundlich adsorption /desorption isotherm data of diuron

Soil	Adsorption				Desorption			
	K_f^{ads} [mL/g]	K_{foc}^{ads} [mL/g]	1/n	R^2	K_f^{des} [mL/g]	K_{foc}^{des} [mL/g]	1/n	R^2
RefeSol 01-A	4.99	504	0.786	0.996	7.88	796	0.834	0.986
RefeSol 03-G	12.52	356	0.843	1.000	15.52	441	0.831	0.997
RefeSol 05-G	10.10	362	0.893	0.999	11.78	422	0.901	0.998
RefeSol 06-A	6.15	293	0.835	0.995	7.76	370	0.813	0.997
LUFA 2.3	4.48	458	0.670	0.993	9.15	934	0.781	0.994

Conclusion

This newly submitted study followed guideline OECD 106 and was considered acceptable by the

RMS, although we disagree with the applicant regarding the exclusion of LUFA 2.3 because of the 1/n value of <0.7. EFSA states that 1/n usually ranges between 0.7 and 1.1 and we agree that values exceeding this range require a closer examination. The Freundlich isotherm was very well fitted (R^2=0.9935) and 1/n was still close to 0.7, so we consider the value as acceptable and included it into the LoEP.

B.8.1.2.2 Adsorption and desorption of metabolites, breakdown and reaction products

KCA 7.1.3.1.2/1 – Brumhard et al, 1998 (study evaluated in the DAR, 2003)

Author:	Brumhard, B. König, T. Sommer, HR.
Title:	Adsorption/Desorption of Desmethyl-Diuron on Different Soils
Date:	19.06.1998
Doc ID:	report No.: MR 575/96
Guidelines:	U. S. Environmental Protection Agency, Pesticide Assessment Guidelines, Subdivision N, Chemistry; Environmental Fate 163-1; Leaching and Adsorption/Desorption Studies. OECD (1981): Organisation for Economic Co-Operation and Development (Hrsg.): Guideline for testing of chemicals, No. 106, Paris, 1-23.
GLP:	yes
Validity:	Acceptable

Material and Methods

The adsorption and desorption behaviour of the metabolite DCPMU of diuron was investigated in four soils at four concentrations. The physical and chemical characteristics of the test soils are provided in Table B.8.1-93.

Table B.8.1-93 Soil characteristics

	BBA 2.1 sand	Borstel loamy sand	Höfchen “im Tal” silt loam	Tonboden clay
Texture analysis				
Sand (2000-50 µm)	89.4 %	77.9 %	3.6 %	15.0 %
Silt (< 50-2 µm)	10.5 %	18.5 %	80.8 %	42.3 %
Clay (< 2 µm)	0.1 %	3.6 %	15.6 %	42.7 %
pH-value				
in H_2O	5.9	5.9	6.0	7.6
in $CaCl_2$	5.3	6.0	5.8	7.4
% organic C	0.7	0.69	2.4	0.64
CEC (meq/100 g)	5.0	5.0	10.0	21.1
Particle density (g/mL)	2.59	2.58	2.5	2.08

Batch equilibrium tests in accordance with OECD 106 were proceeded and the aqueous phase of each sample were analysed on DCPMU concentration after centrifugation, the adsorbed fraction was determined via mass balance calculations (indirect method). Instrumental analytics were conducted using HPLC with UV detection. For mass balancing, the soil was combusted with subsequent analyses after desorption.

Preliminary tests were performed to evaluate DCPMU stability, the ideal soil/solution ratio and the equilibrium time for further testing. Based on these, experiments in the equilibrium were performed with varying DCPMU concentrations (50-5000 µg/L) to calculate isotherms according to the empirical Freundlich equation and the related parameters (K_f, K_{foc}, 1/n) for adsorption and desorption.

Results and Discussion

Table B.8.1-94 and Table B.8.1-95 summarise the Freundlich adsorption and desorption parameters, respectively, for the metabolite DCPMU of diuron.

Table B.8.1-94 Adsorption parameters of DCPMU for Freundlich isotherm

Soil	K_F (mL/g)	1/n	K_{foc} (mL/g)
BBA 2.1, sand	3.5	0.7629	498
Borstel, loamy sand	9.4	0.7561	1358
Höfchen “im Tal”, silt loam	15.6	0.7565	651
Tonboden, clay	4.8	0.7390	744

Table B.8.1-95 Desorption parameters of DCPMU for Freundlich isotherm

Soil	K_F (mL/g)	1/n	K_{foc} (mL/g)
BBA 2.1, sand	5.5	0.8001	786
Borstel, loamy sand	14.0	0.7953	2030
Höfchen “im Tal”, silt loam	22.3	0.7747	929
Tonboden, clay	7.7	0.7871	1205

The adsorption process in the applied concentration range can be accurately described with the Freundlich equation for all test soils. The percentage of adsorption of test substance varied between 40.6 % and 93.6 % of the applied amount depending on soil type and concentration. Running desorption with 0.01 M $CaCl_2$ solution, 4.2 % to 40.5 % of adsorbed DCPMU was desorbed.

Conclusion

The study was evaluated in for previous EU approval of diuron and was considered acceptable. The study followed OECD 106 and after re-evaluation the RMS still considers it acceptable.

KCA 7.1.3.1.2/2 – Heintze, 2002 (study evaluated in monograph, 2003)

Author:	Heintze, A.
Title:	Determination of the Adsorption/desorption behaviour of DCPU in four different soils
Date:	15.03.2002
Doc ID:	20001409/01-PCAD
Guidelines:	OECD (1981): Organisation for Economic Co-Operation and Development (Hrsg.): Guideline for testing of chemicals, No. 106, Paris, 1-23. SETAC-Europe procedures for assessing the environmental fate and ecotoxicity of pesticides, March 1995.
GLP:	yes
Validity:	yes

Material and Methods

The adsorption and desorption properties of the metabolite DCPU of diuron were determined in five soils, following OECD guideline 106 and SETAC requirements. The physical and chemical characteristics of the test soils are provided in Table B.8.1-96.

Table B.8.1-96 Soil characteristics

Soil	BBA 2.1	BBA 2.2	BBA 2.3	“Höfchen im Tal”	BBA S6
Max. water capacity (%)	22.9	39.9	30.3	63.1	43.7

CEC (mval/100g)	3.64	9.97	8.51	15	16.3
Organic C (%)	0.49	1.48	0.76	2.11	1.89
pH (0.01 M $CaCl_2$)	5.7	6.0	7.0	6.7	6.9
Clay (%)	1.3	4.2	7.8	10.3	42.9
Silt (%)	8.9	21.0	27.8	81.5	35.4
Sand (%)	89.8	74.8	64.5	8.2	21.7
Soil texture USDA	Sand	Silty sand	Silty sand	Silt	Clay

Batch experiments were done, the aqueous phases were analysed on DCPU concentrations and the adsorbed fraction was determined via mass balance calculations (indirect method). The analyses were proceeded with HPLC with UV detection. Soil combustion and subsequent analyses were performed for mass balancing. Preliminary tests were performed to figure out the ideal soil:solution ratio for further tests. Adsorption and desorption distribution coefficients and the adsorption/desorption equilibration time were determined using a fixed DCPU concentration (screening test). Based on this, Freundlich Isotherm experiments were performed for adsorption and desorption according to OECD 106.

Results and Discussion

Table B.8.1-97 contains the adsorption and desorption distribution coefficients from the screening test, Table B.8.1-98 summarises the results from the Freundlich isotherm test.

Table B.8.1-97 Determination of DCPU's sorption/desorption distribution coefficients

Soil	**BBA 2.1**	**BBA 2.2**	**BBA 2.3**	**"Höfchen im Tal"**	**BBA S6**
Organic C (%)	0.49	1.48	0.76	2.11	1.89
Adsorption kinetics					
Adsorption (%)	55.3	52.0	44.7	49.8	51.8
kd (cm^3/g)	3.59	10.47	7.81	9.59	10.39
K_{OC} (cm^3/g)	733	707	1028	455	550
log k_{OC}	2.87	2.85	3.01	2.66	2.74
Desorption kinetics					
Adsorption (%)	63.2	59.6	62	60.2	59.9
Desorption (%)	32.1	37.8	32.8	38	34.8
k_d^{des} (cm^3/g)	4.98	14.26	15.77	14.62	14.44
k_{des} (cm^3/g)	1.37	5.87	4.72	5.92	5.16
$K_{d,OC}^{des}$ (cm^3/g)	1016	964	2075	693	764
log $k_{d,OC}^{des}$	3.01	2.98	3.32	2.84	2.88

Table B.8.1-98 Kinetic investigations of DCPU's Freundlich isotherm coefficients

Soil	**BBA 2.1**	**BBA 2.2**	**BBA 2.3**	**"Höfchen im Tal"**	**BBA S6**
Organic C (%)	0.49	1.48	0.76	2.11	1.89
Adsorption isotherms					
1/n	0.796	0.789	0.676	0.757	0.787
K_F^{ads} ($\mu g^{1-1/n}(cm^3)^{1/n}/g$)	4.22	11.38	8.95	11.12	12.02
K_{FOC}^{ads} ($\mu g^{1-1/n}(cm^3)^{1/n}/g$)	861	769	1178	527	636
$K_F^{ads}/(1/n)$ ($\mu g^{1-1/n}(cm^3)^{1/n}/g$)	5.49	14.42	13.24	14.69	15.27
Desorption isotherms					
1/n	0.796	0.778	0.662	0.736	0.781
K_F^{des} ($\mu g^{1-1/n}(cm^3)^{1/n}/g$)	5.07	14.72	11.72	13.9	14.96
K_{FOC}^{des} ($\mu g^{1-1/n}(cm^3)^{1/n}/g$)	1035	995	1542	659	792
$K_F^{des}/(1/n)$ ($\mu g^{1-1/n}(cm^3)^{1/n}/g$)	6.59	18.92	17.7	18.89	19.15

The adsorption parameters of DCPU in the test soils indicate a generally high adsorption which depends on the amount of organic carbon (BBA 2.1, BBA 2.2 and "Höfchen im Tal"), but also on other factors like CEC, silt content or pH value. The latter is shown by BBA 2.3 results, which has the highest K_{oc} at 2-3 fold lower organic carbon than determined in BBA 2.2 and "Höfchen im Tal".
The kinetic evaluations indicate that the differences in adsorption properties were not determined by reaction speed. The equilibrium of adsorption and desorption was reached within 48 hours in all soils.
The adsorption was regarded reversible, because the distribution coefficients calculated from adsorption and desorption were very similar for all soils tested. The same applies for the Freundlich isotherms for adsorption and desorption.

Conclusion

This study was first evaluated in previous EU approval and considered acceptable. The study followed OECD 106 and is still considered acceptable for EU re-approval of diuron. However, the RMS disagrees with the applicant regarding the exclusion of BBA 2.3 because of the 1/n value of <0.7. EFSA states that 1/n usually ranges between 0.7 and 1.1 and we agree that values exceeding this range require a closer examination. The Freundlich isotherm was very well fitted (R^2=0.9985) and 1/n is still close to 0.7, so the RMS considered the value as acceptable and included it into the LoEP.

KCA 7.1.3.1.2/3 – Bramble et al, 1998b (study evaluated in the DAR, 2003)

Author:	Bramble Jr. F.Q. Behmke, F.D. Norwood, G.I.
Title:	Batch equilibrium (adsorption/desorption) of ^{14}C-diuron, fenuron, and N'-(3'chlorophenyl)-N,N-dimethylurea on soil
Date:	06.02.1998
Doc ID:	AMR 4584-97
Guidelines:	U. S. Environmental Protection Agency, Pesticide Assessment Guidelines, Subdivision N, Chemistry; Environmental Fate 163-1;Leaching and Adsorption/Desorption Studies
GLP:	yes
Validity:	no

Material and Methods

The experiments were performed in analogy to KCA 7.1.3.1.1/1. A soil/solution ratio of 1:6 was chosen for the tests with mCPDMU.

Results and Discussion

Table B.8.1-99 and Table B.8.1-100 summarise the results of the screening test and the Freundlich isotherm experiments for mCPDMU.

Table B.8.1-99 Results from screening experiments of adsorption/desorption with mCPDMU

Test soil		**% OM**	**Screening (1 conc. 2 ± 0.5 µg/mL)**					
			Adsorption			**Desorption**		
			K_d	K_{OC}	**K_{OM}**	**K_d**	**K_{OC}**	**K_{OM}**
Myaka	Sand	0.5	0.41	142	83	Nc	Nc	Nc
Donna	Sandy clay loam	0.8	0.37	80	46	Nc	Nc	Nc
Chino	Loam	1.4	2.6	323	188	0.64	79	46
Barclay	Silty clay loam	2.9	1.9	113	65	0.65	39	22
Keyport	Silt loam	7.7	1.8	40	23	0.53	12	6.8

Nc: not calculated

Table B.8.1-100 Results from Freundlich isotherm experiments of adsorption/desorption with mCPDMU

Test soil		**% OM**	**Freundlich Isotherm (0.1-5.0 µg/mL)**							
			Adsorption				**Desorption**			
			K_F	**1/n**	**K_{F_OC}**	**K_{F_OM}**	**K_F**	**1/n**	**K_{F_OC}**	**K_{F_OM}**
Myaka	Sand	0.5	-	-	-	-	-	-	-	-
Donna	Sandy clay loam	0.8	-	-	-	-	-	-	-	-
Chino	Loam	1.4	3.4	0.74	418	242	-	-	-	-
Barclay	Silty clay loam	2.9	2.3	0.69	139	80	-	-	-	-
Keyport	Silt loam	7.7	8.0	0.78	179	104	-	-	-	-

-: not tested

The total recovery range for diuron was 96-102 % in the five test soils. Screening tests revealed that the adsorption was not significant (<10 %) on Myaka and Donna soils and no Freundlich isotherm experiments were conducted with these soils. However, the K_{OC} values were rather low, but in the same range as the other test soils. The results of the Freundlich isotherm tests (K_{FOC} = 139-418) indicate moderate to weak soil adsorption and, consequently, a moderate potential for mobility. Regression constants (1/n) of the Freundlich isotherms were less than 1, indicating that the sorption coefficient (K_d) varied inversely with concentration along the isotherms.

