Renewal Assessment Report

Dimethenamid-P

Volume 3 – B.8 Environmental fate and behaviour

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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 dimethenamid-P in soil under aerobic conditions was investigated in four laboratory studies submitted for first EU Annex I inclusion:

- Krueger & Bade, 1990
- Koenig, 1995
- Koenig, 1995
- Wendt, 1997

For renewal of the dimethenamid-P approval, three additional laboratory soil studies under aerobic conditions were submitted:

- Staudenmaier, 2009a with amendment no. 1 Staudenmaier, 2014a
- Staudenmaier, 2013
- Unsworth, 2014

The studies Staudenmaier, 2013a and Unsworth, 2014 were mainly performed to investigate the stereochemistry and the chiral separation of dimethenamid-P during degradation in soil. The main aim of the study Staudenmaier, 2009a with amendment no. 1 Staudenmaier, 2014a was the elucidation of the unknown lysimeter fractions found in the lysimeter study Burgener, 1996. Therefore, the degradation of dimethenamid-P was investigated under aerobic and anaerobic soil conditions and in a soil photolysis study using normal and exaggerated dimethenamid-P application rates. The new and the previously submitted studies are summarised and evaluated under B.8.1.1.1.

Two new kinetic evaluation studies were submitted to derive modelling and persistence endpoints from aerobic laboratory soil studies Koenig, 1995, Koenig, 1996 and Wendt, 1997 according to FOCUS guidance (2011):

- Platz, 1998
- Bronner, 2010

Additionally, kinetic re-evaluations of the studies Staudenmaier, 2009a with amendment no. 1 Staudenmaier, 2014a, Staudenmaier, 2013, Unsworth, 2014 were performed by the RMS. All kinetic evaluations of the laboratory soil studies under aerobic conditions are summarised and evaluated under B.8.1.2.1. In the study Staudenmaier, 2009a with amendment no. 1 Staudenmaier, 2014a, additional analysis of radioactive material detected in the leachate of a microlysimeter study Fent, 2008 was performed. This is summarised and evaluated under B.8.1.4.2 of this document.

Besides, a laboratory soil study under aerobic conditions was performed with the dimethenamid-P metabolites M656PH054, M656PH047 and M656PH043 that were identified in the unknown lysimeter fractions in order to derive trigger endpoints:

- Class & Heinz, 2014

The study is summarised and evaluated under B.8.1.2.3.

The degradation route and rate of dimethenamid in soil under anaerobic conditions was investigated in the one laboratory studies submitted for first EU Annex I inclusion:

- Bade, 1990

The study is summarised and evaluated under B.8.1.1.2.

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

- Sabat & Yu, 1992
- Nietschmann & YU, 1997

The studies are summarised and evaluated under B.8.1.1.3.

In addition to the laboratory studies, four field dissipation studies with dimethenamid were submitted for first Annex I inclusion:

- Fricker & Hertl, 1995a
- Fricker & Hertl, 1995b
- Carrier & Blanz, 1997
- Carrier, 1997

Since surface processes like volatilisation and soil photolysis cannot be excluded in these studies, two new field studies with dimethenamid-P (Bayer & Marwitz, 2014a & c) and one field study with the soil metabolite M656PH027 (Bayer & Marwitz, 2014b) were performed according to EFSA guidance (2014). For all field studies, storage stability studies either with dimethenamid, dimethenamid-P or/and the metabolite M656PH027 are available:

- Bade, 1990
- Mewis, 2014a
- Mewis, 2014b

The field studies together with the respective storage stability studies are summarised and evaluated under B.8.1.2.5.

Two new kinetic evaluation studies were submitted to derive modelling and persistence endpoints from field studies Bayer & Marwitz, 2014a-c:

- Wiedemann, 2014a
- Wiedemann, 2014b

These studies are also summarised and evaluated under B.8.1.2.5.

The adsorption of dimethenamid-P to soil was investigated in one laboratory study submitted already for first EU Annex I inclusion:

- Tong & Su, 1997

For dimethenamid-P EU approval an addendum of this study was submitted:

- Paulick, 2007

The adsorption of the metabolites M656H023 and M656H027 of dimethenamid-P to soil were investigated in one laboratory study submitted already for first EU Annex I inclusion:

- Mamouni, 1995 with addendum Tong, 1999

For dimethenamid-P EU approval additional studies of dimethenamid-P metabolites were submitted:

- Class & Dorn, 2004 (M656H027)
- Class, 2011a (M656H031)
- Sacchi, 2013 (M656H023, M656H027 and M656H031)
- Class & Walter, 2014a (M656PH043)
- Class & Walter, 2014b (M656PH047)
- Class & Walter, 2014c (M656PH054)

The mobility of dimethenamid in soil was investigated in three column leaching studies submitted already for first EU Annex I inclusion:

- Koenig, 1995a
- Koenig, 1994 & 1995b

Besides one lysimeter study with dimethenamid was performed for first EU Annex I inclusion:

- Burgener, 1996

For the renewal of EU approval several studies were performed to elucidate the unknown radioactive fractions in the leachate of the lysimeter study:

- Fent, 2008
- Staudenmaier, 2009a with amendment no. 1 Staudenmaier, 2014a

- Staudenmaier & Kuhnke, 2014
- Staudenmaier, 2014b

Besides, one study was submitted to evaluate the relevance of the lysimeter study for the agricultural areas of Europe using spatially distributed modelling:

- Haering, 2013a

Additionally, one study was submitted to determine the breakthrough behaviour of the dimethenamid-P metabolites M656PH023 and M656PH027 in a microlysimeter:

- Hein & Baudy, 2013

The results of this study were used to estimate sorption and degradation parameters of these metabolites in the soil column:

- Schroeder, 2014

Two field leaching studies with dimethenamid were submitted for first EU Annex I inclusion:

- Gasser, 1998a & b

Finally, one statement on the plant uptake of dimethenamid-P and one study on the plant uptake factor of the metabolite M656PH027 were submitted for renewal of EU approval:

- Schroeder & McCall, 2014
- Gourlay, 2013

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 is decribed in more detail in the Appendix to this document.
No additional open-literature studies concerning the route and rate of dimethenamid-P in soil were found.

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

B.8.1.1 Route of degradation in soil

B.8.1.1.1 Aerobic degradation

KCA 7.1.1.1/1 – Krueger & Bade, 1990 (study evaluated in the monograph, 2000)

Author:	Krueger, J.P. Bade, T.R.
Title:	Aerobic Soil Metabolism of SAN-582H
Date:	16/07/1990
Doc ID:	90/11105
Guidelines:	U.S. EPA Pesticide Assessment Guide1ines, Subdivision N. Section 162-1 (Oct. 1982)
GLP:	Yes
Validity:	Only acceptable for maximum occurrences of M23

Material and Methods

The aerobic metabolism of dimethenamid (3-^{14}C-thienyl dimethenamid, radiochemical purity 99.3 %; dimethenamid, purity > 98 %) was investigated in Kenyon loam soil (Cedar Falls, Iowa, US). The soil characterisation is given in Table B.8.1.1-1.

Table B.8.1.1-1: Characterisation of the soil system (Krueger & Bade, 1990)

Soil designation		Kenyon loam
Textural class (USDA scheme)		Loam
Origin		Cedar Falls, Iowa (USA)
Particle size distribution (%) **Sand** **Silt** **clay**		 34 41 25
Organic C (%)		2.2
CEC (meq/100 g; cation exchange capacity)		20.4
pH ($CaCl_2$)		6.0
FC (g H_2O/100 g dry soil; field capacity determined at 0.33 bar)		24.4
Microbial counts per gram of soil	**Bacteria**	$3.25\ 10^6$
	Actinomycetes	$7.6\ 10^5$
	Fungi	$5.1\ 10^5$

Duplicate samples of soil treated at a concentration of 2.36 mg/kg of moist soil (2.93 mg/kg of dry soil equivalent to 1.8 kg/ha for a soil depth of 5 cm and a soil density of 1.5 g/cm^3) were incubated in the dark at 25 °C and maintained at 75 % of field capacity for intervals of up to one year. Volatiles were trapped in 1.5 M KOH and ethylen glycol. Soil samples were taken at day 0, 1, 3, 7, 14, 30, 63, 90, 120, 181, 268 and 365 and extracted with methanol/water (1:1). The soil extracts were partitioned with hexane. The extracted soil was hydrolysed under alkaline conditions (1 M KOH, 80 °C) for one hour. The hydrolysis fraction was neutralised with HCl, taken to dryness and extracted with methanol and subsequently with water. The individual extracts were analysed by TLC and HPLC and compared to authentic standards. Isolated fractions were further purified and subjected to GC-MS and/or NMR analysis. The material balance was determined by combustion of the soil residue and radioassay of the extracts for $^{14}CO_2$.

Results and Discussion

The balance of recovered radioactivity for individual incubations ranged from 74.2 to 106.4 % AR and averaged 89.1 % AR.

The active substance was degraded to a residue of 16.3 % AR and 2.3 % TAR after 120 days and one year, respectively. Volatile breakdown products occurred mainly in the form of $^{14}CO_2$ (7.6 % AR at day 120, 17.2 % AR at day 365); organic volatiles were trapped in amounts of 0.6 % AR at the end of the study. Bound residues increased with time and reached a maximum of 21.8 % AR at 120 days and the level was close to that at termination (17.2 % AR). In total, 4 fractions could be isolated by TLC both from the methanol/water and the base hydrolysis extracts. The hexane extracts contained almost exclusively parent compound, the other fractions were isolated from the polar extracts. The distribution of recovered radioactivity among CO_2, dimethenamid and metabolites (sum of methanol/H_2O and basic extract) and non-extractable residue is specified in Table B.8.1.1-2.

The metabolite M656H023 (oxalamide in this study) was the major component, reaching a peak level of 14.4 % AR at day 90 and decreasing to 7.4 % AR at termination. Two further fractions, ‘Fr.4’ and ‘Fr.1A+B’, were isolated by TLC. Fraction 4 increased to an average of 8.5 % AR at day 268 and decreased to 5.7 % AR at termination. Fraction 1A+B represented two compounds in similar quantities and of very similar R_f values on TLC and identical retention times on HPLC. Fr.1A (M656PH027: sulfonate in this study) + B reached a maximum of 9.7 % AR at day 268 and decreased to 8.5 % AR at day 365. Attempts to identify Fraction 4 and Fraction 1B were unsuccessful.

Table B.8.1.1-2: Recovery of radioactivity in % AR and distribution of major metabolites (Krueger & Bade, 1990)

DAT	CO_2	Dimethenamid	M656H023	M656H027* Fr. 1A+B	Fraction 4 (unidentified)	NER	Mass balance**
0	0.0	78.8	0.8	1.3	0.4	5.9	96.8
14	0.6	68.2	5.1	3.4	2.5	11.2	101.9
30	1.5	58.3	3.8	2.1	2.1	10.2	90.9
63	3.5	28.2	8.5	4.2	3.8	10.6	80.1
90	5.9	14.4	14.4	5.9	5.9	16.3	89.7
120	7.6	16.3	11.9	8.1	6.8	21.8	92.6
181	10.0	7.6	9.7	8.5	7.6	15.0	79.2
268	11.9	5.9	8.9	9.7	8.5	17.4	79.4
365	17.2	2.3	7.4	8.5	5.7	17.2	81.9

* The M656PH027 peak contained another compound of equal quantity. The values are the totals for the peak.
** Sum of total volatile, extractable ($MeOH/H_2O$ and base extracts) and non-extractable radioactivity

Conclusion

The study was submitted for the first Annex I inclusion of dimethenamid-P and was considered acceptable at that time. However, after re-evaluation of the study, the RMS concluded that it does not fulfil the requirements of current guidelines anymore. This is mainly due to the low overall recovery which was below 90 % in at least one replicate for 7 of the 9 sampling times and at 3 sampling times where both of the replicates were < 90 %. Excluding the results of all sampling points below < 90 % before kinetic evaluation would not allow the derivation of a meaningful kinetic fit for dimethenamid anymore. Further shortcomings were the study duration which exceeded the recommended 120 days after which the biological activity cannot be guaranteed anymore. Besides, the occurrence of the metabolite M31 was not investigated in the study. The applicant also decided to not include this study in the newly submitted kinetic evaluation studies Platz, 2008 and Bronner, 2010, since when excluding the data points past 120 days no meaningful fit for the two metabolites M656H023 and M656H027 can be obtained anymore.

KCA 7.1.1.1/2 – Koenig, 1995 (study evaluated in the monograph, 2000)

Author: Koenig, M.
Title: Aerobic Degradation of [3-^{14}C-thienyl]-dimethenamid in BBA 2.2 and 2.3 Soils under Laboratory conditions
Date: 19/02/1995
Doc ID: 95/10128
Guidelines: Guideline Part IV, 4-1 "Fate of Plant Protection Products in Soil - Degradation, Conversion and Metabolism" issued by the Federal Biological Research Centre for Agriculture and Forestry, Federal Republic of Germany (1986)
GLP: Yes
Validity: Acceptable

Material and Methods

Aerobic degradation experiments were conducted with two German standard soils BBA 2.2 (loamy sand) and BBA 2.3 (sandy loam). The soil properties are specified in Table B.8.1.1-3.

Table B.8.1.1-3: Characterisation of the soil system (Koenig, 1995)

Soil designation		BBA 2.2	BBA 2.3
Textural class (German scheme)		Loamy sand	Sandy loam
Origin		Germany	Germany
Particle size distribution (%) **0.063 – 2 mm** **0.002 – 0.063 mm** **< 0.002 mm**		 82 12 5	 64 28 8
Organic C (%)		2.29	1.34
CEC (meq/100 g; cation exchange capacity)		9.70	9.50
pH ($CaCl_2$)		5.8	6.6
MWC (g H_2O/100 g dry soil)		9.7	9.5
Microbial biomass determined as µg ATP/kg soil	**day 0**	142	199
	day 119	171	182

Replicate samples of each soil (approximately 60 grams) were treated with dimethenamid (3-^{14}C-thienyl dimethenamid, radiochemical purity > 98.0 %; dimethenamid, purity 99.8 %) at a concentration of 1.92 mg/kg dry soil (corresponding a field rate of 1.44 kg as/ha when assuming a homogenous distribution in the upper 5 cm soil and a soil density of 1.5 kg/L). Soil samples were incubated under aerobic conditions in the dark at 20 °C, maintaining a constant soil humidity of 40 % of the maximum water holding capacity. Volatiles and carbon dioxide were not trapped. After sampling at day 0, 1, 3, 7, 14, 21, 28, 42, 56, 70, 84 and 119, duplicate samples were extracted with MeOH/H_2O (1:1 v/v) and divided into non-polar and polar fractions by solid phase extraction (SPE). The non-polar and polar fractions were analysed for parent compound and metabolites by HPLC and TLC (co-chromatography with authentic standards). Bound radioactive residues were determined by combustion of the soils after extraction.

Results and Discussion

The distribution of extractable radioactivity and bound residues is presented in Table B.8.1.1-4 and Table B.8.1.1-5.

Table B.8.1.1-4: Extractable and bound radioactivity in the soils BBA 2.2 in % AR (Koenig, 1995)

DAT	Extractable radioactiviy	Bound residues	Total recovery
0	98.43	-	-
1	95.77	2.35	98.12
3	92.05	6.01	98.06
7	83.22	13.89	97.11
14	69.93	24.13	94.06
21	63.47	31.12	94.59
28	58.73	34.60	93.33
42	45.07	42.09	87.16
56	41.10	38.00	79.10
70	33.74	44.64	78.38
84	33.94	43.06	77.00
119	25.21	42.32	67.53

Table B.8.1.1-5: Extractable and bound radioactivity in the soils BBA 2.3 in % AR (Koenig, 1995)

DAT	Extractable radioactiviy	Bound residues	Total recovery
0	98.39	-	-
1	96.80	2.18	98.98
3	93.85	7.00	100.85
7	83.70	15.09	98.79
14	72.70	23.67	96.37
21	65.10	30.40	95.50
28	61.61	32.07	93.68
42	49.12	38.19	87.31
56	44.58	36.13	80.71
70	33.89	44.26	78.15
84	31.68	44.85	76.53
119	21.59	43.45	65.04

Total recoveries without CO_2 and volatiles decreased from 98.2 and 99 % at day 0 for the soils BBA 2.2 and BBA 2.3 to 67.5 % and 65 % AR at day 119, respectively. The amount of extractable radioactivity continuously decreased to 25.2 % AR (BBA 2.2) and 21.6 % AR (BBA 2.3) at the end of the incubation. At the same time, bound residues increased to 42.3 % AR (BBA 2.2) and 43.5 % AR (BBA2.3).
The distribution of recovered radioactivity is presented in Table B.8.1.1-6 and Table B.8.1.1-7.

Table B.8.1.1-6: Distribution of the radioactivity in the soil BBA 2.2 in % AR quantified by TLC & HPLC (Koenig, 1995)

DAT	Dimethenamid	M656H023	M656H027	M656H031
0*	98.09	-	-	-
0*	98.77	-	-	-
1	93.52	0.36	0.42	0.36
1	92.03	0.4	0.47	0.33
3	88.39	1.03	0.71	0.55
3	87.18	1.07	0.82	0.64
7	69.38	3.6	2.19	1.94
7	71.06	3.66	2.28	1.62
14	45.21	6.97	5.45	4.22
14	46.81	7.22	5.19	4.37
21	30.54	8.65	8.81	6.31
21	30.07	8.38	7.93	6.85
28	21.60	9.1	10.25	7.05
28	20.41	8.63	10.77	6.84
42	9.10	7.63	10.89	6.53
42	9.70	8.01	10.85	7.11
56	6.58	6.4	10.41	6.06
56	6.31	6.35	10.35	6.05
70	3.47	5.35	9.92	5.5
70	3.52	5.06	9.42	5.07
84	3.40	5.14	9.15	4.94
84	3.67	5.91	9.25	4.39
119	1.62	3.35	7.14	3.64
119	1.62	2.87	7.13	3.55

* no analysis of parent and metabolites, total extractable radioactivity was set for DMTA-P

Table B.8.1.1-7: Distribution of the radioactivity in the soil BBA 2.3 in % AR quantified by TLC & HPLC (Koenig, 1995)

DAT	Dimethenamid	M656PH023	M656PH027	M656PH031
0	99.33*	-	-	-
0	97.44*	-	-	-
1	93.73	0.18	0.58	0.47
1	93.77	0.18	0.83	0.34
3	87.84	0.52	1.25	1.00
3	89.82	0.43	1.09	0.89
7	71.61	1.19	3.28	3.58
7	71.42	1.11	3.24	3.41
14	45.60	2.26	7.17	8.74
14	45.42	1.99	7.91	8.28
21	31.12	2.81	10.15	9.67
21	31.68	2.83	9.55	8.95
28	23.20	3.39	12.09	10.34
28	24.13	3.56	11.89	10.00
42	9.43	3.49	13.32	7.89
42	9.82	3.28	12.05	8.13
56	7.08	2.80	10.04	5.06
56	8.64	2.97	10.78	5.54
70	4.41	2.42	9.32	3.79
70	4.78	2.51	9.62	4.11
84	4.92	2.22	8.00	3.11
84	5.08	1.95	8.45	2.98
119	2.13	1.28	5.71	1.78
119	2.23	0.99	3.33	1.55

* no analysis of parent and metabolites, total extractable radioactivity was set for DMTA-P

Dimethenamid was extensively metabolised leaving 1.6 and 2.2 % AR after 119 days in the soils BBA 2.2 and BBA 2.3. The major degradation products were the metabolites M656H023 (M23 or oxalamide in this study), M656H027 (M27 or sulfonate in this study) and M656H031 (M31 in this study). M656H023 was found with maximum concentrations of 8.9 % and 10.2 % AR at day 28 in the soils BBA 2.2 and BBA 2.3, M656H027 reached maximum concentrations of 10.9 % and 12.7 % on day 42 in the soils BBA 2.2 and BBA 2.3. M656H031 reached maximum concentrations of 6.9 % and 6.8 % in two subsequent samples at day 28 and 42 in the soil BBA 2.2 and remained < 5 % in soil BBA 2.3. All three metabolites declined afterwards. Several other unidentified metabolites were detected which all remained <5 % AR.

Conclusion

The study was considered acceptable for the first Annex I inclusion of dimethenamid-P. After re-evaluation of the study, the RMS concluded that it also fulfils the requirements of current guidelines and is thus still considered acceptable.

The study was performed with dimethenamid instead of dimethenamid-P, however studies both submitted for renewal assessment as well as for the first Annex I inclusion (Wendt, 1997, Nietschman & Yu, 1997, Staudenmaier, 2013a, Unsworth, 2014a) showed that metabolism as well as degradation rates of dimethenamid and dimethenamid-P are virtually identical.

A new kinetic evaluation of the residues of dimethenamid and its soil metabolites was performed by Platz, 2008.

Thus, the DT_{50} and DT_{90} values determined in the study are not presented here anymore.

The soil metabolism of dimethenamid was investigated under aerobic conditions in a loamy sand and in a sandy loam soil at 20 °C and 40 % MWHC. Dimethenamid degraded to 1.6 and 2.2 % after 119 d. The amount of unextractable residues increased to 42.3 and 43.5 % after 119 days. CO_2 and volatiles were not measured. Major metabolites were M656H023, which reached a maximum of 10.2 % after 28 days with subsequent decline, M656H027 which reached a maximum of 12.7 % after 42 days and M656H031 with maxima of 6.9 % after 28 days.

KCA 7.1.1.1/3 – Koenig, 1996 (study evaluated in the monograph, 2000)

Author: Koenig, M.
Title: Aerobic Degradation and Metabolism of [3-^{14}C-Thienyl]-Dimethenamid in Flaach Soil under Laboratory
Date: 07/08/1996
Doc ID: 96/11006
Guidelines: Guidelines for the official testing of plant protection products, part IV, 4-1 of plant protection products in soil- degradation (December 1986)
GLP: Yes
Validity: Acceptable

Material and Methods

Aerobic degradation of dimethenamid (3-^{14}C-thienyl dimethenamid, radiochemical purity > 98.0 %; dimethenamid, purity 99.8 %) was investigated in Switzerland sandy clay loam (Flaach). The soil properties are specified in Table B.8.1.1-8.

Table B.8.1.1-8: Characterisation of the soil system (Koenig, 1996)

Soil designation		Flaach
Textural class (German scheme)		Sandy Clay Loam
Origin		Switzerland
Particle size distribution (%) **0.063 – 2 mm** **0.002 – 0.063 mm** **< 0.002 mm**		 52 24 24
Organic C (%)		1.34
CEC (meq/100 g; cation exchange capacity)		12.6
pH ($CaCl_2$)		7.49
MWC (g H_2O/100 g dry soil) (max. water holding capacity)		Not reported
Microbial biomass determined as µg ATP/kg soil	**day 0**	268
	day 120	270

Replicate samples of each soil (approximately 60 grams) were treated with dimethenamid (3-^{14}C-thienyl dimethenamid, radiochemical purity > 98.0 %; dimethenamid, purity 99.8 %) at a concentration of 1.92 mg/kg dry soil (corresponding to the maximum recommended field rate of 1.44 kg as/ha). Soil samples were incubated under aerobic conditions in the dark at 20 °C, maintaining a constant soil humidity of 40 % of the maximum water holding capacity. Volatiles and carbon dioxide were trapped in ethanediol and 1.5 M KOH. After sampling at day 0, 1, 3, 7, 14, 21, 28, 42, 56, 70, 84 and 120 duplicate samples were extracted with MeOH/H_2O (1:1 v/v) and divided into non-polar and polar fractions by solid phase extraction (SPE). Extracted soil samples were further extracted with methanol/H_2O/0.1 M EDTA (2:2:1 v/v/v). The non-polar and polar fractions were analysed for parent compound and metabolites by HPLC and TLC (co-chromatography with authentic standards). Bound radioactive residues were determined by combustion of the soils after extraction.

Results and Discussion

Total recoveries for individual incubations ranged from 94.4 to 101.7 % AR. The amount of extractable radioactivity continuously decreased to 13.8 % AR at the end of the incubation. 35.8 % AR were mineralised to CO_2 and bound residues increased to 41.4 %.
The distribution of recovered radioactivity is summarised in Table B.8.1.1-6.

Table B.8.1.1-9: Distribution of the radioactivity in the soil Flaach in % AR quantified via TLC (Koenig, 1996)

DAT	Dimethenamid	M656H023	M656H027	M656H031
0	96.5	< 0.1	< 0.1	< 0.1
0	96.8	< 0.1	< 0.1	< 0.1
0	97.0	< 0.1	< 0.1	< 0.1
1	82.9	0.7	1.1	0.3
1	86.7	0.7	1.1	0.3
1	87.4	0.2	0.3	0.1
3	72.8	2.2	2.6	0.7
3	69.9	1.8	2.4	0.6
3	71.9	1.6	2.3	0.7
7	51.4	4.1	5	1.3
7	52.9	4.2	5.9	1.2
7	48.6	4.2	4.8	1.4
14	28.5	7.5	8.5	2.4
14	27.3	7.1	8.5	2.1
14	27.5	7.5	8.3	2.3
21	14.8	8.4	9.3	3.3
21	13.4	6.8	8.7	2.4
21	14.4	8	9.1	2.6
28	7.7	7.2	8.6	4
28	7.3	7.2	8.5	3.6
28	8.1	6.9	8.9	3.3
42	2	4.9	8.1	2.1
42	1.5	4.3	7.7	1.7
42	1.9	4.5	7.4	1.8
56	1.3	3.8	5.9	1.6
56	1	3.1	6	1.6
56	1.1	3.1	5.9	1.4
70	0.9	2.7	5.6	1.8
70	0.7	2.3	5.2	1.5
70	0.7	2.1	5.6	1.3
84	0.6	1.6	4.3	1.2
84	0.4	1.1	3.7	0.9
84	0.5	1.3	3.9	1.1
120	0.4	0.4	2.5	0.5
120	0.3	0.4	2.4	0.5
120	0.3	0.3	2.2	0.3

Dimethenamid was extensively metabolised leaving 0.3 % AR after 120 days in the soil Flaach. The major degradation products were the metabolites M656H023 (oxalamide or M23 in this study) and M656H027 (M27 or sulfonate in this study). M656H023 was found with maximum concentrations of 8.0 % at day 21, M656H027 reached maximum concentrations of 9.1 % on day 21. M656H031 (M31 in this study) reached a maximum concentration of 3.3 % at day 28 thus remained < 5 % in the soil Flaach. All three metabolites declined afterwards. Several other unidentified metabolites were detected which all remained <5 % AR.

Conclusion

The study was considered acceptable for the first Annex I inclusion of dimethenamid-P. After re-evaluation of the study, the RMS concluded that it also fulfils the requirements of current guidelines and is thus still considered acceptable.

The study was performed with dimethenamid instead of dimethenamid-P, however studies both submitted for renewal assessment as well as for the first Annex I inclusion (Wendt, 1997, Nietschman & Yu, 1997, Staudenmaier, 2013a, Unsworth, 2014a) showed that metabolism as well as degradation

rates of dimethenamid and dimethenamid-P are virtually identical.
A new kinetic evaluation of the residues of dimethenamid and its soil metabolites was performed by Latz, 2008. Thus, the DT_{50} and DT_{90} values determined in the study are not presented here anymore.
The soil metabolism of dimethenamid was investigated under aerobic conditions in a sandy clay loam soil at 20 °C and 40 % MWHC. Dimethenamid degraded to 0.3 % after 120 d. The amount of unextractable residues increased to 41.4 % after 120 days and 35.8 % AR were mineralised to CO_2. Major metabolites were M656H023, which reached a maximum of 8.0 % at day 21 with subsequent decline and M656H027 which reached a maximum of 9.1 % on day 21. M656H031 remained < 5 % throughout the study.

KCA 7.1.1.1/4 – Wendt, 1997 (study evaluated in the monograph, 2000)

Author: Wendt, D.R.
Title: Comparative Aerobic Soil Metabolism of SAN 1289H and SAN 582H
Date: 06/03/1997
Doc ID: 97/5257
Guidelines: 40 CFR 158.130, Subdivision N, Guideline Ref. No. 162-1
GLP: Yes
Validity: Acceptable

Material and Methods

The aerobic soil metabolism of ^{14}C-dimethenamid-P (3-^{14}C-thienyl dimethenamid-P, radiochemical purity 96.0 %; dimethenamid-P, purity 98.6 %) and ^{14}C-dimethenamid (3-^{14}C-thienyl dimethenamid, radiochemical purity 98.5 %; dimethenamid, purity 99.7 %) were compared in Elliot clay loam soil (Champaign County, Illinois, USA). The soil characteristics are listed in Table B.8.1.1-10.

Table B.8.1.1-10: Characterisation of the soil system (Wendt, 1997)

Soil designation		Elliot Clay Loam
Textural class (USDA)		Clay loam
Origin		Champaign County, Illinois (USA)
Particle size distribution (%)		
Sand		24
Silt		44
clay		32
Organic C (%)		2.4
CEC (meq/100 g; cation exchange capacity)		15.6
pH ($CaCl_2$)		6.4
FC (g H_2O/100 g dry soil; field capacity determined at 0.33 bar)		33.37
Microbial counts (CFU/g dry soil)	**Aerobic bacteria**	$7.7 \cdot 10^6$
	Actinomycetes	$11 \cdot 10^6$
	Mould	$1.7 \cdot 10^3$

The concentrations of both ^{14}C-dimethenamid-P and ^{14}C-dimethenamid were 1.595 mg/kg moist soil (1.994 mg/kg dry soil equivalent to 1.5 kg/ha for a soil depth of 5 cm and a soil density of 1.5 g/cm^3). Incubation conditions were: aerobic by continuous flow of air, temperature maintained at 23 ± 1 °C, and soil moisture at 75 % of field capacity. Duplicate soil samples were collected at 0, 1, 3, 7, 14, 21, 28, 42, 56, 84, 119 and 182 days. Volatiles were trapped by continuously washing the effluent gas with 1 M NaOH and ethylene glycol. Soil was extracted with methanol, then methanol/0.1 M HCl. The extracts were pooled, concentrated, and characterised by TLC and HPLC. Bound residues were characterised by extraction with 0.1 M NaOH to separate fulvic acid, humic acid, and humin fractions. In addition, exaggerated rate incubations (21 days, 9.5 mg/kg dry soil) were conducted in order to generate products in quantities sufficient for identification by GC-MS. Identification of metabolites was accomplished by co-chromatography with authentic reference standards (TLC and HPLC) and confirmed by MS.

Results and Discussion

The overall mass balances of dimethenamid and dimethenamid-P are presented in Table B.8.1.1-11.

Table B.8.1.1-11: Distribution and overall recovery of dimethenamid-P (DMTA-P) and Dimethenamid (DMTA) in the soil Elliott in % AR (Wendt, 1997)

DAT	CO_2		Bound residues		Total recovery	
	DMTA-P	DMTA	DMTA-P	DMTA	DMTA-P	DMTA
0	0.0	0.0	0.7	0.4	101.5	101.7
1	0.4	0.4	6.3	5.3	97.1	95.3
3	0.8	0.8	10.9	11.3	96.2	97.0
7	1.6	1.5	18.3	19.0	95.8	96.5
14	3.3	3.2	26.8	27.5	96.8	96.5
21	5.2	4.9	33.1	33.2	92.9	94.1
28	7.1	6.7	34.7	34.8	94.3	94.1
42	10.7	10.2	38.0	38.4	94.5	93.8
56	14.0	13.3	38.7	38.7	95.2	95.1
84	18.9	18.5	40.3	43.5	94.2	98.7
119	23.5	23.1	39.9	40.8	92.9	95.0
182	29.2	28.5	39.9	39.5	93.8	94.7

The total recoveries for individual incubations ranged from 91.7 to 102.8 % AR and from 93.5 to 103.6 % AR in the case of dimethenamid-P and dimethenamid, respectively. After the 182 day incubation period, $^{14}CO_2$ accounted for 28-29 % AR for both treatments. Non-extractable residues were found to increase to 40 % AR. Up to 9 % AR and 25 % AR was associated with fulvic acid and humic acid fraction, respectively. The humin fraction contained up to 10 % AR at the end of the study. The distribution of recovered radioactivity of dimethenamid-P and dimethenamid are presented in Table B.8.1.1-12 and Table B.8.1.1-13.

Table B.8.1.1-12: Distribution of the radioactivity in the soil Elliott after degradation of dimethenamid-P (DMTA-P) in % AR quantified by HPLC (Wendt, 1997)

DAT	DMTA-P	M656PH023	M656PH027	M656PH031
0	96.2	n.d.	1.3	n.d.
0	100.7	n.d.	n.d.	n.d.
1	86.4	n.d.	n.d.	n.d.
1	88.5	n.d.	1.5	n.d.
3	69.8	2.8	5.0	2.3
3	77.1	1.7	2.4	2.1
7	59.0	4.3	4.3	4.0
7	54.2	5.8	5.0	3.4
14	31.3	8.2	8.0	6.6
14	33.5	5.2	7.7	6.9
21	19.6	5.1	7.8	8.2
21	20.9	6.1	6.5	8.8
28	13.3	6.0	8.0	9.7
28	15.8	6.0	7.4	8.8
42	6.7	5.0	6.9	8.3
42	8.7	4.2	9.0	9.2
56	8.8	3.9	5.5	9.3
56	8.7	2.9	6.1	8.5
84	6.0	1.9	6.1	8.6
84	4.4	1.5	4.0	6.0
119	3.3	2.0	3.1	5.6
119	2.8	2.3	2.9	4.5
182	1.4	1.2	1.8	4.1
182	1.8	1.9	2.6	3.9

n.d. not detectable

Table B.8.1.1-13: Distribution of the radioactivity in the soil Elliott after degradation of dimethenamid (DMTA) in % AR quantified by HPLC (Wendt, 1997)

DAT	DMTA	M656H023	M656H027	M656H031
0	93.4	n.d.	n.d.	n.d.
0	103.2	n.d.	n.d.	n.d.
1	89.2	n.d.	1.3	n.d.
1	86.6	n.d.	n.d.	n.d.
3	78.2	2.6	3.1	1.0
3	78.1	2.4	2.3	2.6
7	55.6	5.5	3.4	4.5
7	53.0	5.6	4.3	4.6
14	33.7	7.3	7.8	7.6
14	33.2	6.5	8.7	6.7
21	20.9	5.8	7.7	8.7
21	19.9	7.7	6.5	7.6
28	18.2	7.8	6.3	8.0
28	12.7	7.3	8.7	8.6
42	7.8	7.0	5.7	7.4
42	9.0	6.3	4.2	7.2
56	11.4	4.3	3.2	10.3
56	9.0	3.8	4.2	9.4
84	3.9	2.6	3.8	6.5
84	4.4	2.8	4.0	6.9
119	2.6	1.6	4.5	4.6
119	3.4	1.1	4.5	4.5
182	2.0	1.4	3.8	4.3
182	1.7	1.3	2.3	4.2

n.d. not detectable

Dimethenamid-P and dimethenamid were extensively metabolised leaving 1.6 and 1.5 % AR after 182 days of incubation. The major degradation products were the metabolites M656PH023 or M656H023 (oxalamide in this study), M656PH027 or M656H027 (sulfonate in this study) and M656PH031 or M656H031 (STGA in this study), respectively. M656PH023 or M656H023, respectively, were found with maximum concentrations of 7.9 % and 8.2 % AR at day 21 after degradation of dimethenamid-P and dimethenamid, respectively. M656PH027 or M656H027, respectively, reached maximum concentrations of 7.8 % and 8.0 % on day 42 after degradation of dimethenamid-P and dimethenamid, respectively, and M656PH031 or M656H031 (STGA in this study), respectively, reached maximum concentrations of 6.9 % and 6.8 % at day 21 after degradation of dimethenamid-P and dimethenamid, respectively. All three metabolites declined afterwards. Besides, three additional metabolites M656PH032 or M656H032 (TGA in this study), M656PH026 or M656H026 (TLA in this study), M656PH030 or M656H030 (STLA in this study) and M656PH011 or M656H011 (M11 in this study), respectively, were identified which remained all < 5 %.

Conclusion

The study was considered acceptable for the first Annex I inclusion of dimethenamid-P. After re-evaluation of the study, the RMS concluded that it also fulfils the requirements of current guidelines and is thus still considered acceptable.

The soil metabolism of dimethenamid-P and dimethenamid was investigated under aerobic conditions in one clay loam soil at 23 °C and 75 % of field capacity. Dimethenamid-P and dimethenamid degraded to 1.5 - 1.6 % AR after 182 days. $^{14}CO_2$ accounted for 28 - 29 % AR and non-extractable residues increased to 40 % AR after 182 days. Major metabolites were M656PH023 or M656H023 which reached a maximum of 7.9 - 8.2 % after 21 days, M656PH027 or M656H027 which reached a maximum of 7.8 - 8.0 % after 42 days and M656PH030 or M656H030, respectively, with a maximum of 6.9 - 6.8 % at day 21. No differences in degradation and metabolism could be found between dimethenamid-P and dimethenamid.

A new kinetic evaluation of the residues of dimethenamid and its soil metabolites were performed by Bronner, 2010. Thus, the DT_{50} and DT_{90} values determined in the study are not presented here anymore.

KCA 7.1.1.1/5 – Staudenmaier, 2009a with amendment no. 1 Staudenmaier, 2014a (new studies)

Author:	Staudenmaier, H.
Title:	Structure elucidation of metabolites of Dimethenamid in lysimeter leachate
Date:	18/11/2009
Doc ID:	2009/1011362
Guidelines:	OECD 307, BBA IV 4-1, EPA Subdivision N, 162-1
GLP:	Yes
Validity:	Acceptable

Author:	Staudenmaier, H.
Title:	Structure elucidation of metabolites of Dimethenamid in lysimeter leachate – Amendment No 1
Date:	22/01/2014
Doc ID:	2014/1031599
Guidelines:	OECD 307, BBA IV 4-1, EPA Subdivision N, 162-1
GLP:	No - not applicable
Validity:	Acceptable

Aim of study

In the leachate of a lysimeter study with dimethenamid, Burgener, 1996 described under B.8.1.4.2, numerous fractions of unidentified radioactivity were observed. Since no lysimeter leachate was available any more, the material required for structure elucidation had to be newly generated. This was attempted by both, a soil study that used incubations of dimethenamid-P in soil under different conditions and a micro-lysimeter study Fent, 2008 described under B.8.1.4.2.
In the present soil study the soil metabolism of dimethenamid-P was investigated under aerobic, anaerobic and photolytic conditions with the purpose to generate information about the formation of degradation products and to elucidate their structures as far as possible. During the conduct of the study, it turned out that the underlying task - the structure elucidation of metabolites in lysimeter leachate - may be supported by the analysis of the radioactive material detected in the leachate of the microlysimeter study. Therefore, it was decided to additionally use samples of leachate water of the latter study for structure elucidation.
Here, only the investigation and the results of the soil incubations with dimethenamid-P under aerobic, anaerobic and photolytic conditions are described. The comparison of the HPLC chromatograms and the methodology and analysis of the leachate samples of the microlysimeter study as well as the structure elucidation of selected soil and leachate samples or isolated peaks are summarised under B.8.1.4.2 - Staudenmaier, 2009a with amendment no. 1 Staudenmaier, 2014a (new studies). The amendment Staudenmaier, 2014a concerns mainly contains some corrections regarding the new structure proposals and metabolite codes and is thus also describer under B.8.1.4.2 - Staudenmaier, 2009a with amendment no. 1 Staudenmaier, 2014a (new studies).

Material and Methods

Soil from Borstel, Lower Saxony, Germany was used for this study. This is the same soil that was used earlier for the lysimeter study Burgener, 1996 with dimethenamid. The soil characteristics are presented under Table B.8.1.1-14.

Table B.8.1.1-14: Characterisation of the soil system (Staudenmaier, 2009 with amend. 2014)

Origin	Borstel, Lower Saxony, Germany
Textural class (DIN)	sand
Particle size distribution (%) **Sand 0.063 – 2 mm** **Silt 0.002 – 0.063 mm** **Clay < 0.002 mm**	 24 44 32
Organic C (%) **Organic matter [%] ****	0.75 1.29
CEC (cmol / kg)	2.7
pH (H_2O) **pH ($CaCl_2$)**	6.5 5.9
water holding capacity pF0 (g/100g dry weight)	23.0
microbial biomass * **(end of study)** **[mg C/100g dry soil]**	14.5

* determined at the test site according to Anderson & Domsch using a BSB digi
** organic matter = organic carbon x 1.724

All soil samples were treated with a mixture of thienyl-5-^{14}C-labelled and non-radiolabelled dimethenamid-P.

For aerobic soil incubations, soil was treated at a nominal rate of 2.7 mg/ kg of dry soil which corresponds to a field application rate of 2 kg/ha test item (calculated on the basis of an equal distribution in the top 5 cm soil layer and a soil density of 1.5 g/cm^3). Prior to the application, the soil was adjusted to 50 % of the maximum water holding capacity (MWHC). Soil aliquots of 100 g dry soil equivalents were weighed into test vessels and were incubated at 20 °C in the dark. Samples were taken at 0, 2, 7, 14, 28, 58, 89 and 119 days after treatment. At each sampling time, two vessels were taken for sampling. Volatiles were trapped in a trapping system of gas washing flasks containing ethylene glycole and 0.5 M NaOH.
Additional soil was treated at an exaggerated rate of 8 mg dimethenamid-P per kg of dry soil corresponding to a field application rate of 6 kg/ha (calculated on the basis of an equal distribution in the top 5 cm soil layer and a soil density of 1.5 g/cm^3). Therefore, aliquots of 500 g were incubated under aerobic conditions as described above and sampled 58, 89 and 119 days after treatment.

For anaerobic soil incubations, soil aliquots of 100 g dry soil equivalents, treated at the exaggerated rate of 6 kg a.s. per hectare were filled into test vessels and were incubated as described above. After 30 days, the soil in the test vessels was flooded with water in order to establish anaerobic conditions. From day 48 after treatment on, the test vessels were additionally purged with nitrogen. At day 119, one test vessel was sampled.

For the soil photolysis study, untreated soil aliquots of about 45 g each were filled into metal dishes of a soil photolysis apparatus. The soil was treated by pipetting a solution of the test item to the soil surface at a nominal rate corresponding to 6 kg dimethenamid-P per hectare. The photolysis was performed with an intensity of radiation of 3 mW/cm^2 in a Suntest apparatus. After 15 days one test vessel was sampled and worked up and at day 16 the soil of the remaining test vessels was pooled and worked up.

All soil samples were extracted three times with MeOH for about 20 min each by shaking on a laboratory shaker and the phases were separated by centrifugation. The supernatant was decanted, filtered and made up to volume. The extraction procedure was repeated three times with MeOH/H_2O (8:2). For some of the samples a further extraction step with MeOH/H_2O (2:8) was added for the extraction of possible polar metabolites. Aliquots of the pooled extracts were subjected to radio HPLC analysis. Various samples of the soil incubations were investigated by LC-MS/MS analysis, either directly or upon fractionation by HPLC.
Selected extracts of the aerobic soil metabolism, the anaerobic incubation and the soil photolysis were used for structure elucidation either directly or after fractionation.

Results and Discussion

A complete mass balance is only available for the aerobic degradation (normal rate) and in the anaerobic degradation experiments, since the main focus of this study was the generation of suitable amounts of metabolites for structure elucidation. In the aerobic degradation (normal rate) and in the anaerobic degradation experiments, mass balances between 97 – 101.6 % were achieved. The setup of the aerobic degradation at the high rate and the photolysis experiment was not suitable for exact quantification of volatiles and no complete mass balance was thus established.
In the aerobic incubations, the percentage of extractable radioactivity decreased from about 100 % at day 0 to about 38 - 46 % of applied after 119 days. In the anaerobic degradation, it decreased less resulting in 69 % extractable after 119 days. In contrast, in the photolysis experiments low extractability of only 23 - 24 % of applied was observed already after 15 - 16 days.
Bound residues were formed in the aerobic experiments up to 42 % of applied whereas a slightly lower percentage of 27 % was observed in the anaerobic incubation after 119 days. In the photolysis experiment, bound residues increased to 25 - 29 % after 15 - 16 days.
In the aerobic degradation at the low rate, 17.5 % of applied $^{14}CO_2$ was determined after 119 days. Besides $^{14}CO_2$, no other volatile compounds were detected. In the anaerobic soil study only total volatiles were measured which amounted to 3 % after 119 days.

The results of the aerobic incubation at the application rate of 2 kg/ha are shown in Table B.8.1.1-15.

Table B.8.1.1-15: Radio-HPLC analysis of the soil extracts of the incubation with ^{14}C-BAS 656 H under aerobic conditions for an application rate of 2 kg/ha dimethenamid-P (Staudenmaier, 2009 with amend. 2014)

DAT	% TAR											
	^{14}C total	ukn	ukn	M27	ukn	M31	M23	ukn	ukn	ukn	DMTA-P	others [b]
	t_R [a]	23.5	24.1	25.6	27.9	29.0	29.6	30.8	31.7	34.9	37.7	
0	101.2	0.7									100.5	
	100.0	0.4									99.6	
0 mean	100.6	0.5									100.0	
2	94.0		0.3		0.3		0.4			0.2	91.9	0.9
	94.5	0.2	0.3	0.3	0.3	0.1	0.5		0.2	0.1	91.3	0.9
2 mean	94.3	0.1	0.3	0.2	0.3	0.1	0.5		0.1	0.2	91.6	0.9
7	88.3		0.3	0.8		1.0	1.2	0.4	0.4	0.4	81.8	2.0
	89.3		0.5	0.9	1.1	0.9	1.3	0.5	0.4	0.3	82.1	1.3
7 mean	88.8		0.4	0.8	0.5	0.9	1.2	0.5	0.4	0.4	81.9	1.7
14	80.9		0.5	1.4	1.9	2.0	2.8	1.0	0.4		69.1	1.8
	79.7		0.5	1.4	1.8	2.5	2.0	1.0	0.6	0.7	68.0	1.3
14 mean	80.3		0.5	1.4	1.8	2.3	2.4	1.0	0.5	0.3	68.6	1.5
28	70.9	0.5	0.9	2.7	3.1	4.3	2.9	1.6	0.8	0.8	51.4	1.9
	69.7		0.7	2.6	3.1	3.2	4.9	0.6	1.5		51.4	1.7
28 mean	70.3	0.3	0.8	2.6	3.1	3.7	3.9	1.1	1.2	0.4	51.4	1.8
58	54.3	0.7	0.6	4.4		4.3	12.2		0.7	1.0	27.6	2.8
	54.3	0.8	0.7	4.7		4.8	12.2		0.9	1.1	26.8	2.3
58 mean	54.3	0.8	0.7	4.6		4.6	12.2		0.8	1.0	27.2	2.5
89	45.4	1.6		5.4		5.0	12.2		1.3	1.0	15.7	3.2
	44.8	0.8	1.2	5.2		5.1	12.0		1.1	1.0	15.3	3.1
89 mean	45.1	1.2	0.6	5.3		5.0	12.1		1.2	1.0	15.5	3.2
119	37.0	1.1	1.0	5.4		4.3	10.4		0.6	1.0	7.9	5.4
	39.0	0.9	1.2	5.4		4.4	11.6		0.4	1.1	8.1	5.8
119 mean	38.0	1.0	1.1	5.4		4.3	11.0		0.5	1.1	8.0	5.6

ukn unknown compound
[a] t_R approximate retention time in min
[b] each ≤ 1 % TAR
M23 = M656PH023, M27 = M656PH027, M31 = M656PH031

Under aerobic conditions at normal application rate, three metabolites exceeded 5 % TAR at later sampling times: M656PH027 with 5.4 % TAR at day 119, M656PH031 with the maximum of 5.0 % TAR after 89 days and M656PH023 with the maximum of 12.2 % TAR after 58 days. Six other metabolites reached amounts between 1.1 and 3.1 % TAR. Further degradation products in low amounts (<1 % TAR each) were additionally detected. The soil extract from the incubation under aerobic conditions with the high application rates showed the same degradation products as that with the low application rate.

Conclusion

The study is considered acceptable by the RMS.
The soil metabolism of dimethenamid-P was investigated under aerobic conditions in the sand soil Borstel that was earlier used in the lysimeter study Burgener, 1996 at 20 °C and pF 2 at an application rate of 2 kg/ha with the aim to identify the unknown fractions in the leachate of the lysimeter study Burgener, 1996. Additional incubations were performed for selected sampling times under aerobic conditions, under anaerobic conditions and in a photolysis study at an exaggerated application of 6 kg/ha. It has to be noted that the setup of the aerobic soil degradation experiment at a high application rate and the soil photolysis experiment was not suitable for exact quantification of volatiles and no complete mass balance was established. Nevertheless, the study is accepted by the RMS since the main focus of the study was the generation of suitable amounts of metabolites for structure elucidation rather than quantitative aspects like a complete mass balance.

Dimethenamid-P degraded under aerobic conditions and an application rate of 1 kg/ha to 8.0 % AR after 119 days. $^{14}CO_2$ accounted for 17.5 % AR and non-extractable residues increased to 42 % AR after 182 days. Total volatiles in the anaerobic soil study amounted to 3 % after 119 days. 27 % AR non-extractable residues after 119 days and 23 - 24 % AR after 15 - 16 days were observed in the anaerobic incubation and in the photolysis study, respectively.
Major metabolites were M656PH027 with maximum concentrations of 5.4 % TAR at day 119, M656PH031 with a maximum of 5.0 % TAR after 89 days and M656PH023 with a maximum of 12.2 % TAR after 58 days. Chromatograms of the aerobic degradation study under exaggerated application rates showed the same degradation products as that with the low application rate. Under anaerobic conditions, a similar pattern of degradates but with some additional or at least more prominent metabolite peaks as under aerobic conditions was observed in the HPLC chromatograms. Under the influence of light, the pattern of degradates in the HPLC chromatograms was quite dissimilar to that obtained in the incubations in darkness, however the resulting peaks did not match with the HPLC chromatograms of the mini lysimeter leachate samples.
Since the study was performed to elucidate the unknown fractions in the leachate of the lysimeter Burgener, 1996, no kinetic evaluations were performed. However, the RMS is of the opinion that the results of the aerobic incubations at an application rate of 2 kg/ha can also be used to derive degradation endpoints for dimethenamid-P, M656PH027, M656PH031 and M656PH023. Thus, the RMS performed a kinetic evaluation which is described in more detail under **Fehler! Verweisquelle konnte nicht gefunden werden.** - Staudenmaier, 2009a with amendment no. 1 Staudenmaier, 2014a (new studies).
Additionally, structure elucidations of selected anaerobic soil samples, samples of the photolysis study and leachate samples of the mini-lysimeter study Fent, 2008 were performed. These are described in more detail under B.8.1.4.2.

KCA 7.1.1.1/6 – Staudenmaier, 2013 (new study)

Author: Staudenmaier, H.
Title: Chiral analysis of dimethenamid-P after incubation in soil
Date: 18/11/2013
Doc ID: 2012/1073064
Guidelines: None
GLP: yes
Validity: Acceptable

Aim of study

Dimethenamid-P is a chiral compound containing mainly the S-enantiomer. The purpose of the present study was the investigation of the stereochemistry of dimethenamid-P during degradation in soil using chiral separation techniques.

Material and Methods

The study was performed with soil extracts which were obtained from the study KCA 7.1.1.1/5 – Staudenmaier, 2009a with amendment no. 1 Staudenmaier, 2014a where a summary of the soil characteristics, the experimental conditions and the extraction methods of the soil samples can be found.

Extracts of samples from days 0, 28, 58, 89 and 119 DAT were further worked up and investigated by chiral HPLC analysis in the present study.

Since the entire soil extracts were not suitable for analysis on the chiral separation column, the peak of the active substance was first isolated by a chiral HPLC fractionation of soil extracts from the study Staudenmaier, 2009 with amendment 1, Staudenmaier, 2014a. The HPLC run was fractionated and the peak containing dimethenamid-P was further worked up. The collected material for dimethenamid-P was adjusted to volume, mixed and three times partitioned against of ethyl acetate. All extracts were measured by LSC. The ethyl acetate extracts were combined and concentrated to dryness at 40 °C and redissolved in the mobile phase for HPLC analysis. Aliquots of the solution were analysed by LSC and HPLC on a chiral column ((S,S)-Whelk-O-1-Pirkle) to investigate the composition of stereoisomers.
The S-enantiomer was found to separate into two peaks (isomers 1 and 2 in chromatographic order). These were assumed to be conformational isomers which normally interconvert rapidly. In order to investigate whether the two isomers can be interconverted, the peaks were isolated separately and incubated in organic solvent or aqueous solution under various temperature and pH conditions followed by HPLC analysis. The single isomers were isolated by HPLC fractionation using a chiral column. An aliquot of a solution of non-radiolabelled dimethenamid-P was dissolved in n-heptane/isopropanol/tetrahydrofuran (970/20/10, v/v/v) and aliquots thereof were fractionated by HPLC. Corresponding fractions containing isomers 1 and 2 of the S-enantiomer were combined and partly further cleaned up by chiral HPLC fractionation, finally resulting in two fractions containing predominantly isomer 1 or predominantly isomer 2 dissolved in methanol.
Each of the isolated isomers was investigated further by incubation under various conditions: The methanol solutions were diluted with water or buffer (1:10 dilution of the Titrisol buffer concentrate, Merck). Solutions in buffer of pH 4, pH 5, pH 7 and pH 9 were incubated for 5 h, 24 h and 4 days at room temperature. Furthermore, solutions in water were incubated at 50 °C and 70 °C for 1 h, 5.5 h and 24 h. After the incubations the solutions were partitioned three times against ethyl acetate. The organic phase was concentrated to dryness, redissolved in n-heptane/isopropanol/tetrahydrofuran and analysed by chiral HPLC. In a further experiment, the fractions were evaporated to dryness and taken up in organic solvent (HPLC mobile phase: n-heptane/isopropanol/tetrahydrofuran). Aliquots were transferred into HPLC vials, sealed and incubated at 70 °C for 1, 2 or 3 h. After that time the fractions were analysed by chiral HPLC.

Details on the kinetic analysis are described under KCA 7.1.2.1.1/4 - Staudenmaier, 2013.

Results and Discussion

The results of the chiral analysis are given in Table B.8.1.1-16 (in relative percent of the HPLC analyses - % ROI), Table B.8.1.1-17 (in percent of applied - % TAR).

Table B.8.1.1-16: Proportion of enantiomers in soil extracts obtained from soil samples incubated with dimethenamid-P [% ROI in HPLC]

DAT	R-enantiomer [%]	S-enantiomer isomer 1 [%]	S-enantiomer isomer 2 [%]	S-enantiomer isomers 1 + 2 [%]
0	2.6	35.4	62.0	97.4
28	2.7	34.7	62.6	97.3
58	2.5	34.8	62.7	97.5
89	2.4	34.4	63.3	97.7
119	2.3	34.4	63.3	97.7

Table B.8.1.1-17: Proportion of enantiomers in soil extracts obtained from soil samples incubated with dimethenamid-P [% TAR]

DAT	dimethenamid-P [% TAR]	R-enantiomer [% TAR]	S-enantiomer isomer 1 [% TAR]	S-enantiomer isomer 2 [% TAR]	S-enantiomer isomers 1 + 2 [% TAR]
0	100.5	2.6	35.6	62.2	97.8
28	51.4	1.4	17.8	32.2	50.0
58	26.8	0.7	9.3	16.8	26.1
89	15.7	0.4	5.4	9.9	15.3
119	7.9	0.2	2.7	5.0	7.7

The ratio of S- and R-enantiomers was about 97.4 % to 2.6 % at the beginning and almost no change of this ratio was observed during the degradation of dimethenamid-P within 119 days of incubation. Considering this constant ratio, it is concluded that both enantiomers are degraded in soil with the same rate and no conversion of the S-enantiomer to the R-enantiomer or vice versa occurs.
The S-enantiomer was further separated into two peaks, termed isomer 1 and isomer 2. The ratio of these two peaks was 35.4 % to 62.0 % at the beginning and - considering the analytical uncertainty of these not baseline separated peaks - also this ratio remained practically unchanged during degradation.
For the R-enantiomer, no separation into isomers was observed. However this is considered to be a specific feature of the chiral (S,S)-Whelk-O 1 Pirkle column: In the meantime another chiral HPLC system became available which separates also 2 isomers of the R-enantiomer of dimethenamid-P whereas the S-enantiomer is only poorly separated into isomers (non-GLP information). Since the R-enantiomer remains very low in this study this was not further investigated.

Slow, but visible changes of the ratio of the proposed conformational isomers were found during incubation in aqueous solution at room temperature at different pH values in the range of pH 4 to pH 9. This indicates that the isomers tend to interconvert already under mild conditions (see

Table B.8.1.1-18 and Table B.8.1.1-19) thus giving supporting evidence that the isomers are conformers.
The changes were slightly accelerated at 50 °C and - after 1 day at a further increase of the temperature to 70 °C - approached from either side a ratio of the isomers similar to that in the original parent compound (Table B.8.1.1-20 and Table B.8.1.1-21).

Table B.8.1.1-18: Proportion of isomers after incubation of enriched isomer 1 of the S-enantiomer of dimethenamid-P in aqueous solutions of different pH

pH	Incubation time	Isomer 1	Isomer 2
4	5 h	91.2	8.8
	24 h	89.7	10.3
	4 d	87.5	12.5
5	5 h	91.1	8.9
	24 h	87.4	12.6
	4 d	89.7	10.3
7	5 h	91.4	8.6
	24 h	89.2	10.8
	4 d	88.4	11.6
9	5 h	90.9	9.1
	24 h	n.r.*	n.r.*
	4 d	88.6	11.4

* not reported, sample was dried completely by evaporation

Table B.8.1.1-19: Proportion of isomers after incubation of enriched isomer 2 of the S-enantiomer of dimethenamid-P in aqueous solutions of different pH

pH	Incubation time	Isomer 1	Isomer 2
4	5 h	12.7	87.3
	24 h	13.6	86.4
	4 d	13.2	86.8
5	5 h	12.6	87.4
	24 h	13.4	86.6
	4 d	13.1	86.9
7	5 h	12.4	87.6
	24 h	14.2	85.8
	4 d	13.2	86.8
9	5 h	12.5	87.5
	24 h	14.3	85.7
	4 d	13.7	86.3

Table B.8.1.1-20: Proportion of isomers after incubation of enriched isomer 1 of the S-enantiomer of Dimethenamid in aqueous solution at 50 °C and 70 °C

Temperature [°C]	Incubation time	Isomer 1	Isomer 2
-*	0	93.6	6.4
50	1 h	90.3	9.7
	5 h	88.9	11.1
	24 h	86.2	13.8
70	1 h	89.2	10.8
	5 h	84.2	15.8
	24 h	50.1	49.9

* before incubation

Table B.8.1.1-21: Proportion of isomers after incubation of enriched isomer 1 of the S-enantiomer of Dimethenamid in aqueous solution at 50 °C and 70 °C

Temperature [°C]	Incubation time	Isomer 1	Isomer 2
-*	0	93.6	6.4
50	1 h	90.3	9.7
	5 h	88.9	11.1
	24 h	86.2	13.8
70	1 h	89.2	10.8
	5 h	84.2	15.8
	24 h	50.1	49.9

* before incubation

Fast interconversion of the isomers was observed in organic solvent (n-heptane/ isopropanol/ tetrahydrofuran) at an elevated temperature of 70 °C (Table B.8.1.1-22 and Table B.8.1.1-23). Thermodynamic dependency gives evidence that the observed isomers are conformational in nature.

Table B.8.1.1-22: Proportion of isomers after incubation of enriched isomer 1 of the S-enantiomer of dimethenamid-P in organic solution at 70 °C

Incubation time [h]	Isomer 1 [%]	Isomer 2 [%]
0	96.8	3.2
1	62.1	38.0
2	49.8	50.2
3	47.7	52.3

Table B.8.1.1-23: Proportion of isomers after incubation of enriched isomer 2 of the S-enantiomer of dimethenamid-P in organic solution at 70 °C

Incubation time [h]	Isomer 1 [%]	Isomer 2 [%]
0	6.0	94.1
1	34.2	65.8
2	43.6	56.4
3	45.4	54.6

The resulting degradation rates for dimethenamid-P and both enantiomers are described under KCA 7.1.2.1.1/4 - Staudenmaier, 2013.

Conclusion

The study is considered acceptable by the RMS.
The ratio of the S- and R-enantiomers of dimethenamid-P (S-enantiomer and R-enantiomer) during the aerobic degradation of the active substance in a sandy soil was about 97.4 % to 2.6 % at the beginning and almost no change of this ratio was observed within 119 days of incubation. There was no selective degradation of the enantiomers as well as no interconversion between the enantiomers. The S-enantiomer was further separated into two peaks, termed isomer 1 and isomer 2. The ratio of these two peaks was 35.4 % to 62.0 % at the beginning and this ratio remained practically unchanged during the experiment. Additional investigations indicated that these isomers tend to interconvert already under mild conditions at room temperature with this interconversion being accelerated at higher temperature.

KCA 7.1.1.1/7 – Unsworth, 2014 (new study)

Author: Unsworth, R.
Title: Dimethenamid-P: Chiral separation after degradation in soil
Date: 22/01/2014
Doc ID: 2013/1412031
Guidelines: OECD 307 (2002)
GLP: Yes
Validity: Acceptable

Material and Methods

The enantiomeric composition of ^{14}C-dimethenamid-P (thienyl-5-^{14}C dimethenamid-P, radiochemical purity 97 %) and its degradation products was studied in a sandy loam soil (Calke, Derbyshire, UK) with an organic carbon content of 3.9 % and a pH of 4.6 (0.01 M $CaCl_2$). The soil characteristics are listed in Table B.8.1.1-24.

Table B.8.1.1-24: Characterisation of the soil system (Unsworth, 2014)

Parameter	Calke, Derbyshire, UK
Pesticide use	No pesticide sprays have been used since year 2000
Particle size distribution:	
UK classification:	
0.063 mm – 2 mm (%):	68
0.002 mm – 0.063 mm (%):	17
<0.002 mm (%):	15
USDA classification:	
0.05 mm – 2 mm (%):	71
0.002 mm – 0.05 mm (%):	15
<0.002 mm (%):	14
Texture class (UK and USDA):	Sandy Loam
pH in water	5.5
pH in 0.01 M $CaCl_2$	4.6
Organic carbon (%)	3.9
Cation exchange capacity (meq/100 g)	13.9
Soil moisture content (g/100g dry wt)	22.2
Water content at pF 2 (g/100g dry wt)	33.0
Microbial biomass (mgC/kg)	
At 62 day incubation	775 and 574
At end of incubation (120 day)	498 and 582
Microbial biomass (%)	
At 62 day incubation	1.99 and 1.47
At end of incubation (120 day)	and 1.49

Samples of soil adjusted to a moisture content equivalent to pF 2 were treated with [thienyl-5-^{14}C]-dimethenamid-P at a nominal concentration of 2.67 mg/kg, equivalent to a field rate of 2 kg as/ha assuming a uniform incorporation in the top 5 cm depth of soil having a bulk density of 1.5 g/cm^3. Samples were arranged in flow-through systems and incubated in darkness at 20 ± 2 °C for periods of up to 120 days. Radiolabelled volatile metabolites including CO_2 were trapped and quantified.
Samples were taken for analysis immediately after application and after 3, 7, 14, 30, 45, 59, 90 and 120 days of incubation. The following samples were analysed; duplicate replicates for zero-time and 120 days and a single replicate for 14, 30 and 59 days. The remaining samples were stored frozen. Trapping solutions were taken for analysis when the associated sample was taken for analysis. Additionally, all remaining traps were taken for analysis and replaced with fresh media as necessary at 7, 14 days and subsequently at approximately two weekly intervals after application.
Two vessels, established for the determination of microbial biomass, were taken for analysis during incubation (after approximately 60 days). The second set of vessels was taken for analysis after 120

days of incubation. The microbial biomass of the soil was determined by the substrate induced respiration.

The soil samples were extracted with aqueous/organic solvents by shaking them on an orbital shaker for 30 minutes. The zero-time and 14 days samples were extracted at ambient temperature first with methanol as first extraction step and second with methanol/water (80/20, v/v). The 14 days were additionally extracted with methanol/water (50/50, v/v) at ambient temperature. The 30, 59 and 120 days soil samples were extracted at ambient temperature twice with methanol as first and second extraction step, afterwards twice with methanol/water (80/20, v/v) as third and fourth extraction step and as a fifth extraction step with methanol/water (50/50, v/v).
For HPLC analysis, portions of all of the extract solutions were combined in proportion to their total volumes for each sample and duplicate aliquots of the pools taken for radioassay. Extract pools were concentrated under nitrogen gas at approximately 40 °C prior to analysis. The recovery was monitored through the concentration procedure and was determined quantitative. Concentrated extracts were analysed by HPLC and chiral HPLC. Extracts of the soil samples for 120 days were also subjected to LC-MS.
For characterisation of volatile radioactivity, a representative pool of the potassium hydroxide trapping from the 120 day sample was prepared. To this solution, sodium carbonate was added (1 mL trap solution: 0.1 g sodium carbonate). Saturated barium chloride solution was then added (1.5 mL barium chloride: 1 mL trap solution) and the resulting precipitate separated from the mixture by centrifugaiont. An absence of radioactivity in solution was indicative of precipitation of $^{14}CO_2$ as barium carbonate.

Results and Discussion

The microbial biomass of the soil was a mean of 1.7 % (674.5 mg C/kg) of the total organic carbon after 62 days of incubation and 1.4 % (540 mg C/kg) at the end of the incubation period, demonstrating that the soil was microbiologically viable throughout.
The distribution and recovery of radioactivity in the soil samples is given in Table B.8.1.1-25.

Table B.8.1.1-25: Distribution and overall recovery of radioactivity in soil treated with [1^4C]-dimethenamid-P

Days after treatment	extractable radioactiviy	non-extractable residues	total	Volatiles (organics)	Volatiles (CO_2)	material balance
	% TAR					
0	97.61	3.98	101.59	na	na	101.59
	99.8	3.15	102.95	na	na	102.95
0 mean	98.71	3.57	102.27	na	na	102.27
14	70.6	21.77	92.37	nd	4.08	96.45
30	55.47	35.29	90.76	nd	6.94	97.70
59	39.36	45.98	85.34	nd	13.08	98.42
120	30.04	43.58	73.62	nd	19.18	92.80
	30.54	42.42	72.96	nd	26.97	99.93
120 mean	30.3	43.00	73.29	nd	23.08	96.37

na (not applicable)
nd (not detected)

Total recoveries of radioactivity were in the range 92.8 to 103.0 % of the amount of applied radioactivity (% AR). In soil treated with [^{14}C]-dimethenamid-P, extractable radioactivity declined with time, from a mean of 98.7 % at the time of application to a mean of 30.3 % after 120 days. There was a corresponding increase with time in non-extractable radioactivity with a mean value of 43.0 % after 120 days. Volatile radioactivity increased to a mean of 23.1 % after 120 days, which was shown to be associated with $^{14}CO_2$.
The distribution of recovered radioactivity of dimethenamid-P in the soil Calke is presented in Table B.8.1.1-26.

Table B.8.1.1-26: Amount of radioactive components in soil treated with [^{14}C]-dimethenamid-P

		ukn	ukn	ukn	ukn	ukn	ukn	ukn	ukn	ukn
	t_R[a]	3.0	4.5	5.0	6.0	7.0	8.5	10.0	12.0	13.0
DAT	^{14}C total	% TAR								
0	97.61	ND	ND	ND	ND	ND	ND	ND	ND	ND
0	99.80	ND	ND	ND	ND	ND	ND	ND	ND	ND
14	70.60	ND	ND	ND	ND	ND	ND	ND	ND	ND
30	55.47	ND	ND	ND	ND	ND	0.9	ND	ND	ND
59	39.36	0.4	0.4	ND	0.4	ND	2.1	0.2	ND	0.3
120	30.04	0.5	0.2	0.7	1.1	0.3	3.5	0.4	ND	0.4
120	30.54	0.6	0.9	ND	1.0	0.7	3.5	0.5	0.8	0.2
		ukn	ukn	ukn	ukn	ukn	ukn	*M27*	ukn	ukn
	t_R[a]	14.0	14.5	16.0	16.5	17.0	18.2	*19.5*	23.0	24.0
DAT	^{14}C total	% TAR								
0	97.61	ND	ND	ND	ND	ND	ND	ND	ND	ND
0	99.80	ND	ND	ND	ND	ND	ND	ND	ND	ND
14	70.60	ND	ND	ND	ND	ND	ND	1.5	ND	ND
30	55.47	ND	ND	ND	ND	ND	ND	2.4	ND	ND
59	39.36	0.7	0.2	ND	ND	ND	ND	3.2	ND	0.2
120	30.04	0.7	0.5	0.1	0.1	0.3	0.1	3.8	ND	0.2
120	30.54	0.7	0.5	0.4	ND	0.5	ND	3.7	0.2	0.2
		ukn	ukn	ukn	ukn	*M23*	*M31*	ukn	ukn	ukn
	t_R[a]	25.0	25.5	27.0	28.5	*30.0*	*32.5*	34.5	35.5	36.5
DAT	^{14}C total	% TAR								
0	97.61	ND	ND	ND	ND	ND	ND	ND	ND	ND
0	99.80	ND	ND	ND	ND	ND	ND	ND	ND	ND
14	70.60	ND	ND	ND	ND	4.1	2.0	0.4	ND	ND
30	55.47	ND	ND	ND	ND	5.3	2.1	1.0	ND	ND
59	39.36	0.2	0.4	0.6	0.2	6.0	2.2	0.5	0.6	0.3
120	30.04	ND	0.2	0.4	0.1	4.3	1.8	0.5	0.7	0.1
120	30.54	ND	0.5	0.6	ND	4.1	2.1	0.3	0.7	ND

		ukn	ukn	ukn	*BAS 656 H*	others
	t_R[a]	37.5	38.5	40.0		
DAT	^{14}C total	% TAR				
0	97.61	ND	ND	ND	95.8	1.9
0	99.80	ND	ND	ND	98.7	1.1
14	70.60	0.6	0.9	ND	60.5	0.6
30	55.47	0.7	1.2	ND	39.1	2.8
59	39.36	0.8	1.8	0.5	15.2	1.8
120	30.04	0.6	2.3	0.3	4.8	1.3
120	30.54	0.9	1.9	0.3	4.6	1.1

ukn unknown compound
t_R[a] approximate retention time (min)
ND not detected
Others low level radioactivity not considered to constitute a discrete region of interest
M23 = M656PH023, M27 = M656PH027, M31 = M656PH031

Dimethenamid-P was degraded to the major soil metabolites M656PH023 (M23 in this study) with maximum concentrations of 6.0 % on day 59, M656PH027 (M27 in this study) with maximum concentrations of 3.8 % on day 120, M656PH031 (M31 in this study) with maximum concentrations of 2.2 % on day 59. Besides, 27 unidentified metabolites (≤ 3.5% AR) were formed, several of which were polar in nature.
The ratio of the S-entantiomer and the R-enantiomer of dimethenamid-P is given in Table B.8.1.1-27. The ratios of the isomers of the metabolites M656PH023, 27 and M656PH031 are presented in Table B.8.1.1-28.

Table B.8.1.1-27: Ratio of dimethenamid-P isomers in extracts from soil treated with [^{14}C]-dimethenamid-P

Sampling time (days)	T_0	T_0	7	14	30	59	120	120
Component	% proportion							
S-enantiomer	97.2	97.3	97.3	99.1	98.3	97.2	96.0	97.4
R-enantiomer	2.8	2.7	2.7	0.9	1.7	2.8	4.0	2.6

Table B.8.1.1-28: Ratios of metabolite isomers in extracts from soil at 59 days treated with [^{14}C]-dimethenamid-P

Component	Metabolite M656PH023	Metabolite M656PH027	Metabolite M656PH031
	% proportion		
Isomer (1)	52.9	98.3	67.3
Isomer (2)	47.1	1.7	32.7

The proportions of the enantiomers of dimethenamid-P in soil extracts at T_0 (approximately 97 % (S) : 3 % (R) remained similar throughout the 120 days.
The chiral analyses of the metabolites (M656PH023, M656PH027 and M656PH031) were based on methods supplied by the sponsor, which were not developed using enantiomer pure reference standards. Therefore, the chiral analysis results for the metabolites should be treated with caution. More specifically, it is unclear whether the separated peaks do represent the enantiomers or other types of isomers (e.g. rotamers) that were also observed with metabolites of dimethenamid-P.
In the soil extracts at 59 days the proportions of the isomers of M656PH023 were 52.9 % (isomer 1): 47.1 % (isomer 2). For M656PH027 the proportions of the isomers were 98.3 % (isomer 1): 1.7 % (isomer 2). For M656PH031 the proportions of the isomers were 67.3 % (isomer 1): 32.7 % (isomer 2).

Conclusion

The study is considered acceptable by the RMS regarding the degradation pathway of dimethenamid-P and the ratio of the S-entantiomer and the R-enantiomer of dimethenamid-P throughout the incubation. Since it is already stated by the study author, that it is not clear if the peaks of the three metabolites really represent enantiomers or other types of isomers, these data will not be included further.
The soil metabolism of dimethenamid-P was investigated under aerobic conditions in a sandy loam soil at 20 °C and pF 2. Dimethenamid degraded to 4.7 % AR after 120 days. $^{14}CO_2$ accounted for 23.1 % AR and non-extractable residues increased to 43 % AR after 120 days. The metabolites M656PH023, M 27 and M 31 reached maxima of 6.0 % on day 59, 3.8 % on day 120 and 2.2 % on day 59 respectively. Besides, 27 unidentified metabolites (≤3.5 % AR) were formed, several of which were polar in nature. The proportions of the enantiomers of dimethenamid-P in soil extracts at day 0 were approximately 97 % (S) : 3 % (R) and remained similar throughout the 120 days.
A new kinetic evaluation of the residues of dimethenamid-P and its soil metabolites were performed by the RMS which is described under **Fehler! Verweisquelle konnte nicht gefunden werden.** – Unsworth, 2014.

B.8.1.1.2 Anaerobic degradation

KCA 7.1.1.2/ 1 – Bade, 1990 (study evaluated in the monograph, 2000)

Author: Bade, T.R.
Title: Anaerobic soil metabolism of SAN 582 H
Date: 6/9/1990
Doc ID: 90/11111
Guidelines: US-EPA Subdivision N; 161-2
GLP: Yes
Validity: Not acceptable

Material and Methods

Anaerobic degradation of dimethenamid (3-^{14}C-thienyl dimethenamid, radiochemical purity 99.3 %; dimethenamid, purity > 98 %) was investigated in a Kenyon loam soil after aerobic pre-incubation. The soil characterisation is given in Table B.8.1.1-29.

Table B.8.1.1-29: Characterisation of the soil system (Bade, 1990)

Soil designation		Kenyon loam
Textural class (USDA scheme)		Loam
Origin		Cedar Falls, Iowa (USA)
Particle size distribution (%): **sand** **silt** **clay**		 34 41 25
Organic C (%)		2.2
CEC (meq/100 g; cation exchange capacity)		20.4
pH ($CaCl_2$)		6.0
FC (g H_2O/100 g dry soil; field capacity determined at 0.33 bar)		24.4
Microbial counts	**Bacteria**	$3.25 \cdot 10^6$
per gram of soil	**Actinomycetes**	$7.6 \cdot 10^5$
	Fungi	$5.1 \cdot 10^5$

Duplicate samples of soil treated at a concentration of 2.36 mg/kg of moist soil (2.93 mg/kg of dry soil, equivalent to 2.2 kg/ha for a soil depth of 5 cm and a soil density of 1.5 g/cm^3) were incubated in the dark at 25 °C and maintained at 75 % of the 1/3 bar field moisture capacity for 30 days under aerobic conditions. Samples were then transferred into anaerobic jars and an anaerobic state was achieved by using hydrogen plus carbon dioxide generator envelopes. After 7 days the flasks were sparged with nitrogen for 30 minutes and the N_2 passed through traps (ethylene glycol and 1.5 M KOH) connected in series for volatiles. The sparging and trapping were repeated at weekly intervals. Samples were taken on days 0, 1, 3, 7, 14 and 30 (aerobic samples) and on days 58 and 93 (anaerobic samples) and extracted with methanol/water (1:1). The soil extracts were partitioned with hexane. The extracted soil was hydrolysed under alkaline conditions (1 M KOH, 80 °C) for one hour. The hydrolysis fraction was neutralised with HCl, taken to dryness and extracted with methanol and subsequently with water. The individual extracts were analysed by TLC and HPLC and compared to authentic standards. Isolated fractions were further purified and subjected to GC-MS and/or NMR analysis. The material balance was determined by combustion of the soil residue and radioassay of the extracts for $^{14}CO_2$.

Results and Discussion

The balance of recovered radioactivity for individual incubations were in the range from 86.4 to 103.8 % AR. The overall average from duplicate analyses gave a material balance of 96.5 % AR. After 30 days aerobic pre-incubation dimethenamid accounted for 57.9 % AR, the residue of the active

substance declined to 35.4 % AR at the end of the study. Volatile breakdown products ($^{14}CO_2$) accounted for 3.2 % AR at termination. Non-extractable residues (NER) increased with time and reached an average of 18.6 % AR at termination. The distribution of recovered radioactivity among CO_2, dimethenamid and metabolites (sum of methanol/H_2O and basic extract) is presented in Table B.8.1.1-30.

Table B.8.1.1-30: Recovery of radioactivity and distribution of metabolites in % AR (day 0-30 aerobic pre-incubation) (Bade, 1990)

DAT	CO_2	as	M656PH023	M656PH027* Fr.1A+B	Fraction 4**	NER	Balance ***
0	0.0	78.8	0.8	1.3	0.4	5.9	96.8
14	0.6	68.2	5.1	3.4	2.5	11.2	101.9
30	1.5	57.9	3.8	2.1	2.1	10.2	95.1
58	1.9	43.6	7.2	2.5	3.0	16.1	96.2
93	3.2	35.4	8.5	3.4	2.5	18.6	92.6

* The M656PH027 peak contained another compound of equal quantity. The values are the totals for the peak.
** Fraction 4 is postulated as a polar acidic metabolite.
*** Sum of total volatile, extractable (MeOH/H_2O and base extracts) and non-extractable radioactivity

The metabolic profile of dimethenamid under anaerobic conditions is very similar to that found under aerobic conditions. M656PH023 (oxalamide in this study), Fractions 1A (M656PH027 - sulfonate in this study) and 1B, and Fraction 4, the fractions that could be isolated under aerobic conditions, were also found in this study. No additional fractions were separated by TLC.

Conclusion

The study was submitted for the first Annex I inclusion of dimethenamid-P and was considered acceptable as additional information at that time. However, after re-evaluation of the study, the RMS concluded not to consider it acceptable anymore. Only two of the five samples for which dimethenamid and possible metabolites were analysed, were actually incubated under anaerobic conditions. This is in the opinion of the RMS not enough to adequately investigate the fate of dimethenamid under these conditions. Beside, redox potential, pH and oxygen concentration were not measured throughout the anaerobic incubation, thus it is not possible to determine, wether anaerobic conditions were achieved in the test systems or not.

However, dimethenamid-P is not expected to degrade under anaerobic conditions for prolonged periods of time in the representative uses.

B.8.1.1.3 Soil photolysis

KCA 7.1.1.3/ 1 – Sabat & Yu, 1992 (study evaluated in the monograph, 2000)

Author: Sabat, M.
Yu, C.
Title: Photodegradation study on soil
Date: 24/03/1992
Doc ID: 92/12387
Guidelines: US-EPA Subdivision N; 161-3
GLP: Yes
Validity: Only acceptable as route study

Material and Methods

For the investigation of soil photolysis of ^{14}C-dimethenamid (3-^{14}C-thienyl dimethenamid, radiochemical purity 98 %; dimethenamid, analytical reference standard) a 100 gram sample of Kenyon

loam was fortified to produce a concentration of 500 mg/kg (equivalent to 375 g/ha for a soil depth of 5 cm and a soil density of 1.5 g/cm^3. The soil characteristics are given in Table B.8.1.1-31.

Table B.8.1.1-31: Characterisation of the soil system (Sabat & Yu, 1992)

Soil designation	Kenyon loam
Textural class (USDA scheme)	Loam
Origin	Cedar Falls, Iowa (USA)
Particle size distribution (%): **sand** **silt** **clay**	 28 46 26
Organic C (%)	1.9
CEC (meq/100 g; cation exchange capacity)	26.2
pH ($CaCl_2$)	7.4
FC (g H_2O/100 g dry soil; field capacity determined at 0.33 bar)	Not reported

The soil sample was subjected to continuous irradiation under a xenon light (λ < 290 nm filtered out) for 9 days with a light intensity of 8.55 x 10^2 W/m^2. Both irradiated and dark control samples were temperature controlled to 25±1 °C and kept aerated with humidified air. Volatiles and carbon dioxide were trapped with silica gel, 10 % NaOH and ethylene glycol. Subsamples of irradiated soil were collected at day 0, 2, 6 and 9 and extracted with methanol and methanol/water. Analysis of extracts was done using TLC, HPLC and GC-MS.

Results and Discussion

The overall material balance throughout the study ranged from 93.7 % AR to 101 % AR. Racemic dimethenamid degraded to 27 % AR after 9 days, so the irradiation was terminated. The application rate was sufficiently high that some metabolites could be identified. Among these were M656H009 (M9 in this study), M656PH007 (M7 in this study) and M656H011 (M11 in this study) along with trace amounts of a second bicyclic component M656H020 (M20 in this study) and a putative hydroxylated metabolite. The results of this study suggest several degradative pathways: replacement of chlorine by a hydroxyl group, O-demethylation, two modes of cyclisation, and hydroxylation at one of the thiophene methyls or the thiophene itself.
Degradation in the dark controls was minimal and showed that degradation under light is more rapid. The lack of degradation under dark conditions may be due to insufficient moisture content during the incubation compared to the conditions in the aerobic soil metabolism.
The distribution of recovered radioactivity is presented in Table B.8.1.1-32.

Table B.8.1.1-32: Recovery and distribution of radioactivity after soil photolysis (Sabat & Yu, 1992)

Dimethenamid (Kenyon loam)								
DAT	**CO_2**	**as**	**M9**	**M11**	**M7**	**Others**	**Bound Residues**	**Total**
0	0.0	93.3	0.1	0.2	0.1	1.2	6.0	100.9
2	1.3	61.7	5.1	2.6	1.6	12.2	10.8	95.3
6	4.4	40.6	5.8	6.1	2.0	13.5	20.8	93.2
9	5.8	27.0	5.4	4.7	2.1	21.0	27.3	93.3
9 (dark)	-	92.8	0.4	0.2	0.1	1.3	6.6	101.1

M9 = M656H009, M11 = M656H011, M7 = M656H007

Conclusion

The study was considered acceptable for the first Annex I inclusion of dimethenamid-P. After re-evaluation of the study, the RMS concluded that it still fulfils the requirements as route study in soil under photolytic conditions. However, with only four sampling points not enough data points are available according to FOCUS degradation kinetic guidance to determine reliable DT_{50} and DT_{90} values for dimethenamid. Thus, it will not be used as rate study.