Conclusions

The study followed EFA guideline and is in principle in line with OECD 106 and was considered acceptable in the previous EU evaluation. However, this study was not considered acceptable in the renewal of the approval due to the following issues.
The two soils Myaka and Donna had to be excluded, because the adsorption to soil was <10 % in the screening test, while OECD 106 requires a minimum adsorption of 20 % to derive valid Freundlich isotherms. Among other factors like low organic carbon and high sand content, the soil/solution ratio was chosen too low. According to OECD 106 the product of soil/solution ratio * K_d allows the derivation of valid Freundlich parameters if it is above 0.1. For mCPDMU in Myaka and Donna test soils it yielded 0.07 and 0.06, respectively, and could therefore not be considered. However, the soil characteristics of Myaka and Donna correspond with natural soils under agricultural use. Excluding these soils would bias the study results to a best case situation since only the higher adsorption characteristics of the remaining three soils would be considered. To avoid this the RMS decided to exclude the entire study.

B.8.1.3 Mobility in soil

B.8.1.3.1 Column leaching studies

No study was submitted.

B.8.1.3.2 Lysimeter studies

KCA 7.1.4.2/1 – Bergstroem et al, 1996 (study evaluated in the DAR, 2003)

Author:	Bergstroem, L.B. Bramble Jr., F.Q. Aronsson, P.
Title:	Leaching of [phenyl(U)-^{14}C]diuron in Scandinavian soils using field lysimeters
Date:	04.03.1996
Doc ID:	AMR-2619-93
Guidelines:	Letter dated November 2, 1992 from the Danish Environmental Protection Agency: Journal no. M7042-0050, Reference JM/jep/11
GLP:	Yes
Validity:	Yes

Material and Methods

The mobility of the herbicide diuron and its main soil metabolites (DCPMU, DCPU, DCA) were studied under non-steady state flow conditions in two undisturbed sandy soils exposed to northern European climatic conditions. Two lysimeter cores were installed each in Nantuna (5 km from Uppsala, Sweden) and in Langaveka (10 km from Falkenberg, Sweden) with each a length of 1.18 m and an inside diameter of 0.295 m. The duration of the lysimeter tests were 26 month each with a total precipitation (including irrigation) of 1737 mm and an average temperature of 5.8 °C. Black currant bushes were planted on each lysimeter surface to simulate realistic agricultural conditions. The application of diuron was performed in April 1993 at two rates in the two parallel setups each, 2 kg and 4 kg as per ha, representing half (1X) and single (2X) recommended dose. Together with diuron, potassium bromide (KBr) was applied as a conservative tracer to investigate drainage characteristics during the experi-

mental period. All lysimeters received supplemental irrigation to simulate reasonable worst-case conditions with regard to pesticide leaching. The amount of leachate was measured, sampled and analysed. Potassium bromide was determined using adapted flow-injection analysis, radioactivity was detected with LSC and diuron and its metabolites were determined using HPLC with radiochemical detection (LOQ 0.05 µg/L).
The soil characteristics of the two lysimeter are summarised in Table B.8.1-101.

Table B.8.1-101 Soil characteristics

	Clay[a] (%)	Silt[a] (%)	Sand[a] (%)	USDA texture class	OM (%)	OC (%)	CEC (cmol^{c}/ kg)	Bulk dens. (g/cm^{3})	[b]$\theta_{1.0}$ (vol-%)	pH
Långaveka										
Topsoil	1.6	11.5	85.1	Loamy sand	0.9	0.5	3.7	1.48	-[c]	5.8
Subsoil	1.8	6.0	91.6	Sand	0.4	0.2	2.5	1.62	-	5.8
Nåntuna										
Topsoil	9.1	8.2	80.5	Sandy loam	1.1	0.6	-	1.43	17	7.4
Subsoil	0.0	4.6	95.4	Sand	1.0	0.6	-	1.46	6	-

[a] According to the USDA soil textural classes.
[b] Volumetric water content at a tension of 1 m water (estimated field capacity).
[c] Dashes indicate that no measurements were available.

Results and Discussion

Table B.8.1-102 summarises the amount of leachate for each lysimeter as well as the applied radioactivity detected in the leachate and in the soil by the end of the study.

Table B.8.1-102 Amount of leachate and applied radioactivity in leachate and soil of the Langaveka and Nantuna lysimeters at study end

Soil	Treatment	Leachate	Leachate	Soil	Total
	Rate	Vol. (L)	% AR[a]	% AR[a]	% AR[a]
Långaveka	2 kg/ha	40.5	0.7	44.5	45.2
Långaveka	4 kg/ha	45.8	0.6	57.7	58.3
Nåntuna	2 kg/ha	34.4	0.2	58.4	58.6
Nåntuna	4 kg/ha	42.6	0.6	61.9	62.5

[a] percent of the applied radioactivity

Table B.8.1-103 provides the mean concentrations of diuron, DCPMU and DCPU in the leachate. The mean was calculated using the accumulated substance after a certain time interval (1 year, 2 years, 26 months) related to the accumulated amount of leached water in the same time interval.

Table B.8.1-103 Mean concentrations calculated as accumulated substance/accumulated leached water. Calculations were performed by the Danish EPA.

Lysimeter, dose, period	Leachate (L)	Diuron (µg/L)	DCPMU (µg/L)	DCPU (µg/L)
Långaveka, 2 kg/ha				
After 1 year	11.85	0.090	0.132	0.038
After 2 years	31.22	0.042	0.056	0.015
After 26 months	40.37	0.033	0.043	0.011
Långaveka, 4 kg/ha				
After 1 year	17.05	0.357	0.174	0.008
After 2 years	29.59	0.245	0.119	0.005
After 26 months	38.13	0.191	0.093	0.004
Nåntuna, 2 kg/ha				
After 1 year	12.85	0.000	0.000	0.000
After 2 years	25.89	0.001	0.001	0.000

After 26 months	34.37	0.001	0.001	0.000
Nåntuna, 4 kg/ha				
After 1 year	17.29	0.275	0.274	0.096
After 2 years	34.01	0.189	0.158	0.065
After 26 months	42.59	0.155	0.127	0.052

Table B.8.1-104 summarises the concentrations of diuron and its metabolites DCA, DCPMU and DCPU in the lysimeter soils related to soil depth at the end of the study.

Table B.8.1-104 Concentrations of diuron and metabolites in soil at study end

Depth (cm)	**Diuron (µg/kg)**	**DCA (µg/kg)**	**DCPMU (µg/kg)**	**DCPU (µg/kg)**
Långaveka, 2 kg/ha				
0-5	522	54	700	31
5-10	251	13	159	10
10-105	< 50	< 50	< 50	< 50
Långaveka, 4 kg/ha				
0-5	695	83	1345	112
5-10	833	53	756	60
10-20	89	< 50	24	< 50
20-105	< 50	< 50	< 50	< 50
Nåntuna, 2 kg/ha				
0-5	294	51	763	52
5-10	44	60	285	25
10-105	< 50	< 50	< 50	< 50
Nåntuna, 4 kg/ha				
0-5	319	109	1065	63
5-10	81	28	571	57
10-20	15	9	52	2
20-105	< 50	< 50	< 50	< 50

For lysimeters treated with 2 kg as per ha at both locations, annual mean concentrations were below 0.1 µg/L for diuron and the metabolite DCPU. For the metabolite DCPMU, one annual mean concentrations exceeded 0.1 µg/L. The mean concentration after one year at Langaveka was determined to be 0.132 µg/L (Table B.8.1-103).

For lysimeters treated with 4 kg as/ha at both locations, diuron and its metabolite DCPMU were found in the leachate in annual mean concentrations above 0.1 µg/L after the first and the second year. In Langaveka concentrations of diuron were 0.357 µg/L in the first and 0.245 µg/L in the second year. At Nantuna the respective concentrations of diuron were 0.275 and 0.189 µg/L. The metabolite DCPMU were found in slightly lower concentrations, 0.174 and 0.119 µg/L at Langaveka and 0.274 and 0.158 µg/L at Nantuna in year 1 and 2, respectively. DCPU was detected <0.1 µg/L in the leachate at both locations and in both years, whereby in Langaveka the concentrations were clearly below and in Nantuna very close to 0.1 µg/L (Table B.8.1-103).

The highest concentrations in a single leachate sample were 12.5 µg/L diuron, 6.77 µg/L DCPMU and 0.82 µg/L DCPU found in March 1994 at Langaveka after application of 4 kg/ha diuron.

Conclusion

The study was already evaluated in the previous RAR (2003) and considered acceptable. At this re-evaluation the RMS still considers the study as acceptable.

The locations and soils used might reflect worst case conditions due to low temperature, high precipitation rates, high sand and low organic carbon content, but they also represent natural and agriculturally used soils. Thus, the study shows that there is leaching of diuron and DCPMU under particular conditions and with application rates recommended at the time the study was performed. In experiments with the higher application rate of 4 kg/ha, diuron and DCPMU continuously exceeded the trigger of 0.1 µg/L in the leachate, whereas DCPU concentration remained <0.1 µg/L throughout the study. For the tests with the lower application rate of 2 kg/ha, which is similar to the maximum application rate of 1.5 kg/ha of the representative uses in the current re-evaluation, only DCPMU exceeds the trigger value in one of the lysimeters.

B.8.1.3.3 Field leaching studies

No study was submitted.

B.8.2 Fate and behaviour in water and sediment

The hydrolytic degradation of diuron was investigated in two laboratory studies submitted already for first EU approval:

- Williams, 1995
- Hawkins et al, 1988

The direct photochemical degradation of diuron was also investigated in two laboratory studies submitted already for first EU approval:

- Hellpointer, 1991
- Hawkins et al, 1989

No study on the ‘ready biodegradability’ of diuron is available.

For the renewal of the EU approval, one laboratory soil study on the aerobic mineralistaion of diuron in surface water was submitted:

- Swales, 2016

Besides, a study on the fate of diuron in water/sediment systems was submitted already for the first EU approval:

- Sneikus, 2001

For the renewal of the EU approval of diuron, a new kinetic evaluation study of this water/sediment study was submitted:

- Sneikus, 2001.

For first EU approval, a kinetic re-evaluation of the water/sediment study Sneikus, 2001 was performed by

- Schnoeder, 2006

The final results of all acceptable studies regarding the fate and behaviour of diuron and its metabolites in water and sediment are summarised in Volume 1 under 2.8.2.

A search for open literature which included papers in peer-reviewed journals and reports from governments and other agencies in the EU and several other countries was performed by the applicant. The literature search strategy of the applicant and the evaluation of the RMS are described in detail in the Appendix to this document. Relevant studies found by the applicant and the RMS are discussed within the Appendix. No studies concerning the route and rate of diuron in water and sediment, which have to be included in risk assessment, were found.

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

B.8.2.1.1 Hydrolytic degradation

KCA 7.2.1.1/1- Williams, 1995 (study evaluated in the DAR, 2003 in Vol 3, B.2)

Author:	Williams, M.D.
Title:	Hydrolysis of ^{14}C-diuron as a function of pH at 25 ° and 50 °C
Date:	02.11.1995
Doc ID:	42580
Guidelines:	US EPA Guideline, Subdivision N, 161-1, EEC Directive, C.7, Hydrolysis
GLP:	Yes
Validity:	Acceptable

Material and Methods

A hydrolysis study was performed with ^{14}C-diuron labelled in the benzene ring. Hydrolysis was studied at a nominal test concentration of 1.0 µg/L in sterile aqueous buffer solution at pH 4, pH 5, pH 7 and pH 9 and 25±1 °C and 50±1 °C in the dark. The duration of the study was 30 days.
The ^{14}C-acitivity was determined by LSC and the test substance and its hydrolysis products were quantified with HPLC.

Results and Discussion

Total mass balance of the samples ranged from 97.9 to 106.5 %. The DT$_{50}$ values derived for diuron following SFO kinetics and the observed degradation products are presented in Table B.8.2-1.