After artificial irradiation, dimethenamid degraded to 27.0 % after 9 days on a Kenyon loam soil. 5.8 % CO2 and 27.3 % bound residues were formed. Three metabolites M656H009, M656H011 and M656H007 were identified. The metabolite M656H009 occurred twice in concentrations > 5 % with a maximum of 5.8 % on day 6. M656H011 occurred once in a concentration > 5 % with 6.1 % on day 6 and M656H007 remained < 2.5 % throughout the study.

KCA 7.1.1.3/ 2 – Nietschmann & Yu, 1997 (study evaluated in the monograph, 2000)

Author:	Nietschmann, D. Yu, C.
Title:	Comparative photolysis of R,S-dimethenamid (SAN 582 H) and S-dimethenamid (SAN 1289 H) on soil
Date:	10/04/1997
Doc ID:	97/5181
Guidelines:	US-EPA Subdivision N; 161-3
GLP:	Yes
Validity:	Acceptable

Material and Methods

Soil photolysis of ^{14}C-dimethenamid-P (3-^{14}C-thienyl dimethenamid-P, radiochemical purity > 96.0 %; dimethenamid-P, purity 98.6 %) and ^{14}C-dimethenamid (3-^{14}C-thienyl dimethenamid, radiochemical purity > 96 %; dimethenamid, purity 99.7 %) was investigated with 200 gram batches of Elliot clay loam soil at a concentration of about 1.9 mg/kg of dry soil (equivalent to 1.4 kg/ha assuming a soil depth of 5 cm and a soil density of 1.5 g/cm^3). The soil characteristics are given in Table B.8.1.1-33

Table B.8.1.1-33: Characterisation of the soil system (Nietschmann & Yu, 1997)

Soil designation	Elliot clay loam
Textural class (USDA scheme)	Clay loam
Origin	Champaign County, Illinois (USA)
Particle size distribution (%): **sand** **silt** **clay**	 24 44 32
Organic C (%)	2.4
CEC (meq/100 g; cation exchange capacity)	15.6
pH ($CaCl_2$)	6.4
FC (g H_2O/100 g dry soil; field capacity determined at 0.33 bar)	33.37

The soil samples were subjected to continuous irradiation under a xenon light (λ < 290 nm filtered out) for 23 days with a light intensity of 7.83 x 10^2 W/m^2. Both irradiated and dark control samples were temperature controlled to 22±1 °C and kept aerated with humidified air. Volatiles and carbon dioxide were trapped with silica gel, 10 % NaOH and ethylene glycol. Duplicate subsamples of both irradiated and control soil were collected at day 0, 2, 5, 9, 15 and 23 and extracted with methanol and methanol/0.1 M HCl. Extracts were characterised by thin layer chromatography (TLC) and high performance liquid chromatography (HPLC).

Results and Discussion

The overall material balance for the irradiated soil ranged from 98 % AR to 106.7 % AR.
Dimethenamid-P and dimethenamid both showed slow degradation under continuous irradiation on Elliot clay loam soil. The concentrations of the optically active and racemic compounds were 64.3 % AR and 57.6 % AR after 23 days, respectively. Dimethenamid-P and dimethenamid were not degraded in the dark control. During photolysis the increase in $^{14}CO_2$ production, indicated mineralisation of dimethenamid-P and dimethenamid. After the 23 day irradiation period, $^{14}CO_2$ accounted for 10.1 %

AR and 12.3 % AR for dimethenamid-P and dimethenamid, respectively. Characterisation of individual radiocarbon regions showed that the TLC bands were comprised of multiple polar and less polar components, which did not approach 10 % AR, and no further characterisation was performed. The distribution of recovered radioactivity is presented in Table B.8.1.1-34.

Table B.8.1.1-34: Recovery and distribution of radioactivity after soil photolysis (Nietschmann & Yu, 1997)

Dimethenamid-P (Eliot clay loam)									
DAT	**CO_2**	**as**	**Region 1**	**Region 3**	**Region 4**	**Region 5**	**Others ***	**Bound Residues**	**Total**
0	0.0	97.7	0.6	2.3	0.3	0.0	1.5	0.6	103.0
2	0.0	92.0	0.1	2.1	0.8	2.1	3.1	2.0	102.1
5	1.6	85.3	0.5	3.2	1.7	3.1	4.3	3.7	103.3
9	4.1	72.2	0.8	2.7	2.3	3.4	6.7	5.8	98.0
15	7.5	69.0	1.4	2.2	2.4	5.4	7.7	7.8	103.4
23	10.1	64.3	0.4	2.6	2.7	5.5	7.6	9.3	102.5
23 (dark)	0.4	91.0	0.67	1.32	0.62	0.79	1.6	2.3	98.7
Dimethenamid (Eliot clay loam)									
DAT	**CO_2**	**as**	**Region 1**	**Region 3**	**Region 4**	**Region 5**	**Others ***	**Bound Residues**	**Total**
0	0.0	100.2	0.1	1.6	0.7	0.2	1.0	0.7	104.5
2	1.5	91.1	0.0	3.3	1.5	0.6	2.5	2.3	102.8
5	3.4	88.6	0.1	3.5	1.5	1.9	3.7	4.0	106.7
9	6.2	72.9	0.2	4.8	2.9	2.7	6.8	5.6	102.1
15	9.2	65.3	0.3	4.5	3.9	3.7	9.2	7.7	103.8
23	12.3	57.6	0.4	4.8	3.3	3.9	11.0	8.4	101.7
23 (dark)	0.3	97.8	0.3	0.8	0.3	0.3	1.9	2.7	104.4

* Sum of region 6 (<5 % in all samples) and region 7 (= TLC origin)

Conclusion

The study was considered acceptable for the first Annex I inclusion of dimethenamid-P. After re-evaluation of the study, the RMS concluded that it still fulfils the requirements of current guidelines and is thus still acceptable.

After artificial irradiation, racemic dimethenamid and dimethenamid-P degraded to 57.6 – 64.3 % after 23 days on a Elliot clay loam soil. 10.1 - 12.3 % CO_2 and 2.3 - 2.7 % bound residues were formed. No metabolites in concentrations > 5 % were formd. There was no significant difference in the degradation pattern of dimethenamid and dimethenamid-P.

A new kinetic evaluation of the study results according to FOCUS degradation kinetics guidance was performed by the RMS. This is described in more detail under KCA 7.1.2.1.3/ 1 – Nietschmann & Yu, 1997.

B.8.1.2 Rate of degradation

B.8.1.2.1 Aerobic degradation – active substance

KCA 7.1.2.1.1/1 – Platz, 2008 (new study)

Author:	Platz, K.
Title:	Kinetic evaluation of different laboratory soil degradation experiments of Dimethenamid (BAS 656 H) for derivation of modeling endpoints of the parent compound and its metabolites M23, M27 and M656PH031
Date:	03/09/2008
Doc ID:	2008/1048056
Guidelines:	FOCUS kinetics guidance (2006)
GLP:	No (not applicable)
Validity:	Acceptable

Material and Methods

A kinetic re-evaluation of the aerobic soil studies Koenig, 1995 and Koneig, 1996 was performed in order to derive degradation parameters for modeling the environmental fate of dimethenamid and the formation and degradation of its metabolites.
The software package KinGUI version 1.1 was used for parameter estimation. The compartment model used for the estimation approach is described in Figure B.8.1.2-1.

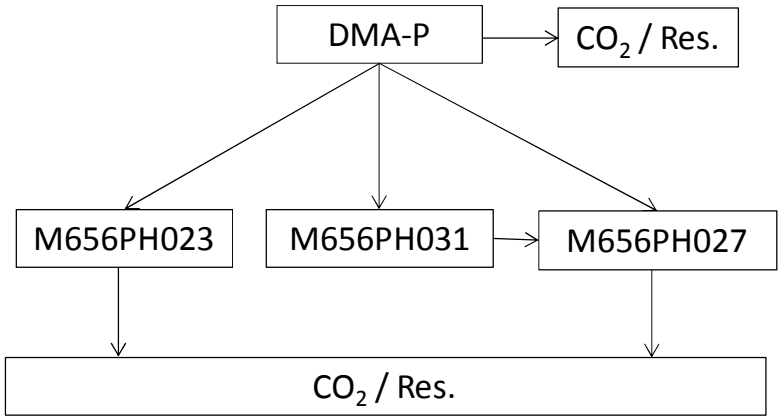


Figure B.8.1.2-1: Metabolism scheme of dimethenamid-P (DMTA-P) used for modelling

The residue data used for modelling are presented in Table B.8.1.1-6, Table B.8.1.1-7 and Table B.8.1.1-9. No further processing was required for the soil residues in soil BBA 2.2 and BBA 2.3. For the soil Flaach the residues of unknown compounds with concentrations >0.1 % AR were added to the dimethenamid residues. The resulting dimethenamid values at day 0 used for kinetic evaluation were 97.2, 96.8 and 97.5 % AR.

Kinetic analysis and calculations of DT_{50} and DT_{90} values were performed for the residues of dimethenamid-P and its metabolites M656PH023 (M23 in this study), M656PH031 (M31 in this study) and M656PH027 (M27 in this study) following the recommendations of the FOCUS Kinetics workgroup (2006).
Kinetic evaluation was performed in a step wise approach. First, only for the parent was modelled using SFO kinetics. Afterwards a kinetic evaluation of dimethenamid-P together with its metabolites M656PH023, M656PH031 and M656PH027 was performed.

Results and Discussion

SFO gave a very good visual and statistical fit for dimethenamid-P in all three soils. Thus, in a second step dimethenamid-P was modelled together with its metabolites M656PH023, M656PH031 and M656PH027 using SFO kinetics. However, no statistically reliable fit could be obtained for M656PH031 and M656PH027. Thus, in a third step the formation fraction from M656PH031 to M656PH027 fixed at 1.0.

The kinetic fits for dimethenamid-P together with its metabolites M656PH023, M656PH027 and M656PH031 using SFO kinetics are presented in Figure B.8.1.2-2, Figure B.8.1.2-3 and Figure B.8.1.2-4. The statistical results can be found in Table B.8.1.2-1, Table B.8.1.2-2 and Table B.8.1.2-3.

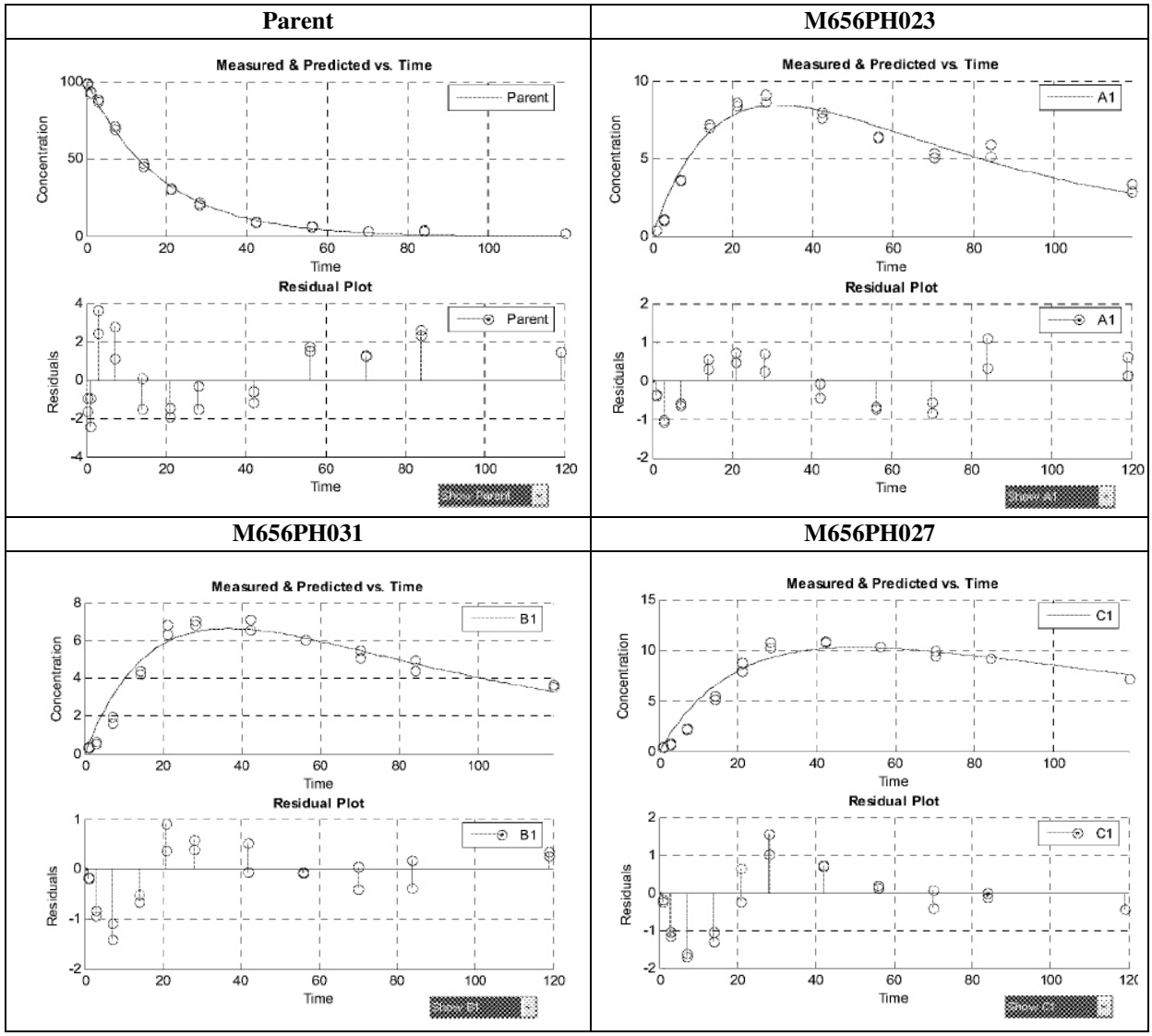


Figure B.8.1.2-2: SFO kinetic fit of dimethenamid-P and the metabolites M656PH023, M656PH031 and M656PH027 -ff from M656PH031 to M656PH027 fixed to 1.0 for the soil BBA 2.2

Table B.8.1.2-1: Statistical parameters using SFO for dimethenamid-P and its metabolites for the soil BBA 2.2

Kinetic model	Parameter	Optimised value	Std. error	p-value (t-test)	% error χ^2 test	DT_{50} (d)	DT_{90} (d)
SFO (parent	M0_parent	99.7055	0.5155	-	3.51	12.81	42.54
	k_ parent	0.0541	7.1e-04	2.0e-078			

+ met)	k_ met_M656PH023	0.0169	0.022	2.8e-011	9.34	40.97	136.11
	ff_met (a.s. → M656PH023)	0.1435	0.0103	-			
	k_ met_M656PH031	0.0113	0.0022	1.2e-06	10.79	61.25	203.48
	ff_met_M656PH031 (a.s. → M656PH031)	0.1007	0.0102	-			
	k_ met_M656PH027	0.0114	0.0017	1.0e-009	9.99	60.58	201.2
	ff_met (a.s. → M656PH027)	0.1251	0.0049	-			
	ff_met (M656PH031 → M656PH027)	1.0	-	fixed			

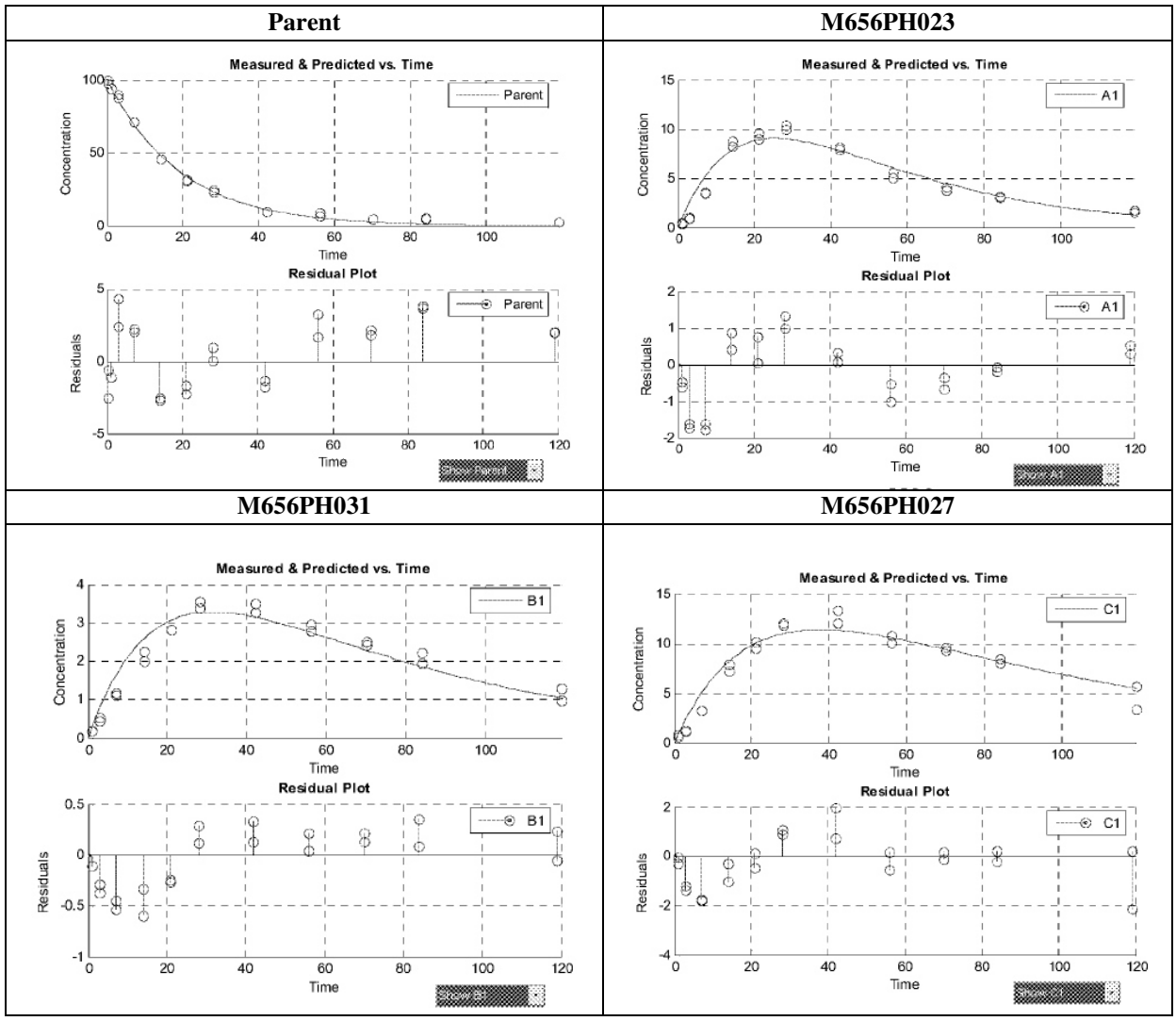


Figure B.8.1.2-3: SFO kinetic fit of dimethenamid-P and the metabolites M656PH023, M656PH031 and M656PH027 -ff from M656PH031 to M656PH027 fixed to 1.0 for the soil BBA 2.3

Table B.8.1.2-2: Statistical parameters using SFO for dimethenamid-P and its metabolites for the soil BBA 2.3

Kinetic model	Parameter	Optimised value	Std. error	p-value (t-test)	% error χ^2 test	DT_{50} (d)	DT_{90} (d)
SFO	M0_parent	99.9578	0.6444	-	4.55 %	13.27	44.10

(parent + met)	k_ parent	0.0522	8.5e-04	1.0e-07			
	k_ met_M656PH023	0.0291	0.0041	1.4e-01	14.68 %	23.81	79.09
	ff_met (a.s. → M656PH023)	0.1891	0.0173	-			
	k_ met_M656PH031	0.0176	0.0071	0.0077	11.06 %	39.43	130.99
	ff_met_M656PH031 (a.s. → M656PH031)	0.1007	0.0158				
	k_ met_M656PH027	0.0159	0.0023	4.8e-01	10.08 %	43.46	144.36
	ff_met (a.s. → M656PH027)	0.1710	0.0074				
	ff_met (M656PH031 → M656PH027)	1.0	-	fixed			

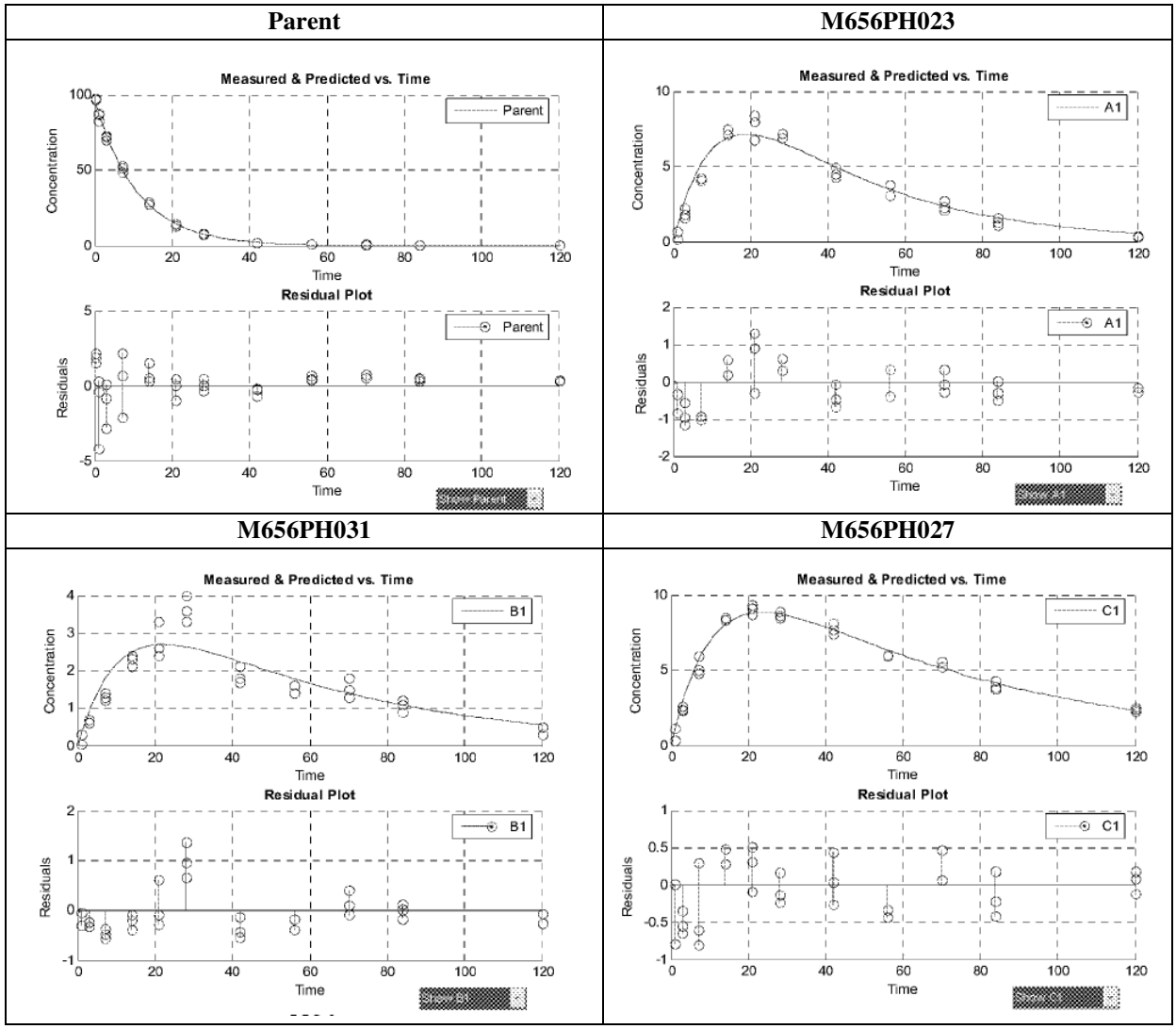


Figure B.8.1.2-4: SFO kinetic fit of dimethenamid-P and the metabolites M656PH023, M656PH031 and M656PH027 -ff from M656PH031 to M656PH027 fixed to 1.0 for the soil Flaach

Table B.8.1.2-3: Statistical parameters using SFO for dimethenamid-P and its metabolites for the soil Flaach

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	95.2943	0.3165	-	2.30 %	7.69	25.55
	k_ parent	0.0901	7.7e-004	2.3e-131			
	k_ met_M656PH023	0.0287	0.0023	1.8e-024	11.61 %	24.13	80.17
	ff_met (a.s. → M656PH023)	0.1282	0.0062	-			
	k_ met_M656PH031	0.0184	0.0039	3.3e-006	19.55 %	37.65	125.08
	ff_met_M656PH031 (a.s. → M656PH031)	0.0425	0.0056	-			
	k_ met_M656PH027	0.0209	0.0015	5.7e-028	4.45 %	33.13	110.07
	ff_met (a.s. → M656PH027)	0.1331	0.0029	-			
	ff_met (M656PH031 → M656PH027)	1.0	-	fixed			

Statistically reliable results could be obtained for dimethenamid-P and the metabolites M656PH023, M656PH031 and M656PH027.
No moisture normalisation to pF2 was performed by the study author. Thus it was performed by the applicant in its dossier. For moisture normalisation standard moisture values
The final DT_{50} and DT_{90} values and formation fractions are summarised in Table B.8.1.2-4. The formation fractions are summarised in Table B.8.1.2-5.

Table B.8.1.2-4: DT_{50} and DT_{90} values of dimethenamid-P and the metabolites M656PH023, M656PH031 and M656PH027 - ff from M656PH031 to M656PH027 fixed to 1.0 (Platz 2008)

Soil BBA 2.2					
Compound	**Kinetic model**	**DT_{50} [d]**	**DT_{90} [d]**	**Moisture correction factor**	**DT_{50} at 20 °C & pF 2 (d)**
Dimethenamid-P	SFO	12.81	42.54	0.768	9.8
M656PH023	SFO	40.97	136.11		31.5
M656PH031	SFO	61.25	203.48		47.1
M656PH027	SFO	60.58	201.2		46.3
Soil BBA 2.3					
Compound	**Kinetic model**	**DT_{50} [d]**	**DT_{90} [d]**	**Moisture correction factor**	**DT_{50} at 20 °C & pF 2 (d)**
Dimethenamid	SFO	13.27	44.10	0.673	9.0
M656PH023	SFO	23.81	79.09		16.0
M656PH031	SFO	39.43	130.99		26.5
M656PH027	SFO	43.46	144.36		29.3
Soil Flaach					
Compound	**Kinetic model**	**DT_{50} [d]**	**DT_{90} [d]**	**Moisture correction factor**	**DT_{50} at 20 °C & pF 2 (d)**
Dimethenamid	SFO	7.69	25.55	0.623	4.8
M656PH023	SFO	24.1	80.17		15.0
M656PH031	SFO	37.7	125.08		23.5
M656PH027	SFO	33.1	110.07		20.6

Table B.8.1.2-5: Formation fractions of the metabolites M656PH023, M656PH031 and M656PH027 -ff from M656PH031 to M656PH027 fixed to 1.0 (Platz 2008)

Compound	**Soil BBA 2.2**	**Soil BBA 2.3**	**Soil Flaach**
	Formation fraction from a.s.		
M656PH023	0.1435	0.1891	0.1282
M656PH031	0.1007	0.0571	0.0425
M656PH027	0.1251	0.1710	0.1331

Conclusion

The study is considered acceptable by the RMS.
For the soils BBA 2.2, BBA 2.3 anf Flaach DT_{50} values of 12.81, 13.27 and 7.7 d together with DT_{90} values of 42.54, 44.10 and 25.55 d, respectively, were derived for dimethenamid using a SFO fit. DT_{50} values for dimethenamid normalised to standard conditions (20 °C and pF2) were 9.8, 9.0 and 4.8 d.

DT_{50} values for the metabolite M656PH023 were 41 d, 23.81 and 24.1 d together with DT_{90} values of 136, 79.1 and 80.17 d in the soils BBA 2.2, BBA 2.3 and Flaach, respectively. DT_{50} values for M656PH023 normalised to standard conditions were 31.5, 16.0 and 15.0 d.
DT_{50} values for M656PH027 were 60.6, 43.5 and 33.1 d with DT_{90} values of 201, 144 and 110 d in the soils BBA 2.2, BBA 2.3 and Flaach, respectively. DT_{50} values for M656PH027 normalised to standard conditions were 46.3, 29.3 and 20.6 d the soils BBA 2.2, BBA 2.3 and Flaach.

For M656PH031, DT_{50} values of 61.3, 39.4 and 37.7 d together with DT_{90} values of 203, 131 and 125 d were found in the soils BBA 2.2, BBA 2.3 and Flaach, respectively. Normalised DT_{50} values for M656PH031 were 47.1, 26.5 and 23.5 d in the soils BBA 2.2, BBA 2.3 and Flaach.
M656PH023 was formed from dimethenamid-P with formation fractions of 0.1435, 0.1891 and 0.1282 in the soils BBA 2.2, BBA 2.3 and Flaach, respectively. M656PH027 were formed from dimethenamid-P with formation fractions of 0.1251, 0.0.1710 and 0.0425 and M656PH031 was formed from dimethenamid-P with formation fractions of 0.1007, 0.0571 and 0.1331 in the soils BBA 2.2, BBA 2.3 and Flaach. The formation fraction from M656PH031 to M656PH027 was fixed to 1.0.

KCA 7.1.2.1.1/2 – Bronner, 2010 (new study)

Author:	Bronner, G.
Title:	Determination of kinetic parameters for the degradation in US-soil of BAS 656 H and its metabolites M23, M27 and M31 in laboratory incubation studies
Date:	17/08/2010
Doc ID:	2010/1135818
Guidelines:	FOCUS kinetics guidance (2006)
GLP:	No (not applicable)
Validity:	Acceptable

Material and Methods

Kinetic re-evaluation of the aerobic soil study Wendt, 1997 according to FOCUS degradation kinetics (2006) was performed to derive degradation parameters for modeling the environmental fate of dimethenamid and the formation and degradation of its metabolites.
The software package KinGUI version 1.1 was used for parameter estimation. The compartment model used for the estimation approach is described in Figure B.8.1.2-1.

For kinetic evaluation the residue data of dimethenamid-P and dimethanemid at day 0 were replaced with the total amount of extractable residues. The metabolite residues at day 0 were not included and the initial values were fixed to 0. The processed residue data used for modelling are presented in Table B.8.1.2-6 and Table B.8.1.2-7.

Table B.8.1.2-6: Distribution of the radioactivity in the soil Elliott after degradation of dimethenamid-P (DMTA-P) in % AR quantified by HPLC

DAT	DMTA-P	M656PH023	M656PH027	M656PH031
0	100.2	-	-	-
0	102.8	-	-	-
1	86.4	-	-	-
1	88.4	-	1.50	-
3	69.8	2.82	4.95	2.26
3	77.0	1.69	2.44	2.07
7	59.0	4.26	4.26	4.01
7	54.1	5.77	4.95	3.45
14	31.3	8.15	8.02	6.58
14	33.5	5.20	7.71	6.89
21	19.6	5.08	7.83	8.15
21	20.9	6.08	6.52	8.77
28	13.3	6.02	8.02	9.65
28	15.8	6.02	7.39	8.77
42	6.71	4.95	6.89	8.27
42	8.71	4.20	8.96	9.15
56	8.84	3.95	5.51	9.27
56	8.65	2.95	6.08	8.52
84	6.02	1.94	6.14	8.59
84	4.4	1.50	4.01	6.02
119	3.32	2.01	3.07	5.64
119	2.82	2.26	2.95	4.45
182	1.38	1.19	1.82	4.14
182	1.82	1.94	2.63	3.95

Table B.8.1.2-7: Distribution of the radioactivity in the soil Elliott after degradation of dimethenamid (DMTA) in % AR quantified by HPLC

DAT	DMTA	M656PH023	M656PH027	M656PH031
0	99.8	-	-	-
0	103.6	-	-	-
1	89.1	-	-	-
1	86.5	-	-	-
3	78.1	2.63	3.07	1.00
3	78.0	2.38	2.26	2.57
7	55.6	5.58	3.38	4.51
7	53.0	5.45	4.32	4.57
14	33.7	7.33	7.83	7.58
14	33.2	6.52	8.65	6.71
21	20.9	5.77	7.71	8.65
21	19.9	7.71	6.45	7.65
28	18.2	7.83	6.33	7.96
28	12.7	7.33	8.71	8.59
42	7.83	7.02	5.70	7.39
42	9.02	6.27	4.20	7.21
56	11.40	4.26	3.20	10.34
56	9.02	3.82	4.20	9.40
84	3.89	2.63	3.76	6.52
84	4.4	2.82	4.01	6.89
119	2.57	1.63	4.51	4.64
119	3.38	1.13	4.51	4.51
182	2.01	1.38	3.82	4.26
182	1.69	1.32	2.26	4.20

Results and Discussion

SFO gave a very good visual and statistical fit for dimethenamid-P in both soils. Thus, in a second step dimethenamid-P was modelled together with its metabolites M656PH023 (= M23 in this study), M656PH031 (= M31 in this study) and M656PH027 (= M27 in this study) using SFO kinetics. However, no statistically reliable fit could be obtained for M656PH031 and M656PH027. Thus, in a third step the formation fraction from M656PH031 to M656PH027 fixed at 1.0.

The kinetic fits for dimethenamid-P together with its metabolites M656PH023, M656PH027 and M656PH031 using SFO kinetics are presented in Figure B.8.1.2-5 and Figure B.8.1.2-6. The statistical results can be found in Table B.8.1.2-8 and Table B.8.1.2-9.

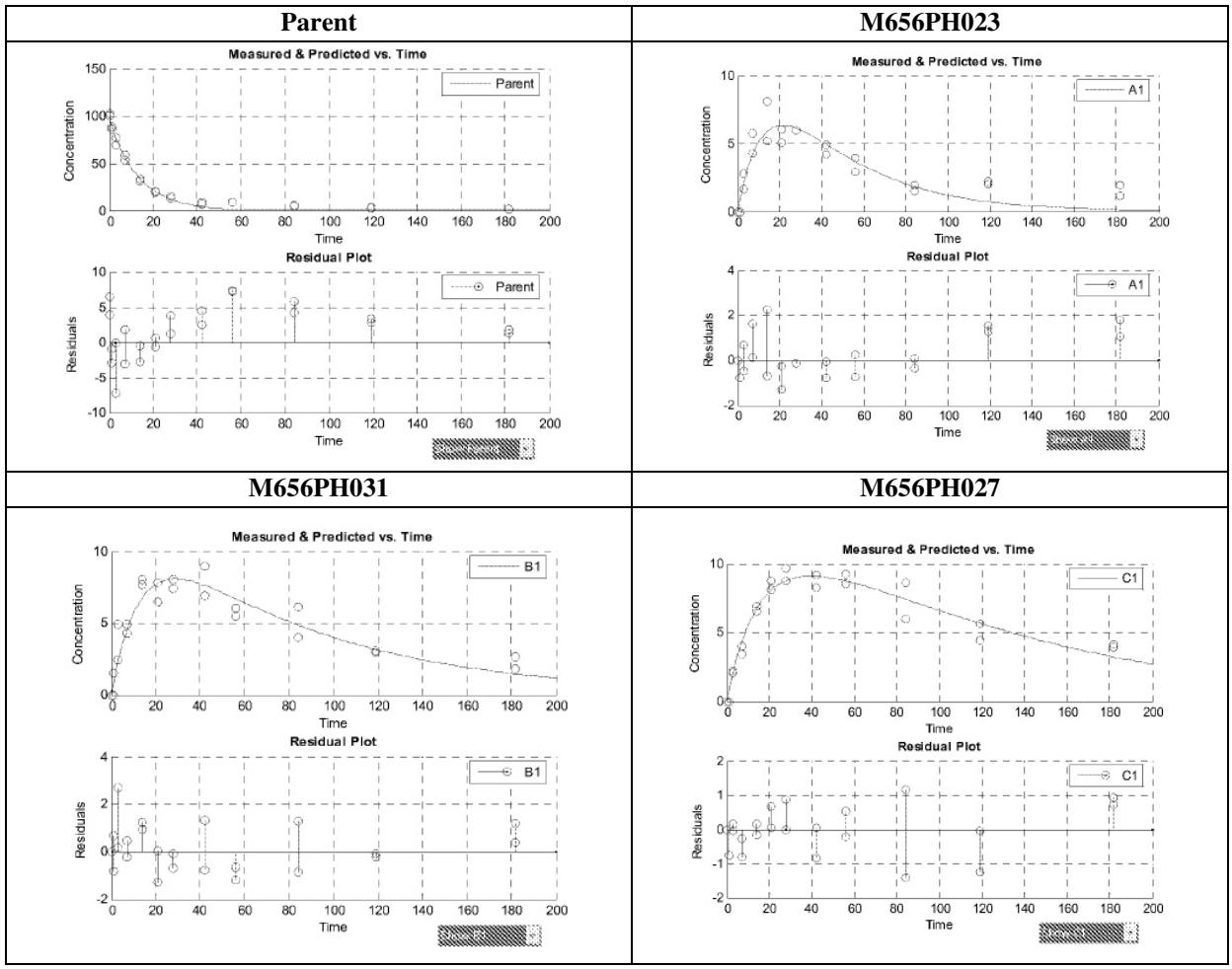


Figure B.8.1.2-5: SFO kinetic fit of dimethenamid-P and the metabolites M656PH023, M656PH031 and M656PH027 -ff from M656PH031 to M656PH027 fixed to 1.0 for the soil Elliott

Table B.8.1.2-8: Statistical parameters using SFO for dimethenamid-P and its metabolites for the soil Elliott

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	96.3172	1.0389	-	8.48 %	9.32	30.97
	k_ parent	0.0743	0.0020	4.1e-055			
	k_ met_M656PH023	0.0264	0.0089	0.0020	19.58 %	26.24	87.17
	ff_met (a.s. → M656PH023)	0.1168	0.0223	-			
	k_ met_M656PH031	0.0124	0.0032	1.3e-004	12.11 %	55.94	185.8
	ff_met_M656PH031 (a.s. → M656PH031)	0.1203	0.0169	-			
	k_ met_M656PH027	0.0152	0.0031	1.9e-006	7.12 %	45.58	151.40
	ff_met (a.s. → M656PH027)	0.1101	0.0087	-			
	ff_met (M656PH031 → M656PH027)	1.0	-	fixed			

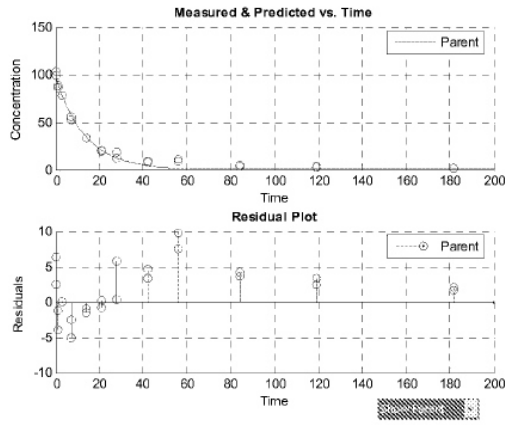
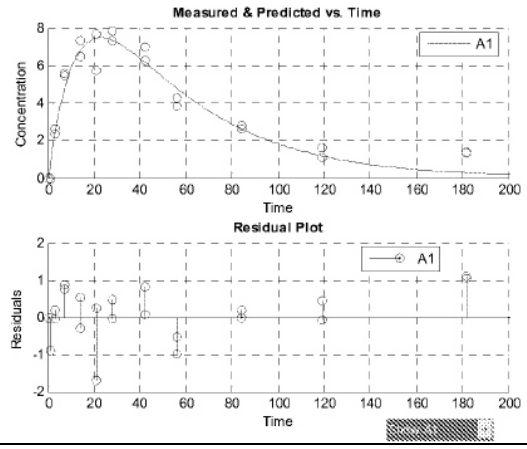
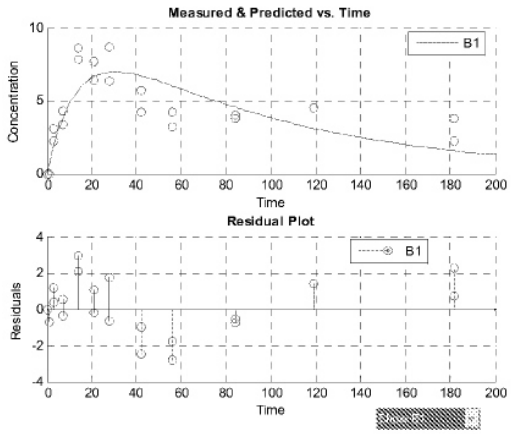
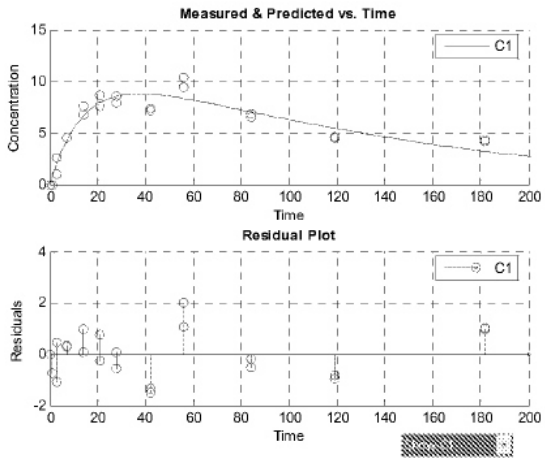
Parent	M656PH023
	
M656PH031	**M656PH027**
	

Figure B.8.1.2-6: SFO kinetic fit of dimethenamid and the metabolites M656PH023, M656PH031 and M656PH027 -ff from M656PH031 to M656PH027 fixed to 1.0 for the soil Elliott

Table B.8.1.2-9: Statistical parameters using SFO for dimethenamid and its metabolites for the soil Elliott

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	97.3005	1.0794	-	8.74 %	9.40	31.23
	k_ parent	0.0737	0.0021	4.1e-054			
	k_ met_M656PH023	0.0231	0.0069	6.1e-004	12.89 %	30.07	99.89
	ff_met (a.s. → M656PH023)	0.1308	0.0213	-			
	k_ met_M656PH031	0.0109	0.0036	0.0015	26.93 %	63.63	211.37
	ff_met_M656PH031 (a.s. → M656PH031)	0.1000	0.0169	-			
	k_ met_M656PH027	0.0140	0.0033	2.2e-005	12.76 %	49.35	163.95
	ff_met (a.s. → M656PH027)	0.1094	0.0087	-			
	ff_met (M656PH031 → M656PH027)	1.0	-	fixed			

Statistically reliable results could be obtained for dimethenamid-P and the metabolites M656PH023, M656PH031 and M656PH027. For modelling purposes the estimated degradation rates were normalised to 20 °C and pF2.

The final DT_{50} and DT_{90} values are summarised in Table B.8.1.2-10. The formation fractions for M656PH023, M656PH031 and M656PH027 are summarised in Table B.8.1.2-11.

Table B.8.1.2-10: DT_{50} and DT_{90} values of dimethenamid-P and the metabolites M656PH023, M656PH031 and M656PH027 - ff from M656PH031 to M656PH027 fixed to 1.0 (Bronner, 2010)

Soil Elliott incubated with dimethenamid-P						
Compound	**Kinetic model**	**DT_{50} [d]**	**DT_{90} [d]**	**Temp. corr. factor**	**Moisture corr. factor**	**DT_{50} at 20 °C & pF 2 (d)**
Dimethenamid-P	SFO	9.32	30.97	1.329	0.924	11.5
M656PH023	SFO	26.24	87.17			37.0
M656PH031	SFO	55.94	485.8			78.1
M656PH027	SFO	45.58	151.4			60.7
Soil Elliott incubated with dimethenamid						
Compound	**Kinetic model**	**DT_{50} [d]**	**DT_{90} [d]**	**Temp. corr. factor**	**Moisture corr. factor**	**DT_{50} at 20 °C & pF 2 (d)**
Dimethenamid	SFO	9.40	31.23	1.329	0.924	11.4
M656PH023	SFO	30.07	99.89			32.2
M656PH031	SFO	63.63	211.4			68.6
M656PH027	SFO	49.35	164.0			56.0

Table B.8.1.2-11: Formation fractions of the metabolites M656PH023, M656PH031 and M656PH027 -ff from M656PH031 to M656PH027 fixed to 1.0

Compound	Soil Elliott incubated with dimethenamid-P	Soil Elliott incubated with dimethenamid
	Formation fraction	Formation fraction
M656PH023	0.117	0.131
M656PH031	0.120	0.100
M656PH027	0.110	0.109

Conclusion

As can be seen when comparing the processed residue data with the original data taken from the study report KCA 7.1.1.1/4 – Wendt, 1997 presented in Table B.8.1.1-12 and Table B.8.1.1-13, there are some differences, that were not explained in this study report. Mainly, the processed residue data are presented with one more digit behind the comma. Thus, it is assumed by the RMS that the study author had access to the original data of Wendt, 1997. However, some of the processed dimethenamid-P residues measured in the first week are slightly lower than the respective residue values in Wendt, 1997 (e.g. 88.4 % dimethenamid-P at day 1 instead of 88.5 % and 78.1 % dimethenamid at day 3 instead of 78.2 %). This is the case for 6 of the residue data of dimethenamid and dimethenamid-P in total and concerns a value of 0.1 % AR. Although, this differences might affect the overall DT_{50} and DT_{90} values mainly for dimethenamid-P and dimethenamid, the effect is considered by the RMS to be very small.
The chi^2 error for the M656PH031 fit were > 15 %, however the visual fits were good, the standard deviations suitably low and the p value remained < 0.05. Thus, also for M656PH031 the resulting DT_{50} and DT_{90} values as well as the formation fractions are considered reliable.
Thus, the resulting DT_{50} and DT_{90} values for dimethenamid-P and dimethenamid and the metabolites M656PH023, M656PH031 and M656PH027 are still considered acceptable by the RMS.

For the soil Elliott, DT_{50} values of 9.32 and 9.40 d together with DT_{90} values of 30.97 and 31.23 d were derived for dimethenamid-P and dimethenamid, respectively, using a SFO fit. DT_{50} values normalised to 20 °C and pF2 were 11.5 d and 11.4 d.
For the metabolite M 23, DT_{50} values were 26.24 d and 30.07 d after formation from dimethenamid-P and dimethenamid, respectively, together with DT_{90} values of 87.17 and 99.89 d. DT_{50} values of M656PH023 normalised to 20 °C and pF2 were 37.0 d and 32.2 d.
For M656PH031, DT_{50} values were 55.94 and 63.63 d after formation from dimethenamid-P and dimethenamid, respectively, with DT_{90} values of 185.8 and 211.4 d. DT_{50} values of M656PH031 normalised to 20 °C and pF2 were 78.1 d and 68.6 d.
DT_{50} values for M656PH027 after formation from dimethenamid-P and dimethenamid, respectively, were 45.58 and 49.53 d with DT_{90} values of 151.4 and 164.0 d. DT_{50} values of M656PH027 normalised to 20 °C and pF2 were 60.7 d and 56 d.
M656PH023, M656PH031and M656PH027 were formed from dimethenamid-P with formation fractions of 0.117, 0.120 and 0.110. The formation fractions for M656PH023, M656PH031 and M656PH027 after formation from dimethenamid were 0.0131, 0.100 and 0.109. The formation fraction from M656PH031 to M656PH027 was fixed to 1.0.

All acceptable persistence and modelling endpoints of dimethenamid-P and its metabolites in soil are summarised in Volume 1 under 2.8.2.

KCA 7.1.2.1.1/3 - Staudenmaier, 2009a with amendment no. 1 Staudenmaier, 2014a (new study)

Author:	Staudenmaier, H.
Title:	Structure elucidation of metabolites of Dimethenamid in lysimeter leachate
Date:	18/11/2009
Doc ID:	2009/1011362
Guidelines:	OECD 307, BBA IV 4-1, EPA Subdivision N, 162-1
GLP:	Yes
Validity:	Acceptable

Aim of the study

Please refer to the study summaries for Staudenmaier, 2009a with amendment no. 1 Staudenmaier, 2014a under B.8.1.1.1 and B.8.1.4.2.

Material and Methods

For details the experimental conditions and the extraction and measurement methodology please refer to KCA 7.1.1.1/5 – Staudenmaier, 2009a with amendment no. 1 Staudenmaier, 2014a.

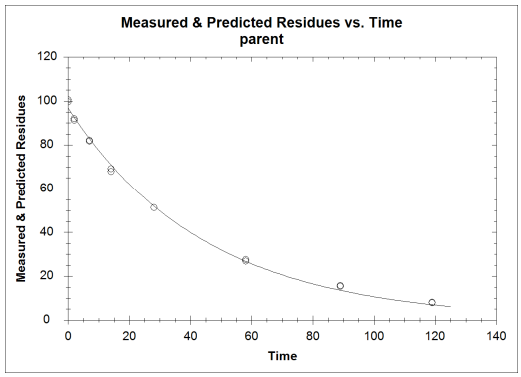
Kinetic analysis and calculations of DT_{50} and DT_{90} values were performed by the RMS for the residues of dimethenamid-P and its metabolites M656PH023, M656PH031 and M656PH027 listed in Table B.8.1.1-15 following the recommendations of the FOCUS Kinetics workgroup. The analysis was conducted by non-linear regression methods employing the software tool KinGUI version 2.
Kinetic evaluation was first performed only for the parent using SFO and FOMC kinetics. Afterwards a kinetic evaluation of dimethenamid-P together with its metabolites M656PH023, M656PH031 and M656PH027 was performed.

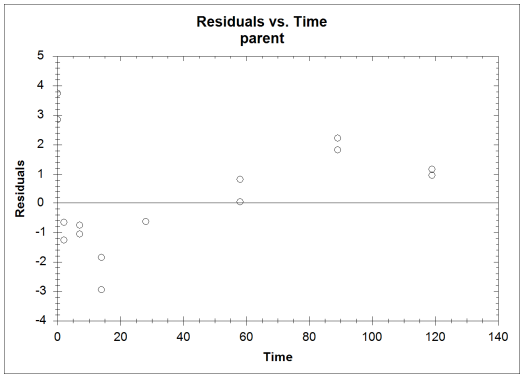
The metabolism pathway of dimethenamid-P for modelling is shown in Figure B.8.1.2-1.

Results and Discussion

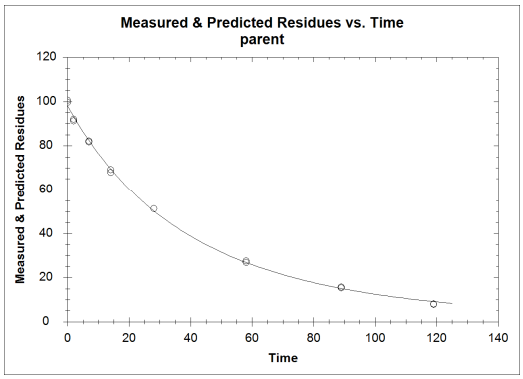
The kinetic fits for dimethenamid-P using SFO and FOMC kinetics are presented in Figure B.8.1.2-7. The statistical results can be found in Table B.8.1.2-12.

SFO





FOMC



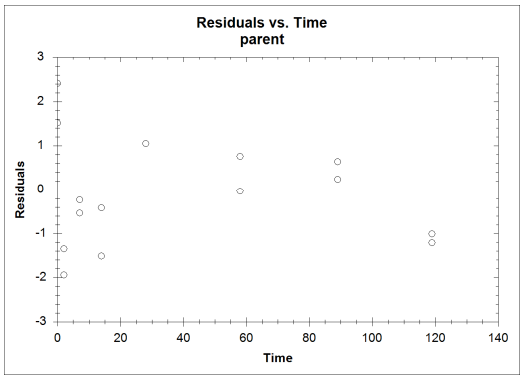


Figure B.8.1.2-7: SFO and FOMC kinetic fit of dimethenamid-P (Staudenmaier, 2009 with amend. Staudenmaier, 2014)

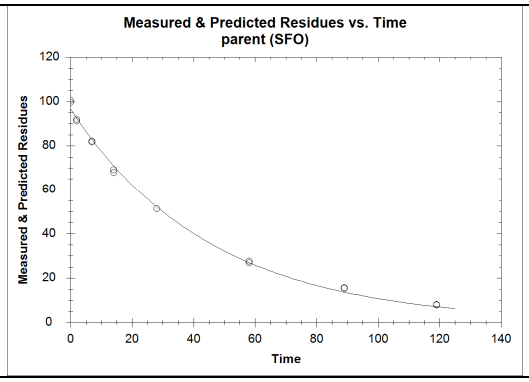
Table B.8.1.2-12: Statistical parameters using SFO and FOMC for dimethenamid-P (Staudenmaier, 2009 with amend. Staudenmaier, 2014)

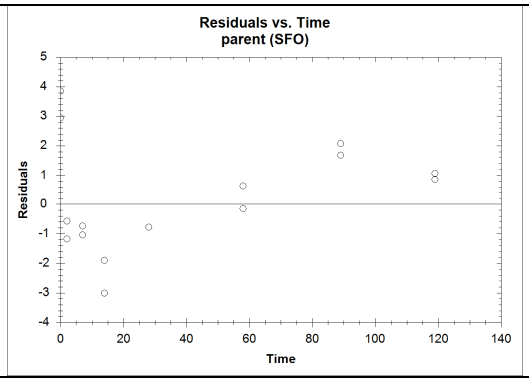
Kinetic model	Parameter	Optimised value	Std. error	p-value (t-test)	% error χ^2 test	DT_{50} (d)	DT_{90} (d)	Visual assessment
SFO	M0_parent	96.748352	0.841198	< 2e-16	2.58 %	31.29	103.93	Very good
	k_ parent	0.022155	0.000573	6.22e-16				
FOMC	M0_parent	98.0872	0.6803	< 2e-16	1.73 %	29.18	114.4	Very good
	α_parent	5.0946	1.3006	0.000884				
	β_parent	200.2064	58.1537	0.002184				

SFO gave a very good visual and statistical fit for dimethenamid-P and the FOMC fit was only marginally better. Thus, in a second step dimethenamid-P was modelled together with its metabolites M656PH023, M656PH031 and M656PH027 using SFO for dimethenamid-P. However, no statistically reliable fit could be obtained for M656PH031 and M656PH027. Thus, in a third step the formation fraction from M656PH031 to M656PH027 fixed at 1.0.

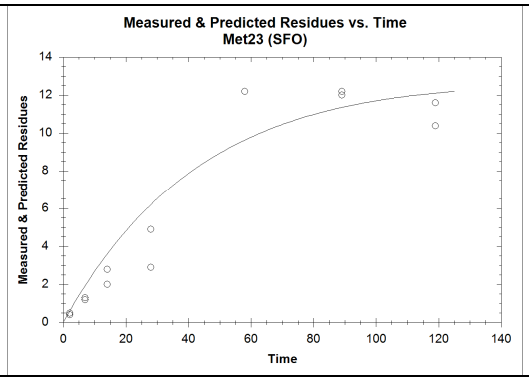
The kinetic fits for dimethenamid-P together with its metabolites M656PH023, M656PH027 and M656PH031 using SFO kinetics are presented in Figure B.8.1.2-8: SFO kinetic fit of dimethenamid-P and the metabolites M656PH023, M656PH031 and M656PH027 -ff from M656PH031 to M656PH027 fixed to 1.0 (Staudenmaier, 2009 with amend. Staudenmaier, 2014)". The statistical results can be found in Table B.8.1.2-13.

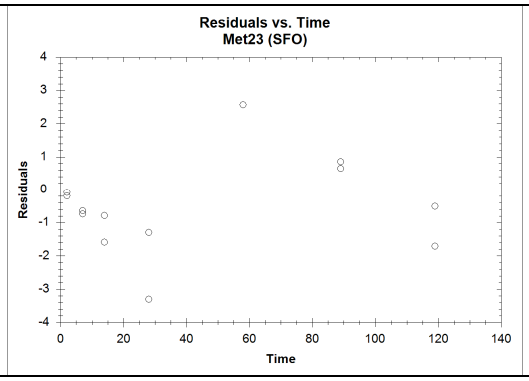
Parent





M656PH023





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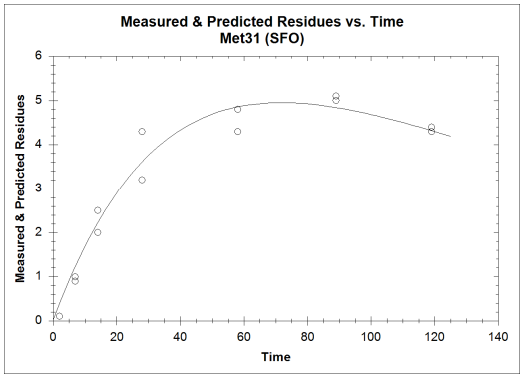
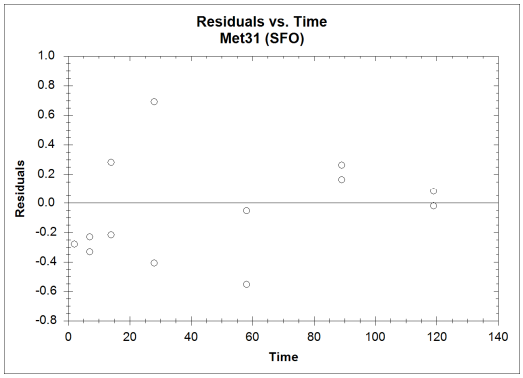
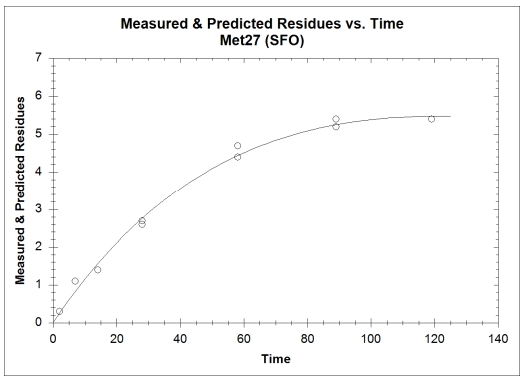




M656PH027



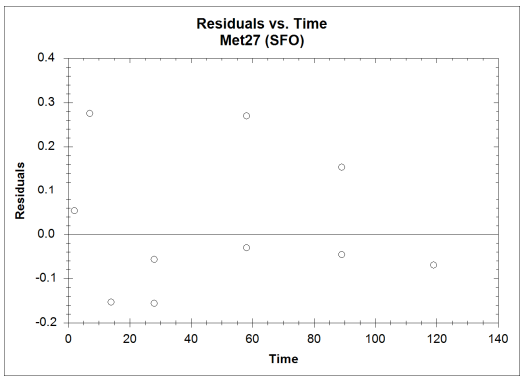


Figure B.8.1.2-8: SFO kinetic fit of dimethenamid-P and the metabolites M656PH023, M656PH031 and M656PH027 -ff from M656PH031 to M656PH027 fixed to 1.0 (Staudenmaier, 2009 with amend. Staudenmaier, 2014)

Table B.8.1.2-13: Statistical parameters using SFO for dimethenamid-P and its metabolites (Staudenmaier, 2009 with amend. Staudenmaier, 2014)

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	96.6404595	0.8494592	< 2e-16	2.83	31.49	104.6
	k_ parent	0.0220143	0.0005701	< 2e-16			
	k_ met_M656PH023	0.0004708	0.0022419	0.417	19.9 %	1472	4860
	ff_met (a.s. → M656PH023)	0.14048	0.0195836	-			
	k_ met_M656PH031	0.0081354	0.0012013	9.05e-09	5.6 %	85.20	283.03
	ff_met_M656PH031 (a.s. → M656PH031)	0.09178	0.0073124	-			
	k_ met_M656PH027	0.0079516	0.0012127	1.92e-08	3.72 %	87.17	289.58
	ff_met (a.s. → M656PH027)	0.05882	0.0044324	-			
	ff_met (M656PH031 → M656PH027)	1.0		fixed			

Statistically reliable results could be obtained for dimethenamid-P and the metabolites M656PH031 and M656PH027 but not for M656PH023. The resulting DT_{50} values were normalised to standard conditions of pF2 using the measured maximum water holding capacity of the soil. The final DT_{50} and DT_{90} values are summarised in Table B.8.1.2-14. The final formation fractions are presented in Table B.8.1.2-15.

Table B.8.1.2-14: DT_{50} and DT_{90} values of dimethenamid-P and the metabolites M656PH031 and M656PH027 - ff from M656PH031 to M656PH027 fixed to 1.0 (Bronner, 2010)

Soil Borstel					
Compound	**Kinetic model**	**DT_{50} [d]**	**DT_{90} [d]**	**Moisture corr. factor**	**DT_{50} at 20 °C & pF 2 (d)**
Dimethenamid-P	SFO	31.49	104.6	0.971	30.6
M656PH031	SFO	85.2	283		82.7
M656PH027	SFO	87.2	289.6		82.2

Table B.8.1.2-15: Formation fractions of the metabolites M656PH031 and M656PH027 -ff from M656PH031 to M656PH027 fixed to 1.0 (Staudenmaier, 2009 with amend. Staudenmaier, 2014)

Compound	Soil Borstel
	Formation fraction
M656PH031	0.0918
M656PH027	0.0588

Conclusion

A kinetic evaluation of the residues of the study Staudenmaier, 2009a with amendment no. 1 Staudenmaier, 2014a was performed by the RMS.
A DT_{50} value of 31.49 d together with a DT_{90} value of 104.6 d was derived for dimethenamid-P using a SFO fit. DT_{50} values for the metabolites M656PH031 and M656PH027 were 85.2 d and 87.2 d, respectively, with DT_{90} values of 283 d and 289.6 d. M656PH031 and M656PH027 were formed from dimethenamid-P with formation fractions of 0.0918 and 0.0588, respectively. The formation fraction from M656PH031 to M656PH027 was fixed to 1.0. No statistically reliable fit could be obtained for M656PH023. DT_{50} values of dimethenamid-P, M656PH031 and M656PH027 under reference conditions of 20 °C and pF2 are 30.6 d, 82.7 d and 82.2 d, respectively.
All acceptable endpoints of dimethenamid-P and its metabolites in soil are summarised in Volume 1 under 2.8.2.

KCA 7.1.2.1.1/4 - Staudenmaier, 2013 (new study)

Author:	Staudenmaier, H.
Title:	Chiral analysis of dimethenamid-P after incubation in soil
Date:	18/11/2013
Doc ID:	2012/1073064
Guidelines:	None
GLP:	yes
Validity:	Acceptable

Aim of the study

Please refer to the study summary of Staudenmaier, 2013 described under B.8.1.1.1.

Material and Methods

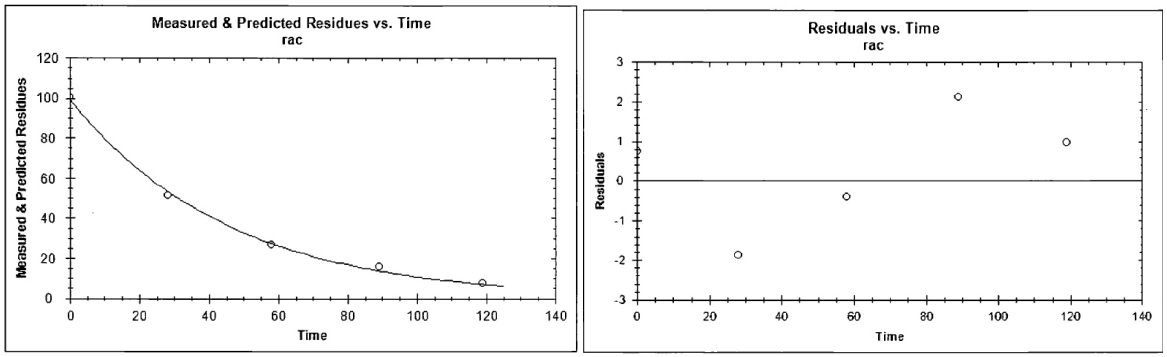
For details on the experimental conditions and the extraction and measurement methodology please refer to Staudenmaier, 2009a with amendment no. 1 Staudenmaier, 2014a described under B.8.1.1.1. For details on the additional sample work up and the methodology of chiral HPLC analysis please refer to study summary of Staudenmaier, 2013 described under B.8.1.1.1.

Kinetic analysis and calculations of DT_{50} and DT_{90} values were performed for the residues listed in Table B.8.1.1-17 following the recommendations of the FOCUS Kinetics workgroup using SFO and FOMC. The analysis was conducted by non-linear regression methods employing the software tool KinGUI 2.

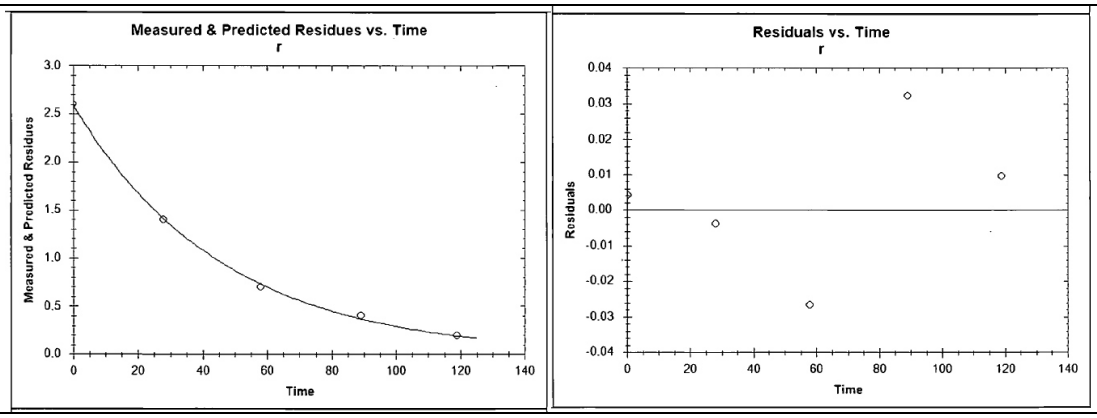
Results and Discussion

For results on the chiral analysis throughout the incubation and under different conditions please refer to KCA 7.1.1.1/6 – Staudenmaier, 2013.
Both, the S- and the R-enantiomer, separately and the total sum of enantiomers have been evaluated following the steps in the flowcharts proposed by the FOCUS Kinetics guidance document. SFO resulted in statistically very good fits for all evaluations and is the most appropriate kinetic model. The visual fits using SFO are presented in Figure B.8.1.2-9. The statistical parameters for the SFO fit can be found in Table B.8.1.2-16.

Sum of enantiomers (= dimethenamid-P)



R-enantiomer



S-enantiomer

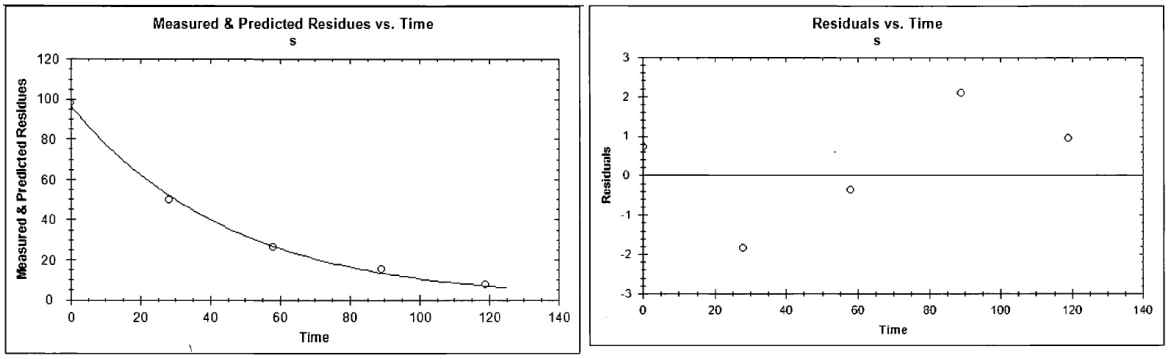


Figure B.8.1.2-9: SFO of sum of enantiomers, the R-enantiomer and the S-enantiomer (Staudenmaier, 2013a)

Table B.8.1.2-16: Statistical parameters using SFO for sum of both enantiomer and for the R-enantiomer and the S-enantiomer separately (Staudenmaier, 2013a)

Kinetic model	Parameter	Optimised value	Std. error	p-value (t-test)	% error χ^2 test
Sum of enantiomers (= dimethenamid-P)					
SFO	M_0_parent	99.760579	1.708592	5.53e-06	2.74 %
	k_ parent	0.022415	0.000779	4.61e-05	
R-enantiomer					
SFO	M_0_parent	2.5957595	0.0250499	9.91e-07	1.46 %
	k_ parent	0.0219529	0.0004064	6.99e-06	
S-enantiomer					
SFO	M_0_parent	97.07	1.614	5.06e-06	2.77 %
	k_ parent	2.241e-02	7.956e-04	4.91e-05	

A summary of the resulting DT_{50} and DT_{90} values is provided in Table B.8.1.2-17.

Table B.8.1.2-17: DT_{50}/DT_{90} of the enantiomers of dimethenamid-P in the soil Borstel (Staudenmaier, 2013a)

Compund	Kinetic model	DT_{50} [d]	DT_{90} [d]
Sum of enantiomers (= dimethenamid-P)	SFO	30.9	102.7
R-enantiomer	SFO	31.6	104.9
S-enantiomer	SFO	30.9	102.8

The kinetic evaluation shows that there is no significant difference between the degradation of racemic dimethenamid and the R- and S-enantiomers of dimethenamid-P individually. All substances degrade at the same rate, i.e. the rate of degradation is within the confidence intervals of all three kinetic analyses. Similar degradation rates also demonstrate that there is no interconversion between isomers. Interconversion would lead to differing kinetics between the enantiomers. This is also backed-up analysing the ratio of S- and R-enantiomer over time, which does not show a significant and continuous increase/decrease over time.

Conclusion

The study is considered acceptable by the RMS.
DT_{50} values of 30.9 days, 30.9 days and 31.6 days were estimated for the sum of both enantiomers, the S- and the R-enantiomer, respectively, using the SFO model. The kinetic evaluation showed that there is no significant difference between the degradation of the total sum of isomers, as well as the R- and S-enantiomer individually. All substances degrade with the same rate, i.e. the rate of degradation is within the confidence intervals of all three kinetic analyses.

All acceptable persistence and modelling endpoints of dimethenamid-P and its metabolites in soil are summarised in Volume 1 under 2.8.2.

KCA 7.1.2.1.1/5 – Unsworth, 2014a (new study)

Author: Unsworth, R.
Title: dimethenamid-P: Chiral separation after degradation in soil
Date: 22/01/2014
Doc ID: 2013/1412031
Guidelines: OECD 307 (2002)
GLP: Yes
Validity: Acceptable

Aim of the study

Please refer to the study summary of Unsworth, 2014a described under B.8.1.1.1.

Material and Methods

For details the experimental conditions and the extraction and measurement methodology please refer to the study summary of Unsworth, 2014a described under B.8.1.1.1.

Kinetic analysis and calculations of DT_{50} and DT_{90} values were performed for the residues of dimethenamid-P and its metabolites M656PH023, M656PH031 and M656PH027 listed in Table B.8.1.1-26 by the RMS following the recommendations of the FOCUS Kinetics workgroup. The analysis was conducted by non-linear regression methods employing the software tool KinGUI version 2.
Kinetic evaluation was first performed only for the parent using SFO and FOMC kinetics. Afterwards a kinetic evaluation of dimethenamid-P together with its metabolits M656PH023, M656PH031 and

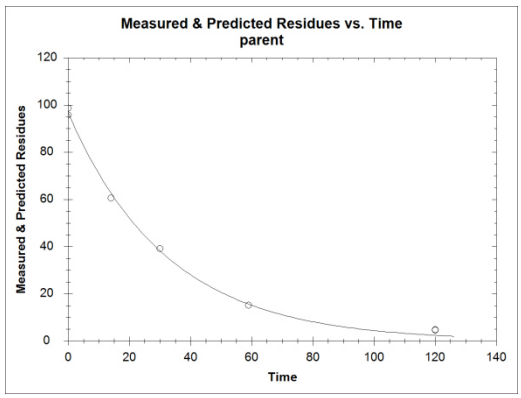
M656PH027 was performed.

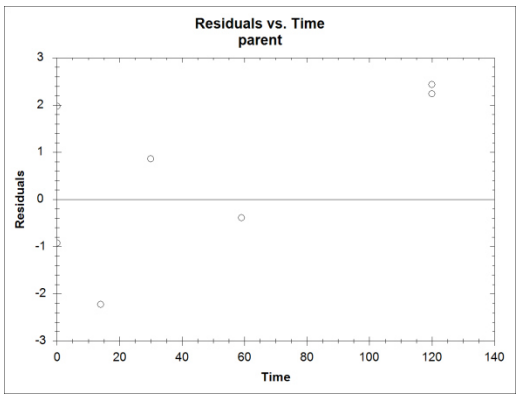
The metabolism pathway of dimethenamid-P for modelling is shown in Figure B.8.1.2-1.

Results and Discussion

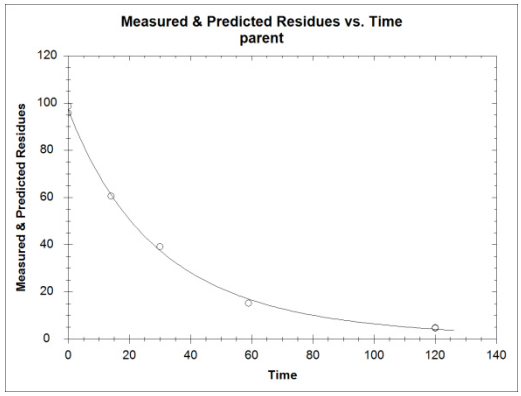
The kinetic fits for dimethenamid-P using SFO and FOMC kinetics are presented in Figure B.8.1.2-10. The statistical results can be found in Table B.8.1.2-18.

SFO





FOMC



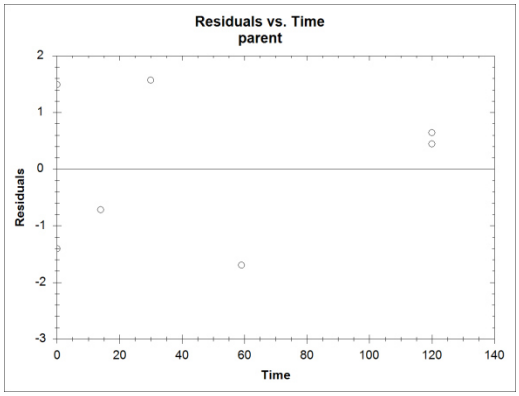


Figure B.8.1.2-10: SFO and FOMC kinetic fit of dimethenamid-P

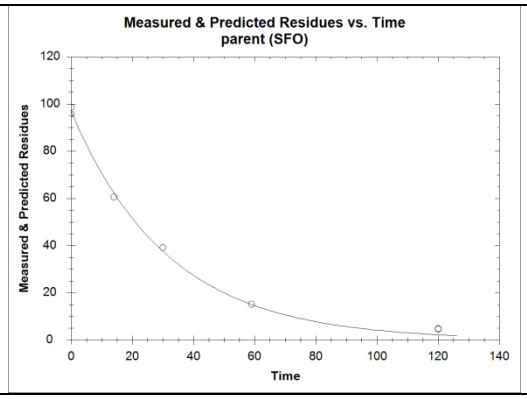
Table B.8.1.2-18: Statistical parameters using SFO and FOMC for dimethenamid-P

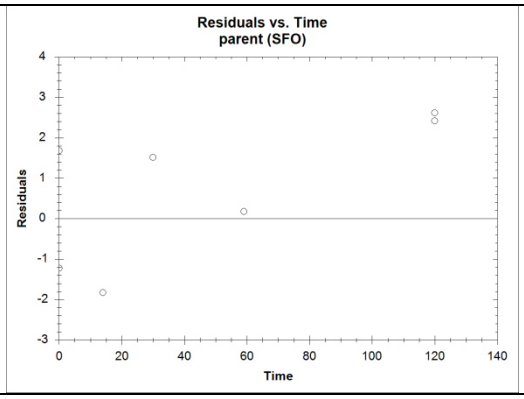
Kinetic model	Parameter	Optimised value	Std. error	p-value (t-test)	% error χ^2 test	DT_{50} (d)	DT_{90} (d)	Visual assessment
SFO	M0_parent	96.723966	1.423254	6.53e-09	2.75 %	22.04	74.43	Very good
	k_ parent	0.030935	0.001336	1.40e-06				
FOMC	M0_parent	97.2034	1.1427	5.73e-08	1.81 %	21.39	81.39	Very good
	α_parent	6.1655	3.0734	0.0577				
	β_parent	179.7592	99.2489	0.0722				

SFO gave a good visual and statistically more reliable fit for dimethenamid-P than FOMC. Thus, in a second step dimethenamid-P was modelled together with its metabolites M656PH023, M656PH031 and M656PH027 using SFO for dimethenamid-P. However, no statistically reliable fit could be obtained for M656PH031 and M656PH027. Thus, in a third step the formation fraction from M656PH031 to M656PH027 was fixed at 1.0.

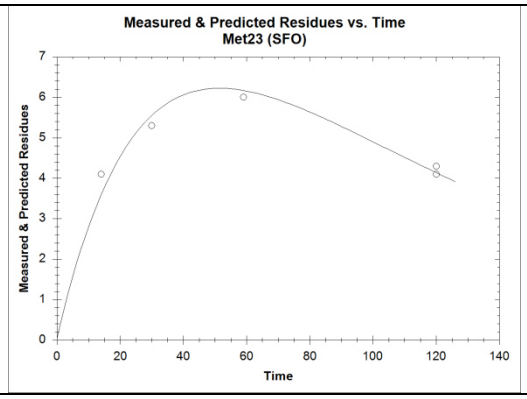
The kinetic fits for dimethenamid-P together with its metabolites M656PH023, M656PH027 and M656PH031 using SFO kinetics are presented in Figure B.8.1.2-11. The statistical results can be found in Table B.8.1.2-19.

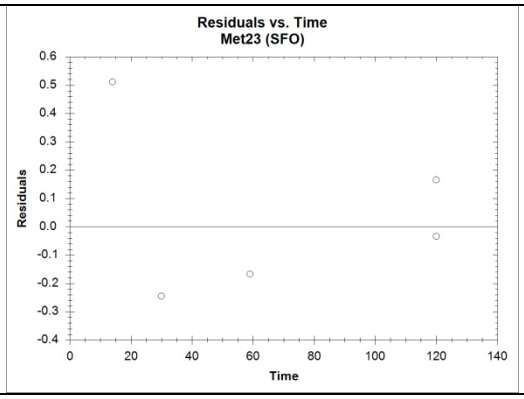
Parent



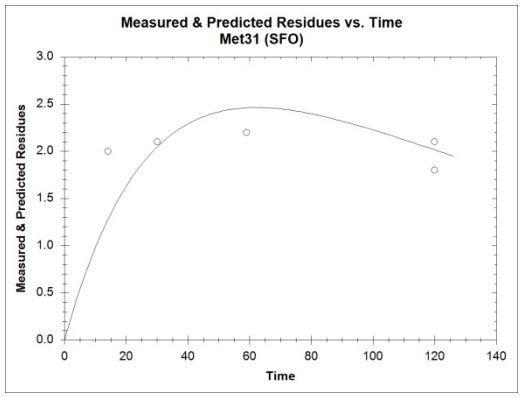


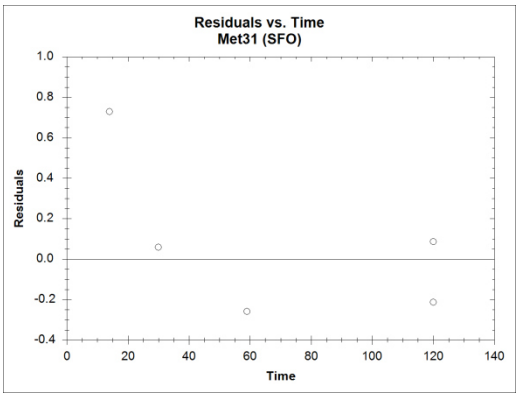
M656PH023



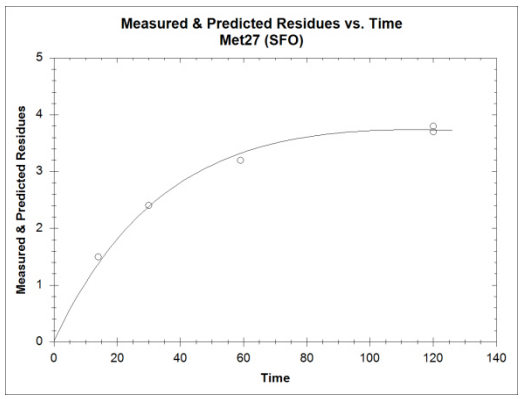


M656PH031





M656PH027



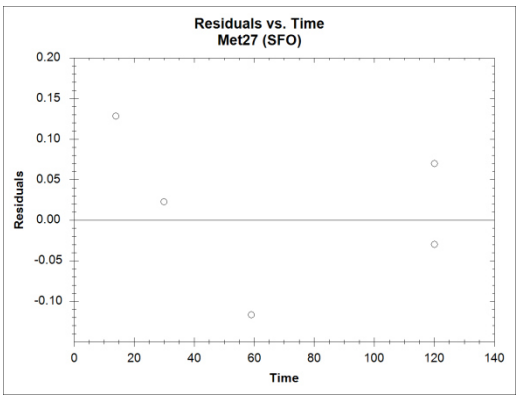


Figure B.8.1.2-11: SFO kinetic fit of dimethenamid-P and the metabolites M656PH023, M656PH031 and M656PH027 -ff from M656PH031 to M656PH027 fixed to 1.0

Table B.8.1.2-19: Statistical parameters using SFO for dimethenamid-P and the metabolites M656PH023, M656PH031 and M656PH027-ff from M656PH031 to M656PH027 fixed to 1.0

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	97.019956	1.539394	< 2e-16	3.85 %	21.93	72.84
	k_ parent	0.031612	0.001470	2.01e-12			
	k_ met_M656PH023	0.010841	0.001265	3.03e-07	4.08 %	63.94	212.4
	ff_met (a.s. → M656PH023)	0.11210	0.008060	-			
	k_ met_M656PH031	0.006711	0.002629	0.0115	12.42 %	103.29	343.12
	ff_met_M656PH031 (a.s. → M656PH031)	0.03853	0.007284	-			
	k_ met_M656PH027	0.004646	0.001786	0.0105	1.97 %	149.2	495.64
	ff_met (a.s. → M656PH027)	0.03902	0.003115	-			
	ff_met (M656PH031 → M656PH027)	1.0	-	fixed			

Statistically reliable results could be obtained for dimethenamid-P and its metabolites. The final DT_{50} and DT_90 values and formation fractions are summarised in Table B.8.1.2-20.