Table B.8.2-1 Hydrolysis DT$_{50}$ values of diuron

pH	Temp (°C)	DT$_{50}$ (d)	Degradation products
4	25	798	None <5 %
	50	25.7	52.5 % 3,4-dichloraniline on day 29 7.41 % & 7.11 % degradation A on day 29 and 30
5	25	313	None <5 %
	50	55.6	34.3 % 3,4-dichloraniline on day 28
7	25	insignificant. degradation*	None <5 %
	50	insignificant. degradation **	9.06 & 9.7 % 3,4-dichloraniline on day 29 and 30
9	25	insignificant. degradation***	None <5 %
	50	109	20.8 % degradate D on day 28

* no decrease of diuron (101.6 % at study end)
**decrease of diuron from 100 to 95.1 %
*** no decrease of diuron (101.4 % at study end)

Conclusion

The study was submitted for the section physical-chemical properties in the previous EU approval and was evaluated and considered acceptable in Volume 3, B.2. It was again only submitted for the section physical-chemical properties but it is summarised also in this section to account for the respective data requirement. The study was re-evaluated by the RMS according to the actual OECD 111 guideline and is still considered acceptable. Under temperatures representative to natural environmental conditions best (25 °C), diuron is stable to hydrolysis at pH 4, pH 5, pH 7 and pH 9.

KCA 7.2.1.1/2- Hawkins et al, 1988 (study evaluated in the DAR, 2003 in Vol 3, B.2)

Author:	Hawkins, D.R. Kirkpatrick, D. Shaw, D.
Title:	The Hydrolytic Stability of ^{14}C-Diuron
Date:	21.04.1988
Doc ID:	AMR-908-87
Guidelines:	US EPA Guideline, Subdivision N, 161-1
GLP:	Yes
Validity:	Acceptable

Material and Methods

A hydrolysis study was performed with ^{14}C-diuron labelled in the benzene ring. Hydrolysis was studied at a nominal test concentration of 10 ppm in sterile aqueous buffer solution at pH 5, pH 7 and pH 9 and 25±1 °C in the dark. The duration of the study was 30 days.
The ^{14}C-acitivity was determined by LSC and the test substance and its hydrolysis products were quantified with TLC and HPLC.

The ^{14}C-acitivity was determined by LSC and the test substance and its hydrolysis products were quantified with TLC. Besides, selected samples were analysed with HPLC.

Results and Discussion

Total recoveries of the applied radioactivity were greater than 97 % at all times. Unaltered diuron accounted for more than 96 % applied radioactivity at all times and all pH values. Thus, diuron is considered stable to hydrolysis at 25±1 °C at pH 5, pH 7 and pH 9. No degradation products in concentrations >2 % were found.

Conclusion

The study was submitted for the section physical-chemical properties in the previous EU approval and was evaluated and considered acceptable in Volume 3, B.2. It was again only submitted for the section of the physical-chemical properties but it is summarised also in this section to account for the respective data requirement. The study was re-evaluated by the RMS according to the actual OECD 111 guideline and is still considered acceptable although no measurements were performed at pH 4. At 25 °C, diuron is stable to hydrolysis at pH 5, pH 7 and pH 9.

B.8.2.1.2 Direct photochemical degradation

KCA 7.2.1.2/1 – Hellpointer, 1991 (study evaluated in the DAR, 2003 in Vol 3, B.2)

Author:	Hellpointer, E.
Title:	Determination of the quantum yield and assessment of the environmental half-life of the direct photodegradation of diuron in water
Date:	19.3.1991
Doc ID:	PF 3486
Guidelines:	Phototransformation of Chemicals in Water, Part A, UBA, 1989
GLP:	Yes (signatur of study authors is missing)
Validity:	Acceptable

Material and Methods

The quantum yield of direct photodegradation of diuron (99.7 % purity) in pure water was determined using the ECETOC method. Therefore the degradation of diuron was determined using polychromatographic light in 5 nm steps for the wavelengths from 295 to 400 nm and in 10 nm steps from 401 nm on. The degradation experiment was conducted in a merry-go-round irradiation apparatus fitted with a mercury immersion lamp. The intensity of the light acting on the test solution was measured by means of the chemical actinometer uranyloxalate. The concentration of diuron in the samples was determined by reversed phase-HPLC and the respective UV-signal was evaluated using external acetonitrile standards. The quantum yield was calculated using the computer program QUANT.

Results and Discussion

The UV-absorption spectrum of diuron in highly pure water shows a maximum at 211 nm and a maximum at 248 nm. The absorption of diuron ends with Ɛ = 730 L/mole cm at 295 nm to Ɛ = 20 L/mole cm in the environmentally relevant range of wavelengths. Degradation rates of 0.2754 h^{-1} and 0.3077 h^{-1} were determined in the two degradation experiments with diuron. In both experiments accelerated degradation took place with increasing duration of exposure. This is explained by the secondary photodegradation mechanisms induced by exposure of the primary photoproducts of diuron, in the course of which diuron molecules may be attacked and degraded additionally. Quantum yields of 2.54 and 2.33 10^{-2} were calculated for the two experiments resulting in a mean quantum yield of 0.0243.

Conclusion

The study was submitted for the section physical-chemical properties in the previous EU approval and was evaluated and considered acceptable in Volume 3, B.2. It was again only submitted for the section of the physical-chemical properties but it is summarised also in this section to account for the respective data requirement. The study was re-evaluated by the RMS according to the actual OECD 316 guideline where the determination of the quantum yield is described as an additional option. The study is still considered acceptable, although the degradation rates of diuron were not determined in buffered solution but in pure water without buffer.

KCA 7.2.1.2/2 – Hawkins et al, 1989 (study evaluated in the DAR, 2003 in Vol 3, B.2)

Author:	Hawkins, D.R. Kirkpatrick, D. Shaw, D. Mobbs, J.
Title:	The photodegradation of ^{14}C-diuron in water
Date:	30.08.1989
Doc ID:	AMR-909-87
Guidelines:	US EPA Guideline, Subdivision N, 161-2
GLP:	Yes
Validity:	partly acceptable

Material and Methods

The photolysis of ^{14}C- diuron has been studied in an aqueous solution buffered at pH 7.0. The initial concentration of diuron in the solution was 10 ppm. A xenoc arc simulated sunlight source including a filter for light of wavelength < 290 nm was used for continuous irradiation for 15 days. One day of irradiation was determined to be equivalent to 4.8 days of natural sunlight assuming a 12-hour day length. At a latitude of 52°N Irradiated and dark control solutions were maintained at 25 ± °C under sterile conditions. The test vessels were connected to a series of traps to collect volatile compounds.
The ^{14}C-acitivity was determined by LSC and the test substance and its hydrolysis products were quantified with TLC. Since under irradiated conditions, diuron degraded to several polar compounds, three different solvent systems B, D and F of increasing polarity were used for further separation of the fractions. Besides, selected samples were analysed with HPLC. For HPLC analysis, the samples were extracted 3 x 2 mL dichloromethane for ca. 15 seconds shaking each. The combined extracts were dried under nitrogen at ambient temperature and re-dissolved in 1 mL acetonitrile.

Results and Discussion

The total recovery of the irradiated test solutions and the dark controls were between 86.5 – 100.4 %. 16.4 % volatiles radioactivity was found after 15 days which accounted mostly for CO_2.

The radioactive distribution of the irradiated samples using TLC solvent B and F is presented in Table B.8.2-2 and Table B.8.2-3. No results of the fractions using TLC solvent D were presented in the study report however it was stated also in solvent D no separation of the fraction 'Polars' was possible. The radioactive distribution of the dark controls is presented in Table B.8.2-4.

Table B.8.2-2 Distribution of the radioactivity in the irradiated samples with diuron after TLC with system B

Day	Diuron	Polars B*	B1	B2	B3	B4,B5	B6, B7	zone a
	% applied radioactivity							
0	98.8	0.6^{+}					0.8^{+}	
3	77.8	11.2	2	1.4	1.5	1.2	1.9	0.3
7	51.7	25.1	3.9	5	1.8	1.9	2.3	0.6
11	39.3	33.9	4.1	5.9	2.2	1.9	2	0.5
15	33.2	35.3	5.1	7.2	2.2	1.7	1.9	0.1

* polar radioactivity that could not be separated in system B
\+ concentrations of the combined TLC fractions

Table B.8.2-3 Distribution of the radioactivity in the irradiated samples with diuron after TLC with system F

Day	Polars F	F1	Zone P	F2	Zone q	F3	F4	F5, F6, F7	F8	F9**	F10**	Zone r	Others
	% applied radioactivity												
0	1.1^{+}										98.5	0.5	-
3	2.5	1.9	1.1	2.7	1.6	3.6	6	3.5	3.1	69.6^{+}		<0.1	1.7
7	4.6	3.2	1.8	3.8	2.2	4.9	7.5	5.3	4.9	49.8^{+}		<0.1	4.3
11	5.1	3.7	2.5	4.2	2.3	5.4	8.5	5.4	6.1	41.5^{+}		<0.1	5.3
15	5.9	5	3	4.6	2.7	5.5	7	6.4	6	34.7^{+}		<0.1	5.9

** Thought to consist of diuron plus TLC fraction B3-B7
\+ concentrations of the combined TLC fractions

Table B.8.2-4 Distribution of the radioactivity in the dark control samples with diuron after TLC with system B

Day	Diuron	zone x	zone y
	% applied radioactivity		
0	97.8	0.8	1.3
3	98.6	0.7	0.8
7	98.4	1.3	0.4
11	98.4	1	0.7
15	97.4	0.8	1

Under irradiated conditions, diuron decreased form 98.8 to 33.2 %. Several radioactive fractions above 5 % but not above 10 % at study end were found in the irradiated samples which were not elucidated any further. None of the observed peaks corresponded to 3,4-dichloroaniline, DCPU, DCPMU, TCAB or TCAOB.
No degradation of diuron under dark conditions was observed.

For diuron an experimental DT$_{50}$ of 9.0 d was derived equivalent to a DT$_{50}$ of 43 d under natural sunlight conditions assuming 12 h sun per day.

Conclusion

The study was submitted for the section physical-chemical properties in the previous EU approval and was evaluated and considered acceptable in Volume 3, B.2. It was again only submitted for the section of the physical-chemical properties but it is summarised also in this section to account for the respective data requirement. The study was re-evaluated by the RMS according to the actual OECD 316 guideline. The study still fulfills most of the requirements of the current guideline. However, the total recovery was below 90 % in the two irradiated samples at day 11 and in two out of four irradiated samples at day 15. Besides, several unknown compounds were found above 5 % at the end of study while 33.2 % diuron was still present. Thus, these compounds might reach concentrations > 10 % if irradiation would be continued and should be elucidated. Also the lacking separation of the Polars using TLC system B and fraction F9 and F10 is considered unsatisfactory and the interpretation of fraction F9 and F10 is ambigious.

The RMS believes that the study is not sufficient to elucidate degradation pathway of the aqueous diuron photolysis under natural environmental conditions and a new photolysis study or OECD 309 study under irradiated conditions should be performed.

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

B.8.2.2.1 ‘Ready biodegradability’

No study is available, therefore the active substance diuron is considered as not ‘readily biodegradable’ by default.

B.8.2.2.2 Aerobic mineralisation in surface water

KCA 7.2.2.2/1 – Swales, 2016 (new study)

Author:	Swales, S.
Title:	[^{14}C]-diuron:aerobic mineralisation in surface water and suspended sediment
Date:	23.03.2016
Doc ID:	3200983 (714-001)
Guidelines:	OECD 309
GLP:	Yes
Validity:	Acceptable

Material and Methods

The mineralisation and degradation of ^{14}C-diuron (>99 % puritiy, 12.2 MBq/mg) was assessed in the laboratory in a natural water system with 0.02 g/L suspended sediment.

Water and sediment were collected on 5th October 2015 from a Lake at Studley Royal, Ripon UK, where no pesticides were applied in the immediate vicinity in the last 5 years. The water was collected from 0-5 cm through a 100 µm sieve straight into a clean plastic container. The sediment from top 5 cm and passed through a 2 mm sieve into a clean container. The characteristics of the surface water system are presented in Table B.8.2-5.

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Table B.8.2-5 Characteristics of the surface water system

Parameter [unit]		**Value**
Water		
pH on the 5th of October	n.a.	8.74
Total organic carbon (TOC) [mg/L]		5.7
Dissolved organic carbon (DOC) [mg/L]		3.8
Biological oxygen demand (BOD_5) [mg O_2/L]		2.51
Total nitrogen [%]		0.000375
Total phosphorus [mg/L PO_4^{3-}]		1.24
Suspended solids [mg/L]		1.8
Hardness as $CaCO_3$ [mg/L]		138
Alkalinity [mg $CaCO_3$/L]		126
Nitrite [mg/L NO_2-N]		
Nitrate [mg /L NO_3-N]		
Sediment		
UK particle Size Distribution (PSD)	Sand (2000 – 63 µm) [%]	53
	Silt (63 – 2 µm) [%]	33
	Clay (< 2 µm) [%]	14
	Textural Class	Sandy loam
USDA	Sand (2000 – 50 µm) [%]	57
	Silt (50 – 2 µm) [%]	29
	Clay (< 2 µm) [%]	14
	Textural Class	Sandy loam
Organic carbon (OC) [%]		2.0
Organic Matter (OM) [%]		3.4
pH on the 5th of Oct	n.a.	8.55
pH on the 16th of Oct	H_2O	7.2
	0.01M $CaCl_2$	6.7

A preliminary test was conducted at the highest proposed test concentration (95 µg/L) using test water containing amended sediment (0.02 g/L). Test vessels were incubated for up to 7 days and samples were removed and analysed at 0 DAT and 7 DAT, in order to determine an approximate degradation rate and establish sampling times for the main test. No degradation of diuron was observed in the 7 day period and the main test sampling times were selected accordingly.