Table B.8.1.2-20: DT_{50}/DT_{90} and formation fractions of dimethenamid-P and its metabolites M656PH023, M656PH031 and M656PH027 in the soil Calke (Unsworth, 2014a)

Compund	Kinetic model	DT_{50} [d]	DT_{90} [d]	Formation fraction
dimethenamid-P	SFO	21.93	74.84	-
M656PH023	SFO	63.94	212.4	0.1121 (a.s.→ M656PH023)
M656PH031	SFO	103.29	343.12	0.03853 (a.s.→ M656PH031)
M656PH027	SFO	149.2	495.64	0.03902 (a.s.→ M656PH027)
				1.0 (M656PH031→ M656PH027)

Conclusion

A kinetic evaluation of the residues of the study Unsworth, 2014a was performed by the RMS.
A DT_{50} value of 21.93 d together with a DT_{90} value of 74.84 d was derived for dimethenamid-P using a SFO fit. DT_{50} values for the metabolites M656PH023, M656PH031 and M656PH027 were 63.94 d, 103.3 d and 149.2 d, respectively, with DT_{90} values of 212.4 d, 343.12 d and 495.64 d. M656PH023 was formed from dimethenamid-P with a formation fraction of 0.1121. M656PH031 and M656PH027 were formed from dimethenamid-P with formation fractions of 0.03853 and 0.03902, respectively. The formation fraction from M656PH031 to M656PH027 was fixed to 1.0.

All acceptable persistence and modelling endpoints of dimethenamid-P and its metabolites in soil are summarised in Volume 1 under 2.8.2.

B.8.1.2.2 Aerobic degradation – metabolites

KCA 7.1.2.1.2/ 1 – Class & Heinz, 2014 (new study)

Author:	Class, T. Heinz, N.
Title:	Aerobic soil degradation of the three dimethenamid-P metabolites M656PH054 (Reg.No. 5920718), M656PH047 (Reg.No. 5917260), M656PH043 (Reg.No. 5917262) in three soils (OECD Guideline 307)
Date:	26/02/2014
Doc ID:	2013/1348091
Guidelines:	OECD 307 (2002), BBA VI 4-1 (December 1986), EPA OPPTS 835.4100 (Oct 2008)
GLP:	Yes
Validity:	Acceptable

Material and Methods

The aerobic degradation of the three dimethenamid-P metabolites M656PH054 (Reg No. 5920718), M656PH047 (Reg No. 5917260), M656PH043 (Reg No. 5917262) was investigated in three soils, a loamy sand (Li10), a sandy loam (LUFA 5M) and (LUFA 2.2) (soil class according to DIN) in order to derive trigger endpoints.
The soil characteristics are listed in Table B.8.1.2-21.

Table B.8.1.2-21: Characterisation of the soil systems (Class & Heinz, 2014)

Soil specification	Li10	LUFA 2.2	LUFA 5M
Textural class (USDA)	Loamy sand	Sandy loam	Loamy sand
Particle size distribution (%)			
clay <0.002 mm	5.6	12.0	6.1
Silt 0.002 – 0.050 mm	11.6	27.7	11.1
Clay 0.05 – 2.0 mm	82.8	60.3	82.8
Total nitrogen (%)	0.09	0.16	0.12
TOC (total organic carbon) (%)	0.84	1.47	2.03
pH ($CaCl_2$)	6.4	5.4	7.2
pH (H_2O)	6.9	5.9	7.9
Effective cation exchange capacity (cmol/kg)	5.3	7.6	11.4
Max. water holding capacity (g/100 g dry soil)	25.1	29.5	25.2
Microbial biomass (mg C/ 100 g)	18.5	30.7	26.5
Bulk density (g/L)	1369	1227	1367

The soils were kept under aerobic conditions at about 5 °C for about 12 days, then water was adjusted to 40 % of MWHC and the soils were acclimatised 21 days at room temperature in the dark. The nominal application rate of none-radiolabelled M656PH054, M656PH047 and M656PH043 dosed to bulk soil was 0.5 mg/kg (based on dry soil weight). Assuming a soil depth of 5 cm and a soil density of 1.5 g/cm^3 this corresponds to a theoretical field application rate of about 375 g/ha. Upon correction for the purity of the test item M656PH047, the actual application rate of M656PH047 was 0.127 mg/kg equivalent to approximetaly 50 g/ha. Incubation flasks with 50 g of dosed dry soil equivalents were placed in thermostated cabinet(s) set to 20±1 °C and thus be kept in the dark. The dosed soil samples were incubated for various intervals up to 118 days prior to extraction.
The soil samples were extracted with 25 mL of methanol by shaking for 30 minutes on a horizontal shaker and sonication for 10 minutes in an ultrasonic bath, followed by centrifugation (5 minutes at 4000 rpm). The extraction was repeated two more times with each 25 mL of methanol/water (1/1;v/v), the extracts were combined and diluted to exactly 100 mL (V_{End}) with methanol. An aliquot of the final extract was diluted by a factor DF of 5 with methanol/water (1/1; v/v) and analysed by liquid chromatography with tandem mass spectrometric detection (LC/MS/MS).

The observed results of the metabolites in the incubated soil samples (expressed as µg/kg) were fitted using the software package KinGUI version 2 according to FOCUS kinetic guidance in order to derive trigger endpoints. Therefore, SFO and FOMC kinetics were modelled first. Where FOMC resulted in a better fit than SFO, additionally DFOP was tested.

Results and Discussion

Since incubations were performed in flasks open to the atmosphere without collection of volatiles and also bound residues were not measured, the determination of an overall mass balance was only possible for day 0. Recoveries at day 0 ranged from 98.1 – 100.0 % for the soil Li10, from 84.7 – 93.3 % for the soil LUFA 2.2 and from 90.6 – 98.6 % for the soil LUFA 5M.
The residues of M656PH054, M656PH047 and M656PH043 during the incubations are presented in Table B.8.1.2-22, Table B.8.1.2-23 and Table B.8.1.2-24.

Table B.8.1.2-22: Residues of M656PH054 in the soils Li10, LUFA 2.2 and LUFA 5M in % AR

Days	Soil Li10	Soil LUFA 2.2	Soil LUFA 5M
	M656PH054 (%AR)		
0	98.5	92.7	98.6
0	100.0	84.7	90.9
0	98.1	93.3	96.9
2	93.1	87.4	74.4
2	92.8	89.7	80.0
7	84.3	76.5	68.3
7	86.0	77.2	64.9
14	72.1	69.9	57.7
14	72.7	76.5	58.7
21	65.8	63.1	53.3
21	63.0	59.3	44.9
29	56.3	54.4	35.4
29	56.5	51.2	30.8
43	45.7	41.1	25.5
43	37.8	39.6	24.6
61	28.8	33.9	13.1
61	31.3	31.6	12.4
75	25.7	32.0	7.50
75	28.3	30.4	6.77
90	17.3	26.1	0.89
90	19.7	28.0	1.70
105	11.8	26.4	98.6
105	12.5	26.3	90.9
118	10.6	26.0	96.9
118	10.8	26.4	74.4

Table B.8.1.2-23: Residues of M656PH0047 in the soils Li10, LUFA 2.2 and LUFA 5M in % AR

Days	Soil Li10	Soil LUFA 2.2	Soil LUFA 5M
	M656PH0047 (in %AR)		
0	97.5	95.8	98.6
0	104.0	89.8	92.6
0	99.9	100.0	99.8
2	101.0	93.8	82.6
2	99.8	95.3	88.9
7	101.0	94.8	90.8
7	101.0	94.3	82.4
14	96.1	91.0	91.8
14	94.0	98.0	92.0
21	87.2	89.5	84.2
21	86.4	83.6	77.6
29	86.9	77.9	71.3
29	87.1	77.2	65.6
43	80.9	71.4	66.5
43	75.3	72.8	65.3
61	74.9	53.9	49.3
61	76.7	51.8	49.0
75	68.6	50.8	28.2
75	71.6	49.0	26.9
90	53.9	45.7	8.68
90	59.4	48.5	11.7
105	36.6	44.4	3.06
105	38.0	44.9	2.38
118	36.0	43.3	1.71
118	37.2	43.4	1.10

Table B.8.1.2-24: Residues of M656PH0043 in the soils Li10, LUFA 2.2 and LUFA 5M in % AR

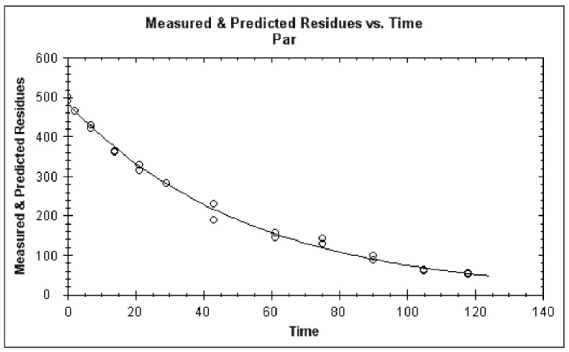
Days	Soil Li10	Soil LUFA 2.2	Soil LUFA 5M
	M656PH0043 (in %AR)		
0	95.2	92.5	95.5
0	104.0	86.4	90.7
0	99.4	97.6	97.3
2	93.7	88.9	70.4
2	93.5	92.1	76.9
7	73.0	71.8	49.9
7	72.9	71.9	49.0
14	60.0	61.6	35.2
14	60.2	70.2	34.3
21	53.2	57.1	29.1
21	52.6	54.5	23.4
29	45.8	47.4	13.0
29	44.0	45.1	11.4
43	34.6	36.7	5.57
43	28.1	35.3	5.35
61	22.2	32.2	2.19
61	24.6	28.7	1.55
75	24.2	30.2	1.15
75	26.9	27.2	1.14
90	19.2	24.0	95.5
90	20.2	25.8	90.7
105	16.0	24.0	97.3
105	17.8	23.6	70.4
118	14.8	22.1	76.9
118	15.1	23.5	49.9

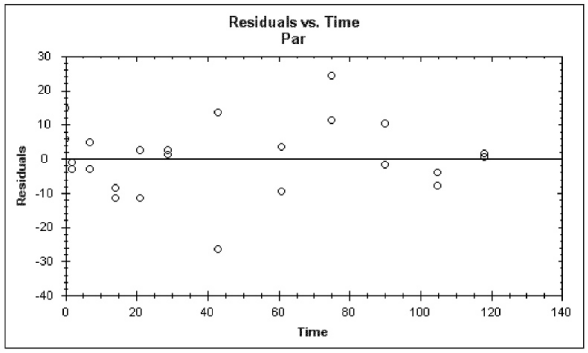
The statistical results of the kinetic evaluation are given in Table B.8.1.2-25, Table B.8.1.2-26 and Table B.8.1.2-27. The best kinetic fits for M656PH054, M656PH00047 and M656PH00043 are shown in Figure B.8.1.2-12, Figure B.8.1.2-13 and Figure B.8.1.2-14.

Table B.8.1.2-25: Statistical parameters for M656PH054

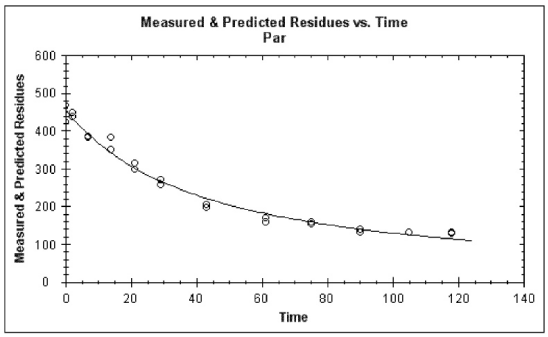
Soil Li10								
Kinetic model	**Parameter**	**Optimised value**	**Std. error**	**p-value (t-test)**	**% error χ^2 test**	**Visual assessment**	**DT_{50} (d)**	**DT_{90} (d)**
SFO	M0 (µg/kg)	485.1	4.035	< 2e-16	2.35 %	Very good	36.74	122.4
	k	0.01887	2.84e-04	< 2e-16				
FOMC	M0 (µg/kg)	485.19	3.752	< 2e-16	2.44 %	Very good	36.67	121.92
	α	927.173	186.408	3.19e-05				
	β	49031	10434	6.12e-05				
DFOP	M0 (µg/kg)	493.5	6.464	< 2e-16	2.15 %	Very good	35.54	123.92
	k_1	0.1921	0.2998	0.2645				
	k_2	1.821e-02	7.486e-4	< 2e-16				
	g	4.515e-02	3.106e-2	0.0808				
Soil LUFA 2.2								
Kinetic model	**Parameter**	**Optimised value**	**Std. error**	**p-value (t-test)**	**% error χ^2 test**	**Visual assessment**	**DT_{50} (d)**	**DT_{90} (d)**
SFO	M0 (µg/kg)	4309	10.5	< 2e-6	7.4 %	acceptable	50.59	168.04
	k	1.370e-02	8.524e-04	6.06e-14				
FOMC	M0	457.2391	8.7092	< 2e-16	4.1 %	Very good	40.21	334.14
	α	1.0738	0.1195	1.22e-05				
	β	44.3364	12.8556	0.00120				
DFOP	M0 (µg/kg)	455.8	6.936	< 2e-16	3.21 %	Very good	38.60	??
	k_1	2.806e-02	5.379e-03	2.09e-05				
	k_2	1.798e-09	4.623e-03	0.538.604				
	g	0.7558	0.1423	1.69e-05				
Soil LUFA 5M								
Kinetic model	**Parameter**	**Optimised value**	**Std. error**	**p-value (t-test)**	**% error χ^2 test**	**Visual assessment**	**DT_{50} (d)**	**DT_{90} (d)**
SFO	M0 (µg/kg)	440.8	10.12	< 2e-16	6.7 %	good	21.91	72.77
	k	3.164e-02	1.37e-03	1.37e-13				
FOMC	M0 (µg/kg)	454.24	11.04	< 2e-16	8.41 %	good	19.29	64.17
	α	703.03	1663.32	0.339				
	β	19558.76	46333.18	0.339				
DFOP	M0 (µg/kg)	440.80	10.62	< 2e-16	7.40 %	good	21.91	72.77
	k_1	0.03166	0.04197	0.231				
	k_2	0.03164	0.003516	5.83e-08				
	g	0.06668	0.3545	0.427				

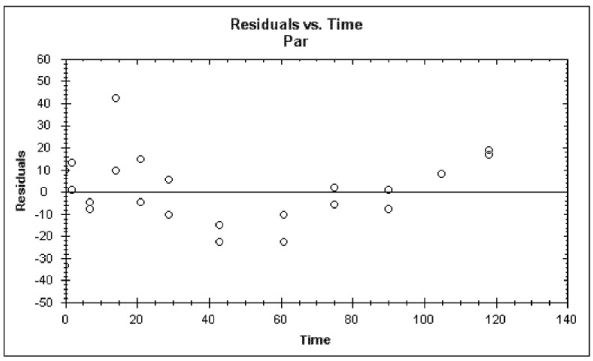
Soil Li10 (SFO)



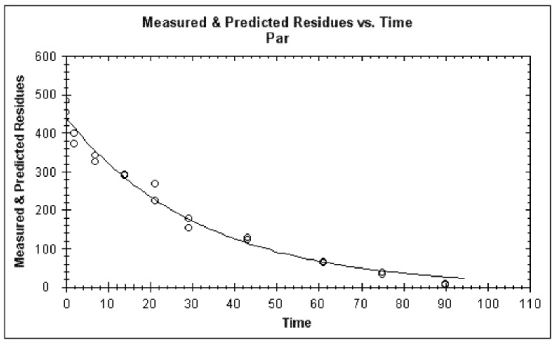


Soil LUFA 2.2 (FOMC)





Soil LUFA 5M (SFO)



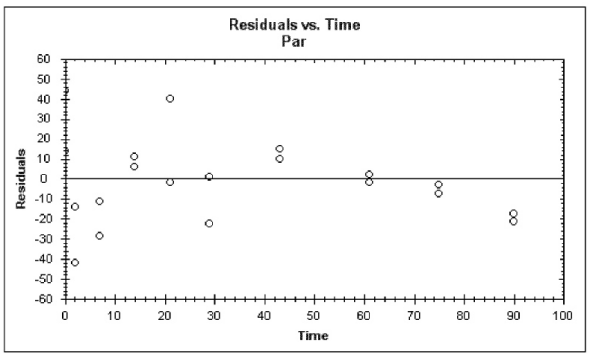


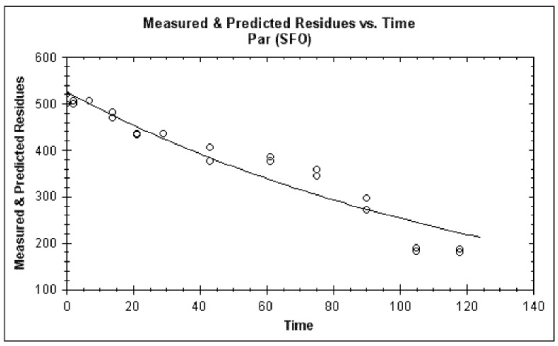
Figure B.8.1.2-12: M656PH054: SFO kinetic fit of for the soils Li10 and LUFA 5M and FOMC kinetic fit for the soil LUFA 2.2

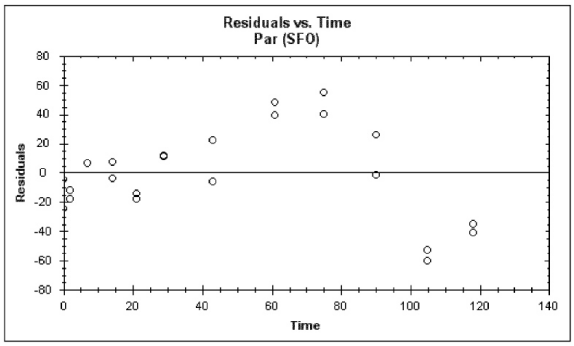
For M656PH054, SFO resulted in acceptable fits for all three soils, however for soil LUFA 2.2 the FOMC was more appropriate. No statistically reliable fits could be obtained for all three soils using DFOP.

Table B.8.1.2-26: Statistical parameters for M656PH0047 (Class & Heinz, 2014)

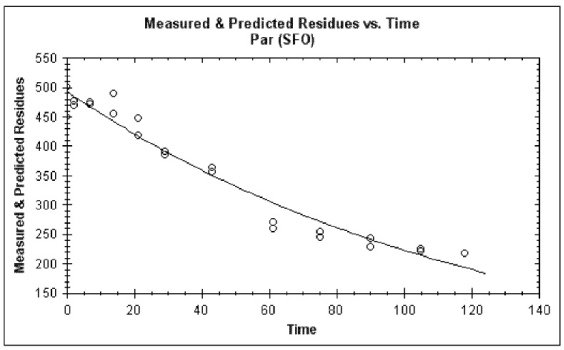
Soil Li10								
Kinetic model	**Parameter**	**Optimised value**	**Std. error**	**p-value (t-test)**	**% error χ^2 test**	**Visual assessment**	**DT_{50} (d)**	**DT_{90} (d)**
SFO	M0 (µg/kg)	524.7	10.65	< 2e-16	6.03 %	acceptable	94.56	314.12
	k	7.330e-03	4.792e-4	1.65e13				
FOMC	M0 (µg/kg)	537.62	49.18	1.99e-10	6.78 %	acceptable	83.96	279.4
	α	449.22	1098.74	0.343				
	β	54370	133088	0.344				
Soil LUFA 2.2								
Kinetic model	**Parameter**	**Optimised value**	**Std. error**	**p-value (t-test)**	**% error χ^2 test**	**Visual assessment**	**DT_{50} (d)**	**DT_{90} (d)**
SFO	M0 (µg/kg)	492.7	8.22	< 2e-16	4.46 %	acceptable	87.06	289.21
	k	7.962e-03	4.145e-4	1.54e-15				
FOMC	M0 (µg/kg)	495.53	9.615	< 2e-16	4.59 %	acceptable	86.47	342.53
	α	4.808	8.369	0.286				
	β	557.633	1049.157	0.300				
Soil LUFA 5M								
Kinetic model	**Parameter**	**Optimised value**	**Std. error**	**p-value (t-test)**	**% error χ^2 test**	**Visual assessment**	**DT_{50} (d)**	**DT_{90} (d)**
SFO	M0 (µg/kg)	507.7	2.158	< 2e-16	15.79 %	poor	42.810	142.21
	k	0.0162	1.545e-3	2.57e-10				
FOMC	M0 (µg/kg)	542.05	24.27	< 2e-16	19.7 %	poor	32.22	107.17
	α	653.80	1435.93	0.327				
	β	30376	66779	0.327				

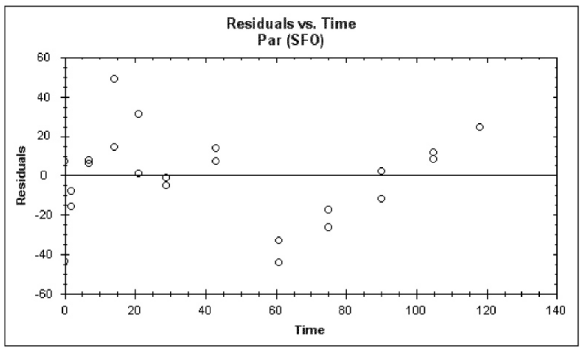
Soil Li10



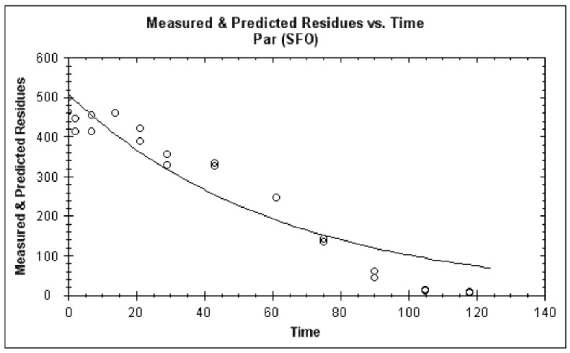


Soil LUFA 2.2.





Soil LUFA 5M



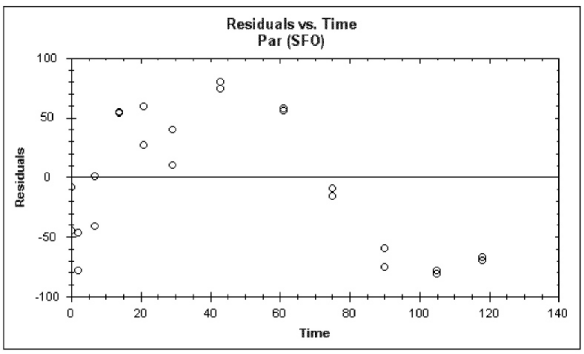


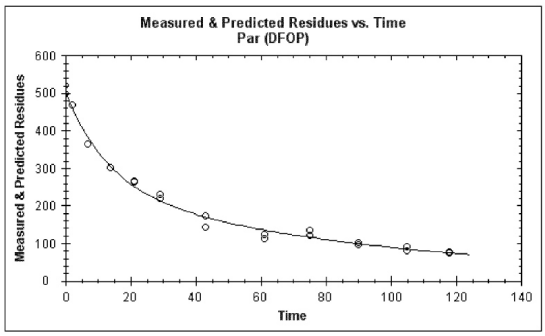
Figure B.8.1.2-13: M656PH047: SFO kinetic fits for the soils Li10, LUFA 2.2. and LUFA 5M

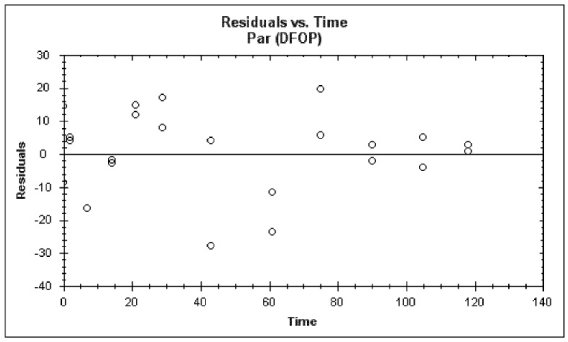
For M656PH0047, SFO resulted in acceptable fits for all three soils. SFO fits were more appropriate and statistically more reliable than FOMC.

Table B.8.1.2-27: Statistical parameters for M656PH0043

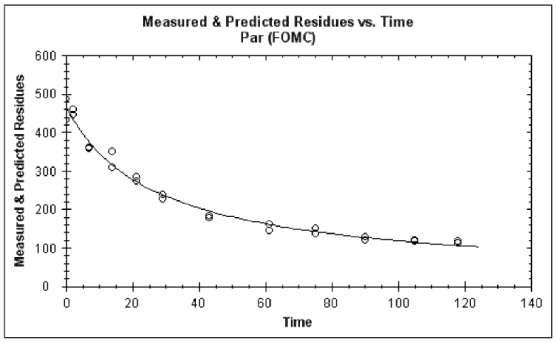
Soil Li10								
Kinetic model	**Parameter**	**Optimised value**	**Std. error**	**p-value (t-test)**	**% error χ^2 test**	**Visual assessment**	**DT_{50} (d)**	**DT_{90} (d)**
SFO	M0 (µg/kg)	459.7	14.12	< 2e-16	11.37 %	poor	32.05	106.48
	k	2.162e-02	1.753e-3	1.16e-11				
FOMC	M0 (µg/kg)	508.01	5.72	< 2e-16	3.42 %	Very good	20.81	197.8
	α	0.95559	0.08661	1.68e-10				
	β	19.52691	3.07802	1.19e-06				
DFOP	M0 (µg/kg)	505.6	7.862	< 2e-16	3.86 %	Very good	20.74	153.78
	k_1	7.705e-02	1.740e-2	0.000129				
	k_2	1.037e-02	2.206e-3	2.61e-05				
	g	0.5072	8.092e-2	2.02e-06				
Soil LUFA 2.2								
Kinetic model	**Parameter**	**Optimised value**	**Std. error**	**p-value (t-test)**	**% error χ^2 test**	**Visual assessment**	**DT_{50} (d)**	**DT_{90} (d)**
SFO	M0 (µg/kg)	426.0	13.15	< 2e-16	10.12 %	acceptable	44.15	146.7
	k	1.570e-02	1.286e-3	1.42e-11				
FOMC	M0 (µg/kg)	469.64	9.1105	< 2e-16	3.53 %	Very good	29.57	363.94
	α	0.7944	0.1047	9.55e-08				
	β	21.2284	5.1658	0.00025				
DFOP	M0 (µg/kg)	463.94	7.7408	< 2e-16	3.19 %	Very good	29.21	494.75
	k_1	0.041459	0.009114	9.76e-05				
	k_2	0.002336	0.003808	0.273				
	g	0.6823	0.12949	1.86e-05				
Soil LUFA 5M								
Kinetic model	**Parameter**	**Optimised value**	**Std. error**	**p-value (t-test)**	**% error χ^2 test**	**Visual assessment**	**DT_{50} (d)**	**DT_{90} (d)**
SFO	M0 (µg/kg)	444.0	11.09	< 2e-16	8.07 %	good	10.17	33.77
	k	6.818e-02	3.927e-3	4.18e-12				
FOMC	M0 (µg/kg)	456.12	12.01	< 2e-16	7.08 %	good	8.88	38.08
	α	3.3827	1.7197	0.0340				
	β	39.04943	25.0716	0.0701				

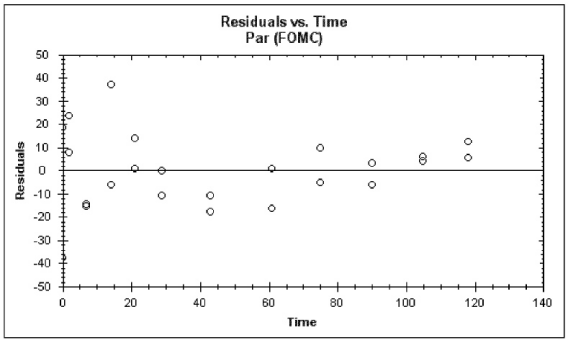
Soil Li10 (DFOP)



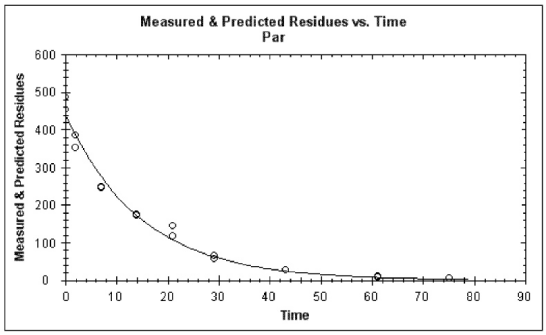


Soil LUFA 2.2 (FOMC)





Soil LUFA 5M (SFO)



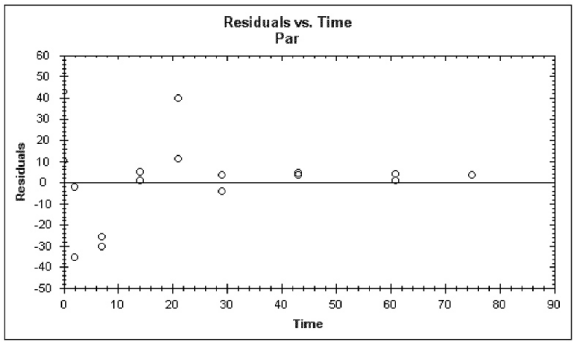


Figure B.8.1.2-14: M656PH043: DFOP kinetic fit of in the soil Li10, FOMC kinetic fit for the soil LUFA 2.2 and SFO kinetic fits for the soil LUFA 5M

For M656PH0043, SFO resulted in acceptable fits for all three soils. FOMC seemed statistically more appropriate for all soils than SFO, but for soil Lufa 5M the t-test failed for the parameter β. For soil Lufa 2.2 the χ^2 error of the DFOP (Double-First-Order in Parallel) analysis was even lower than for FOMC, but the t-test failed on the rate k_2. For soil Li10 the χ^2 error of the DFOP fit was slightly larger than the FOMC model, all parameters are estimated statistically sound. Since DFOP kinetics can be used to derive modelling endpoints, and there is practically no difference between FOMC and DFOP, DFOP was considered as best-fit model.

The resulting DT_{50} and DT_{90} values of M656PH054, M656PH047 and M656PH043 to be used as persistence endpoints are presented in Table B.8.1.2-28, Table B.8.1.2-29 and Table B.8.1.2-30.

Table B.8.1.2-28: DT_{50} and DT_{90} values of M656PH054– trigger endpoints

Soil	Soil type	Persistence endpoints		
		DT_{50} [d]	DT_{90} [d]	Kinetic model
Li10	Loamy sand	37	122	SFO
LUFA 2.2	Sandy loam	40	334	FOMC
LUFA 5M	Loamy sand	22	73	SFO

Table B.8.1.2-29: DT_{50} and DT_{90} values of M656PH047– trigger endpoints

Soil	Soil type	Persistence endpoints		
		DT_{50} [d]	DT_{90} [d]	Kinetic model
Li10	Loamy sand	95	314	SFO
LUFA 2.2	Sandy loam	87	289	SFO
LUFA 5M	Loamy sand	43	142	SFO

Table B.8.1.2-30: DT_{50} and DT_{90} values of M656PH043– trigger endpoints

Soil	Soil type	Persistence endpoints		
		DT_{50} [d]	DT_{90} [d]	Kinetic model
Li10	Loamy sand	21	154	DFOP
LUFA 2.2	Sandy loam	30	364	FOMC
LUFA 5M	Loamy sand	10	34	SFO

Conclusion

The study is considered acceptable by the RMS.
M656pH054 degraded in two loamy sands and one sandy loam under aerobic conditions with DT_{50} values from 22 – 40 d and DT_{90} values from 73 – 334 d. DT_{50} values for M656PH047 ranged from 43 – 95 d with DT_{90} values from 142 – 314 d. M656PH043 degraded with DT_{50} values from 10 – 30 d and DT_{90} values from 34 – 364 d.
All acceptable persistence and modelling endpoints of dimethenamid-P and its metabolites in soil are summarised in Volume 1 under 2.8.2.

B.8.1.2.3 Anaerobic degradation

No acceptable study on the anaerobic degradation rate of dimethenamid-P is available. However, it is not considered necessary by the RMS, since dimethenamid-P is not expected to degrade under anaerobic conditions for prolonged periods of time in the representative uses.

B.8.1.2.4 Soil photolysis

KCA 7.1.2.1.3/ 1 – Nietschmann & Yu, 1997 (study evaluated in the monograph, 2000)

Author:	Nietschmann, D. Yu, C.
Title:	Comparative photolysis of R,S-dimethenamid (SAN 582 H) and S-dimethenamid (SAN 1289 H) on soil
Date:	10/04/1997
Doc ID:	97/5181
Guidelines:	US-EPA Subdivision N; 161-3
GLP:	Yes
Validity:	Acceptable

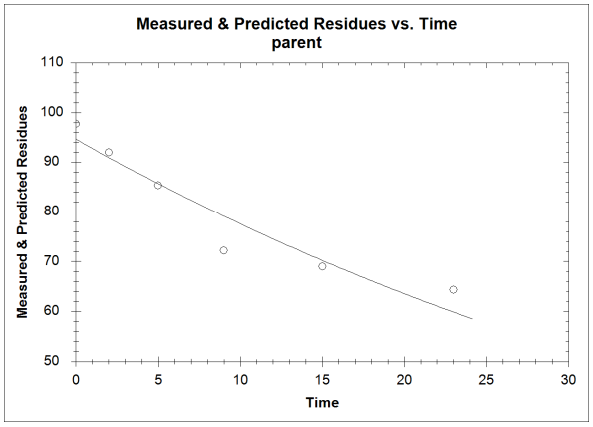
Material and Methods

For details on the experimental conditions and the extraction and measurement methodology please refer to KCA 7.1.1.3/ 2 – Nietschmann & Yu, 1997.
Kinetic analysis and calculations of DT_{50} and DT_{90} values were performed for the residues of dimethenamid-P and dimethenamid listed in Table B.8.1.1-34 by the RMS following the recommendations of the FOCUS Kinetics workgroup. The analysis was conducted by non-linear regression methods employing the software tool KinGUI version 2.

Results and Discussion

The statistical results for dimethenamid and dimethenamid-P can be found in Table B.8.1.2-31 and Table B.8.1.2-32. The SFO kinetic fits, that were finally chosen for dimethenamid and dimethenamid-P, are presented in Figure B.8.1.2-15 and Figure B.8.1.2-16.

SFO



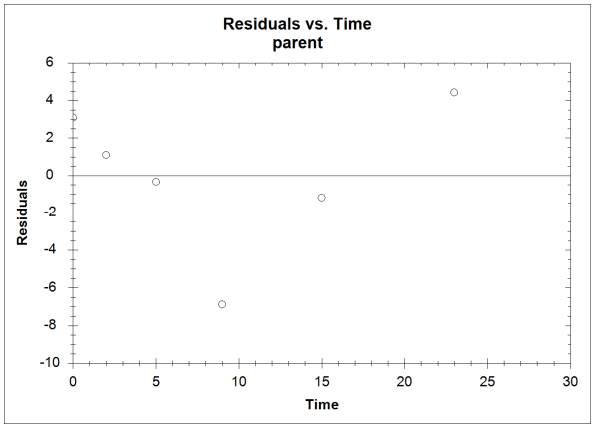
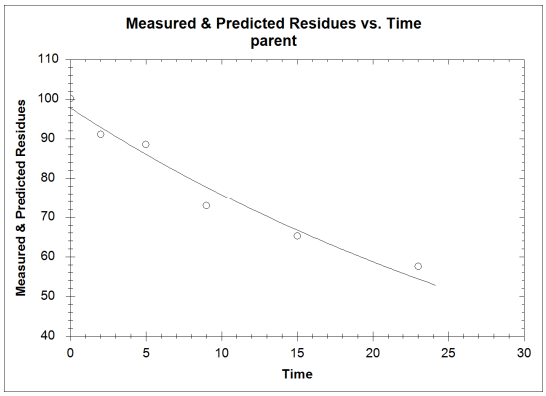


Figure B.8.1.2-15: SFO kinetic fit of dimethenamid-P after soil photolysis

Table B.8.1.2-31: Statistical parameters using SFO and FOMC for dimethenamid-P

Kinetic model	Parameter	Optimised value	Std. error	p-value (t-test)	% error χ^2 test	DT_{50} (d)	DT_{90} (d)	Visual assessment
SFO	M0	94.5999	2.9856	2.96e-06	3.62 %	34.84	115.74	poor
	k	0.019895	0.003275	0.00186				
FOMC	M0	98.56868	2.53408	1.87e-05	2.16 %	63.59	21033	good
	α	0.28167	0.11154	0.0429				
	β	5.92513	4.35397	0.1334				
DFOP	M0	98.61	2.500	0.000321	2.07 %	???	???	good
	k1	0.10697	9.525e-02	0.189458				
	k2	4.394e-09	2.112e-2	0.500				
	g	3.840e-01	3.91e-01	0.21386				
HS	M0	98.30	1.242	7.97e-05	1.12 %	53.78	236.04	Very good
	k1	3.260e-02	2.739e-03	0.00349				
	k2	8.816e-03	4.020e-3	0.07979				
	tb	9.321	1.878	0.01914				

SFO



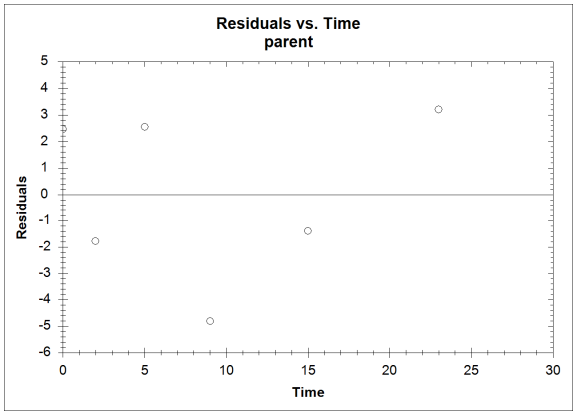


Figure B.8.1.2-16: Kinetic fits of dimethenamid after soil photolysis

Table B.8.1.2-32: Statistical parameters using SFO and FOMC for dimethenamid

Kinetic model	Parameter	Optimised value	Std. error	p-value (t-test)	% error χ^2 test	DT_{50} (d)	DT_{90} (d)	Visual assessment
SFO	M0	97.742225	2.428997	1.14e-06	2.93 %	27.21	90.38	good
	k	0.025476	0.002732	0.000368				
FOMC	M0	100.0559	2.7348	2.25e-05	2.44 %	31.5	533.73	good
	α	0.6628	0.4639	0.124				
	β	17.0670	16.9567	0.194				
DFOP	M0	100.0	3.110	0.000483	2.69 %	37.36	??	good
	k1	6.703e-02	0.1233e	0.3206				
	k2	2.550e-08	7.515e-02	0.500				
	g	0.5445	1.396	0.367				
HS	M0	99.8156	2.7086	0.00368	2.46 %	32.141	134.77	good
	k1	0.032404	0.005888	0.015734				
	k2	0.015682	0.009755	0.1246				
	tb	11.3090	5.6767	0.092285				

While biphasic kinetics appeared visually more suitable to describe photolytic degradation of dimethenamid-P, no statistically reliable fits could be obtained using the respective kinetic models FOMC, DFOP and HS.
For dimethenamid SFO gave a visually and statistically acceptable fit and no statistically reliable fits could be obtained using the respective kinetic models FOMC, DFOP and HS.
Thus SFO was chosen as most suitable kinetic model both for dimethenamid-P and for dimethenamid.
The resulting DT_{50} and DT_{90} values for dimethenamid-P and dimethenamid are presented in Table B.8.1.2-33.

Table B.8.1.2-33: DT_{50} and DT_{90} values of dimethenamid-P and dimethenamid after photolytic degradation on the soil Elliot

Compound	Persistence endpoints		
	DT_{50} [d]	**DT_{90} [d]**	**Kinetic model**
dimethenamid-P	34.84	115.74	SFO
dimethenamid	27.21	90.38	SFO

Conclusion

A kinetic evaluation of the residues of the study Nietschmann & Yu, 1997 was performed by the RMS.
After artificial irradation, dimethenamid-P and dimethenamid degraded on a clay loam soil with DT_{50} values between 27.21 – 34.84 d and DT_{90} values between 90.38 – 115.7 d following SFO kinetics.

All acceptable persistence and modelling endpoints of dimethenamid-P and its metabolites in soil are summarised in Volume 1 under 2.8.2.

B.8.1.2.5 Field studies

Soil dissipation studies

KCA 7.1.2.2.1/ 1– Fricker & Hertl, 1995 a & b, Carrier & Blanz, 1997 and Carrier, 1997 (studies evaluated in the monograph, 2000)

Author:	Fricker, P. Hertl, P.
Title:	Mobility and dissipation of residues of dimethenamid from field soil after application of SAN 582 H 900 EC under field conditions in Germany, 1993 (Field soil dissipation/leaching study)
Date:	20/02/1995
Doc ID:	BASF RegDoc.# 95/10130 BOD 1999-499
Guidelines:	BBA IV, 4-1- field dissipation; study fulfils the requirements of SETAC
GLP:	Yes
Validity:	Acceptable to derive persistence endpoints

Author:	Fricker, P. Hertl, P.
Title:	Dissipation of residues of dimethenamid from field soil after application of SAN 582 H 900 EC under field conditions in France, 1992. (Field soil dissipation/leaching study)
Date:	22/3/1995
Doc ID:	BASF RegDoc.# 95/10133 BOD 1999-500
Guidelines:	BBA IV, 4-1 - field dissipation, study fulfils the requirements of SETAC
GLP:	Yes
Validity:	Acceptable to derive persistence endpoints

Author:	Carrier, M. N. Blanz, J.
Title:	Dissipation of residues of dimethenamid from field soil after application of SAN 582 H 900 EC under field conditions in France, 1992. (Field soil dissipation/leaching study)
Date:	14/03/1997
Doc ID:	BASF RegDoc.# 97/11507 BOD 1999-501
Guidelines:	BBA IV, 4-1 - field dissipation
GLP:	Yes
Validity:	Acceptable to derive persistence endpoints

Author:	Carrier, M. N.
Title:	Dissipation of residues of dimethenamid from field soil after application of SAN 582 H 900 EC under field conditions in Italy, 1992. (Field soil dissipation/leaching study)
Date:	23/09/1997
Doc ID:	BASF RegDoc.# 97/11508 BOD 1999-502
Guidelines:	BBA IV, 4-1 - field dissipation
GLP:	Yes
Validity:	Acceptable to derive persistence endpoints

Material and Methods

The four field soil dissipation studies have been performed for the first EU approval of dimethenamid to investigate the degradation and dissipation of dimethenamid and to determine the concentrations of the metabolites M656H023 (M23 or oxalamide in the study) and M656H027 (M27 or sulfonate in the study) in soil. In total, 9 trials were conducted: 2 trials at locations in Germany, 4 trials in France and 3 trials in Italy. General data regarding the trials are given in Table B.8.1.2-34.