In the main test, surface water containing 0.02 g/L suspended sediment (100 mL) was dispensed into test vessels (250 mL, ca. 6 cm diameter amber glass reagent bottles). Sterilised water samples were dispensed into sterilised vessels in a laminar flow cabinet to maintain sterility. Additional incubation groups were set up for the sodium [^{14}C]-benzoate reference samples which were used to demonstrate that the microbial population was viable in the test system. Control groups contained test water and reference standard or test water, reference standard and acetonitrile (86 µL) to assess the impact of the organic solvent on the test system.

The study also included two untreated blank control vessels in which oxygen content and pH were measured without contaminating the probes used in their measurement. One of the replicates was treated with acetonitrile (86 µL) to provide a comparison of water qualities following treatment of the test samples (A, B and C) with acetonitrile. All test vessels were maintained in the dark in a temperature controlled room at 20 ± 2 °C.

Test vessels were treated with ^{14}C-diuron three days after collection of the test system (5 October 2015). Test vessels were gently shaken after application to distribute the test item in the water. The test item [^{14}C]diuron was supplied as an ethanol solution. The solvent was removed under nitrogen and the test item was reconstituted in acetonitrile (4 mL) to form a stock solution. The concentration was determined by LSC as 1.19 mg/mL. The stock solution was diluted with acetrontrile to prepare the application solution. The concentration of the application solution was 0.111 mg/mL (determined by LSC). The nominal application rates for the test item (95 µg/L and 10 µg/L) and sodium [^{14}C]-benzoate (10 µg/L) were achieved by applying selected volumes of application solutions drop wise to the water surface of the test vessels.

Dissolved oxygen and pH were measured in the blank controls whenever test samples were removed for analysis.

Duplicate test vessels were removed for analysis from non-sterile groups treated with diuron at 0, 7, 14, 21, 28, 46 and 60 day after treatment (DAT). The sterilised samples were removed at 60 DAT. Corresponding traps were collected for sampled vessels or replenished with fresh solutions every four weeks as necessary. Traps connected to test vessels of reference substance were collected and replenished accordingly at 4, 8, 12, 14, 18, 21, 28, 35 and 60 DAT.

For characterisation of low dose samples, a weighed subsample of the test water was concentrated (centrifugal evaporation) to dryness before being reconstituted in acetonitrile:water (1:1 v:v) and transferred to a pre-weighed vial. Following centrifugation (2000 rpm, 5 minutes) the vial and contents were re-weighed. Aliquots of these solutions were submitted to LSC and HPLC analyses for the low dose (10 µg/L) samples, whereas measurements were conducted directly in aliquots of the test system water for the high dose (96 µg/L) and sterile samples.

The nature of the radioactivity trapped in the sodium hydroxide traps was not investigated as the levels of trapped volatiles was ≤ 2 % AR but assumed to be $^{14}CO_2$.

HPLC was conducted with a C18 column (Ace 5 C18 (5 µm, 250 x 4.6 mm) using a gradient of 1 % trifluoroacetic acid in water and tetrahydrofuran at a flow rate of 1 mL/min:

TLC was conducted with solvents chloroform, methanol and acetic acid (90:8:2 v/v/v). Following chromatography, radiolabelled compounds were detected by preparation of a radioluminogram of the TLC plate using a Fuji BAS 1500 Bio-image analyser and non radiolabelled compounds were visualised under UV light at 254 nm. Chromatograms were evaluated from the radioluminograms using the associated software (Tina version 2.09 g), with Rf values being used to determine the identity of each region.

The presence of diuron in the samples was confirmed by LC-MS/MS comparison to non radiolabelled reference standards. In addition, it was also confirmed by LC-MS/MS that the peak obtained in the test samples was due solely to diuron.

The limit of detection (LOD) for chromatographic analysis by HPLC was estimated based on the smallest metabolite with values of 1.1 % AR for 10 µg/L samples and 0.5 % AR for 96 µg/L samples. No limit of detection for TLC was determined as it was used as confirmatory method.

To obtain degradation rates for diuron, SFO was fitted to the residues measured in the low and the high dosed samples using the kinetic program CAKE v.2.

Results and Discussion

During the incubation, water parameters (pH and oxygen content) were measured in control vessels. No systematic differences between the groups (low dose, high dose and sterile) were encountered. During incubation the oxygen content of the water ranged from 7.61 to 8.62 mg/L demonstrating aerobic conditions and the pH of the water was measured to be in the range of 8.08 to 8.76.

The mass balances and the radioactive distribution of the low and high test concentrations in the viable samples are provided in Table B.8.2-6.

Table B.8.2-6 Recovery and distribution of radioactivity (% of AR) in lake water containing suspended sediment after application of [^{14}C]diuron (mean values of replicates)

Low concentration (10 µg/L)						
Time (d)	**Diuron**	**Unknown metabolites**	**Unresolved background**	**total NaOH traps**	**Vessel wash**	**Mass balance**
0	96.5	nd	0.3	-	1.4	98.3
7	96.3	nd	1.0	0.1	1.9	99.3
14	95.1	nd	0.2	0.2	1.5	97.0
21	93.9	nd	1.0	0.3	1.4	96.5
28	93.5	nd	0.4	0.4	2.2	96.5
46	92.0	nd	1.3	1.2	2.3	96.8
60	88.2	0.5	1.0	2.00	3.2	94.8
High concentration (96 µg/L)						
Time (d)	**Diuron**	**Unknown metabolites**	**Unresolved background**	**total NaOH traps**	**Vessel wash**	**Mass balance**
0	96.1	nd	0.9	-	1.0	97.9
7	95.7	nd	1.1	0.1	1.8	98.7
14	96.4	nd	0.1	0.2	1.2	97.9
21	94.0	nd	0.3	0.2	1.2	95.7
28	93.8	nd	0.9	0.2	2.4	97.3
46	94.2	0.7	0.6	0.3	1.3	97.1
60	94.9	0.4	0.4	0.4	1.1	97.2

Mean mass balance of the high and low test concentrations were in the range 94.8 to 99.3 % AR in the viable test vessels.

In the low dose samples, diuron decreased from 96.5 % to 88.2 % after 60 d of incubation. In the high dose samples, decrease of diuron was insignificant with 96.1 % diuron at day 0 and 94.9 % diuron at day 60. Degradation products in water accounted for < 1 % AR. Besides, 2 % and 0.4 % CO_2 was formed in the low and high dose samples, respectively. Non-extractable residues in the suspended sediment were not determined.

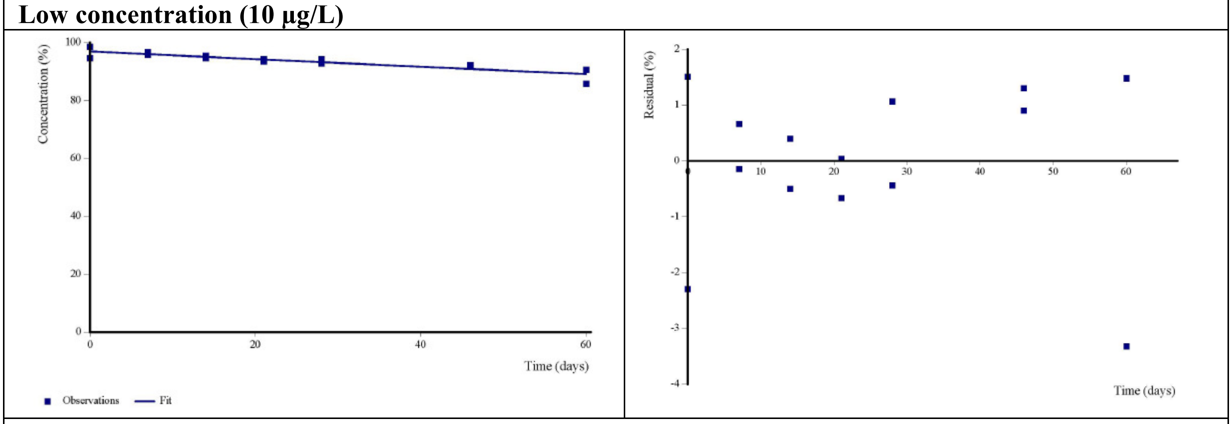
In the sterile vessels, a mass balance of 102 % AR was achieved while no degradation of diuron was observed (99.8 % AR at day 60).

The degradation rates for diuron in the low and the high concentration experiments are presented in Table B.8.2-7. The visual fits and residual plots are presented in Figure 8.2-1.

Table B.8.2-7 Degradation rates of diuron in lake water containing suspended sediment applying SFO

Experiment	**Degradation rate constant**	**Prob.>t**	**Chi^2 (%)**	**Visual fit**	**DT$_{50}$**	**DT$_{90}$**
Low concentration (10 µg/L)	0.001411	1.29E-005	1.01	good	491	1630
High concentration (96 µg/L)	2.82E-004	0.07123	1.01	good	2460	8160

Low concentration (10 µg/L)



High concentration (96 µg/L)

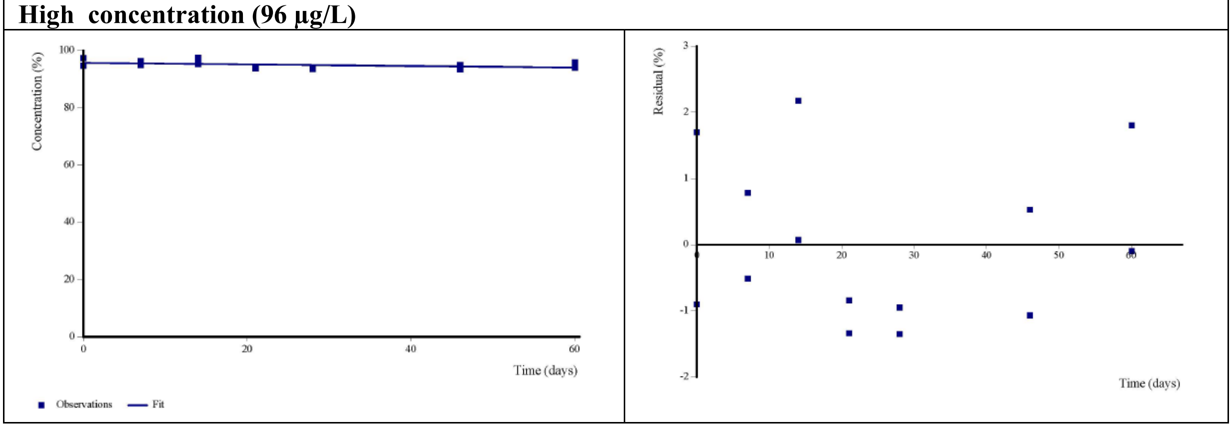


Figure B.8.2-1 **Kinetic fits and residual plots of diuron in lake water containing suspended sediment applying SFO**

A statistically measurable degradation rate could only be determined for the low dose experiments. For the high dose experiment, the t-test returned a probability <0.05, thus there is no significant difference of the degradation rate to zero.

Conclusion

The study was evaluated by the RMS against the requirements of OECD 309 and is considered acceptable.
The degradation of diuron was investigated in lake water from a Lake at Studley Royal, Ripon UK with 0.02 g/L suspended sediment under aerobic conditions at 20 °C. In the low dose experiment with 10 µg/L diuron, the test substance decreased from 96.5 % to 88.2 % after 60 d of incubation. A DT_{50} of 491 d and a DT_{90} of 1630 d was extrapolated for the low dose experiments applying SFO kinetics. In the high dose experiments, decrease of diuron was insignificant with 96.1 % diuron at day 0 and 94.9 % diuron at day 60. No degradation rates could be obtained for this experiment.
Degradation products in water accounted for < 1 % AR in both experiments.

B.8.2.2.3 Water/sediment studies

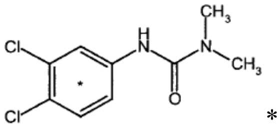
KCA 7.2.2.3/1 – Sneikus, 2001 (study evaluated in the DAR, 2003)

Author:	Sneikus, J.
Title:	Aerobic degradation and metabolism of diuron in the water-sediment system
Date:	05.12.2001
Doc ID:	GP01-006 M1511091-8 (994-07019)
Guidelines:	SETAC-Europe (1995)
GLP:	Yes
Validity:	Acceptable for Hoenninger Pond, not acceptable for river Erft

Material and Methods

The degradation and partitioning behaviour of [phenyl-UL-^{14}C]diuron and its metabolites was investigated in two different water/sediment systems under laboratory conditions. The test material is described in Table B.8.2-8.