Table B.8.1.2-34: Location & duration and application rates for the 9 field dissipation trials performed with dimethenamid (EC formulation)

Study	Trial no	Location	Duration	Application rate kg a.s/ha
Fricker & Hertl, 1995a DocID 95/10130	R10283	Niederaula, Germany	26 May 1993 – 25 March 1994	1.4
	R10284	Goslar, Germany	25 May 1993 – 24 March 1994	1.4
Fricker & Hertl, 1995b DocID 95/10133	R10242	Brevelay, France	12 May 1992 – 9 November 1992	1.4
	R10243	Degre, France	4 May 1992 – 3 November 1992	1.4
Carrier & Blanz, 1997 DocID 97/11507	R10244	Vergoignan, France	5 May 1992 – 5 November 1992	1.5
	R10245	Cestas, France	5 May 1992 – 5 November 1992	1.4
Carrier, 1997 97/11508	R10246	Budrio, Italy	20 May 1992 – January 1993	1.4
	R10247	Mezzolara, Italy	20 May 1992 – January 1993	1.5
	R10248	Argenta, Italy	20 May 1992 – January 1993	1.5

Data with regard to soil parameters, application and weather conditions are summarised in Table B.8.1.2-35.

Table B.8.1.2-35: Soil properties and climatic conditions for the 9 field dissipation trials performed with dimethenamid (EC formulation)

Trial no	Soil type	Soil properties			Average temp. [°C]	Cumulative Precipitation [mm]
		% C_{org}	CEC meq/100g	pH		
R10283	Loamy sand	0.9	7.6	6.5	8.5	696
R10284	Silty loam	1.2	14.8	7.6	8.8	701
R10242	Sandy silty loam	1.5	7.7	5.9	15.1	477
R10243	Loam	1.1	8	6.0	11.8	300
R10244	Sand	0.5	3.95	6.1	18.0	744
R10245	Sandy loam	1.2	3.28	4.9	18.0	779
R10246	Sandy loam	0.7	10.6	7.4	15.3	413
R10247	Sandy loam	0.4	9.15	7.4	15.3	431
R10248	Loam	0.9	16.2	7.4	15.1	478

The trials were performed using the formulated product Frontier (SAN 582 H 900 EC) containing 900 g dimethenamid/L. The nominal application rate was always 1.6 L of product/ha corresponding to 1440 g dimethenamid/ha. The initial concentration of dimethenamid in the top 10 cm soil layer following application at this rate was estimated as 0.96 mg/kg. The formulated product was always sprayed onto uncropped (bare) soil with knapsack sprayers and an attached sprayboom. On 10 – 11 sampling dates soil cores were taken up to at least 180 DAT (days after treatment) and to a maximum of 330 DAT. Sampling depth was 0-30 cm (trial R10283 on days 14 – 120, trial R10284 on days 7 – 120, the trials R10244, R10245, R10246 on days 30 – 186, trial R10247 on days 7 – 122, trial R10248 on days 14 – 245), 0-40 cm (trial R10283 on days 0 – 7, R10284 on days 0 – 3) or 0-50 cm (trial R10242, trial R10243, trial R10246 on days 0 – 21, trial R10247 on days 0 – 3 and trial R10248 on days 0 – 7). The soil samples were separated in 10 cm segments. Following extraction with methanol/water (6:4) and solid phase extraction clean-up analysis was done using an HPLC/DAD method, which was able to determine dimethenamid and its metabolites M656H023 and M656H027 to a limit of determination of 0.01 mg/kg soil. Fortification experiments at concentration levels between 0.01 and 1.8 mg/kg resulted in average recoveries of 83.1 – 98.4 % (dimethenamid), 79.7 – 91.9 % (oxalamide metabolite) and 84.6 – 99.1 % (sulfonate metabolite). Soil control samples revealed no dimethenamid residues equivalent to or above the limit of determination.

The LOD for the field trials R10283 & R10284 was 0.003 µg/g. The LOD for the field trials R10242

& R10243 was 0.005 µg/g. For the field trials R10244 und R10245, the LOD was 0.0061 µg/g and for the field trials R10246, R10247 and R10248. The LOQ for all field trials was 0.01 µg/g.

DT_{50} and DT_{90} values in the studies were derived using Timme & Frehse and Gustaffson models and are thus not according to current FOCUS degradation kinetics anymore. Since the DT_{50} and DT_{90} values of dimethenamid and its metabolites could still be used for persistence calculations and as trigger endpoints, an attempt was made by the RMS to derive new degradation rates according to the current FOCUS degradation kinetic guidance.
Therefore the residue data were first processed according to FOCUS degradation kinetic guidance. Afterwards a kinetic re-evaluation was performed by non-linear regression methods employing the software tool KinGUI version 2.
New DT_{50} and DT_{90} values were only derived for dimethenamid, since due to the poor quality and the few available residue data it was not considered likely by the RMS, that reliable DT_{50} and DT_{90} values for the metabolites could be obtained.

Results and Discussion

The application rate verification results for all field soil dissipation studies with dimethenamid, which were obtained by comparing the actual and theoretical 0 day concentration of dimethenamid in the 0-10 cm soil layer are given in Table B.8.1.2-36.

Table B.8.1.2-36: Application rate verification for dimethenamid in field soil dissipation studies

Trial no.	Location	Recovery in % of applied amount corrected for procedural recoveries
R10283	Niederaula, Germany	92
R10284	Goslar, Germany	86
R10242	Brevelay, France	175
R10243	Degre, France	66
R10244	Vergoignan, France	73.7
R10245	Cestas, France	102.5
R10246	Budrio, Italy	65.4
R10247	Mezzolara, Italy	73.9
R10248	Argenta, Italy	75.1

In the two field trials R10283 and R10284 conducted in Germany, dimethenamid was only found in the top 10 cm layer with exception of the samples collected up to day 7 after application. Significant quantities of the metabolites were found in the day 0 samples. Metabolites M656H023 and M656H027 in concentrations above the limit of determination were exclusively found in the top 10 cm layer. Maximum concentrations of M656H023 on the two sites were 0.053 mg/kg (day 14) and 0.052 mg/kg (day 7). Maximum concentrations of M656H027 on the two sites were 0.026 mg/kg (day 21) and 0.048 mg/kg (day 7). At the end of the studies 120 days after application neither dimethenamid nor metabolites could be detected. The cumulative residues over all sampled soil depths of dimethenamid, M656H023 and M656H027 in the two field trials R10283 and R10284 are presented in Table B.8.1.2-37.

Table B.8.1.2-37: Residues of dimethenamid (=DMTA), M656H023 (=M23) and M656H027 (M=27) in field soil dissipation trials R10283 and R10284 performed in Germany

Trial R10283				Trial R10284			
DAT	DMTA [µg/g]	M23 [µg/g]	M27 [µg/g]	DAT	DMTA [µg/g]	M23 [µg/g]	M27 [µg/g]
0	0.754	0.01	0.027	0	0.591	0.016	0.024
3	0.385	0.018	n.d.	3	0.476	0.012	0.02
7	0.28	0.033	0.017	7	0.056	0.052	0.048
14	0.095	0.053	0.022	14	0.077	0.034	0.041
21	0.092	0.048	0.026	21	0.031	0.024	0.028
29	0.056	0.046	0.016	29	0.018	0.017	0.023
61	0.017	0.023	n.d.	60	0.004	n.d.	n.d.
91	0.004	0.018	0.01	91	n.d.	n.d.	n.d.
120	n.d.	n.d.	n.d.	120	n.d.	n.d.	n.d.

In the two field trials R10242 and R10243 conducted in the north west of France the major fraction of dimethenamid was localised in the upper 10 cm of the soil horizon. Some of the samples collected during the first two weeks after application contained residues up to 0.057 mg/kg in the 10-30 cm layer. No dimethenamid residues were detected at a depth below 10 cm in any of the samples collected on day 28 or later. No residues were detected in the two bottom soil layers (30-50 cm) during the entire study period. At site R10242 the metabolite M656H023 was detected only during the first month after application at three occasions in the 0-10 cm layer (max. 0.03 mg/kg on day 0). One week after application 0.012 mg/kg were found in the 10-20 cm layer. At site R10243 where the degradation of dimethenamid was slower M656H023 detections were confined to the 0-10 cm layer (max. 0.059 mg/kg on day 60) with the exception of one finding on day 21 (0.01 mg/kg). At site R10242, apart from occasional findings below the limit of determination, M656H027 residues were found in three samples (max. 0.015 mg/kg on day 28). At site R10243, M656H027 was detected in the top soil layer in most of the samples (max. 0.039 mg/kg on day 60); three samples up to day 60 from deeper soil layers contained traces of M656H027. At the end of the studies 183 days after application dimethenamid was found only in amounts at or below the limit of determination. Metabolite M656H023 was not detected, Metabolite M656H027 was found at 0.01 mg/kg only on one site.
The cumulative residues over all sampled soil depths of dimethenamid, M656H023 and M656H027 in the two field trials R10242 and R10243 are presented in Table B.8.1.2-38.

Table B.8.1.2-38: Residues of dimethenamid (= DMTA), M656H023 (= M23) and M656H027 (= M27) in field soil dissipation trials R10242 and R10243 performed in Northern France

Trial R10242				Trial R10243			
DAT	DMTA [µg/g]	M23 [µg/g]	M27 [µg/g]	DAT	DMTA [µg/g]	M23 [µg/g]	M27 [µg/g]
0	1.684	0.03	n.d.	0	0.631	n.d.	n.d.
3	0.596	n.d.	0.021	3	0.553	0.013	0.014
7	0.56	0.026	0.015	7	0.557	0.011	0.009
15	0.26	n.d.	0.026	14	0.284	n.d.	n.d.
22	0.117	n.d.	0.015	21	0.385	0.01	0.006
28	0.149	0.23	0.015	28	0.482	0.036	0.035
59	0.025	n.d.	0.022	60	1.94	0.059	0.049
86	0.011	n.d.	0.01	91	0.063	0.03	0.021
120	0.009	n.d.	0.005	120	0.029	0.031	0.02
181	0.009	n.d.	n.d.	183	0.012	n.d.	0.01

In the two field trials R10244 and R10245 conducted in the south west of France, no dimethenamid residues above the limit of determination were found in layers deeper than 10 cm at Vergoignan (R10244). During the study period more than 98 % of dimethenamid residues were located in the 0-10 cm layer. At Cestas (R10245) dimethenamid concentrations above the limit of determination were found in 10-20 cm and 20-30 cm depth in the samples taken on day 0, 57 and 90 and in the

10-20 cm sample of day 30. 81.7 % of dimethenamid residues were located in the uppermost 10 cm of the soil horizon, 11.9 % and 6.4 % in the 10-20 cm and 20-30 cm horizon, respectively. At Vergoignan (R10244) metabolite M656H023 was detected occasionally up to day 57 in all three soil layers but only one finding was above the limit of determination (0-10 cm on day 21 0.015 mg/kg). At Cestas (R10245) M656H023 was not detected at levels above the limit of determination. At Vergoignan (R10244) also metabolite M656H027 was detected occasionally up to day 57 in all three soil layers but only one finding was above the limit of determination (10-20 cm on day 14 0.018 mg/kg). At Cestas (R10245) M656H027 was not detected at levels above the limit of determination. At the end of the studies 184 days after application dimethenamid was detected below the limit of determination at Vergoignan (0-30 cm) and at a concentration of 0.023 mg/kg at Cestas (0-10 cm, 10-30 cm: < 0.01 mg/kg). Residues of the metabolite M656H023 were not detected; traces of the metabolite M656PH027 were only found in the 20-30 cm layer (< 0.01 mg/kg).
The cumulative residues over all sampled soil depths of dimethenamid, M656H023 and M656H027 in the two field trials R10244 and R10245 are presented in Table B.8.1.2-39.

Table B.8.1.2-39: Residues of dimethenamid (= DMTA), M656H023 (= M23) and M656H027 (= M27)in field soil dissipation trials R10244 and R10245 performed in Southern France

Trial R10244				Trial R10245			
DAT	DMTA [µg/g]	M23 [µg/g]	M27 [µg/g]	DAT	DMTA [µg/g]	M23 [µg/g]	M27 [µg/g]
0	0.612	0.023	0.015	0	0.786	n.d.	< 0.01
2	0.546	n.d.	0.01	2	0.183	n.d.	< 0.01
8	0.42	0.012	<0.01	8	0.546	< 0.01	< 0.01
14	0.387	<0.01	0.028	14	0.373	n.d.	n.d.
21	0.3	0.02	0.011	21	0.209	n.d.	< 0.01
30	0.115	0.017	0.017	30	0.298	< 0.01	< 0.01
57	0.02	<0.01	0.015	57	0.112	< 0.01	< 0.01
90	<0.01	n.d.	n.d.	90	0.078	< 0.01	< 0.01
120	<0.01	n.d.	n.d.	120	0.026	n.d.	< 0.01
184	<0.01	n.d.	n.d.	184	0.035	n.d.	< 0.01

In the three field trials R10246, R10247 and R10248 conducted in northern Italy no residues of dimethenamid above the limit of determination were found in layers deeper than 10 cm later than 7 days after the application. During the overall study duration, the percentages of dimethenamid present in the upper 10 cm of the soil horizon were 98.1 %, 96.9 % and 98.2 % for the three sites. Metabolite M656PH023 was not detected in soil layers deeper than 10 cm. Maximum concentrations in the 0-10 cm layer were 0.021 mg/kg (day 21), 0.013 mg/kg (day 21 and 30) and 0.037 mg/kg (day 122) for the trials R10246, R10247 and R10248, respectively. Metabolite M656PH027 was not detected at concentrations above the limit of determination in soil layers deeper than 10 cm. Maximum concentrations of M656PH027 in the 0-10 cm layer were 0.022 mg/kg (day 14), 0.039 mg/kg (day 30) and 0.049 mg/kg (day 60 and 93) for the three trials. At Budrio (R10246) neither dimethenamid nor the metabolites were detected at the end of the study (day 186). At Mezzolara (R10247) dimethenamid and metabolite M656PH023 were found in traces in the 0-10 cm layer (< 0.01 mg/kg) at the end of the study (day 122). At Argenta (R10248), at the end of the study (day 245) traces of dimethenamid and the metabolite M656PH027 were detected in the upper soil layer and in the 20-30 cm layer, respectively.
The cumulative residues over all sampled soil depths of dimethenamid, M656PH023 and M656PH027 in threee two field trials R10246, R10247 and R10248 are presented in Table B.8.1.2-40.

Table B.8.1.2-40: Residues of dimethenamid (=DMTA), M656H023 (=M23) and M656H027 (=M27) in field soil dissipation trials R10246, R10247 and R10248 performed in Italy

Trial R10246				Trial R10247			
DAT	**DMTA [µg/g]**	**M23 [µg/g]**	**M27 [µg/g]**	**DAT**	**DMTA [µg/g]**	**M23 [µg/g]**	**M27 [µg/g]**
0	0.525	n.d.	n.d.	0	0.67	n.d.	n.d.
3	0.285	n.d.	< 0.01	3	0.672	n.d.	n.d.
7	0.286	n.d.	< 0.01	7	0.312	n.d.	n.d.
14	0.216	0.019	0.022	14	0.23	< 0.01	n.d.
21	0.103	0.021	0.02	21	0.144	0.013	0.03
30	0.057	0.013	0.019	30	0.113	0.013	0.039
60	0.015	0.012	0.015	60	0.028	< 0.01	0.025
94	< 0.01	0.013	n.d.	93	< 0.01	n.d.	0.017
122	< 0.01	0.019	n.d.	122	< 0.01	< 0.01	n.d.
186	n.d.	n.d.	n.d.	0	0.67	n.d.	n.d.

Trial R10248			
DAT	**DMTA [µg/g]**	**M23 [µg/g]**	**M27 [µg/g]**
0	0.673	n.d.	n.d.
3	0.567	< 0.01	n.d.
7	0.413	n.d.	n.d.
14	0.354	n.d.	n.d.
25	0.256	0.01	0.02
30	0.144	0.01	0.044
60	0.033	0.028	0.049
93	0.017	0.03	0.049
122	0.011	0.037	0.041
186	n.d.	n.d.	0.013

For kinetic re-evaluation, all data values between LOD and LOQ were replaced with 1/2 x (LOD + LOD), all values < LOD were replaced with ½ LOD and the sample points after the first non-detect were omitted. Kinetic evaluations were first only performed for dimethenamid. of the kinetic evaluation are given in Table B.8.1.2-41 to Table B.8.1.2-49.

Table B.8.1.2-41: Statistical parameters for dimethenamid-P for the field trial R10283

Kinetic model	Parameter	Optimised value	Std. error	p-value (t-test)	% error χ^2 test	DT_{50} (d)	DT_{90} (d)	Visual assessment
SFO	M0	0.76235	0.04408	5.92e-06	14.76 %	2.92	9.64	poor
	k	0.23886	0.03350	0.000421				
FOMC	M0	0.76656	0.04236	2.74e-05	13.7 %	2.63	12.34	acceptable
	α	2.5500	2.05039	0.141				
	β	8.114	8.6806	0.194				
DFOP	M0	0.76845	0.000173	0.000173	12.87 %	2.67	11.69	good
	k1	0.29788	0.07105	0.012376				
	k2	0.03065	0.05110	0.295451				
	g	0.89629	0.65004	0.002835				
HS	M0	0.76150	0.05742	0.000463	17.53 %	2.96	??	poor
	k1	0.23440	0.06096	0.015523				
	k2	0.25363	0.15131	0.096141				
	tb	2.98723	1.52820	0.072799				

Table B.8.1.2-42: Statistical parameters for dimethenamid-P for the field trial R10284

Kinetic model	Parameter	Optimised value	Std. error	p-value (t-test)	% error χ^2 test	DT_{50} (d)	DT_{90} (d)	Visual assessment
SFO	M0	0.61897	0.07404	0.0002	29.34 %	3.91	13.0	acceptable
	k	0.17706	0.04640	0.006211				
FOMC	M0	0.6190e	8.280e-02	0.000856	31.7 %	3.91	13.02	acceptable
	α	4.501e+02	9.313e+03	0.481883				
	β	2.539e+03	5.260e+04	0.481903				
DFOP	M0	0.6200	0.09454	0.00370	34.79 %	3.86	13.31	acceptable
	k1	0.1831	0.07962	0.05253				
	k2	7.131e-06	2.842e-01	0.5000				
	g	0.9862	0.1522	0.00373				
HS	M0	0.5835	0.04962	0.00066	17.11 %	2.75	??	poor
	k1	0.02620	NA	NA				
	k2	0.50387	0.21567	0.0508				
	tb	NA	NA	NA				

Table B.8.1.2-43: Statistical parameters for dimethenamid-P for the field trial R10242

Kinetic model	Parameter	Optimised value	Std. error	p-value (t-test)	% error χ^2 test	DT_{50} (d)	DT_{90} (d)	Visual assessment
SFO	M0	1.60110	0.15923	1.03e-05	28.57 %	3.24	10.76	poor
	k	0.21410	0.06157	0.00515				
FOMC	M0	1.68193	0.06787	1.42e-07	12.45 %	1.93	21.80	Very good
	α	0.84066	0.18297	0.00186				
	β	1.50665	0.73374	0.04292				
DFOP	M0	1.686501	0.035696	4.01e-08	6.40 %	0.57	21.99	poor
	k1	3.681103	22.716962	0.43881				
	k2	0.068307	0.007479	0.000132				
	g	0.550993	0.03853	5.05e-06				
HS	M0	1.686498	0.035694	4.01e-08	6.40 %	2.02	21.99	good
	k1	0.343894	0.209025	0.080421				
	k2	0.068309	0.007481	0.00013				
	tb	2.905431	2.202846	0.11218				

Table B.8.1.2-44: Statistical parameters for dimethenamid-P for the field trial R10243

Kinetic model	Parameter	Optimised value	Std. error	p-value (t-test)	% error χ^2 test	DT_{50} (d)	DT_{90} (d)	Visual assessment
SFO	M0	0.60046	0.048598	8.58e-07	17.91 %	35.13	116.7	acceptable
	k	0.019733	0.004427	0.00106				
FOMC	M0	0.6006	0.005206	4.14e-06	18.81 %	35.08	116.85	acceptable
	α	0.03137	5.6e+03	0.478				
	β	1.586e+04	2.837e+05	0.478				
DFOP	M0	0.63416	0.086327	0.000163	19.45 %	31.89	121.23	acceptable
	k1	0.276987	0.627039	0.337077				
	k2	0.018015	0.005799	0.01472				
	g	0.111957	0.20927	0.30595				
HS	M0	0.633490	0.091146	0.00022	19.54 %	32.40	118.12	acceptable
	k1	0.049680	NA	NA				
	k2	0.018775	0.005206	0.00564				
	tb	2.745927	NA	NA				

Table B.8.1.2-45: Statistical parameters for dimethenamid-P for the field trial R10244

Kinetic model	Parameter	Optimised value	Std. error	p-value (t-test)	% error χ^2 test	DT_{50} (d)	DT_{90} (d)	Visual assessment
SFO	M0	0.61544	0.02563	1.71e-07	8.19 %	16.47	54.72	good
	k	0.042079	0.004166	2.73e-05				
FOMC	M0	0.6155	0.02812	1.85e-06	8.75 %	16.46	54.78	good
	α	4.955e+02	4.036e-03	0.454				
	β	1.176e-04	9.59e+04	0.454				
DFOP	M0	0.61545	0.03139	19..e-05	9.44 %	16.47	54.72	good
	k1	0.04208	NA	NA				
	k2	0.04208	0.01027	0.00742				
	g	0.21406	NA	NA				
HS	M0	0.59859	0.017419	2.14e-06	4.95 %	20.02	38.60	poor
	k1	0.034624	0.003556	0.000312				
	k2	0.089542	0.021987	0.007595				
	tb	21	1.0303	1.71e-05				

Table B.8.1.2-46: Statistical parameters for dimethenamid-P for the field trial R10245 (without data point at day 2)

Kinetic model	Parameter	Optimised value	Std. error	p-value (t-test)	% error χ^2 test	DT_{50} (d)	DT_{90} (d)	Visual assessment
SFO	M0	0.76089	0.058278	1.8e-06	15.96 %	16.22	53.87	acceptable
	k	0.042741	0.007262	0.000304				
FOMC	M0	0.79311	0.05008	2.01e-06	12.94 %	13.64	78.17	good
	α	1.69056	0.84885	0.0468				
	β	26.9162	19.2253	0.1055				
DFOP	M0	0.79522	0.054159	1.32e-05	13.57 %	13.72	82.63	good
	k1	0.089427	0.055647	0.0845				
	k2	0.016749	0.012415	0.1176				
	g	0.602436	0.331017	0.0642				
HS	M0	0.78600	0.06763	4.14e-05	16.57 %	14.8	63.98	good
	k1	0.10710	NA	NA				
	k2	0.03278	0.01108	0.0158				
	tb	2.76491	NA	NA				

Table B.8.1.2-47: Statistical parameters for dimethenamid-P for the field trial R10246

Kinetic model	Parameter	Optimised value	Std. error	p-value (t-test)	% error χ^2 test	DT_{50} (d)	DT_{90} (d)	Visual assessment
SFO	M0	0.45829	0.03991	1.31e-05	17.82 %	10.8	33.50	acceptable
	k	0.06874	0.01408	0.00138				
FOMC	M0	0.4934	0.0522	0.000112	17.08 %	7.18	47.87	acceptable
	α	1.3622	1.2233	0.1581				
	β	108270	15.9686	0.2636				
DFOP	M0	0.517602	0.031507	4.05e-05	11 %	6.67	39.42	acceptable
	k1	3.363238	24.784848	0.44931				
	k2	0.049145	0.009132	0.00288				
	g	0.305892	0.081671	0.01001				
HS	M0	0.5176	0.031568	4.05e-05	11 %	6.67	39.42	acceptable
	k1	0.174137	0.139086	0.13939				
	k2	0.049144	0.009131	0.00288				
	tb	2.921175	3.15519	0.20349				

Table B.8.1.2-48: Statistical parameters for dimethenamid-P for the field trial R10247

Kinetic model	Parameter	Optimised value	Std. error	p-value (t-test)	% error χ^2 test	DT_{50} (d)	DT_{90} (d)	Visual assessment
SFO	M0	0.70807	0.05501	6.76e-06	16.34 %	9.06	30.08	good
	k	0.07655	0.01377	0.000716				
FOMC	M0	0.72015	0.06188	4.11e-05	16.82 %	8.37	34.84	good
	α	3.80421	6.17169	0.282				
	β	41.887	79.8512	0.311				
DFOP	M0	0.72192	0.06848	0.000229	17.88 %	8.23	36.81	good
	k1	0.10592	0.07657	0.1194				
	k2	0.02400	0.05710	0.34795				
	g	0.79720	0.58285	0.1216				
HS	M0	0.67575	0.07349	0.000388	17.32 %	9.52	27.21	poor
	k1	0.02957	NA	NA				
	k2	0.09094	0.026	0.01248				
	tb	2.8049	Na	NA				

Table B.8.1.2-49: Statistical parameters for dimethenamid-P for the field trial R10248

Kinetic model	Parameter	Optimised value	Std. error	p-value (t-test)	% error χ^2 test	DT_{50} (d)	DT_{90} (d)	Visual assessment
SFO	M0	0.647313	0.026415	1.52e-07	7.9 %	15.1	50.84	good
	k	0.045289	0.004508	2.82e-05				
FOMC	M0	0.6475	0.02886	1.64e-06	8.42 %	15.29	50.92	good
	α	0.03097	NA	NA				
	β	6.825e+3	NA	NA				
DFOP	M0	0.677379	0.035723	2.28e-05	7.64 %	13.80	54.18	good
	k1	0.409206	0.477565	0.21991				
	k2	0.039837	0.006618	0.00192				
	g	0.134433	0.115679	0.15490				
HS	M0	0.6751	0.03776	2.88e-05	7.97 %	14.25	52.66	good
	k1	0.07631	0.02028	0.485891				
	k2	0.04191	5.446e-03	0.000767				
	tb	2.789	1.642e+02	0.4936				

For the field trial R10283, a statistically reliable fit could only be obtained when applying SFO. However, the resulting visual fit was poor and did not represent the residues well. Thus, no acceptable fit could be obtained for this trial.

For the field trial R10284, none of the applied kinetic models resulted in a statistically and visually acceptable fit.

FOMC gave a statistically and visually acceptable fit for the field trial R10242.

For the trials R10243, R10245, R10246 and R10247, The χ2 error was slightly above 15 %, however the remaining statistical parameters and the visual fit were still acceptable. Thus, SFO was chosen for these trials. For R10245 an acceptable fit could only be obtained when omitting the dimethenamid residues of day 2 as an outlier.

For the remaining field trials R10244 and R10248, SFO gave statistically and visually the most acceptable fits. The visual fits and residual plots of the kinetic models chosen for R10244, R10245, R10246, R10247 and R10248 are presented in Figure B.8.1.2-19 and Figure B.8.1.2-20. Since no reliable fit could be obtained for R10283 and R10284, only the dimethenamid residues are shown in Figure B.8.1.2-17.

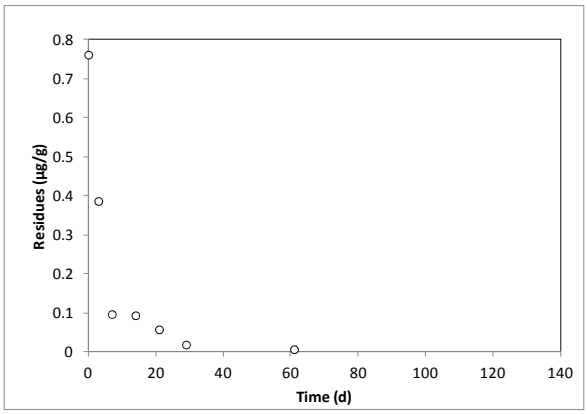
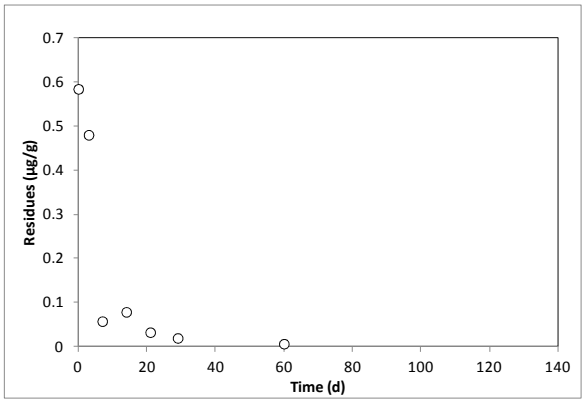
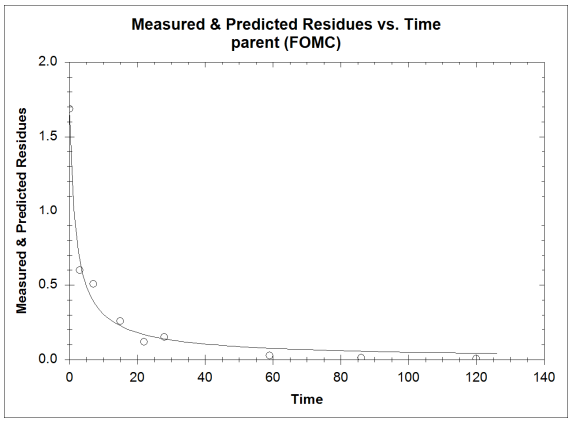
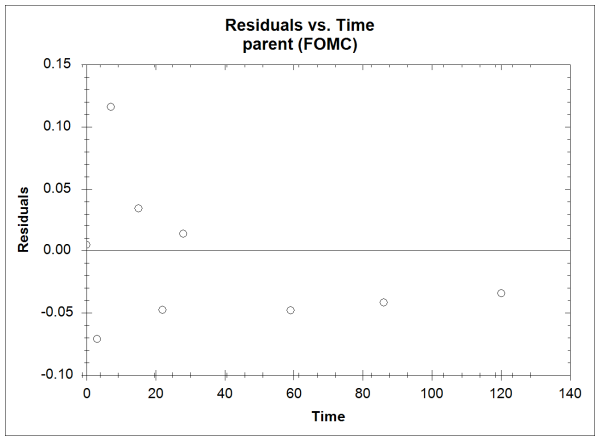
Trial R10283	Trial R10284
	

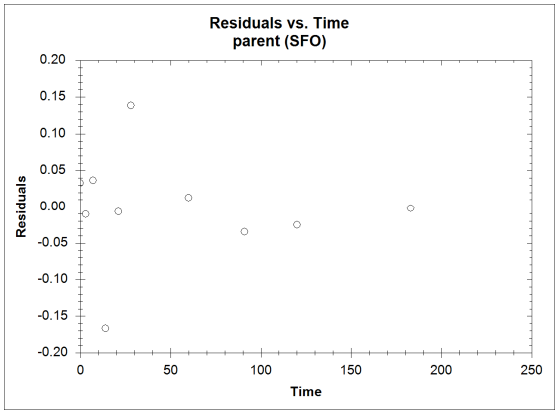
Figure B.8.1.2-17: Residues of dimethenamid in the field trials R10283 and R10284 (no reliable kinetic fit could be obtained)

Trial R10242 (FOMC)





Trial R10243 (SFO)



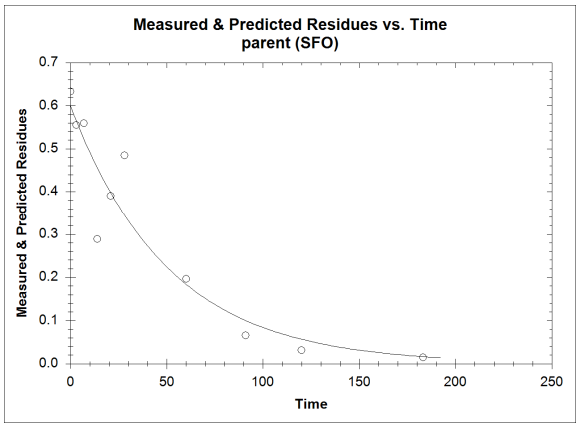
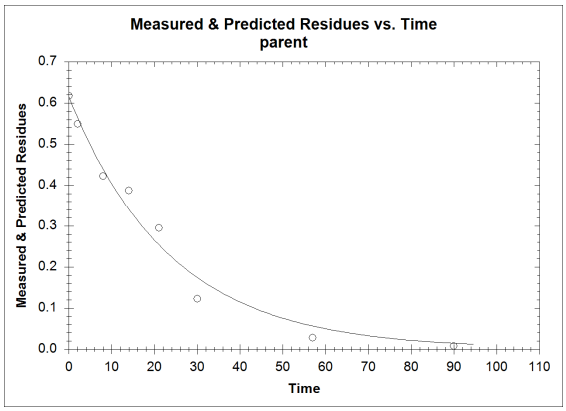
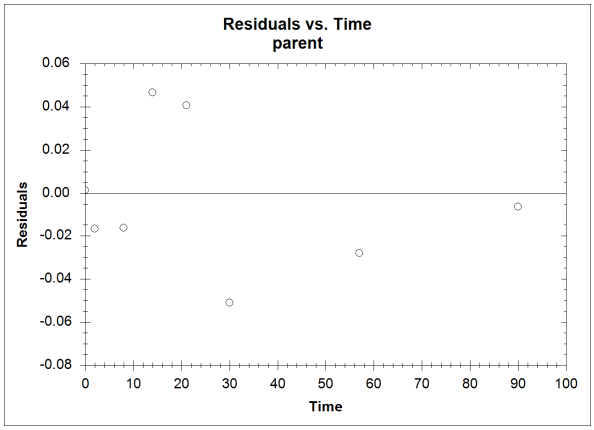


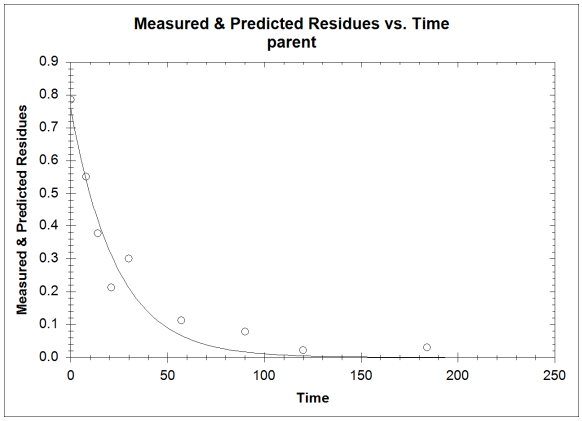
Figure B.8.1.2-18: Kinetic fits of dimethenamid in the field trials R10242 and R10243

Trial R10244 (FOMC)





Trial R10245 (SFO)



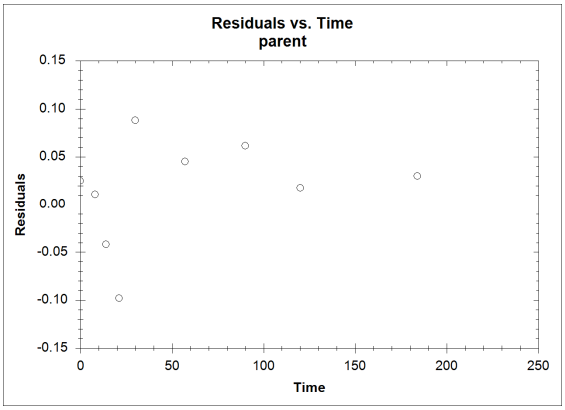
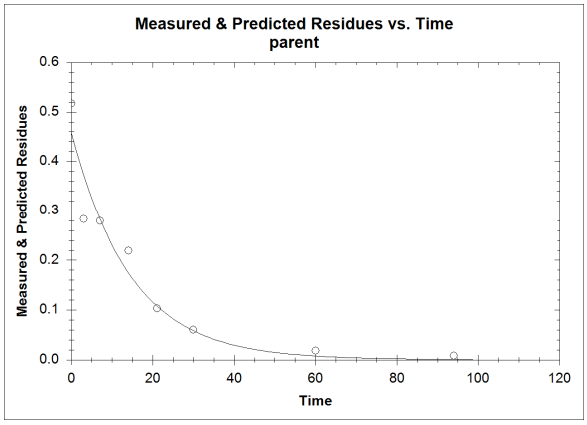
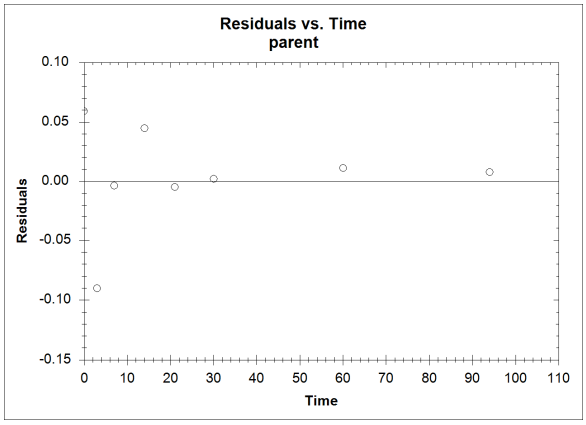


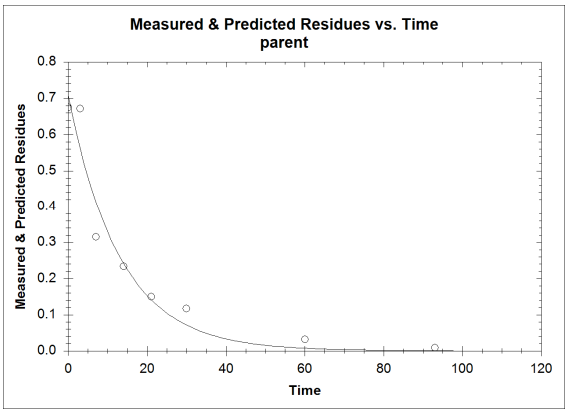
Figure B.8.1.2-19: Kinetic fits of dimethenamid in the field trials R10244 and R10245

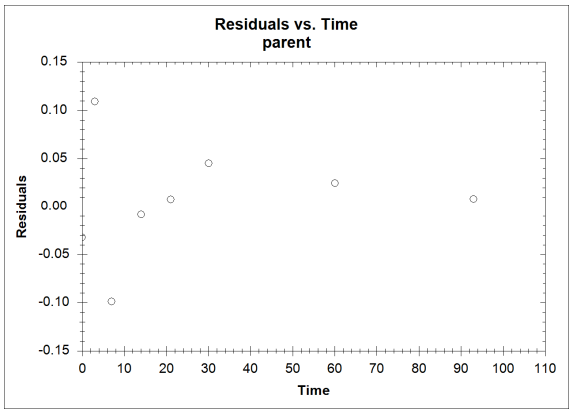
Trial R10246 (SFO)



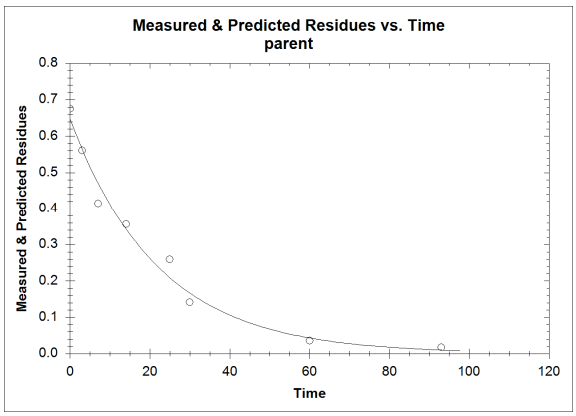


Trial R10247 (SFO)





Trial R10248 (SFO)



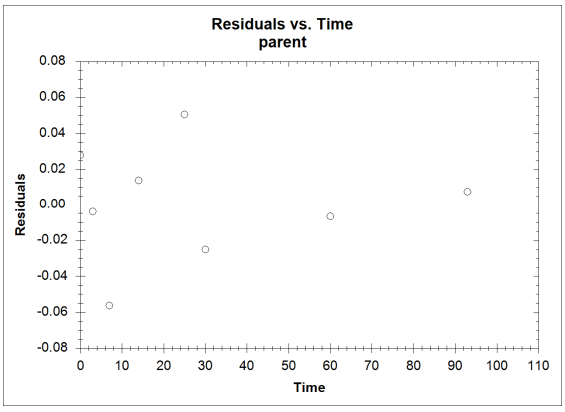


Figure B.8.1.2-20: Kinetic fits of dimethenamid in the field trials R10246, R10247 and R10248

The final DT_{50} and DT_{90} values for dimethenamid are summarised in Table B.8.1.2-50.

Table B.8.1.2-50: DT_{50} and DT_{90} values of dimethenamid in the field dissipation studies

Field trial	Persistence endpoints		
	DT_{50} [d]	**DT_{90} [d]**	**Kinetic model/ kinetic parameter**
R10283	-[1)]	-[1)]	-[1)]
R10284	-[1)]	-[1)]	-[1)]
R10242	1.93	21.80	FOMC, α: 0.841, β: 1.057
R10243	35.12	116.7	SFO
R10244	16.47	54.72	SFO
R10245	16.22	53.87	SFO
R10246	10.08	33.50	SFO
R10247	9.06	30.08	SFO
R10248	15.31	50.84	SFO

[1)] No statistically reliable fit could be obtained

Conclusion

The field dissipation studies were considered acceptable as additional information for the first Annex 1 approval of dimethenamid-P. After re-evaluation of the study, the RMS concluded that the study are still considered acceptable to be used for persistence calculations of dimethenamid.
The dissipation of dimethenamid was investigated at 9 field trials throughout Europe. DT_{50} of dimethenamid ranged from 1.93 – 35.12 d with DT_{90} values between 21.8 – 116.7 d.
The metabolite M656H023 was found at a maximum concentration of 13.44 % AR (= 0.23 µg/g) at day 28at the trial R10242. The metabolite M656H027 was found at a maximum concentration of 7.99 % AR [Jwö1](= 0.049 µg/g), at day 60 and 93 at the trial R10284. Further metabolites were not investigated.
The results of all acceptable field studies of dimethenamid-P and its metabolites are summarised in Volume 1 under 2.8.2.

KCA 7.1.2.2.1/ 2– Bade, 1990 (study evaluated in the monograph, 2000)

Author: Bade, T.R.
Title: Stability of SAN 582 H and its metabolites in stored frozen soil samples QAU #89/11/27
Date: 02/04/1990
Doc ID: BASF DocID 92/12382, BOD 1999-503
Guidelines: US-EPA, Subdivision N, 164-1
GLP: Yes
Validity: Acceptable

Material and Methods

Two approaches were used to determine the storage stability of dimethenamid residues in frozen soils. The first approach was to fortify control samples of soil with dimethenamid and metabolite M656PH023 and compare the concentrations found immediately after fortification and after storage. The second approach was to reanalyse radioactive samples from the soil metabolism study.

Results and Discussion

In the first approach, the stability of dimethenamid and M656PH023 in fortified and frozen soil samples was shown for up to 30 months. In the second approach, the stability of dimethenamid and its soil metabolites M656PH023 and M656PH027 was demonstrated over a period of three years.

Conclusion

The study was considered acceptable for the first Annex I inclusion of dimethenamid and is still considered acceptable by the RMS now.

KCA 7.1.2.2.1/ 3– Bayer & Marwitz, 2014a (new study)

Author:	Bayer, H Marwitz, A.
Title:	Field soil dissipation study of BAS 656 H (dimethenamid-P) in the formulation BAS 656 12 H on bare soil at four different sites in Europe, 2011-2013
Date:	05/03/2014
Doc ID:	BASF DocID 2013/1343457, study code 380194
Guidelines:	NAFTA Guidance Document for Conducting Terrestrial Field Dissipation Studies Regulatory Directive DIR2006-01 (March 2006), EPA 835.6100, SETAC, EFSA Guidance to obtain DT_{50} values in soil (2010), SANCO/825/00 rev. 8.1 (16 November 2010), SANCO/3029/99 rev. 4 (11 July 2000)
GLP:	Yes
Validity:	Acceptable

Material and Methods

The dissipation of dimethenamid-P (BAS 656 H) applied in the product BAS 656 12 H and its metabolites M656PH023 (M23 in study), M656PH027 (M31 in study) and M656PH031 (M31 in study) under field conditions were investigated at four sites in Europe representative of Northern and Southern EU conditions. One trial each was performed in Germany (L110061), Northern France (L110062), Southern France (L110063) and Spain (L110064). The soil characteristics of the respective sites are presented in Table B.8.1.2-51.

Table B.8.1.2-51: Soil characteristics of the trial sites used to investigate the field dissipation of dimethenamid-P

Trial	**L110061**			**L110062**		
Location	**Goch-Nierswalde, Germany**			**Stotzheim, France (North)**		
Soil properties	**0 - 30 cm**	**30 - 60 cm**	**60 - 90 cm**	**0 - 30 cm**	**30 – 60 cm**	**60 - 90 cm**
Soil class (DIN 4220)	Sandy silt (Us)	Sandy silt (Us)	Sandy silt (Us)	Medium clay silt (Ut3)	Medium silt clay (Ut3)	Silty loam (Lu)
sand [%]	22.7	19.2	22.1	16.5	12.6	15.1
silt [%]	74.9	74.8	70.7	69.8	70.7	64.3
clay [%]	2.5	6.1	7.3	13.6	16.6	20.6
Soil class (USDA)	Silt loam	Silt loam	Silt loam	Silt loam	Silt loam	Silt loam
sand [%]	33.6	29.0	29.9	15.1	17.6	17.3
silt [%]	64.9	65.7	62.7	66.4	66.2	61.8
clay [%]	1.6	5.3	7.5	18.5	16.1	20.9
Total organic C [%]	1.75	0.50	0.14	1.7	0.71	0.69
Organic matter [%] *	3.02	0.86	0.24	2.93	1.22	1.19
pH [$CaCl_2$]	5.85	5.60	4.44	7.11	7.25	7.01
pH [H_2O]	6.50	6.67	5.55	8.02	8.14	7.91
CEC [mval Ba/100g dry weight]	9.5	4.3	3.7	14.8	13.8	13.2
MWHC [g/100g dry weight]	48.9	52.7	51.2	58.1	51.3	48.2
pF 2.0 [g/100g dry weight]**	23.7	17.7	21.4	25.1	27.2	29.1
pF 2.5 [g/100g dry weight]**	21.8	17.0	16.6	22.7	25.5	25.6
Dry bulk density [g/cm3]***	1.28	-	-	1.15	-	-
Soil taxonomy	Pseudogley-Cambisol / Pseudogley-Paracambisol			Haplic Calcisol		
Trial	**L110063**			**L110064**		
Location	**Meauzac, France (South)**			**Utrera, Spain**		
Soil properties	**0 - 40 cm**	**40 - 90 cm**		**0 - 15 cm**	**15 – 30 cm**	**30 – 90 cm**
Soil class (DIN 4220)	Silty loamy sand (Slu)	Poor loamy sand (Sl2)		Pure sand (Ss)	Pure sand (Ss)	Sandy clay loam (Lts)
sand [%]	45.7	81.4		86.2	85.6	52.2
silt [%]	43.4	13.5		9.1	9.4	15.3
clay [%]	10.9	5.1		4.6	4.9	32.4
Soil class (USDA)	Sandy loam	Loamy sand		Sand	Sand	Silt clay loam
sand [%]	53.0	84.1		88.1	87.7	53.4
silt [%]	36.2	11.0		7.7	8.0	10.7
clay [%]	10.8	4.8		4.1	4.3	35.9
Total organic C [%]	1.30	0.94		0.48	0.33	0.37
Organic matter [%] *	2.24	1.62		0.83	0.57	0.64
pH [$CaCl_2$]	7.55	7.76		6.93	7.00	6.36
pH [H_2O]	8.50	8.90		7.77	7.90	7.42
CEC [mval Ba/100g dry weight]	9.0	5.0		4.7	4.8	22.8
MWHC [g/100g dry weight]	44.0	34.9		28.0	27.4	45.7
pF 2.0 [g/100g dry weight]**	18.6	8.4		12.0	12.9	33.1
pF 2.5 [g/100g dry weight]**	17.2	8.9		10.0	10.5	30.7
Dry bulk density [g/cm3]***	1.53	-		1.66	-	-
Soil taxonomy	Endoeutric Albeluvisol			Eutric Planosols		

* organic matter = organic carbon x 1.724
** water retention characteristics, soil moisture at 0.1 or 0.33 bar
*** samples taken at 10-20 cm depth (mean of 3 replicates)
CEC = cation exchange capacity
MWHC = maximum water holding capacity

All sites represent typical regions of agricultural practice representative for growing crops including maize, which is among the most important crops for the use of dimethenamid-P. No dimethenamid-P

or product from a similar chemical class had been used on the test plots in the previous three years. The crop and pesticide history of the trial sites is presented in Table B.8.1.2-52.

Table B.8.1.2-52: Management history of the trial sites in the previous years (non-GLP)

Trial	Location	Year	Crops grown	Pesticides used
L110061	Goch-Nierswalde, Germany	2008	green manuring	no pesticides applied
		2009	green manuring	no pesticides applied
		2010	alfalfa	pyridat
		2011*	green manuring	no pesticides applied
L110062	Stotzheim, France (North)	2008	maize	nicosulfuron, mesotrione, dicamba
		2009	vine nursery	oryzalin+diuron, glufosinate+ammonium, oxyfluorfen+propyzamide, fosetyl-aluminium+folpet+cymoxanil, dimethomorph+folpet, chlorpyriphos-methyl, folpet+mandipropamid, sulfur micro, copper oxychloride
		2010	maize	nicosulfuron, mesotrione, dicamba
		2011*	none	glyphosate
L110063	Meauzac, France (South)	2008	maize	bentazone+dicamba, foramsulfuron
		2009	maize	bentazone+dicamba, foramsulfuron
		2010	maize	bentazone+dicamba, foramsulfuron
		2011*	none	no additional pesticide applied
L110064	Utrera, Spain	2008	mustard	no additional pesticide applied
		2009	corn	pendimethalin, abamectin
		2010	sunflower	pendimethalin
		2011*	fallow field	no additional pesticide applied

The trial sites consisted of an untreated (size: 30 - 90 m^2) and a treated plot (size: 324 - 630 m^2), the latter being subdivided into 3 subplots A, B and C that were assigned for replicates.

The product BAS 656 12 H, formulated as an emulsifiable concentrate (EC), was broadcast applied to bare soil in a single application at a nominal rate of 1008 g a.s./ha using a target water volume of 300 L/ha. Applications were conducted between early April and late May 2011 using a calibrated boom sprayer. The actual application rates determined by quantifying the amount of spray discharged ranged from 944 to 1048 g a.s./ ha for all trials. Results from spray broth analysis for the individual trial sites revealed concentrations in the range of 1.96 to 2.41 g/L corresponding to 58-72 % of the target concentration of 3.34 g/L. Dose verification conducted via application monitors yielded recovery values for the individual trial sites ranging from 721 to 855 g/ha and thus 72 to 85 % of the target rate. Since spray broth concentrations were already lower than expected in all trials, it is assumed that the product had not been properly mixed before bottling or use. However, no adverse effect on the validity of the study is expected by the lower application rate since the amount of dimethenamid-P applied is more than enough to be able to determine its degradation behaviour.

Further details of application are presented in Table B.8.1.2-53.

Table B.8.1.2-53: Application parameters of field trial sites treated with BAS 656 12 H (EC, 720 g/L)

Trial Country	Application method	No. of applications	Subplot (m²)	Application rate per treatment				Application date
				nominal	actual*	dose verification**		
				[g a.s/ha]	[g a.s./ha]	[g a.s/ha]	% of nominal	
L110061 Germany	broadcast spray to bare soil	1	A (133.5)	1008	1012	717	71	24-May-2011
			B (133.5)	1008	1042	698	69	
			C (133.5)	1008	1037	748	74	
			Average	1008	1030	721	72	
L110062 France (North)	broadcast spray to bare soil	1	A (168)	1008	1010	825	82	24-May-2011
			B (168)	1008	992	807	80	
			C (168)	1008	1048	933	93	
			Average	1008	1017	855	85	
L110063 France (South)	broadcast spray to bare soil	1	A (210)	1008	944	878	87	20-May-2011
			B (210)	1008	1018	781	77	
			C (210)	1008	1026	629	62	
			Average	1008	996	762	76	
L110064 Spain	broadcast spray to bare soil	1	A (108)	1008	1024	823	82	08-Apr-2011
			B (108)	1008	1048	791	78	
			C (108)	1008	1036	808	80	
			Average	1008	1036	807	80	

Immediately after application of the test item, the plots were covered with a layer of sand of approximately 6 mm depth to protect the applied product from surface processes like photolysis or volatilisation, and to exclude any potential impact on the degradation of the test item caused by any of these processes. Only at the control plot and at sub-subplot 3 of replicate A of trial L110062, a layer of sand of 25-30 mm was applied due to a technical mishap. The affected sub-subplot of the treated plot was sampled shortly afterwards (0 DAT) and consequently, there is no adverse effect on the validity of the study. The layer of sand was controlled up to at least 28 days after application and was renewed when needed. It remained intact until at least 28 days. Within this time period of 28 days, the individual fields received a total precipitation (rain and irrigation) of 85 mm (Germany), 82 mm (France North), 51 mm (France South) and 103 mm (Spain), respectively.
No tillage or fertilisation was performed during the course of the study from first to last sampling and no crops were grown throughout any of the trials. The plots were kept free of vegetation via the application of glyphosate or glufosinate ammonium.
Rainfall was supplemented with irrigation at sites in Germany (195 mm), Northern France (130 mm), Southern France (313 mm) and Spain (687 mm) and the total water input was at least 102 % of the historical average rainfall during the study period at the test sites.
Actual weather data are based on records of appropriate weather stations located on-site. Monthly summary results on temperature, precipitation and irrigation are presented in Table B.8.1.2-54.

Table B.8.1.2-54: Summary of climatic conditions at field trial sites used to investigate the dissipation of dimethenamid-P

Trial	L110061			L110062			L110063			L110064		
Location	Goch-Nierswalde			Stotzheim			Meauzac			Utrera		
	Germany			France (North)			France (South)			Spain		
Climatic conditions	T_{mean} Air [°C]	Prec. [mm]	Irrigation [mm]	T_{mean} Air [°C]	Prec. [mm]	Irrigation [mm]	T_{mean} Air [°C]	Prec. [mm]	Irrigation [mm]	T_{mean} Air [°C]	Prec. [mm]	Irrigation [mm]
Month		∑	∑		∑	∑		∑	∑		∑	∑
Apr 11	-	-	-	-	-	-	-	-	-	19.6	70.0	7.9
May 11	15.0	10.0	10.0	16.4	7.8	0.0	18.4	2.2	0.0	23.4	28.0	30.5
Jun 11	16.1	89.0	0.0	17.3	102.0	3.0	18.6	49.8	22.6	26.9	3.0	90.0
Jul 11	15.6	112.4	10.0	16.3	97.8	10.9	19.3	81.8	23.0	27.7	0.0	90.3
Aug 11	16.9	136.2	0.0	18.5	95.2	14.9	21.8	0.4	47.0	28.3	0.0	86.1
Sep 11	15.4	54.2	5.0	16.0	75.8	0.0	19.7	14.2	59.0	25.6	15.0	61.1
Oct 11	10.8	78.4	0.0	9.2	35.2	8.7	13.7	17.2	38.0	22.5	70.5	43.3
Nov 11	6.7	8.4	50.0	5.1	2.4	0.0	11.2	19.2	36.0	15.5	88.5	0.0
Dec 11	5.5	146.6	0.0	4.9	101.8	0.0	7.4	66.4	0.0	11.5	14.5	5.1
Jan 12	4.1	122.0	0.0	3.3	58.4	0.0	5.7	33.2	0.0	9.8	40.0	16.3
Feb 12	0.4	24.2	0.0	-2.1	2.8	0.0	0.7	2.4	0.0	7.9	0.5	24.5
Mar 12	8.1	23.8	20.0	8.1	10.2	3.5	10.2	28.4	17.0	13.7	8.0	29.7
Apr 12	8.2	79.8	0.0	8.9	50.6	25.9	10.7	101.0	19.0	15.9	59.5	11.1
May 12	14.4	70.0	10.0	15.4	33.4	0.0	16.6	70.8	0.0	23.6	23.0	23.1
Jun 12	14.6	122.2	0.0	17.2	96.2	0.0	20.0	58.6	0.0	26.6	0.0	43.8
Jul 12	16.9	148.0	10.0	17.9	89.0	10.7	20.1	31.2	18.0	27.4	0.0	46.8
Aug 12	18.4	45.0	25.0	18.9	37.2	17.0	22.6	67.6	0.0	28.1	0.0	46.2
Sept 12	13.5	48.8	30.0	14.0	44.8	21.9	18.0	20.2	17.0	24.6	78.0	31.4
Oct 12	10.0	84.6	10.0	8.9	81.6	0.0	14.4	36.6	16.0	20.0	127.0	-
Nov 12	6.5	34.6	0.0	5.8	93.4	0.0	8.7	57.8	0.0	15.8	135.5	-
Dec 12	4.3	121.0	0.0	3.2	66.2	0.0	6.3	97.0	0.0	12.4	37.0	-
Jan 13	1.8	46.2	0.0	1.3	20.0	0.0	4.6	129.2	0.0	11.9	49.5	-
Feb 13	1.2	37.6	0.0	0.0	37.8	0.0	4.3	61.8	0.0	11.1	55.0	-
Mar 13	2.8	39.8	15.0	2.6	24.6	0.0	8.8	89.0	0.0	14.6	165.5	-
Apr 13	8.4	45.2	0.0	9.6	72.6	13.1	11.5	74.6	0.0	16.2	1.0	-
May 13	12.4	0.2	0.0	13.0	58.4	0.0	14.1	40.8	0.0	-	-	-

Replicate soil specimens (8 per treated subplot and 10 or 15 per control plot) were taken at intervals up to about 725 days and down to a maximum soil depth of 90 cm. At day 0, immediately after application, the treated plots were sampled down to 10 cm only. The detailed sampling intervals are presented in Table B.8.1.2-55.

Table B.8.1.2-55: Summary of sampling intervals at each field trial site

Trial	Country	Sampling intervals [days after treatment]
L110061	Germany	-1, 0, 3, 6, 10, 16, 28, 59, 85, 120, 150, 175, 233, 366, 540, 710
L110062	France (North)	-11, 0, 3, 6, 10, 16, 28, 58, 92, 120, 154, 176, 233, 358, 548, 721
L110063	France (South)	-1, 0, 3, 6, 10, 19, 28, 59, 94, 123, 153, 180, 243, 364, 550, 725
L110064	Spain	-1, 0, 3, 6, 10, 17, 31, 60, 95, 116, 151, 179, 236, 355, 544, 725

Untreated specimens were collected from the control plot at three occasions, one or eleven days before application down to a depth of 90 cm, and after about one and two years to a depth of 10 cm each.
Soil cores were cut into 10 cm sections. Soil segments of the same depth and subplot from a defined sampling event were pooled and homogenised and a representative sub-sample of each depth was taken for residue analysis. All soil specimens were stored at about -18 °C within a maximum of 8 hours and 30 minutes after sampling and remained frozen until analysis.

In order to demonstrate stability of the residues in soil during storage and any shipments, shipment verification specimens were prepared at selected sampling occasions by fortifying untreated soil from

the field sites with known amounts of dimethenamid-P. These specimens were stored and shipped under the same conditions as the actual residue specimens. Analysis of the shipping verification specimens on dimethenamid-P yielded an average recovery value of 112 % across all sites confirming residue stability during all storage and shipment procedures.
Soil specimens and application monitors were analysed for dimethenamid-P and metabolites M656PH023, M656PH027 and M656PH031 according to BASF method L0109/02. The analytical method involved extraction of the soil with methanol/water (60/40, v/v). The final determination of the analytes was performed by HPLC-MS/MS with a limit of quantification (LOQ) of 0.005 mg/kg for each analyte. The limit of detecition (LOD) was set at 0.0015 mg/kg.
Field soil specimens from the treated plot were analysed down to a maximum of 50 cm or to a depth until at least two consecutive soil segments were free of quantifiable residues (< LOQ). Analysis was performed until a maximum of 366 days after treatment (DAT).
Spray broth specimens were diluted to the appropriate concentration and analysed for dimethenamid-P using HPLC-MS/MS.
Residue values of dimethenamid-P and metabolites M656PH023, M656PH027 and M656PH031 in mg/kg dry soil were converted to residue rates in g/ha taking into account the actual dry soil density of the individual field samples, and were summed up for all depths between 0 and 50 cm analysed. Residue values were not corrected for procedural recoveries except for results obtained from petri dish and shipment verification analysis.

Results and Discussion

No residues above 30 % of the LOQ of dimethenamid-P and its metabolites M656PH023, M656PH027 and M656PH031 were detected in any of the untreated control samples proving that there were no interferences of the untreated soil material with the analytical procedures used.
Procedural recovery experiments performed with untreated field soil specimens spiked with a mix of dimethenamid-P and its metabolites M656PH023, M656PH027 and M656PH031 at different concentration levels yielded overall mean recovery rates between 93 and 96 %.
Field soil specimens from the treated plots were analysed down to a depth until at least two consecutive soil segments were free of quantifiable residues (< LOO of 0.005 mg/kg, maximum depth of 50 cm).
The residue data of dimethenamid-P, M656PH023, M656PH027 and M656PH031 summed up for all depth between 0 and 50 cm and converted to g/ha are presented in Table B.8.1.2-56, Table B.8.1.2-57, Table B.8.1.2-58 and Table B.8.1.2-59.

Table B.8.1.2-56: Total residues of dimethenamid-P under field conditions in soil calculated to g/ha and summed up for all depths analysed

Trial Country	L110061 Goch-Nierswalde, Germany			L110062 Stotzheim, France		
DAT	Replicate A [g/ha]	Replicate B [g/ha]	Replicate C [g/ha]	Replicate A [g/ha]	Replicate B [g/ha]	Replicate C [g/ha]
0	672	740	722	530	623	888
3	590	765	715	752	806	884
6	354	727	778	733	832	848
10	391	502	499	768	646	623
16	276	317	483	458	398	536
28	447	420	163	223	155	149
58-59	108	65	54	7.2	7.3	5.7
85-92	42	48	42	0	0	0
120	19	35	31	0	0	0
150-154	19	28	17	0	0	0
175-176	13	27	21	0	0	0
233	16	21	12	0	0	0
358-366	0	0	0	0	0	0
Trial Country	**L110063 Meauzac, France**			**L110064 Utrera, Spain**		
DAT	**Replicate A [g/ha]**	**Replicate B [g/ha]**	**Replicate C [g/ha]**	**Replicate A [g/ha]**	**Replicate B [g/ha]**	**Replicate C [g/ha]**
0	858	719	804	937	884	997
3	747	761	761	583	896	628
6	759	758	603	691	681	876
10	538	779	762	348	758	681
17-19	338	371	217	610	505	457
28-31	122	159	123	284	155	174
59-60	14	15	8.6	16	17	19
94-95	0	0	0	0	0	0
116-123	0	0	0	0	0	0
151-153	0	0	0	0	0	0
179-180	0	0	0	0	0	0
236-243	0	0	0	0	0	0
355-364	0	0	0	0	0	0

DAT = days after treatment
calculations are based on actual dry soil density for individual soil layers
residue values <0.005 mg/kg (<LOQ) were reported and treated as zero

Table B.8.1.2-57: Total residues of M656PH023 under field conditions in soil calculated to g/ha and summed up for all depths analysed

Trial Country	L110061 Goch-Nierswalde, Germany			L110062 Stotzheim, France		
DAT	Replicate A [g/ha]	Replicate B [g/ha]	Replicate C [g/ha]	Replicate A [g/ha]	Replicate B [g/ha]	Replicate C [g/ha]
0	0	0	0	0	0	0
3	0	0	0	0	0	0
6	0	0	0	0	0	0
10	0	0	0	5.6	0	6.7
16	0	0	26	7.3	15	13
28	26	0	0	11	7.9	10
58-59	0	0	0	0	0	0
85-92	0	0	0	0	0	0
120	0	0	0	0	0	0
150-154	0	0	0	0	0	0
175-176	0	0	0	0	0	0
233	0	0	0	0	0	0
358-366	0	0	0	0	0	0
Trial Country	**L110063 Meauzac, France**			**L110064 Utrera, Spain**		
DAT	**Replicate A [g/ha]**	**Replicate B [g/ha]**	**Replicate C [g/ha]**	**Replicate A [g/ha]**	**Replicate B [g/ha]**	**Replicate C [g/ha]**
0	0	0	0	0	0	0
3	0	0	0	0	0	0
6	0	0	0	0	0	0
10	0	0	0	0	0	0
17-19	17	15	13	12	17	15
28-31	20	30	26	40	33	26
59-60	0	0	0	16	16	14
94-95	0	0	0	0	0	0
116-123	0	0	0	0	0	0
151-153	0	0	0	0	0	0
179-180	0	0	0	0	0	0
236-243	0	0	0	0	0	0
355-364	0	0	0	0	0	0

DAT = days after treatment
calculations are based on actual dry soil density for individual soil layers
residue values <0.005 mg/kg (<LOQ) were reported and treated as zero

Table B.8.1.2-58: Total residues of M656PH027 under field conditions in soil calculated to g/ha and summed up for all depths analysed

Trial Country	L110061 Goch-Nierswalde, Germany			L110062 Stotzheim, France		
DAT	Replicate A [g/ha]	Replicate B [g/ha]	Replicate C [g/ha]	Replicate A [g/ha]	Replicate B [g/ha]	Replicate C [g/ha]
0	0	0	0	0	0	0
3	0	0	0	0	0	0
6	0	0	0	0	0	0
10	0	0	0	0	0	0
16	0	0	8.5	6.4	6.6	7.3
28	22	8.2	10	31	34	29
58-59	28	36	32	0	9.7	0
85-92	18	21	13	0	0	0
120	0	0	0	0	0	0
150-154	0	0	0	0	0	0
175-176	0	0	0	0	0	0
233	0	0	0	0	0	0
358-366	0	0	0	0	0	0
Trial Country	**L110063 Meauzac, France**			**L110064 Utrera, Spain**		
DAT	**Replicate A [g/ha]**	**Replicate B [g/ha]**	**Replicate C [g/ha]**	**Replicate A [g/ha]**	**Replicate B [g/ha]**	**Replicate C [g/ha]**
0	0	0	0	0	0	0
3	0	0	0	0	0	0
6	0	0	0	0	0	0
10	0	0	0	0	0	0
17-19	22	22	11	10	15	0
28-31	26	45	31	48	37	28
59-60	12	0	10	40	32	23
94-95	0	0	0	0	21	19
116-123	0	0	0	10	24	0
151-153	0	0	0	0	0	0
179-180	0	0	0	0	0	0
236-243	0	0	0	0	0	0
355-364	0	0	0	0	0	0

DAT = days after treatment
calculations are based on actual dry soil density for individual soil layers
residue values <0.005 mg/kg (<LOQ) were reported and treated as zero

Table B.8.1.2-59: Total residues of M656PH031 under field conditions in soil calculated to g/ha and summed up for all depths analysed

Trial Country	L110061 Goch-Nierswalde, Germany			L110062 Stotzheim, France		
DAT	Replicate A [g/ha]	Replicate B [g/ha]	Replicate C [g/ha]	Replicate A [g/ha]	Replicate B [g/ha]	Replicate C [g/ha]
0	0	0	0	0	0	0
3	0	0	0	0	0	0
6	0	0	0	0	0	0
10	0	0	0	0	0	0
16	0	0	11	6.4	13	15
28	12	6.9	0	36	23	25
58-59	0	0	0	0	0	0
85-92	0	0	0	0	0	0
120	0	0	0	0	0	0
150-154	0	0	0	0	0	0
175-176	0	0	0	0	0	0
233	0	0	0	0	0	0
358-366	0	0	0	0	0	0
Trial Country	**L110063 Meauzac, France**			**L110064 Utrera, Spain**		
DAT	**Replicate A [g/ha]**	**Replicate B [g/ha]**	**Replicate C [g/ha]**	**Replicate A [g/ha]**	**Replicate B [g/ha]**	**Replicate C [g/ha]**
0	0	0	0	0	0	0
3	0	0	0	0	0	0
6	0	0	0	0	0	0
10	0	0	0	0	0	0
17-19	13	8.3	8.4	10	13	17
28-31	16	21	20	45	32	37
59-60	0	0	0	12	13	14
94-95	0	0	0	0	0	0
116-123	0	0	0	0	0	0
151-153	0	0	0	0	0	0
179-180	0	0	0	0	0	0
236-243	0	0	0	0	0	0
355-364	0	0	0	0	0	0

DAT = days after treatment
calculations are based on actual dry soil density for individual soil layers
residue values <0.005 mg/kg (<LOQ) were reported and treated as zero

Dimethenamid-P degraded fast at all four European field sites. The total amount of dimethenamid-P residues detected in the soil profiles decreased from an average of 781 g/ha at day 0 to values between 6 and 108 g/ha after 2 months. At sites in Northern France, Southern France and Spain, no residues above the LOQ (0.005 mg/kg) were detectable any longer after 95 days at the latest. At the site in Germany, no residues above the LOQ were left after 1 year.
The main proportion was always measured in the top 0-10 cm soil layer and only small amounts of the compound were detected in the 10-20 cm layer. No residues above the LOQ were detected below 20 cm in any sample. Altogether, it can be concluded that dimethenamid-P does not show any significant tendency to move into deeper soil layers indicating low potential for dimethenamid-P residues to leach to groundwater.
Metabolites M656PH023, M656PH027 and M656PH031 were temporarily detected in small amounts at all sites reaching maximum amounts of 40 g/ha, 48 g/ha, und 45 g/ha, respectively. Thereafter residues declined again and were no longer detected after 151 days at the latest. All metabolites were only found in the top 0-20 cm soil layer, except for 1 single detect of M656PH027 in the 20-30 cm layer at the site in Spain. No residues of the three metabolites above the LOQ were observed in deeper soil layers in any sample at any site.

Conclusion

The study is considered acceptable by the RMS.
Dimethenamid-P degraded fast under field conditions in soil at all four European field sites. The total amount of dimethenamid-P residues in the soil profiles decreased from an average of 781 g/ha at day 0 to values between 6 and 108 g/ha after 2 months. At sites in Northern France, Southern France and Spain, no residues above the LOQ (0.005 mg/kg) were detectable any longer after 95 days at the latest. At the site in Germany, no residues above the LOQ were left after 1 year. Dimethenamid-P residues were exclusively detected in the upper 20 cm of the soils. No residues above the LOQ were detected below 20 cm in any sample. Altogether, it can be concluded that dimethenamid-P does not show any significant tendency to move into deeper soil layers indicating low potential for dimethenamid-P residues to leach to groundwater.
Metabolites M656PH023, M656PH027 and M656PH031 were temporarily detected in low amounts at all sites reaching maximum amounts of 4.20 % AR (= 40 g/ha), 5.04 % (= 48 g/ha), und 8.56 % AR (= 45 g/ha), respectively. All metabolites were only found in the top 0-20 cm soil layer, except for 1 single detect of M656PH027 in the 20-30 cm layer at the site in Spain. No residues of the three metabolites above the LOQ were observed in deeper soil layers in any sample at any site.
DT_{50} and DT_{90} values for dimethenamid-P and its metabolites to be used for persistence calculations and modelling are derived in two separate studies described under Wiedemann, 2014a and Wiedemann, 2014b.

KCA 7.1.2.2.1/ 4 Bayer & Marwitz, 2014b (new study)

Author:	Bayer, H. Marwitz, A.
Title:	Field soil dissipation study of M27 (metabolite of BAS 656 H, Dimethenamid) in the formulation EXP 360714 H-AA on bare soil at four different sites in Europe, 2011-2013
Date:	03/06/2014
Doc ID:	BASF DocID 2013/1343459, study code 404430
Guidelines:	NAFTA Guidance Document for Conducting Terrestrial Field Dissipation Studies Regulatory Directive DIR2006-01 (March 2006), EPA 850.6100, SETAC, EFSA Guidance to obtain DT_{50} values in soil (2010), SANCO/825/00 rev. 8.1 (16 November 2010), SANCO/3029/99 rev. 4 (11 July 2000)
GLP:	Yes
Validity:	Acceptable

Material and Methods

The dissipation of M656PH027 (M27 in study), a metabolite of dimethenamid-P (BAS 656 H) under field conditions was investigated at four sites in Europe representative of Northern and Southern EU conditions. Trials were performed in Germany (trial L110330), Northern France (trial L110331), Southern France (trial L110332) and in Spain (trial L110333). All sites represent typical regions of agricultural practice representative for growing crops including maize which is among the most important crops for the use of dimethenamid. The soil characteristics of the respective sites are presented in Table B.8.1.2-60.

Table B.8.1.2-60: Soil characteristics of the trial sites used to investigate the field dissipation of M656PH027

Trial	**L110330**			**L110331**	
Location	**Goch-Nierswalde, Germany**			**Stotzheim, France (North)**	
Soil properties	**0 - 30 cm**	**30 - 60 cm**	**60 - 90 cm**	**0 - 28 cm**	**28 – 90 cm**
Soil class (DIN 4220)	Sandy silt (Us)	Sandy silt (Us)	Medium silty sand (Su3)	Sandy loamy silt (Uls)	Silty loam (Lu)
sand [%]	18.1	25.7	70.3	28.8	27.7
silt [%]	77.1	67.5	25.3	56.4	50.6
clay [%]	4.9	6.7	4.5	14.7	21.7
Soil class (USDA)	Silt loam	Silt loam	Sandy loam	Silt loam	Loam
sand [%]	25.9	33.5	74.0	30.6	28.8
silt [%]	69.3	59.1	20.9	54.9	47.9
clay [%]	4.7	7.3	5.0	14.6	23.3
Total organic C [%]	1.65	0.28	0.12	0.83	0.34
Organic matter [%]*	2.84	0.48	0.21	1.43	0.59
pH [$CaCl_2$]	6.36	5.95	5.03	5.47	6.40
pH [H_2O]	7.07	7.04	6.39	6.40	7.50
CEC [mval Ba/100g dry weight]	9.6	3.5	2.8	8.5	12.1
MWHC [g/100g dry weight]	52.7	47.0	34.3	49.5	47.9
pF 2.0 [g/100g dry weight]**	32.6	17.5	8.2	19.0	24.8
pF 2.5 [g/100g dry weight]**	18.0	15.8	7.3	17.8	18.4
Dry bulk density [g/cm^3]***	1.28	-	-	1.19	-
Soil taxonomy	Anthrosole			Haplic Calcisol	

Trial	**L110332**		**L110333**		
Location	**Meauzac, France (South)**		**Utrera, Spain**		
Soil properties	**0 - 40 cm**	**40 - 90 cm**	**0 - 15 cm**	**15 – 30 cm**	**30 – 90 cm**
Soil class (DIN 4220)	Silty loamy sand (Slu)	Poor silty sand (Su2)	Poor clay sand (St2)	High loamy sand (Sl4)	Sandy clay loam (Lts)
sand [%]	45.4	85.0	85.5	69.6	51.3
silt [%]	43.7	11.1	8.8	14.5	17.8
clay [%]	11.0	3.9	5.6	15.9	30.9
Soil class (USDA)	Loam	Loamy sand	Loamy sand	Sandy clay loam	Sandy clay loam
sand [%]	51.5	87.0	86.3	70.4	52.8
silt [%]	36.7	8.6	6.7	9.5	15.6
clay [%]	11.9	4.3	6.9	20.3	31.5
Total organic C [%]	1.38	0.80	0.38	0.34	0.30
Organic matter [%]*	2.38	1.38	0.66	0.59	0.52
pH [$CaCl_2$]	7.49	7.01	6.92	6.66	6.72
pH [H_2O]	8.44	7.66	7.93	7.75	7.77
CEC [mval Ba/100g dry weight]	9.0	4.0	5.0	12.2	20.4
MWHC [g/100g dry weight]	42.2	32.1	27.8	36.4	43.0
pF 2.0 [g/100g dry weight]**	18.0	7.2	10.7	35.3	36.7
pF 2.5 [g/100g dry weight]**	14.0	6.0	7.8	19.8	30.2
Dry bulk density [g/cm^3]***	1.59	-	1.61	-	-
Soil taxonomy	Endoeutric Albeluvisol		Planosol eutrico		

* organic matter = organic carbon x 1.724
** water retention characteristics, soil moisture at 0.1 or 0.33 bar
*** samples taken at 10-20 cm depth (mean of 3 replicates)
CEC = cation exchange capacity; MWHC = maximum water holding capacity

All sites represent typical regions of agricultural practice representative for growing crops including maize, which is among the most important crops for the use of dimethenamid-P. No product M656PH027 or dimethenamid-P or its structural analogues had been used on the test plots in the previous three years. The crop and pesticide history of the trial sites is presented in Table B.8.1.2-61.

Table B.8.1.2-61: Management history of the trial sites in the previous years (non-GLP)

Trial	Location	Year	Crops grown	Pesticides used
L110330	Goch-Nierswalde, Germany	2008	green manuring	no pesticides applied
		2009	green manuring	no pesticides applied
		2010	alfalfa	pyridat
		2011*	green manuring	no pesticides applied
L110331	Stotzheim, France (North)	2008	maize	nicosulfuron, mesotrione, dicamba
		2009	vine nursery	glufosinate-ammonium, oryzalin+diuron, oxyfluorfen+propyzamide, fosetyl-aluminium+folpet+cymoxanil, dimethomorph+folpet, chlorpyriphos-methyl, folpet+mandipropamid, sulfur micro, copper oxychloride
		2010	maize	nicosulfuron, mesotrione, dicamba
		2011*	none	glyphosate
L110332	Meauzac, France (South)	2008	maize	bentazone+dicamba, foramsulfuron
		2009	maize	bentazone+dicamba, foramsulfuron
		2010	maize	bentazone+dicamba, foramsulfuron
		2011*	none	no additional pesticide applied
L110333	Utrera, Spain	2008	fallow field	no additional pesticide applied
		2009	phacelia, tanacetifolia	no additional pesticide applied
		2010	wheat	fenpropimorph
		2011*	fallow field	no additional pesticide applied

* until start of trial

The trial sites consisted of an untreated control plot (size: 30 - 90 m^2) and a treated plot (size: 324 - 630 m^2), the latter being subdivided into 3 subplots A, B and C that were assigned for replicates.

The product EXP 360714 H-AA, formulated as a soluble concentrate (SL), was broadcast applied to bare soil in a single application at a nominal rate of 250 g a.s./ha using a target water volume of 300 L/ha. Applications were conducted between early May and early June 2011 using a calibrated boom sprayer. The actual application rates determined by quantifying the amount of spray discharged ranged from 249 to 254 g a.s./ha (mean from each trial), with an average of 253 g as/ha. Results from spray broth analysis for the individual trial sites revealed concentrations between 90 and 100 % of the nominal value with an average of 94 % across all sites. Dose verification conducted via application monitors yielded recovery values for the individual sites ranging from 100 to 108 % of the target rate and an average recovery of 103 % over all sites. Further details of application are presented in Table B.8.1.2-62.

Table B.8.1.2-62: Application parameters of field trial sites treated with M656PH027 (SL, 100 g/L)

Trial Country	Application method	No. of appli-cations	Subplot (m^2)	Application rate per treatment				Application Date
				nominal	actual*	dose verification**		
				[g a.s/ha]	[g a.s./ha]	[g a.s/ha]	% of nominal	
L110330 Germany	broadcast spray to bare soil	1	A (133.5)	250	251	265	106	24-May-2011
			B (133.5)	250	250	214	86	
			C (133.5)	250	258	280	112	
			Average	250	253	253	101	
L110331 France (North)	broadcast spray to bare soil	1	A (168)	250	239	261	104	07 June-2011
			B (168)	250	249	244	98	
			C (168)	250	258	268	107	
			Average	250	249	258	103	
L110332 France (South)	broadcast spray to bare soil	1	A (210)	250	257	216	86	24-May-2011
			B (210)	250	258	348	139	
			C (210)	250	246	245	98	
			Average	250	254	269	108	
L110333 Spain	broadcast spray to bare soil	1	A (108)	250	259	239	96	10-May-2011
			B (108)	250	255	242	97	
			C (108)	250	249	267	107	
			Average	250	254	250	100	

* determined by calculation of spray liquid applied
** determined by means of petri dishes filled with soil

Immediately after application of the test item, the plots were covered with a layer of sand of approximately 6 mm depth to protect the applied product from surface processes like photolysis or volatilisation, and to exclude any potential impact on the degradation of the test item caused by any of these processes. The application of sand was conducted until complete coverage of the soil surface. The layer of sand was controlled up to at least 28 days after application and was renewed when needed. It remained intact until at least 28 days. Within this time period of 28 days, the individual fields received a total precipitation (rain and irrigation) of 85 mm (Germany), 99 mm (France North), 62 mm (France South) and 51 mm (Spain), respectively.

No tillage or fertilisation was performed during the course of the study and no crops were grown throughout any of the trial. The plots were kept free of vegetation via the application of glyphosate or glufosinate ammonium. Rainfall was supplemented with irrigation at sites in Germany (195 mm), Northern France (120 mm), Southern France (321 mm) and Spain (671 mm) and the total water input was at least 92 % of the historical average rainfall during the study period at the test sites.

Actual weather data are based on records of appropriate weather stations located on-site. Monthly summary results on temperature, precipitation and irrigation are presented in Table B.8.1.2-63.