Table B.8.2-8 Test material

Radiolabelled test item	
Test material	[Phenyl-UL-^{14}C]Diuron
Lot #	329/1
Structure	 *position of phenyl-UL-^{14}C-label
Specific radioactivity	3.57 MBq/mg
Radiochemical purity	>98 %
CAS #:	330-54-1 (unlabelled)
Non-radiolabelled test item	
Test material:	Diuron
IUPAC name:	3-(3,4-dichlorophenyl)-1,1-dimethylurea
Purity:	99.7 %
Reference compounds	
DCPMU	N'-3,4-dichlorophenyl)-N-methylurea
m-CPDMU	m-chlorophenyl-dimethyl urea
3,4-DCA	3,4-dichloroaniline

The two natural water/sediment systems used in the study were taken from River Erft (Neuss, Germany) and Hoenniger Weiher (close to Wipperfürth, Germany). Plants and stones were removed from the systems and the sediment was sieved through a 2 mm sieve prior to use. The water was filtered through a 0.2 mm sieve before added to the test vessels. Characterisation data of the water/sediment system are presented in Table B.8.2-9.

Table B.8.2-9 Characteristics of the water/sediment systems

Designation of water/sediment system	River Erft	Hoenniner Pond
Origin	Neuss, Germany	Hönnige, Germany
Sampling date	31st of January 2001	31st of January 2001
Water		
pH value	7.5*	6.5*
TOC [mg C/L]	29.0*	12.0*
DOC [mg C/L]	10.0*	9.0*
Hardness [°DH]	18.0*	5.8*
Total nitrogen [mg N/L]	6.1*	5.9*
Total phosphorus [mg P/L]	2.0*	0.53*
Oxygen saturation [%]	86.0*	95.1*
Redox potential [mV]	360*	364*
Sediment		
Texture (DIN 19682)	silty loam	sandy loamy silt
% sand (2000 – 63 µm)	11.9	24.4
% silt (63 – 2 µm)	63.4	62.3
% clay (< 2 µm)	24.7	13.3
pH value ($CaCl_2$)	7.0	5.9
pH value (H_2O)	7.4	6.3
Organic matter [%]	9.8	7.6
TOC [%]	5.6	4.5
CEC [meq Ba/100 g DM]	26	15
Total nitrogen [%]	0.3	0.4
Total phosphorus [%]	0.41	0.08

* measured after field sampling

130 mL of aqueous sediment was weighted into each incubation flask (volume : 1 L, diameter: 10.5 cm), equal to 55.0 g sediment (dry weight) of the River Erft and 70.6 g (dry weight) of the Hoenniger Pond to achieve a height of 1.5 cm in the test vessels. 390 mL of the filtered water was added to each incubation vessel corresponding to a height of 4.5 cm (ratio water: sediment was 3:1, v:v). Test systems were pre-incubated for 13 days in darkness at 20 °C. 3.46 mg diuron was applied to each test vessel corresponding to a single use rate of 4.0 g as/ha. Resulting concentration in water was approximately 7 mg as/L. A trapping system was connected to the test system to trap CO_2 and volatiles. The test vessels were incubated in the dark at a temperature of 19.9 ± 0.8 °C for a maximum of 120 days. During incubation the water phase was slightly stirred without disturbing the sediment. Duplicate samples were taken for analysis immediately after application and after 7, 14, 28, 55, 91 and 120 days of incubation.

The supernatant was separated from the sediment. Aliquots of the supernatant were adjusted to alkaline pH by adding sodium hydroxide and used for determination of $^{14}CO_2$. Further aliquots of the water were taken for measurement by LSC. Additionally, aliquots were spotted on plates for quantification of compounds with TLC. Sediment samples were extracted with a series of steps. The sediment was extracted with a mixture of acetonitrile and water (4:1, v:v) for 45 min and supernatants and sediment were separated via centrifugation. Afterwards sediments were extracted three times with acetonitrile. Extracts were combined and aliquots were measured by LSC. Additionally, aliquots were spotted on plates for quantification of compounds with TLC. Selected water and sediment extracts were subjected to HPLC analysis to confirm the TLC results. Remaining sediment was air-dried and afterwards radioassayed by combustion/LSC. For determination of $^{14}CO_2$ trapped in the soda lime trap and to determine dissolved $^{14}CO_2$ & ^{14}-cabonates in water, 18 % HCL was used to dissolve the soda lime or added to the water. Liberated $^{14}CO_2$ was swept out and absorbed in 3 vials (in series) filled with a cooled mixture of Carbosorb and PermafluorE (Canberra Packard Co.) followed by LS measurement. The polyurethane trap for volatile organic compounds was extracted with ethyl acetate by ultrasonification for 2 minutes and extracts were radioassayed.

Results

The total recovery was in the range of 91.3 to 103.4 % in the test system River Erft. The respective mean values was calculated to be 97.5 % AR. For the test system Hoenniger Pond, the material balance was in the range of 97.5 to 103.3 % AR with a corresponding mean value of 100.8 % AR.
Mineralization of 29.7 % and 2.05 % CO_2 were reached after 120 d in the in the test system River Erft and Hoenniger Pond, respectively , while 45.9 % and 17.5 % non- extractable residues were formed. The material balance of applied radioactivity in both test systems is presented in Table B.8.2-10.
The amount of diuron in the test system River Erft decreased to non-detectable amounts after 120 days in the water phase. Maximum occurrence in the sediment layer of the River Erft was 73.5 % AR at day 28 and decreased to 10.2 % AR after 120 days. In the test system Hoenniger Pond, diuron decreased from 92.0 % at day 0 to 10.3 % AR after 120 days in the water phase. Maximum occurrence of 64.0 % AR of diuron in the sediment layer was observed after 91 days and decreased to 60.2 % AR after 120 days. One major metabolite, mCPDMU, was observed in the test system Hoenninger Pond and amounts to 15.2 % AR after 55 days in the total system of which 6.7 % was detected in the water phase (1 x >5 %) and 8.5 % in the sediment extract (2 x >5 %). DCPMU was also observed and identified in both water/sediment systems, but never exceeded 5 % of applied radioactivity. Details are presented in Table B.8.2-11 and Table B.8.2-12.

Table B.8.2-10 Total mass balance in % AR in water/sediment systems River Erft and Hönninger Pond (mean values)

Day after application	**River Erft**					
	Not extracted sediment	**Extracted sediment**	**Water phase**	**CO_2**	**Volatiles**	**Recovery**
0	0.90	8.54	90.58	n.d.	n.d.	100.01
7	4.21	51.13	43.53	0.17	<0.01	99.03
14	10.04	58.69	31.62	0.68	<0.01	101.04
28	10.11	75.00	17.63	0.68	<0.01	103.42
55	33.83	50.87	5.79	4.34	0.04	94.87
91	44.24	24.27	0.84	22.28	0.04	91.67
120	45.92	15.63	0.68	29.70	0.04	91.97
Day after application	**Hoenninger Pond**					
	Not extracted sediment	**Extracted sediment**	**Water phase**	**CO_2**	**Volatiles**	**Recovery**
0	1.19	9.90	92.17	n.d.	n.d.	103.25
7	5.04	57.51	38.02	0.14	<0.01	100.71
14	8.00	62.12	29.91	0.61	0.02	100.65
28	9.87	64.22	25.77	1.33	<0.01	101.20
55	14.66	61.84	21.92	1.56	0.01	99.99
91	14.70	67.57	14.67	1.56	<0.01	98.51
120	17.48	68.64	13.42	2.05	<0.01	101.60

Table B.8.2-11 Distribution of radioactivity in % AR in water/sediment system River Erft

Day after application	Diuron	mCPDMU	DCPMU	Others	Origin
Supernatant water					
0	89.0	n.d.	n.d.	n.d.	0.2
0	90.8	n.d.	n.d.	n.d.	0.3
7	43.1	n.d.	n.d.	n.d.	n.d.
7	43.3	n.d.	n.d.	n.d.	0.7
14	29.2	n.d.	n.d.	n.d.	2.1
14	30.5	n.d.	n.d.	n.d.	1.5
28	17.2	n.d.	n.d.	n.d.	0.5
28	17.3	n.d.	n.d.	n.d.	0.3
55	n.d.	n.d.	n.d.	n.d.	1.1
55	6.5	n.d.	n.d.	n.d.	3.9
91	0.4	n.d.	n.d.	0.2	0.4
91	n.d.	n.d.	n.d.	n.d.	0.5
120	n.d.	n.d.	n.d.	n.d.	0.8
120	n.d.	n.d.	n.d.	n.d.	0.5
Sediment extract					
0	8.6	n.d.	n.d.	n.d.	0.2
0	8.0	n.d.	n.d.	n.d.	0.5
7	51.4	n.d.	n.d.	n.d.	0.2
7	50.5	n.d.	n.d.	n.d.	0.2
14	62.2	n.d.	0.5	n.d.	0.5
14	53.5	n.d.	0.4	n.d.	0.2
28	76.2	n.d.	1.0	n.d.	0.5
28	70.8	n.d.	0.7	n.d.	0.8
55	34.8	n.d.	2.2	0.4	1.1
55	59.8	n.d.	2.2	n.d.	1.2
91	23.3	n.d.	7.5	n.d.	2.1
91	14.2	n.d.	1.2	n.d.	0.2
120	6.1	n.d.	2.6	0.6	1.6
120	11.3	n.d.	4.3	0.5	1.3

n.d.: not detected (< 0.2 %)

Table B.8.2-12 Distribution of radioactivity in % AR in water/sediment system Hoenniger Pond

Day after application	Diuron	mCPDMU	DCPMU	Others	Origin
Supernatant water					
0	91.8	n.d.	n.d.	n.d.	n.d.
0	92.2	n.d.	n.d.	n.d.	0.2
7	41.2	n.d.	n.d.	n.d.	n.d.
7	34.7	n.d.	n.d.	n.d.	n.d.
14	26.6	n.d.	n.d.	n.d.	0.5
14	29.7	0.2	n.d.	n.d.	2.8
28	22.3	1.6	n.d.	n.d.	1.3
28	23.8	1.3	0.2	n.d.	1.1
55	12.6	10.9	n.d.	n.d.	0.6
55	16.4	2.5	n.d.	n.d.	0.8
91	13.8	n.d.	0.3	n.d.	0.4
91	13.2	1.2	0.2	n.d.	0.2
120	10.0	3.3	0.5	n.d.	0.6
120	10.5	1.2	0.3	n.d.	0.4
Sediment extract					
0	10.1	n.d.	n.d.	n.d.	n.d.
0	9.4	n.d.	n.d.	n.d.	n.d.
7	56.3	n.d.	n.d.	n.d.	n.d.
7	58.7	n.d.	n.d.	n.d.	n.d.
14	62.1	n.d.	0.2	3.2	n.d.
14	58.0	n.d.	0.4	n.d.	0.3
28	54.1	7.3	1.0	n.d.	0.4
28	61.3	2.7	1.3	n.d.	0.4
55	43.2	13.2	1.2	22.0	0.3
55	58.2	3.9	1.3	n.d.	0.5
91	62.5	0.9	2.4	n.d.	n.d.
91	65.5	1.8	1.8	n.d.	n.d.
120	55.5	4.4	4.0	1.3	1.0
120	64.8	1.8	3.4	n.d.	1.0

n.d.: not detected (< 0.2%)

Conclusion

The study was accepted for the first EU approval. However, after re-evaluation of the study conditions against current the requirements of the currently valid guideline for performing water/sediment studies, OECD 308, one major deviation was found:
In the original study report it is stated on page 11, that the water and sediment samples from the river Erft were collected, since diuron and 3,4-dichloroaniline were detected in the water of the river in the past. Thus, it was expected that due to the earlier findings, that the microorganisms in this system would be able to metabolise diuron and its metabolite 3,4-dichloraniline. In the OECD 308 guideline however, it is stated, that a sediment should not be used, if it has been contaminated with the test substance or its structural analogy within the previous 4 years. Since diuron exhibits faster degradation in the river Erft then in the Hoenninger Pond, an adaption of the microorganisms in the river system cannot be ruled out. Thus, we believe that the results from the river Erft should be excluded and the study should is considered only acceptable for the system Hoenninger Pond.

In the system Hoenninger Pond, diuron decreased from 92.0 % at day 0 to 10.3 % AR after 120 days in the water phase. Maximum occurrence of 64.0 % AR of diuron in the sediment layer was observed after 91 days and decreased to 60.2 % AR after 120 days. One major metabolite, mCPDMU, was observed in the test system Hoenninger Pond and amounts to 6.7 % in the water phase (1 x >5 %) and

8.5 % in the sediment after 55 days (2 x >5 % in consecutive samples). Mineralisation of 2.05 % was reached, while 17.5 % non- extractable residues were formed after 120 d.

A new kinetic evaluation of the study results according to FOCUS degradation kinetics (2006) was performed for the first EU approval of diuron, which is summarised below (Schnoeder, 2006). Thus, the original DT_{50} and DT_{90} values of the study report are not included in this summary anymore.

KCA 7.2.2.3/2 – Schnoeder, 2006 (study evaluated in the Addendum, 2007)

Author:	Schnoeder, F.
Title:	Environmental fate endpoints for diuron and its metabolites – data review amd kinetic calculations with model maker 4.0
Date:	23.03.2006
Doc ID:	DuPont-19861 (994-07008)
Guidelines:	FOCUS degradation kinetics, 2006
GLP:	No, not applicable
Validity:	not acceptable

Material and Methods

In this study a kinetic re-evaluation was performed of the laboratory aerobic soil studies Mackie & Hall, 1994 and deVries, 1996 with diuron and the laboratory aerobic soil studies Hennecke (2005a & b) with the metabolites DCPMU and DCPU, respectively, the field dissipation studies Pogàny, 1993 and Rouchard et al, 2000 with diuron and the water/sediment study Sneikus, 2001 with diuron.
Here only the kinetic re-evaluation of water/sediment study Sneikus, 2001 is summarised. The summary of the kinetic re-evalution of laboratory studies Mackie & Hall, 1994 and deVries, 1996 with diuron and Hennecke (2005a & b) with DCPMU and DCPU, respectively, can be found under B.8.1.1.6 and B.8.1.1.7. The summary of the kinetic re-evalution of the field dissipation studies Pogàny, 1993 and Rouchard et al, 2000 can be found under B.8.1.1.10.

The kinetic re-evaluation of the experimental results from the study Sneikus, 2001, which investigated the degradation of diuron in two water/sediment systems, was performed according to FOCUS kinetic guidance (2005). Degradation and dissipation rates for diuron and its metabolite mCPDMU in the total system, the water layer and/or the sediment layer to be used as persistence and as modelling endpoints were derived using the program ModelMaker version 4.0. The mean values of the residues presented in Table B.8.2-11 were used for kinetic re-evaluation. The kinetic models SFO, FOMC, HS and DFOP were tested as recommended by FOCUS Kinetics Guidance (FOCUS, 2005).

For the active substance diuron, degradation half-lives at Level P I for total system and dissipation half-lives for the water phase and the sediment phase were calculated. At Level P-II, a first order kinetics model was used to describe degradation within the water and sediment compartment as well as transfer rates between both compartments.

An attempt was made to derive dissipation or degradation endpoints for the metabolite mCPDMU, which are derived from the decline data of the metabolite in the water column, sediment and total system by fitting curves to the data from the maximum value onwards. However, fits for the water and sediment phase were considered inappropriate due to the fact only three data points were available. Besides, degradation of mCPDMU for the whole system was assessed under consideration of parent data and respective formation of the metabolite from diuron. The resulting endpoints for mCPDMU were consistent with those obtained from the fit of the decline phase in the total system and thus considered to be appropriate.

Results and Discussion

The persistence endpoints and modelling endpoints for diuron in water/sediment system are summarised in Table B.8.2-13 and Table B.8.2-14.
Diuron dissipates from the water phase of the water/sediment systems with DT_{50} values of 7.9 and 3.3

d and DT_{90} values of 26.2 and 151 d. For the sediment, dissipation DT_{50} values of 34.4 d and 1000 d and a DT_{90} values of 114 d were derived. In the total system, diuron degradates with DT_{50} values of 48.0 and 234 d and DT_{90} values of 159 and 773 d.
Level P-II modelling of diuron resulted in default values of 1000 days for the water phase (River Erft) and for sediment (Hönniger pond). Thus, the geometric mean DT_{50} value for total systems 105.7 days was proposed as input for modelling
The persistence and modelling endpoint For mCPDMU, a DT_{50} of 21.5 days and DT_{90} of 71.5 days in the total system Hönniger pond were considered to most realistically reflect the behaviour of mCPDMU in water/sediment systems (see Table B.8.2-15).

Table B.8.2-13: Persistence endpoints for diuron in water/sediment systems

System	Water phase [days]			Sediment phase [days]			Total system [days]			Kinetic level
	DT_{50}	DT_{90}	Model	DT_{50}	DT_{90}	Model	$DegT_{50}$	$DegT_{90}$	Model	
River Erft	7.9	26.2	SFO	34.4	114.4	SFO*	48.0	159.4	SFO	P-I
Hönniger pond	3.3	151.1	FOMC	1000	-	-	232.6	772.8	SFO	P-I

* fit from peak

Table B.8.2-14: Modelling endpoints for diuron in water/sediment systems

System	Water phase [days]			Sediment phase [days]			Total system [days]		
	$DegT_{50}$	Model	Kinetic level	$DegT_{50}$	Model	Kinetic level	$DegT_{50}$	Model	Kinetic level
River Erft	1000	-	P-II	48.0	SFO	P-I	48.0	SFO	P-I
Hönniger pond	232.6	SFO	P-I	1000	-	P-II	232.6	SFO	P-I

Table B.8.2-15: Persistence and modelling endpoints for the metabolite mCPDMU in water/sediment systems

System	Total system [days]			Kinetic level
	$DegT_{50}$	$DegT_{90}$	Model	
Hönniger pond	21.5	77271.5	SFO	P-I

Conclusion

The kinetic re-evaluation was considered acceptable for the last EU approval, however when re-evaluating the study for renewal of approval of diuron, several deviations from FOCUS kinetics guidance (2006, 2014) were found:
First, mean values were used instead of separate replicate values for the kinetic-re-evaluation. Second, values just after detectable samples were not set to ½ * <LOD (this only concerns water phase of river Erft). Besides, the Level P-I degradation rates of diuron in the sediment phase of river Erft were derived with only four time points although FOCUS (2006, 2014) recommends a minimum of five (the same was tried was Hönninger Weiher, however no reliable fit could be obtained, since there was no decline).
Besides, the degradation rates of mCPDMU were statistically not reliable (χ^2 of 77 % and t-test failed (p-value of 0.1127)) and should thus not be used.
Finally, results of Level II kinetic modelling are generally not considered acceptable anymore. No adsorption properties of the substances are entered in the model, thus the model arbitrary attributes changes in residues to adsorption/desorption processes or to degradation processes. This leads to an over-parameterisation of the model where several statistically reliable solutions are possible.

Due to the deviations and since considerably different degradation rates were obtained when repeating the kinetic evaluation according to FOCUS (2006, 2014), the RMS re-run the kinetic evaluation at P-I Level for the water/sediment system Weiher Hoenninger as described below. No kinetic re-evaluation was performed by the RMS for the system River Erft, since the degradation rates of this system are not considered acceptable due to pre-adaption of the microorganisms (see conclusion of the study Sneikus, 2001).

Re-Calculations of RMS:

For kinetic re-evaluation, the residue data of diuron presented in Table B.8.2-12 were used. No pre-processing of the residues of the system Hoenninger Weiher were necessary, since diuron remained above the detection limit throughout the study duration. For determination degradation rates of diuron in the total system, the residues of the water phase and of the sediment phase were summed up.
The kinetic model CAKE, version 3.1 was used for kinetic re-calculations.
The statistical results of the different kinetic models applied to describe the dissipation of diuron from the water phase of the system Hoenninger Weiher are presented in Table B.8.2-16. The visual fit and the residual plot of the FOMC kinetic, which describes the dissipation of diuron from the water phase best, are presented in Figure B.8.2-2.

The statistical results of the different kinetic models applied to describe the degradation of diuron in the total system Hoenninger Weiher are presented in Table B.8.2-17.
A statistically reliable could only be obtained using SFO kinetics, however the visual fit and the residual plot shows a clear biphasic trend as shown in Figure B.8.2-3.

Table B.8.2-16 Statistical results of the kinetic models describing the dissipation of diuron from the water phase of the system Hoenninger Weiher (re-calculation of the RMS)

Kinetic model	Parameter	Optimised value	Std. error	p-value (t-test)	% error χ^2 test	DT_{50} (d)	DT_{90} (d)	Visual assessment
SFO	M_0_parent	86.38	8.009	N/A	27.4	8.9	29.6	poor
	k_ parent	0.07793	0.01599	1.92E-004				
FOMC	M_0_parent	91.99	1.476	N/A	2.67	4.22	182	Very good
	α_parent	0.4571	0.03795	N/A				
	β_parent	1.188	0.304	N/A				
DFOP	M_0_parent	91.97	1.685	N/A	3.8	4.99	124	Very good
	k1_parent	0.2467	0.03309	1.09E-005				
	k2_parent	0.009239	0.001553	7.06E-005				
	g_parent	0.6864	0.02775	N/A				
HS	M0_parent	92	1.79	N/A	4.38	5.48	119	good
	k1_parent	0.1265	0.007288	4.26E-009				
	k2_parent	0.01025	0.001448	1.70E-005				
	tb_parent	9.353	0.7361	N/A				

FOMC

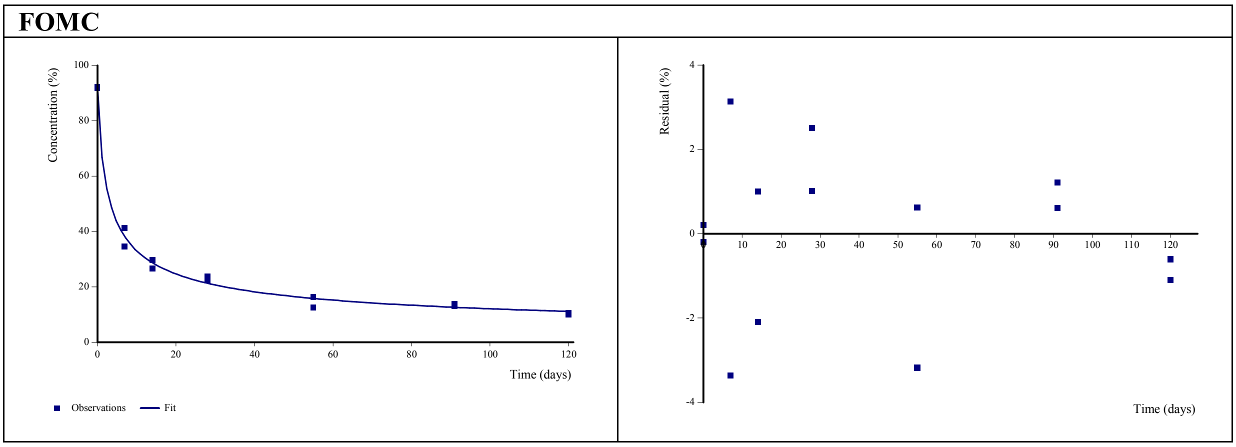


Figure B.8.2-2 **FOMCS kinetic fit and residual plot for the dissipation of diuron from the water phase of the system Hoenninger pond**

Table B.8.2-17 **Statistical results of the kinetic models describing the degradation of diuron in the total system Hoenninger Weiher (re-calculation of the RMS)**

Kinetic model	**Parameter**	**Optimised value**	**Std. error**	**p-value (t-test)**	**% error χ^2 test**	**DT_{50} (d)**	**DT_{90} (d)**	**Visual assessment**
SFO	M_0_parent	93.91	3.79	N/A	7.05	232	769	Poor
	k_ parent	0.002993	7.77E-004	0.001145				
FOMC	M_0_parent	102.7	5.141	N/A	4.98	1.29E+03	>10,000	good
	α_parent	0.1257	0.05435	N/A				
	β_parent	5.205	6.906	N/A				
DFOP	M_0_parent	103.2	4.673	N/A	4.53	>10,000	>10,000	good
	k1_parent	0.04815	0.04286	0.1438				
	k2_parent	4.80E-014	0.002538	0.5				
	g_parent	0.3126	0.181	N/A				
HS	M0_parent	101.1	3.75	N/A	3.87	>10,000	>10,000	good
	k1_parent	0.008427	0.002571	0.004158				
	k2_parent	2.95E-024	0.001425	0.5				
	tb_parent	41.9	13.55	N/A				

SFO

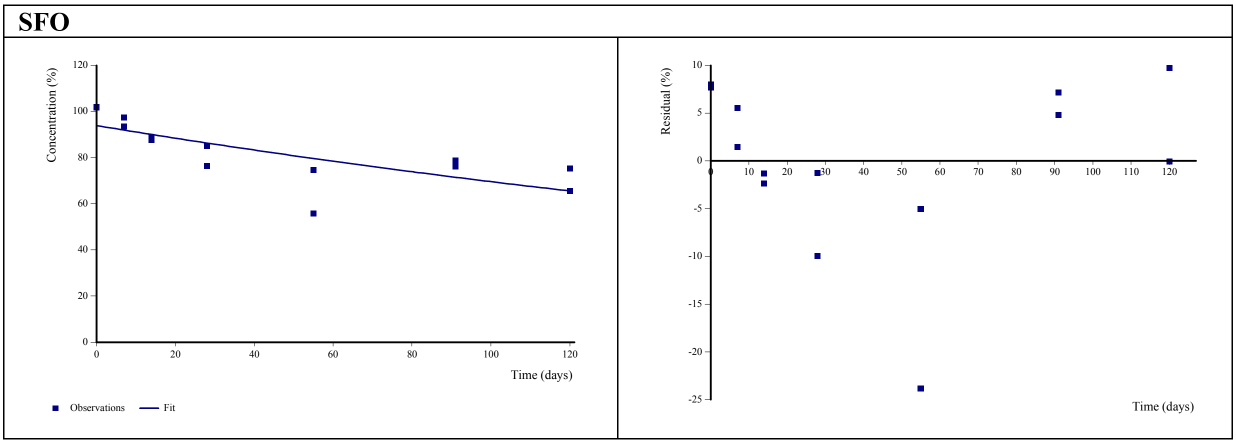


Figure B.8.2-3 **SFO kinetic fit and residual plot for the degradation of diuron in the total system Hoenninger pond**

The following endpoints are presented in Table B.8.2-18 and Table B.8.2-19 suggested to be used for persistence calculations and for modelling of diuron in water and sediment.

Table B.8.2-18: Persistence endpoints for diuron in the water/sediment system Weiher Hönninger (Level P-I, re-calculations of the RMS)

System	**Water phase [days]**			**Total system [days]**		
	$DisT_{50}$	**$DisT_{90}$**	**Model**	**$DegT_{50}$**	**$DegT_{90}$**	**Model**
Hönniger pond	4.22	182	FOMC	1000	1000	default

Table B.8.2-19: Modelling endpoint for diuron in the water/sediment system Weiher Hönninger (Level P-I, re-calculations of the RMS)

System	**Total system [days]**	
	$DegT_{50}$	**Model**
Hönniger pond	1000	default

B.8.2.3 Degradation in the saturated zone

No study on the degradation of diuron or its metabolites in the saturated zone was submitted.

B.8.3 Fate and behaviour in air

The photochemical oxidation of diurond in air was estimated in one study submitted for the actual EU re-approval:

- Shao-Franz & Klein, 2016

Besides, the volatilisation of diuron in the formulated product Diuron Bayer WP 80 from dolomite, lava and soil was investigated in one field study submitted for first EU approval:

- Fritz, 1992

The final results of all acceptable studies regarding the fate and behaviour of diuron and its metabolites in air are summarised in Volume 1 under 2.8.3.

A search for open literature which included papers in peer-reviewed journals and reports from governments and other agencies in the EU and several other countries was performed by the applicant. The literature search strategy of the applicant and the evaluation of the RMS are described in detail in the Appendix to this document. Relevant studies found by the applicant and the RMS are discussed within the Appendix. No studies concerning the fate of diuron in air, which have to be included in risk assessment, were found.

B.8.3.1 Route and rate of degradation in air

KCA 7.3.1/1 – Shao-Franz & Klein, 2016 (new study)

Author:	Shao-Franz, W. Klein, C.
Title:	Estimation of the atmospheric residence time of the active substance diuron using the Atkinson method related to the supplementary dossier – M-CA section 7 for diuron
Date:	01.03.2016
Doc ID:	PP169-00016 (781-002)
Guidelines:	None
GLP:	No, not applicable
Validity:	Acceptable

Material and Methods

The photochemical and oxidative decomposition of the active substance diuron in air was evaluated on theoretical calculation according to Atkinson using the actual program AopWin v1.92.

Results and Discussion

Diuron was estimated to degrade with a DT_{50} of 0.983 days i.e. 11.8 hours in the atmosphere assuming a 12-hr day and a concentration of 1.5×10^6 OH/cm^3.

Conclusion

The estimation of the atmospheric half-life of the active substance diuron is considered acceptable by the RMS.

KCA 7.3.1/2 – Fritz, 1992 (study evaluated in monograph, September 2003)

Author:	Fritz, R.
Title:	Determination of the volatilisation of diuron in a field experiment
Date:	11.11.1992
Doc ID:	PF-3787
Guidelines:	BBA Guidelines for the Testing of Plant Protection Products in Registration Procedures, Part IV, 6-1, July 1990
GLP:	yes
Validity:	Not acceptable

Material and Methods

The volatilisation behaviour of Phenyl-UL-^{14}C diuron (>99 % purity) was determined in accordance with the BBA guideline IV, 6-1. Three trials were carried out under field conditions in a container arrangement with a target area of 1 m^2. Diuron was formulated as Diuron Bayer WP 80.

The product was applied to three different target areas presented in Table B.8.3-1. The application scheme is given in Table B.8.3-3.

Table B.8.3-1 Target areas used to investigate the volatilisation behavior of diuron

Dolomite	A material that is used on road verges, paths and roads, open spaces, railway tracks and embankments.
Lava	Used as granule for top layers on open spaces and paths.
Loamy sand	With a low content of organic matter. Serves as model area for ditches and fallow land

The soil characteristics of the loamy sand are given in Table B.8.3-2.

Table B.8.3-2 Soil characteristics

Soil	Loamy sand
Source	Monheim (Rhineland), field plot A20
Texture analysis (USDA)	
Sand	72.4 %
silt	22.6 %
Clay	5.0 %
pH (in $CaCl_2$)	6.4
pH (in water)	6.9
Org. C (%)	1.4
T-value (meq/ 100g)	8

A pre-emergence treatment, i.e. a spray application to surfaces without vegetation, was chosen as indication. Application rates were 568.5 mg as/m on dolomite, 592.5 on the lava and 576.7 mg as/m^2 on the sand soil.

Table B.8.3-3 Target areas used to investigate the volatilisation behavior of diuron

Trial no.	Time of application (hours)	Trial period	Target area
1	8.15	2-3 April 1992	Dolomite
2	10.30	6-7 April 1992	Lava
3	10.10	7-8 April 1992	Light sand

For analysis the top 2-3 cm of the soil were scraped off and extracted twice with methanol for 1 hour each. After centrifugation, the total radioactivity in the extracts was measured with LSC. The distribution of the radioactivity was determined with TLC and HPLC.

During the experiment, air temperature, humidity, wind velocity and rainfall were recorded at ground level and prevailing wind direction, wind velocity and duration and intensity of sunshine were recorded at 2 m above ground.

Results and Discussion

The recovery rates of all three target areas are given in Table B.8.3-4. The distribution of the radioactivity is presented in Table B.8.3-5.

Table B.8.3-4 Recovery rates of radioactivity applied to dolomite, lava and soil

Trial no.	Initial deposit (%)	1 hour (%)	3 hours (%)	6 hours (%)	24 hours (%)
1	100	107.5	105.0	108.2	111.1
2	100	92.7	97.7	96.4	96.5
3	100	105.8	106.7	108.3	117.0
Mean of three trials	100	102.0	103.1	104.3	108.2

Table B.8.3-5 Distribution of the radioactivity in the top layer (% of the radioactivity applied, average over all three target areas)

	Initial deposit	1 hour	3 hours	6 hours	24 hours
Diuron	73.3	73.5	76.4	72.0	79.7
Unknown extracted	4.1	2.2	2.4	6.1	5.1
Unextracted residues	22.6	26.3	24.3	26.2	23.4
Total	100.0	102.0	103.1	104.3	108.2

No diuron evaporated from the different target areas within 24 hours after application. The analyses of these material extracts showed that after this period, the majority of the recovered radioactivity was assignable to unchanged diuron.

Conclusion

The study was considered acceptable for the last EU approval. However after re-evaluation of the study for EU re-approval it is not considered acceptable anymore, since the formulation Diuron Bayer WP 80 is not the representative formulation of diuron. Besides, no uses of diuron in the current representative SC formulation on roads, lanes and yards are intended for EU re-approval.

B.8.3.2 Transport via air

No study on the transport of diuron or its metabolites via air was submitted.

B.8.3.3 Local and global effects

No study on the local and global effects of diuron or its metabolites was submitted.

B.8.4 Monitoring data concerning fate and behaviour of the active substance, metabolites, degradation and reaction products

B.8.4.1 Monitoring data of groundwater

Publications concerning monitoring data of diuron in groundwater that were found during the literature report are assessed and summarised in the Appendix to Volume 3, B.8 if relevant.
No additional monitoring data of diuron or its metabolites were submitted.

B.8.4.2 Monitoring data of surface water

Relevant publications concerning findings of diuron in surface water that were found during the literature report are assessed and summarised in the Appendix to Volume 3, B.8 if relevant.
No additional monitoring data of diuron or its metabolites were submitted.

B.8.4.3 Monitoring data of air

Relevant publications concerning findings of diuron in air water that were found during the literature report are assessed and summarised in the Appendix to Volume 3, B.8 if relevant.
No additional monitoring data of diuron or its metabolites were submitted.

B.8.5 References relied on

B.8.5.1 References cited but not submitted:

- Draft Assessment Report (DAR) of Diuron (September 2003)
- Final Addendum to the DAR of Diuron (March 2004)
- Revised DAR of Diuron (September 2003/Revised October 2007)
- Review Report for the active substance Diuron, SANCO/2184/2008 rev 3, 10 July 2008
- EFSA (2014): EFSA Guidance Document for evaluating laboratory and field dissipation studies to obtain DegT50 values of active substances of plant protection products and transformation products of these active substances in soil. EFSA Journal 2014;12(5):3662, 37 pp.
- FOCUS (2005): Guidance Document on Estimating Persistence and Degradation Kinetics from Environmental Fate Studies on Pesticides in EU Registration. Report of the FOCUS Work Group on Degradation Kinetics, EC Document Reference Sanco/10058/2005 version 2.0, 434 pp. (corresponding to FOCUS (2006) as cited in studies already evaluated according to 91/414/EC)
- FOCUS (2006): Guidance Document on Estimating Persistence and Degradation Kinetics from Environmental Fate Studies on Pesticides in EU Registration. Report of the FOCUS Work Group on Degradation Kinetics, EC Document Reference Sanco/10058/2005 version 2.0, 434 pp.
- FOCUS (2011): Generic Guidance for Estimating Persistence and Degradation Kinetics from Environmental Fate Studies on Pesticides in EU Registration. Report of the FOCUS Work Group on Degradation Kinetics. 23 November 2011, version 1.0, 436 pp.
- FOCUS (2014): Generic Guidance for Estimating Persistence and Degradation Kinetics from Environmental Fate Studies on Pesticides in EU Registration. Report of the FOCUS Work Group on Degradation Kinetics. 18 November 2014, version 1.1, 440 pp.

B.8.5.2 Reference list sorted by Annex point

Data point	Author(s)	Year	Title Report No. (Doc. No.) Source (where different from company) GLP or GEP status, Published or not	Verte-brate study Y/N	Data protec-tion claim-ed Y/N	Justifica-tion if data protec-tion is claimed	Owner	Previous-ly submitted Y/N
KCA 7.1.1.1/01	Hawkins, D.R. Kirkpatrick, D. Shaw, D. Chan. S.C.	1990	THE METABOLISM OF [PHENYL(U)-^{14}C]DIURON IN KEYPORT SILT LOAM SOIL UNDER AEROBIC CONDITIONS Report No.: AMR-1202-88 HRC/DPT 189/891860 (994-07002) Huntingdon Research Centre, Huntingdon, United Kingdom GLP, unpublished BVL no. 3056333	N	N	Study was part of the original dossier	Lanxess & DuPont	Y IIA, 7.1.1.1.1/01 IIA, 7.1.1.2.1/02
KCA 7.1.1.1/02	Mackie, J.A. Hall, B.E.	1994	THE DEGRADATION OF [PHENYL(U)-^{14}C]-DIURON IN SOIL UNDER AEROBIC CONDITIONS Report No.: AMR 2603-93 9923 (994-07003) Inveresk Research Institute, Tranent, Scotland, United Kingdom GLP, unpublished BVL no. 3056334	N	N	Study was part of the original dossier	DuPont	Y IIA, 7.1.1.1.1/02 IIA, 7.1.1.2.1/01
KCA 7.1.1.1/03	de Vries, R.	1996	DETERMINATION OF THE METABOLISM AND DEGRADATION RATE OF DIURON IN SOIL Report No.: 157826 (994-07004) NOTOX B.V., ´s-Hertogenbosch, The Netherlands GLP, unpublished BVL no. 3056335	N	N	Study was part of the original dossier	Lanxess	Y IIA, 7.1.1.1.1/03 IIA, 7.1.1.2.1/03
KCA 7.1.1.2/01	Yu, W.C.	1988	ANAEROBIC SOIL METABOLISM OF [PHENYL(U)-^{14}C]DIURON Report No.: AMR 552-86 12300 (994-07006) Cambridge Analytical Associates Inc., Boston, Massachusetts, USA GLP, unpublished BVL no. 3056337	N	N	Study was part of the original dossier	DuPont	Y IIA, 7.1.1.1.2/02
KCA 7.1.1.3/01	Hennecke, D.	2005	SOIL PHOTOLYSIS OF DIURON Report No.: GAB-008/7-06 (994-07007) Fraunhofer, Institut Molekularbiologie und Angewandte Oekologie GLP, unpublished BVL no. 3056338	N	N	Study was part of the original dossier	Lanxess & DuPont	Y IIA, 7.1.1.1.2/03

Data point	Author(s)	Year	Title Report No. (Doc. No.) Source (where different from company) GLP or GEP status, Published or not	Verte-brate study Y/N	Data protec-tion claim-ed Y/N	Justifica-tion if data protec-tion is claimed	Owner	Previous-ly submitted Y/N
KCA 7.1.2.1.1/01	Hawkins, D.R. Kirkpatrick, D. Shaw, D. Chan. S.C.	1990	THE METABOLISM OF [PHENYL(U)-^{14}C]DIURON IN KEYPORT SILT LOAM SOIL UNDER AEROBIC CONDITIONS Report No.: AMR-1202-88 HRC/DPT 189/891860 (994-07002) Huntingdon Research Centre, Huntingdon, United Kingdom GLP, unpublished BVL no. 3056341	N	N	Study was part of the original dossier	Lanxess & DuPont	Y IIA, 7.1.1.1.1/01 IIA, 7.1.1.2.1/02
KCA 7.1.2.1.1/02	Drechsler, S. Klein, C.	2016	ASSESSMENT OF THE DEGRADATION KINETICS OF DIURON IN SOIL UNDER LABORATORY CONDITIONS ACCORDING TO THE RECOMMENDATIONS OF THE FOCUS REPORT ON DEGRADATION KINETICS (2006, 2014) Report No.: na (782-002) Scientific Consulting Company, Bad Kreuznach, Germany Not GLP, unpublished BVL no. 3088872	N	Y	New study necessary for the approval renewal of Diuron	Arysta LifeScience Benelux Sprl	N
KCA 7.1.2.1.1/03	Drechsler, S. Klein, C.	2016	RAW DATA TO ASSESSMENT OF DEGRADATION KINETICS OF DIURON IN SOIL UNDER LABORATORY CONDITIONS ACCORDING TO THE RECOMMENDATIONS OF THE FOCUS REPORT ON DEGRADATION KINETICS (2006, 2014) Report No.: na (782-007) Scientific Consulting Company, Bad Kreuznach, Germany Not GLP, unpublished BVL no. 3088873	N	Y	New study necessary for the approval renewal of Diuron	Arysta LifeScience Benelux Sprl	N
KCA 7.1.2.1.1/04	Mackie, J.A. Hall, B.E.	1994	THE DEGRADATION OF [PHENYL(U)-^{14}C]-DIURON IN SOIL UNDER AEROBIC CONDITIONS Report No.: AMR 2603-93 9923 (994-07003) Inveresk Research Institute, Tranent, Scotland, United Kingdom GLP, unpublished BVL no. 3056340	N	N	Study was part of the original dossier	DuPont	Y IIA, 7.1.1.1.1/02 IIA, 7.1.1.2.1/01

Data point	Author(s)	Year	Title Report No. (Doc. No.) Source (where different from company) GLP or GEP status, Published or not	Verte-brate study Y/N	Data protec-tion claim-ed Y/N	Justifica-tion if data protec-tion is claimed	Owner	Previous-ly submitted Y/N
KCA 7.1.2.1.1/05	de Vries, R.	1996	DETERMINATION OF THE METABOLISM AND DEGRADATION RATE OF DIURON IN SOIL Report No.: 157826 (994-07004) NOTOX B.V., ´s-Hertogenbosch, The Netherlands GLP, unpublished BVL no. 3056342	N	N	Study was part of the original dossier	Lanxess	Y IIA, 7.1.1.1.1/03 IIA, 7.1.1.2.1/03
KCA 7.1.2.1.1/06	Schnoeder, F.	2006	ENVIRONMENTAL FATE ENDPOINTS FOR DIURON AND ITS METABOLITES - DATA REVIEW AND KINETIC CALCULATIONS WITH MODEL MAKER 4.0 Report No.: DuPont-19861 (994-07008) DuPont de Nemours (Deutschland) GmbH, Bad Homburg, Germany Not GLP, unpublished BVL no. 3056339	N	N	Study was part of the original dossier	Lanxess & DuPont	Y IIA, 7.1.1.2/01 IIA, 7.2.1.3.2/02
KCA 7.1.2.1.2/01	Hennecke, D.	2005	AEROBIC SOIL DEGRADATION OF 3,4 DICHLOROPHENYL METHYLUREA (DCPMU) Report No.: GAB-010/7-90 (994-07009) Fraunhofer-Institute for Molecular Biology and Applied Ecology (IME), Schmallenberg, Germany GLP, unpublished BVL no. 3056343	N	N	Study was part of the original dossier	Lanxess & DuPont	Y IIA, 7.1.1.2.1/04
KCA 7.1.2.1.2/02	Hennecke, D.	2005	AEROBIC SOIL DEGRADATION OF 3,4 DICHLOROPHENYL UREA (DCPU) Report No.: GAB-009/7-90 (994-07010) Fraunhofer, Institut Molekularbiologie und Angewandte Oekologie GLP, unpublished BVL no. 3056344	N	N	Study was part of the original dossier	Lanxess & DuPont	Y IIA, 7.1.1.2.1/05

Data point	Author(s)	Year	Title Report No. (Doc. No.) Source (where different from company) GLP or GEP status, Published or not	Verte-brate study Y/N	Data protec-tion claim-ed Y/N	Justifica-tion if data protec-tion is claimed	Owner	Previous-ly submitted Y/N
KCA 7.1.2.1.2/03	Schnoeder, F.	2006	ENVIRONMENTAL FATE ENDPOINTS FOR DIURON AND ITS METABOLITES - DATA REVIEW AND KINETIC CALCULATIONS WITH MODEL MAKER 4.0 Report No.: DuPont-19861 (994-07008) DuPont de Nemours (Deutschland) GmbH, Bad Homburg, Germany Not GLP, unpublished BVL no. 3056355	N	N	Study was part of the original dossier	Lanxess & DuPont	Y IIA, 7.1.1.2/01 IIA, 7.2.1.3.2/02
KCA 7.1.2.1.3/01	Yu, W.C.	1988	ANAEROBIC SOIL METABOLISM OF [PHENYL(U)-^{14}C]DIURON Report No.: AMR 552-86 12300 (994-07006) Cambridge Analytical Associates Inc., Boston, Massachusetts, USA GLP, unpublished BVL no. 3056337	N	N	Study was part of the original dossier	DuPont	Y IIA, 7.1.1.1.2/02
KCA 7.1.2.2.1/04	Pogány, E.	1993	DISSIPATION OF DIURON IN SOILS UNDER FIELD CONDITIONS Report No.: 2138/91 (994-07011) Bayer AG, Leverkusen, Germany GLP, unpublished BVL no. 3056345	N	N	Study was part of the original dossier	Lanxess	Y IIA, 7.1.1.2.2/01 IIA, 7.1.3.3/02
KCA 7.1.2.2.1/05	Sommer, H.	1993	STORAGE STABILITY OF DIURON IN SOIL Report No.: RA-112/93 (994-07001) Bayer AG, Leverkusen, Germany GLP, unpublished BVL no. 3056332	N	N	Study was part of the original dossier	Lanxess	Y IIA, 7/01
KCA 7.1.2.2.1/08	Drechsler, S. Klein, C.	2016	ASSESSMENT OF DEGRADATION KINETICS OF DIURON IN SOIL UNDER FIELD CONDITIONS ACCORDING TO THE RECOMMENDATIONS OF THE FOCUS REPORT ON DEGRADATION KINETICS (2006, 2014) Report No.: na (782-006) Scientific Consulting Company, Bad Kreuznach, Germany Not GLP, unpublished BVL no. 3088884	N	Y	New study necessary for the approval renewal of Diuron	Arysta LifeScience Benelux Sprl	N

Data point	Author(s)	Year	Title Report No. (Doc. No.) Source (where different from company) GLP or GEP status, Published or not	Verte-brate study Y/N	Data protec-tion claim-ed Y/N	Justifica-tion if data protec-tion is claimed	Owner	Previous-ly submitted Y/N
KCA 7.1.2.2.1/09	Drechsler, S. Klein, C.	2016	RAW DATA TO ASSESSMENT OF DEGRADATION KINETICS OF DIURON IN SOIL UNDER FIELD CONDITIONS ACCORDING TO THE RECOMMENDATIONS OF THE FOCUS REPORT ON DEGRADATION KINETICS (2006, 2014) Report No.: na (782-008) Scientific Consulting Company, Bad Kreuznach, Germany Not GLP, unpublished BVL no. 3088885	N	Y	New study necessary for the approval renewal of Diuron	Arysta LifeScience Benelux Sprl	N
KCA 7.1.3.1.1/02	Derz, K.	2009	DETERMINATION OF THE ADSORPTION/DESORPTION OF PREVENTOL A 6 Report No.: LAN-001/7-13 (731-001) Fraunhofer-Institute for Molecular Biology and Applied Ecology (IME), Schmallenberg, Germany GLP, unpublished BVL no. 3088887	N	Y	New study necessary for the approval renewal of Diuron	Lanxess	N
KCA 7.1.3.1.2/01	Brumhard, B. Koenig, T. Sommer, H.	1998	ADSORPTION/DESORPTION OF DESMETHYL-DIURON ON DIFFERENT SOILS Report No.: MR 575/96 (994-07016) Bayer AG, Leverkusen, Germany GLP, unpublished BVL no. 3056349	N	N	Study was part of the original dossier	Lanxess	Y IIA, 7.1.2/02
KCA 7.1.3.1.2/02	Heintze, A.	2002	DETERMINATION OF THE ADSORPTION/DESORPTION BEHAVIOUR OF DCPU IN FOUR DIFFERENT SOILS Report No.: GP01-25 20001409/01-PCAD (994-07017) Arbeitsgemeinschaft GAB Biotechnologie GmbH & IFU Umweltanalytik GmbH, Niefern-Öschelbronn, Germany GLP, unpublished BVL no. 3056351	N	N	Study was part of the original dossier	Lanxess & DuPont	Y IIA, 7.1.2/03

Data point	**Author(s)**	**Year**	**Title Report No. (Doc. No.) Source (where different from company) GLP or GEP status, Published or not**	**Verte-brate study Y/N**	**Data protec-tion claim-ed Y/N**	**Justifica-tion if data protec-tion is claimed**	**Owner**	**Previous-ly submitted Y/N**
KCA 7.1.4.2/01	Bergstroem, L.F. et al.	1996	LEACHING OF [PHENYL(U)-^{14}C]DIURON IN SCANDINAVIAN SOILS USING FIELD LYSIMETERS Report No.: AMR-2619-93 (994-07018) Swedish University of Agricultural Sciences, Uppsala, Sweden GLP, unpublished BVL no. 3056352	N	N	Study was part of the original dossier	DuPont	Y IIA, 7.1.3.3/01
KCA 7.2.1.1/01	Williams, M.D.	1995	HYDROLYSIS OF ^{14}C-DIURON AS A FUNCTION OF pH AT 25°C AND 50°C Report No.: 42580 (994-01019) ABC Laboratories, Inc., Columbia, Missouri, USA GLP, unpublished BVL no. 2803351	N	N	Study was part of the original dossier	DuPont	Y IIA, 2.9.1/02
KCA 7.2.1.1/02	Hawkins, D.R. Kirkpatrick, D. Shaw, D	1988	THE HYDROLYTIC STABILITY OF 14C-DIURON Report-no. AMR-908-87 GLP, unpublished BVL no. 2803352	N	N	Study was part of the original dossier	DuPont	Y IIA, 2.9.1/01
KCA 7.2.1.2/01	Hawkins, D.R. Kirkpatrick, D. Shaw, D. Mobbs, J.	1989	THE PHOTODEGRADATION OF ^{14}C-DIURON IN WATER Report No.: AMR-909-87 HRC/DPT 179/881179 (994-01020) Huntingdon Research Centre, Ltd., Cambridgeshire, United Kingdom GLP, unpublished BVL no. 2803353	N	N	Study was part of the original dossier	Lanxess & DuPont	Y IIA, 2.9.2/01
KCA 7.2.1.2/02	Hellpointner, E.	1991	DETERMINATION OF THE QUANTUM YIELD AND ASSESSMENT OF THE ENVIRONMENTAL HALF-LIFE OF THE DIRECT PHOTODEGRADATION OF DIURON IN WATER Report No.: PF 3486 (994-01021) Bayer AG, Leverkusen, Germany GLP, unpublished BVL no. 2803354	N	N	Study was part of the original dossier	Lanxess	Y IIA, 2.9.3/01

Data point	Author(s)	Year	Title Report No. (Doc. No.) Source (where different from company) GLP or GEP status, Published or not	Verte-brate study Y/N	Data protec-tion claim-ed Y/N	Justifica-tion if data protec-tion is claimed	Owner	Previous-ly submitted Y/N
KCA 7.2.2.2/01	Swales, S.	2016	[^{14}C]-DIURON: AEROBIC MINERALISATION IN SURFACE WATER AND SUSPENDED SEDIMENT Report No.: 3200983 (714-001) Smithers Viscient (ESG) Ltd., Harrogate, United Kingdom GLP, unpublished BVL no. 3088888	N	Y	New study necessary for the approval renewal of Diuron	Arysta LifeScience Benelux Sprl	N
KCA 7.2.2.3/01	Sneikus, J.	2001	AEROBIC DEGRADATION AND METABOLISM OF DIURON IN WATER-SEDIMENT SYSTEM Report No.: GP01-006 M1511091-8 (994-07019) Bayer AG, Leverkusen, Germany GLP, unpublished BVL no. 3056354	N	N	Study was part of the original dossier	Lanxess & DuPont	Y IIA, 7.2.1.3.2/01
KCA 7.3.1/01	Shao-Franz, W. Klein, C.	2016	ESTIMATION OF THE ATMOSPHERIC RESIDENCE TIME OF THE ACTIVE SUBSTANCE DIURON USING THE ATKINSON METHOD RELATED TO THE SUPPLEMENTARY DOSSIER - M-CA SECTION 7 FOR DIURON Report No.: na (781-002) Scientific Consulting Company, Bad Kreuznach, Germany Not GLP, unpublished BVL no. 3088889	N	Y	New study necessary for the approval renewal of Diuron	Arysta LifeScience Benelux Sprl	N