Table B.8.1.2-63: Summary of climatic conditions at field trial sites used to investigate the dissipation of M656PH027

Trial	L110330			L110331			L110332			L110333		
Location	Goch-Nierswalde			Stotzheim			Meauzac			Utrera		
	Germany			France (North)			France (South)			Spain		
Climatic conditions	T_{mean} Air [°C]	Prec. [mm]	Irriga-tion [mm]	T_{mean} Air [°C]	Prec. [mm]	Irriga-tion [mm]	T_{mean} Air [°C]	Prec. [mm]	Irriga-tion [mm]	T_{mean} Air [°C]	Prec. [mm]	Irriga-tion [mm]
Month		∑	∑		∑	∑		∑	∑		∑	∑
May 11	15.0	10.0	10.0	-	-	-	18.1	2.2	0.0	23.4	28.0	30.5
Jun 11	16.1	89.0	0.0	17.2	88.4	0	18.6	49.8	22.0	26.9	3.0	90.9
Jul 11	15.6	112.4	10.0	16.3	97.8	10.5	19.3	81.8	27.5	27.7	0.0	91.7
Aug 11	16.9	136.2	0.0	18.5	95.2	16.7	21.8	0.4	49.5	28.3	0.0	91.0
Sep 11	15.4	54.2	10.0	16.0	75.8	0.0	19.7	14.2	61.1	25.6	15.0	54.6
Oct 11	10.8	78.4	0.0	9.2	35.2	8.7	13.7	17.2	39.2	22.5	70.5	38.6
Nov 11	6.7	8.4	50.0	5.1	2.4	0.0	11.2	19.2	33.3	15.5	88.5	0.0
Dec 11	5.5	146.6	0.0	4.9	101.8	0.0	7.4	66.4	0	11.5	14.5	5.0
Jan 12	4.1	122.0	0.0	3.3	58.4	0.0	5.7	33.2	0	9.8	40.0	17.6
Feb 12	0.4	24.2	0.0	-2.1	2.8	0.0	0.7	2.4	0	7.9	0.5	23.6
Mar 12	8.1	23.8	20.0	8.1	10.2	3.5	10.2	28.4	18.2	13.7	8.0	30.2
Apr 12	8.2	79.8	0.0	8.9	50.6	26.3	10.7	101.0	18.7	15.9	59.5	10.7
May 12	14.4	70.0	10.0	15.4	33.4	0.0	16.6	70.8	0	23.6	23.0	23.1
Jun 12	14.6	122.2	0.0	17.2	96.2	0.0	20.0	58.6	0	26.6	0.0	43.7
Jul 12	16.9	148.0	10.	17.9	89.0	10.1	20.1	31.2	16.9	27.4	0.0	45.5
Aug 12	18.4	45.0	25.0	18.9	37.2	20.8	22.6	67.6	0	28.1	0.0	44.3
Sept 12	13.5	48.8	25.0	14.0	44.8	23.2	18.0	20.2	17.2	24.6	78.0	30.5
Oct 12	10.0	84.6	10.0	8.9	81.6	0.0	14.4	36.6	17.0	20.0	127.0	0.0
Nov 12	6.5	34.6	0.0	5.9	55.8	0.0	9.1	30.4	0	18.1	40.5	0.0
Dec 12	4.3	121.0	0.0	-	-	-	-	-	-	-	-	-
Jan 13	1.8	46.2	0.0	-	-	-	-	-	-	-	-	-
Feb 13	1.2	37.6	0.0	-	-	-	-	-	-	-	-	-
Mar 13	2.8	39.8	15.0	-	-	-	-	-	-	-	-	-
Apr 13	8.4	45.2	0.0	-	-	-	-	-	-	-	-	-
May 13	12.3	0.2	0.0	-	-	-	-	-	-	-	-	-

The actual air temperature recorded at the field sites during the study period was similar to the historic values. Whereas the sites in Northern Europe (Germany and Northern France) received more rain during the study period compared to the historical values, rainfall was less than the historic values in Southern Europe (Southern France, Spain). Due to additional irrigation, the total water input at the test sites during the study was at least 92 % of the historical average rainfall, which is considered sufficient to allow the cultivation of crops like maize.

Replicate soil specimens (8 per treated subplot and 10 or 15 per control plot) were taken at intervals up to about 710 days and down to a maximum soil depth of 90 cm. At day 0, immediately after application, the treated plots were sampled down to 10 cm only. The detailed sampling intervals are presented in Table B.8.1.2-64.

Table B.8.1.2-64: Summary of sampling intervals at each field trial site

Trial	Country	Sampling intervals [days after treatment]
L110330	Germany	-1, 0, 3, 6, 10, 17, 31, 60, 85, 120, 150, 175, 237, 363, 541, 710
L110331	France (North)	-8, 0, 3, 6, 10, 16, 28, 58, 92, 121, 153, 184/185, 233, 359, 535
L110332	France (South)	0, 3, 6, 10, 16, 29, 59, 93, 125, 153, 183, 248, 367, 541
L110333	Spain	-1, 0, 3, 6, 10, 16, 29, 59, 91, 120, 149, 176, 238, 363, 546

Untreated specimens were collected from the control plot at three occasions, one or eleven days before application down to a depth of 90 cm, and after about one and two years to a depth of 10 cm each.
Soil cores were cut into 10 cm sections. Soil segments of the same depth and subplot from a defined

sampling event were pooled and homogenised and a representative sub-sample of each depth was taken for residue analysis. All soil specimens were stored at about -18 °C within a maximum of 8 hours and 30 minutes after sampling and remained frozen until analysis.
In order to demonstrate stability of the residues in soil during storage and shipment, shipment verification specimens were prepared at selected sampling occasions by fortifying untreated soil from the field sites with known amounts of M656PH027. These specimens were stored and shipped under the same conditions as the actual residue specimens. Analysis of the shipping verification specimens on M656PH027 yielded an average recovery value of 89 % across all sites confirming residue stability during all storage and shipment procedures.
Soil specimens and application monitors were analysed for M656PH027 and metabolite M656PH023 according to BASF method L0109/02. The analytical method involved extraction of the soil with methanol/water (60/40, v/v). The final determination of the analytes was performed by LC-MS/MS with a limit of quantification (LOQ) of 0.005 mg/kg for each analyte. Field soil specimens from the treated plot were analysed down to a depth until at least two consecutive soil segments were free of quantifiable residues (< LOQ). Analysis was performed until a maximum of 248 days after treatment (DAT).
Spray broth specimens were diluted to the appropriate concentration and analysed for dimethenamid-P using HPLC-MS/MS.
Residue values of M656PH027 and metabolite M656PH023 in mg/kg dry soil were converted to residue rates in g/ha taking into account the actual dry soil density of the individual field samples, and were summed up for all depths between 0 and 60 cm analysed. Residue values were not corrected for procedural recoveries except for results obtained from petri dish and shipment verification analysis.

Results and Discussion

No residues above 30 % of the LOQ of any analyte were detected in any of the untreated control samples proving that there were no interferences of the untreated soil material with the analytical procedure used.
Procedural recovery experiments performed with untreated soils spiked with the two metabolites M656PH023 and M656PH027 at concentrations of 0.005, 0.01, and 0.05 mg/kg yielded overall mean recovery rates of 99 % for each individual analyte, confirming the validity of the analytical method used in this study.
Field soil specimens from the treated plots were analysed down to a depth until at least two consecutive soil segments were free of quantifiable residues (< LOO of 0.005 mg/kg, maximum depth of 60 cm).
The residue data of M656PH023 and M656PH027 summed up for all depth between 0 and 60 cm and converted to g/ha are presented in Table B.8.1.2-65.

Table B.8.1.2-65: Total residues of M656PH027 under field conditions in soil calculated to g/ha and summed up for all depths analysed

Trial Country	L110330 Goch-Nierswalde, Germany			L110331 Stotzheim, France		
DAT	Replicate A [g/ha]	Replicate B [g/ha]	Replicate C [g/ha]	Replicate A [g/ha]	Replicate B [g/ha]	Replicate C [g/ha]
0	158	140	171	176	176	192
3	155	149	212	144	150	141
6	182	148	211	111	102	160
10	254	136	131	72	91	109
16 - 17	164	101	113	72	65	77
28 - 31	108	49	75	37	44	38
58 - 60	53	48	38	0	0	0
85 - 92	36	21	0	0	0	0
120 - 121	0	0	0	0	0	0
150 - 153	0	0	0	0	0	0
175 - 185	0	0	0	0	0	0
233 - 237	0	0	0	0	0	0
Trial Country	**L110332 Meauzac, France**			**L110333 Utrera, Spain**		
DAT	**Replicate A [g/ha]**	**Replicate B [g/ha]**	**Replicate C [g/ha]**	**Replicate A [g/ha]**	**Replicate B [g/ha]**	**Replicate C [g/ha]**
0	164	171	216	184	163	127
3	180	201	151	164	167	185
6	195	132	149	171	121	220
10	186	187	128	148	160	137
16	142	177	126	153	91	86
29	34	31	44	66	63	69
59	0	0	0	28	43	0
91 - 93	0	0	0	0	19	0
120 - 125	0	0	0	0	0	0
149 - 153	0	0	0	0	0	0
176 - 183	0	0	0	0	0	0
238 - 248	0	0	0	0	0	0

DAT = days after treatment
calculations are based on actual dry soil density for individual soil layers
residue values <0.005 mg/kg (<LOQ) were reported and treated as zero

M656PH027 degraded fast under field conditions in soil at all four European field sites. The total amount of M656PH027 residues detected in the soil profiles decreased from an average of 170 g/ha at day 0 to an average of 55 g/ha after 1 month. No residues above the LOQ (0.005 mg/kg) were detectable any longer after 4 months at the latest.
M656PH027 residues were mainly detected in the top 0-30 cm layer of the soils. No residues above the LOQ were detected below 40 cm in any sample at any site. Altogether, it can be concluded that M656PH027 shows a moderate tendency to move into deeper soil layers indicating moderate potential for M656PH027 residues to leach to groundwater.
Metabolite M656PH023 was not present in the soil samples. No residues of M656PH023 above the LOQ were detected in any sample at any site.

Conclusion

The study is considered acceptable by the RMS.
M656PH027, a metabolite of dimethenamid, degraded fast under field conditions in soil at all four European field sites. The total amount of M656PH027 residues detected in the soil profiles decreased from an average of 170 g/ha at day 0 to an average of 55 g/ha after 1 month. No residues above the LOQ (0.005 mg/kg) were detectable any longer after 4 months at the latest.
M656PH027 residues were mainly detected in the top 0-30 cm layer of the soils and no residues above the LOQ were detected below 40 cm in any sample at any site. Altogether, it can be concluded that

M656PH027 shows moderate tendency to move into deeper soil layers indicating moderate potential for M656PH027 residues to leach to groundwater.
Metabolite M656PH023 was also monitored during the study. No residues of M656PH023 above the LOQ were detected in any sample at any site.
DT_{50} and DT_{90} values for M656PH027 to be used for persistence calculations and modelling are derived in two separate studies described under under Wiedemann, 2014a and Wiedemann, 2014b.

KCA 7.1.2.2.1/ 5– Bayer & Marwitz, 2014c (new study)

Author:	Bayer, H. Marwitz, A.
Title:	Field soil dissipation study of BAS 656 H (dimethenamid-P) in the formulation BAS 769 00 H on bare soil at two different sites in Europe, 2011-2013
Date:	05/12/2014
Doc ID:	BASF DocID 2013/1343460, study code 380194_1
Guidelines:	NAFTA Guidance Document for Conducting Terrestrial Field Dissipation Studies Regulatory Directive DIR2006-01 (March 2006), EPA 835.6100, SETAC Procedures for assessing the environmental fate and behaviour and ecotoxicity of pesticides (March 1995), EFSA Scientific Opinion on field dissipation studies (2010), SANCO/825/00 rev. 8.1 (16 November 2010), SANCO/3029/99 rev. 4 (11 July 2000)
GLP:	Yes
Validity:	Acceptable

Material and Methods

The dissipation of dimethenamid-P (BAS 656 H) applied in the product BAS 769 00 H and its metabolites M656PH023 (M23 in study), M656PH027 (M27 in study)and M656PH031 (M31 in study) under field conditions were investigated at two sites in Europe representative of Northern EU conditions. One trial each was performed in Germany (L110482) and one in the United Kindom (L110481). The soil characteristics of the respective sites are presented in Table B.8.1.2-66.

Table B.8.1.2-66: Characteristics of the trial sites used to investigate the field dissipation of dimethenamid-P

Trial	L110481		L110482		
Location	Wilson, United Kingdom		Lentzke, Germany		
Soil properties	0 - 30 cm	30 - 90 cm	0 - 38 cm	38 – 66 cm	66 - 90 cm
Soil class (DIN 4220)	Silty loam (Lu)	Poor clay loam (Lt2)	Poor loamy sand (Sl2)	Poor loamy sand (Sl2)	Poor loamy sand (Sl2)
sand [%]	18.7	33.9	72.3	72.3	74.5
silt [%]	56.9	37.7	22.4	21.2	19.7
clay [%]	24.5	28.4	5.2	6.6	5.7
Soil class (USDA)	Silt loam	Silty clay loam	Sandy loam	Sandy loam	Loamy sand
sand [%]	21.2	37.1	75.4	74.2	76.7
silt [%]	56.3	35.5	19.5	18.8	17.3
clay [%]	22.5	27.4	5.1	7.0	6.0
Total organic C [%]	2.48	0.65	0.62	0.17	0.09
Organic matter [%]*	4.28	1.12	1.07	0.29	0.16
pH [$CaCl_2$]	6.84	7.27	5.73	6.04	6.22
pH [H_2O]	7.22	8.31	6.64	7.16	7.22
CEC [mval Ba/100g dry weight]	25.1	17.8	4.2	3.7	3.2
MWHC [g/100g dry weight]	63.8	53.2	43.9	37.9	37.9
pF 2.0 [g/100g dry weight]**	34.9	25.1	14.1	15.5	13.8
pF 2.5 [g/100g dry weight]**	29.0	21.1	12.3	10.8	10.7
Dry bulk density [g/cm^3]***	1.26	-	1.57	-	-
Soil taxonomy	Dystric Cambisol		Albic-Luvisols, Albeluvisol, and Cambisol		

* organic matter = organic carbon x 1.724
** water retention characteristics, soil moisture at 0.1 or 0.33 bar
*** samples taken at 10-20 cm depth (mean of 3 replicates)
CEC = cation exchange capacity
MWHC = maximum water holding capacity

The selected fields represented typical regions of agricultural practice with soils representative for growing crops including oilseed rape, which is among the most important crops for the use of dimethenamid-P. No dimethenamid-P or product from a similar chemical class had been used on the test plots in the previous three years. The crop and pesticide history of the trial sites is presented in Table B.8.1.2-67.

Table B.8.1.2-67: Management history of the trial sites in the previous years (non-GLP)

Trial	Location	Year	Crops grown	Pesticides used
L110481	Wilson, United Kingdom	2008	winter wheat	tebuconazole, chlorothalonil, epoxiconazole, trinexapac-ethyl, amidosulfuron, chlormequat, cyproconazole, propiconazole
		2009	winter wheat	iodosulphuron-methyl-sodium, mesosulfuron-methyl, amidosulfuron, chlormequat, chlorothalonil, cyproconazole, propiconazole, epoxiconazole, trinexapac-ethyl, tebuconazole, prothioconazole, lambda-cyhalothrin
		2010	bare soil	glyphosate
		2011*	bare soil	glyphosate
L110482	Lentzke, Germany-East	2008	winter wheat	tritosulfuron, fluroxypyr, flurasulam, pinoxaden, chloquintocet
		2009	winter wheat	glyphosate
		2010	clover	glyphosate
		2011*	carrots	glyphosate, pendimethalin

* until start of trial

The trial area at each site was divided into two plots, one untreated control plot (size: 18 - 36 m^2) and one treated plot (size: 324 m^2). The treated plot consisted of three equal sized subplots A, B and C that

were assigned for replicates.

The product BAS 769 00 H, formulated as an emulsifiable concentrate (EC), was broadcast applied to bare soil in a single application at a nominal rate of 600 g a.s./ha using a target water volume of 300 L/ha. Applications were conducted in early and in late September 2011 using a calibrated boom sprayer. The actual application rates determined by quantifying the amount of spray discharged ranged from 582 to 626 g a.s./ha for all trials, with an average of 606 g a.s./ha. Results from spray broth analysis revealed a concentration of 102 % of the nominal value. Dose verification conducted via application monitors yielded recovery values for the individual trial sites ranging from 81 to 92 % of the target rate and an average recovery of 87 % over both sites. Further details of application are presented in Table B.8.1.2-68.

Table B.8.1.2-68: Application parameters of the field trial site treated with BAS 769 00 H (EC, 200 g/L)

Trial Country	Application Method	No. of applica-tions	Subplot (m^2)	Application rate per treatment				Application Date
				nominal	actual*	dose verification**		
				[g a.s/ha]	[g a.s./ha]	[g a.s/ha]	% of nominal	
L110481 Wilson United Kingdom	broadcast spray to bare soil	1	A (108)	600	611	481	80	27-Sep-2011
			B (108)	600	600	470	78	
			C (108)	600	606	499	83	
			Average	600	606	484	81	
L110482 Lentzke Germany	broadcast spray to bare soil	1	A (108)	600	610	550	92	9-Sep-2011
			B (108)	600	582	532	89	
			C (108)	600	626	580	97	
			Average	600	606	553	92	

* determined by calculation of spray liquid applied
** determined by means of petri dishes filled with soil

Immediately after application of the test item, the plots were covered with a layer of sand of approximately 4 mm depth to protect the applied product from surface processes like photolysis or volatilisation, and to exclude any potential impact on the degradation of the test item caused by any of these processes. The application of sand was conducted until complete coverage of the soil surface. The layer of sand was controlled up to 27 (Germany) or 29 days after application (UK) and was renewed when needed. It remained intact until at least 27 and 29 days, respectively. Within this time period of 27/29 days, the individual fields received a total precipitation (rain and irrigation) of 25 mm (United Kingdom) and 22 mm (Germany), respectively.

No tillage or fertilisation was performed during the course of the study and no crops were grown throughout any of the trials. The plots were kept free of vegetation via the application of glyphosate. Rainfall was supplemented with irrigation at the site in Germany (111 mm). The field in UK was not irrigated due to adequate rainfall. The total water input at trial sites in United Kingdom and Germany was at least 103 % of the historical average rainfall during the study period.

Actual weather data are based on records of appropriate weather stations located on-site. Monthly summary results on temperature, precipitation and irrigation are presented in Table B.8.1.2-69.

Table B.8.1.2-69: Summary of climatic conditions at field trial sites used to investigate the dissipation of dimethenamid-P

Trial	L110481			L110482		
Location	Wilson			Lentzke		
	United Kingdom			Germany		
Climatic conditions	T_{mean} Air [°C]	Prec. [mm]	Irrigation [mm]	T_{mean} Air [°C]	Prec. [mm]	Irrigation [mm]
Month		∑	∑		∑	∑
Sep 11	18.0	0.0	0.0	13.0	16.6	0.0
Oct 11	12.7	37.6	0.0	7.9	36.8	0.0
Nov 11	9.5	41.0	0.0	2.4	6.0	0.0
Dec 11	6.2	55.6	0.0	2.6	67.8	0.0
Jan 12	5.3	13.8	0.0	-0.1	52.4	0.0
Feb 12	4.2	14.2	0.0	-3.3	23.6	0.0
Mar 12	7.4	26.4	0.0	6.7	10.4	0.0
Apr 12	7.0	104.6	0.0	7.8	24.0	20.2
May 12	11.7	37.2	0.0	13.9	29.0	31.8
Jun 12	13.5	138.4	0.0	14.8	55.4	9.1
Jul 12	15.5	50.0	0.0	17.6	127.4	0.0
Aug 12	16.2	23.6	0.0	17.8	22.4	26.3
Sept 12	12.7	24.8	0.0	13.7	30.0	23.8
Oct 12	9.3	62.6	0.0	8.4	59.8	0.0
Nov 12	6.6	106.4	0.0	4.7	30.0	0.0
Dec 12	4.9	134.2	0.0	-0.1	33.8	0.0
Jan 13	3.7	36.6	0.0	-0.2	63.2	0.0
Feb 13	3.0	31.8	0.0	-0.5	27.2	0.0
Mar 13	2.5	60.8	0.0	2.6	1.0	0.0

The actual air temperature recorded at the field sites during the study period was similar to the historic values. Whereas the site in UK received slightly more rain during the study period compared to historical values, rainfall was less than historic values at the site in Germany. Due to additional irrigation of the field in Germany, the total water input at both test sites during the study was at least 103 % of the historical average rainfall, which is considered sufficient to allow the cultivation of crops like oilseed rape.

Replicate soil specimens (8 per treated subplot and 10 or 15 per control plot) were taken at intervals up to about 548 days and down to a maximum soil depth of 90 cm. At day 0, immediately after application, the treated plots were sampled down to 10 cm only. The detailed sampling intervals are presented in Table B.8.1.2-70.

Table B.8.1.2-70: Summary of sampling intervals at each field trial site

Trial	Country	Sampling intervals [days after treatment]
L110481	United Kingdom	-1, 0, 3, 6, 10, 17, 29, 62, 85, 122, 154, 182, 246, 367, 548
L110482	Germany	-4, 0, 3, 6, 10, 17, 27, 59, 87, 123, [150±5]*, 185, 242, 353, 545

* 150 ± 5 DAT sampling could not be performed due to unfavourable weather conditions

Untreated specimens were collected from the control plot at two occasions, one or four days before application down to a depth of 90 cm, and after about one year to a depth of 10 cm.
Soil cores were cut into 10 cm sections. Soil segments of the same depth and subplot from a defined sampling event were pooled and homogenised and a representative sub-sample of each depth was taken for residue analysis. All soil specimens were stored at about -18 °C within a maximum of 8 hours after sampling and remained frozen until analysis.
In order to demonstrate stability of the residues in soil during storage and any shipments, shipment verification specimens were prepared at selected sampling occasions by fortifying untreated soil from the field sites with known amounts of dimethenamid-P. These specimens were stored and shipped under the same conditions as the actual residue specimens. Analysis of the shipping verification specimens on dimethenamid-P yielded an average recovery value of 77 % across the two sites

confirming residue stability during all storage and shipment procedures.
Soil specimens were analysed for dimethenamid-P and metabolites M656PH02), M656PH027 and M656PH031 according to BASF method L0109/02. Application monitors (Petri dish samples) were analysed for dimethenamid-P. The analytical method involved extraction of the soil with methanol/water (60/40, v/v). The final determination of the analytes was performed by LC-MS/MS with a limit of quantification (LOQ) of 0.005 mg/kg for each analyte. Field soil specimens from the treated plot were analysed down to a depth until at least two consecutive soil segments were free of quantifiable residues (< LOQ). Analysis was performed to a maximum of 367 days after treatment (DAT).
Spray broth specimens were diluted to the appropriate concentration and analysed for dimethenamid-P using HPLC-MS/MS.
Residue values of dimethenamid-P and metabolites M656PH023, M656PH027 and M656PH031 in mg/kg dry soil were converted to residue rates in g/ha taking into account the actual dry soil density of the individual field samples, and were summed up for all depths between 0 and 50 cm analysed. Residue values were not corrected for procedural recoveries except for results obtained from petri dish and shipment verification analysis.

Results and Discussion

No residues above 30 % of the LOQ of any analyte were detected in any of the untreated control samples proving that there were no interferences of the untreated soil material with the analytical procedures used.
Procedural recovery experiments performed with untreated field soils spiked with the four analytes at concentration levels of 0.005, 0.01 and 0.05 mg/kg yielded overall mean recovery rates between 85 and 93 % for the individual analytes, confirming the validity of the analytical method used in this study.
Field soil specimens from the treated plots were analysed down to a depth until at least two consecutive soil segments were free of quantifiable residues (< LOO of 0.005 mg/kg, maximum depth of 60 cm).
The residue data of dimethenamid-P, M656PH023, M656PH027 and M656PH031 summed up for all depth between 0 and 50 cm and converted to g/ha are presented in Table B.8.1.2-71, Table B.8.1.2-72, Table B.8.1.2-73 and Table B.8.1.2-74.

Table B.8.1.2-71: Total residues of dimethenamid-P under field conditions in soil calculated to g/ha and summed up for all depths analysed

Trial Country	L110481 Wilson, United Kingdom			L110482 Lentzke, Germany		
	Replicate A	Replicate B	Replicate C	Replicate A	Replicate B	Replicate C
DAT	[g/ha]	[g/ha]	[g/ha]	[g/ha]	[g/ha]	[g/ha]
0	708	570	496	456	459	416
3	530	251	485	353	293	326
6	588	416	222	283	295	249
10	287	341	395	217	236	305
17	418	348	191	150	153	170
27-29	253	175	212	78	86	81
59-62	125	136	158	50	50	35
85-87	92	147	77	31	42	24
122-123	52	79	49	40	38	31
154	58	69	58	*	*	*
182-185	69	30	43	22	15	13
242-246	0	8.1	13	0	0	0
367	0	0	0			

* no sample taken due to bad weather conditions
calculations are based on actual dry soil density for individual soil layers
residue values <0.005 mg/kg (<LOQ) were reported and treated as zero
DAT = days after treatment

Table B.8.1.2-72: Total residues of M656PH023 under field conditions in soil calculated to g/ha and summed up for all depths analysed

Trial Country	L110481 Wilson, United Kingdom			L110482 Lentzke, Germany		
DAT	Replicate A	Replicate B	Replicate C	Replicate A	Replicate B	Replicate C
	[g/ha]	[g/ha]	[g/ha]	[g/ha]	[g/ha]	[g/ha]
0	0	0	0	0	0	0
3	0	0	0	0	0	0
6	0	0	0	0	0	0
10	0	0	0	0	0	0
17	11	6.6	7.5	0	0	0
27-29	13	6.1	15	0	0	0
59-62	7.2	7.0	16	0	0	0
85-87	0	0	0	0	0	0
122-123	0	0	0	0	0	0
154	0	0	0	*	*	*
182-185	0	0	0	0	0	0
242-246	0	0	0	0	0	0
367	0	0	0			

* no sample taken due to bad weather conditions
calculations are based on actual dry soil density for individual soil layers
residue values <0.005 mg/kg (<LOQ) were reported and treated as zero
DAT = days after treatment

Table B.8.1.2-73: Total residues of M656PH027 under field conditions in soil calculated to g/ha and summed up for all depths analysed

Trial Country	L110481 Wilson, United Kingdom			L110482 Lentzke, Germany		
DAT	Replicate A	Replicate B	Replicate C	Replicate A	Replicate B	Replicate C
	[g/ha]	[g/ha]	[g/ha]	[g/ha]	[g/ha]	[g/ha]
0	0	0	0	0	0	0
3	0	0	0	0	0	0
6	0	0	0	0	0	0
10	0	0	0	0	0	0
17	14	13	7.5	0	0	0
27-29	20	12	23	0	0	0
59-62	38	35	48	0	0	0
85-87	42	30	36	0	0	0
122-123	22	28	12	0	0	0
154	40	31	24	*	*	*
182-185	53	28	26	0	0	0
242-246	0	0	0	0	0	0
367	0	0	0			

* no sample taken due to bad weather conditions
calculations are based on actual dry soil density for individual soil layers
residue values <0.005 mg/kg (<LOQ) were reported and treated as zero
DAT = days after treatment

Table B.8.1.2-74: Total residues of M656PH031 under field conditions in soil calculated to g/ha and summed up for all depths analysed

Trial Country	L110481 Wilson, United Kingdom			L110482 Lentzke, Germany		
DAT	Replicate A	Replicate B	Replicate C	Replicate A	Replicate B	Replicate C
	[g/ha]	[g/ha]	[g/ha]	[g/ha]	[g/ha]	[g/ha]
0	0	0	0	0	0	0
3	0	0	0	0	0	0
6	0	0	0	0	0	0
10	0	0	0	0	0	0
17	12	0	11	0	0	0
27-29	8.8	0	8.7	0	0	0
59-62	0	0	9.3	0	0	0
85-87	0	0	0	0	0	0
122-123	0	0	0	0	0	0
154	0	0	0	*	*	*
182-185	0	0	0	0	0	0
242-246	0	0	0	0	0	0
367	0	0	0			

* no sample taken due to bad weather conditions
calculations are based on actual dry soil density for individual soil layers
residue values <0.005 mg/kg (<LOQ) were reported and treated as zero
DAT = days after treatment

Dimethenamid-P degraded fast under field conditions in soil at both European field sites. The total amount of dimethenamid-P residues in the soil profiles decreased from an average of 518 g/ha at day 0 to an average of 32 g/ha (range: 13-69 g/ha) after six months. No residues above the LOQ (0.005 mg/kg) were detectable any longer after 8 or 12 months. At the site in Germany, no residues above the LOQ were left after 242 days.
Residues of dimethenamid-P were exclusively detected in the upper 10 cm of the soils. Therefore, it can be concluded that dimethenamid-P does not show any tendency to move into deeper soil layers indicating low potential for dimethenamid-P residues to leach to groundwater.
The metabolites M656PH023, M656PH027 and M656PH031 were temporarily detected in small amounts only at the site in the United Kingdom reaching maximum amounts of 3.17 % Ar (= 16 g/ha), 7.37 % (= 53 g/ha), and 2.14 % (= 12 g/ha), respectively. Thereafter, residues declined again and were no longer detected after 182 days at the latest. At the site in Germany, no residues of the three metabolites above the LOQ (0.005 mg/kg) were detected in any sample. Metabolites M656PH023 and M656PH031 were exclusively found in the top 0-10 cm soil layer. Metabolite M656PH027 was detected in the 0-30 cm soil layer.

Conclusion

The study is considered acceptable by the RMS.
Dimethenamid-P degraded fast under field conditions in soil at two European field sites in Germany and the United Kingdom. The total amount of dimethenamid-P residues in the soil profiles decreased from an average of 518 g/ha at day 0 to an average of 32 g/ha after six months. No residues above the LOQ (0.005 mg/kg) were detectable any longer after 8 or 12 months. DT_{50} values are supposed to be low and are presented in separate modelling reports.
Dimethenamid-P residues were exclusively detected in the upper 10 cm of the soils. Therefore, it can be concluded that dimethenamid-P does not show any tendency to move into deeper soil layers indicating low potential for dimethenamid-P residues to leach to groundwater.
The metabolites M656PH023, M656PH027 and M656PH031 were temporarily detected only at the site in the United Kingdom reaching maximum amounts of 16 g/ha, 53 g/ha, and 12 g/ha, respectively. At the site in Germany, no residues of the three metabolites above the LOQ (0.005 mg/kg) were detected in any sample.
The metabolites M656PH023 and M656PH031 were only found in the top 0-10 cm soil layer.

Metabolite M656PH027 was detected in the 0-30 cm layer.
DT_{50} and DT_{90} values for dimethenamid-P and its metabolites to be used for persistence calculations and modelling are derived in two separate studies described under Wiedemann, 2014a and Wiedemann, 2014b..

KCA 7.1.2.2.1/ 6–Mewis, 2014a (new study)

Author:	Mewis, A.
Title:	Determination of the storage stability of dimethenamid-P and its metabolites M23, M27 and M31 in 4 soils under deep frozen conditions
Date:	13/03/2014
Doc ID:	BASF DocID 2013/1348019
Guidelines:	EPA 860.1380
GLP:	Yes
Validity:	Acceptable

Material and Methods

The storage stability of dimethenamid-P (CAS No 163515-14-8, puritiy 96.4 %) and its metabolites M656PH023 (M23 in this study, puritiy 98.8 %), M656PH027 (M27 in this study, sodium salt, three batches puritiy 97.1 %, 97.4 % & 97.1 %) and M656PH031 (M31 in this study, puritiy 98.7 %) in deep-frozen soil over a storage period of up to 29 months was examined in four soils from the trials L110061, L110062, L110063 and L110064 of the field study
KCA 7.1.2.2.1/ 3– Bayer & Marwitz, 2014a.
The homogenised soil samples were stored deep-frozen. 5 g of matrix sample was fortified at 0.1 mg/kg (20 x LOQ) of each analyte (separate systems). The test items were distributed to the entire sample with a solvent volume of maximum 500 µL per sample. For each storage interval and matrix a set of at least 4 samples (2 samples for analysis plus 2 backup samples) was prepared.
The temperatures in the freezer were recorded during the entire storage period; temperatures ranged from a minimum of -25 °C to a maximum of -14 °C with a mean temperature of -22 °C. The samples were analysed at least in duplicate, after fortification and storage for 0, 1, 2, 4, 8, 12, 18 and 29 months. In addition, blank matrix samples and freshly fortified recovery samples were analysed at the analysis dates.
For the determination of dimethenamid-P and its metabolites, soil samples were analysed by method L0109/02. The samples were extracted twice with 20 mL of methanol/water (60:40, v/v). The final determination was performed by HPLC-MS/MS detection using at least two characteristic fragment ions.

Results and Discussion

Residues of dimethenamid-P and its metabolites M656PH023, M656PH027 and M656PH031 were determined after deep-frozen storage for 0, 1, 2, 4, 8, 12, 18 and 29 months. The results are given in Table B.8.1.2-75, Table B.8.1.2-76, Table B.8.1.2-77 and Table B.8.1.2-78.

Table B.8.1.2-75: Results of the storage stability of dimethenamid-P in soil

Test item	Storage period	Recovery [% of initial amount]			
		Soil L110061	Soil L110062	Soil L110063	Soil L110064
Dimethenamid-P	0 months	100	100	100	100
	1 months	110	110	110	109
	2 months	102	96	97	100
	4 months	98	95	95	94
	8 months	83	85	83	90
	12 months	92	90	93	93
	18 months	87	88	93	90
	29 months	104	103	99	99

Table B.8.1.2-76: Results of the storage stability of M656PH023 in soil

Test item	Storage period	Recovery [% of initial amount]			
		Soil L110061	Soil L110062	Soil L110063	Soil L110064
M656PH023	0 months	100	100	100	100
	1 months	105	105	102	100
	2 months	99	106	96	98
	4 months	104	106	103	101
	8 months	78	92	96	89
	12 months	86	85	77	84
	18 months	84	77	75	85
	29 months	89	85	84	87

Table B.8.1.2-77: Results of the storage stability of M656PH027 in soil

Test item	Storage period	Recovery [% of initial amount]			
		Soil L110061	Soil L110062	Soil L110063	Soil L110064
M656PH027	0 months	100	100	100	100
	1 months	102	98	94	96
	2 months	107	107	101	102
	4 months	110	104	102	101
	8 months	86	91	88	89
	12 months	97	91	93	90
	18 months	96	86	91	91
	29 months	92	88	87	84

Table B.8.1.2-78: Results of the storage stability of M656PH031 in soil

Test item	Storage period	Recovery [% of initial amount]			
		Soil L110061	Soil L110062	Soil L110063	Soil L110064
M656PH031	0 months	100	100	100	100
	1 months	95	101	103	105
	2 months	98	107	102	104
	4 months	99	105	104	103
	8 months	91	104	91	97
	12 months	78	86	77	86
	18 months	79	91	80	90
	29 months	77	95	86	94

The recovery values in this study did not fall below 70 % of the initial value at any time point and for each analyte. Thus, residues of dimethenamid-P and its metabolites M656PH023, M656PH027 and M656PH031 can be regarded as stable in the matrix soil for at least 29 months.

Conclusion

The study is considered acceptable by the RMS.
The deep-frozen storage stability of dimethenamid-P and its metabolites M656PH023, M656PH027 and M656PH031 in four soils was investigated over a storage period of up to 29 months. Residues of dimethenamid-P and its metabolites M656PH023, M656PH027 and M656PH031 can be regarded as stable in the matrix soil for at least 29 months of storage under deep-freeze conditions.

KCA 7.1.2.2.1/ 7–Mewis, 2014b (new study)

Author:	Mewis, A.
Title:	Determination of the storage stability of dimethenamid-P and its metabolites M23, M27 and M31 in 2 soils under deep frozen conditions
Date:	24/03/2014
Doc ID:	BASF DocID 2013/1348029
Guidelines:	EPA 860.1380
GLP:	Yes
Validity:	Acceptable

Material and Methods

The storage stability of dimethenamid-P (CAS No 163515-14-8, puritiy 96.4 %) and its metabolites M656PH023 (M23 in the study, puritiy 98.8 %), M656PH027 (M27 in the study, sodium salt, three batches puritiy 97.1 %, 97.4 % & 97.1 %) and M656PH031 (M31 in the study, puritiy 98.7 %) in deep-frozen soil over a storage period of up to 23 months was examined in two soils from the trials L110481 and L110482 of the field study KCA 7.1.2.2.1/ 5– Bayer & Marwitz, 2014c.
Two homogenised soil samples from the field trials were stored deep-frozen. 5 g of matrix sample was fortified at 0.1 mg/kg (20 x LOQ) of each analyte (separate systems). The test items were distributed to the entire sample with a solvent volume of maximum 500 µL per sample. For each storage interval and matrix a set of at least 4 samples (2 samples for analysis plus 2 backup samples) was prepared.
The temperatures in the freezer were recorded during the entire storage period; temperatures ranged from a minimum of -25 °C to a maximum of -14 °C with a mean temperature of -22 °C. The samples were analysed at least in duplicate, after fortification and storage for 0, 1, 2, 4, 8, 12 and 23 months. In addition, blank matrix samples and freshly fortified recovery samples were analysed at the analysis dates.
For the determination of dimethenamid-P and its metabolites, soil samples were analysed by method L0109/02. The samples were extracted twice with 20 mL of methanol/water (60:40, v/v).
The final determination was performed by HPLC-MS/MS detection using at least two characteristic fragment ions.

Results and Discussion

Residues of dimethenamid-P and its metabolites M656PH023, M656PH027 and M656PH031 were determined after deep-frozen storage for 0, 1, 2, 4, 8, 12 and 23 months. The results are given in

Table B.8.1.2-79: Results of the storage stability of dimethenamid-P in soil

Test item	Storage period	Recovery [% of initial amount]	
		Soil L110481	Soil L110482
dimethenamid-P	0 months	100	100
	1 months	115	109
	2 months	106	100
	4 months	127	119
	8 months	127	121
	12 months	101	101
	23 months	99	98

Table B.8.1.2-80: Results of the storage stability of M656PH023 in soil

Test item	Storage period	Recovery [% of initial amount]	
		Soil L110481	Soil L110482
M656PH023	0 months	100	100
	1 months	102	102
	2 months	95	91
	4 months	112	114
	8 months	111	102
	12 months	105	105
	23 months	101	97

Table B.8.1.2-81: Results of the storage stability of M656PH027 in soil

Test item	Storage period	Recovery [% of initial amount]	
		Soil L110481	Soil L110482
M656PH027	0 months	100	100
	1 months	111	109
	2 months	102	97
	4 months	120	121
	8 months	106	109
	12 months	113	114
	23 months	92	92

Table B.8.1.2-82: Results of the storage stability of M656PH031 in soil

Test item	Storage period	Recovery [% of initial amount]	
		Soil L110481	Soil L110482
M656PH031	0 months	100	100
	1 months	107	103
	2 months	98	100
	4 months	115	115
	8 months	115	98
	12 months	90	88
	23 months	86	86

The recovery values in this study did not fall below 80 % of the initial value at any time point and for each analyte. Thus, residues of dimethenamid-P and its metabolites M656PH023, M656PH027 and M656PH031 can be regarded as stable in the matrix soil for at least 23 months.

Conclusion

The study is considered acceptable by the RMS.
The deep-frozen storage stability of dimethenamid-P and its metabolites M656PH023, M656PH027 and M656PH031 in two soils was investigated over a storage period of up to 23 months. Residues of dimethenamid-P and its metabolites M656PH023, M656PH027 and M656PH031 can be regarded as stable in the matrix soil for at least 23 months of storage under deep-freeze conditions.

KCA 7.1.2.2.1/ 8–Wiedemann, 2014a (new study)

Author:	Wiedemann, G.
Title:	Calculation of persistence half-lives from terrestrial field dissipation studies with dimethenamid-P and its metabolite M27 according to Focus kinetics
Date:	02/12/2014
Doc ID:	BASF DocID 2014/1031649, study code CALC-1833
Guidelines:	FOCUS Degradation Kinetics (2011) Sanco/10058/2005 version 2.0
GLP:	No (not applicable)
Validity:	Acceptable

Aim of the study

Two field dissipation studies Bayer & Marwitz, 2014a & c (six trials) with the active substance dimethenamid-P and one study Bayer & Marwitz, 2014b (four trials) with the dimethenamid-P soil metabolite M656H027 (M27 in the study) were evaluated to derive non-normalised persistence endpoints following the recommendations of the guidelines by the FOCUS work group on degradation kinetics (FOCUS, 2011).

Material and Methods

All replicate values were used in the optimisation without averaging. The main part of the residues was found in 0 - 20 cm depth; below 40 cm, no residues > LOQ were detected in any of the samplings. For modelling, the observed residues in the different layers were added.
In the parent study, the main metabolites M656PH023 (M23 in study), M656PH027 and M656PH031 (M31 in the study) were analysed. However, in many trials not enough data points were available to perform a kinetic evaluation: Degradation of M656PH023 was assessed in three out of six trials with dimethenamid-P, degradation of M656PH027 as metabolite in five trials. Degradation of M656PH031 could not be assessed in any of the trials.
LOQ and LOD (limit of quantification / detection) were 0.005 mg kg^{-1} and 0.001 mg kg^{-1} in all trials. Concentrations given as "< LOQ" were treated according to the guidance of FOCUS (2011): The first sample < LOQ after or before a sample with detection of M656PH027 was set to 0.5 x (LOQ + LOD). All following samples < LOQ were ignored. This rule was applied temporally and also spatially; i.e. if M656PH027 was detected in layer 0 – 10 cm but not in any layer below, the value for layer 10 – 20 cm was set to 0.5 x (LOQ + LOD).
The processed residues for dimethenamid-P and its metabolites used for kinetic evaluation are presented in Table B.8.1.2-83 to Table B.8.1.2-92.

Table B.8.1.2-83: Total residues of dimethenamid-P and its metabolites under field conditions in soil processed for kinetic evaluation (trial L110061)

Trial Country	dimethenamid-P			M656PH027		
DAT	Replicate A [g/ha]	Replicate B [g/ha]	Replicate C [g/ha]	Replicate A [g/ha]	Replicate B [g/ha]	Replicate C [g/ha]
0	674.1	742.5	724.3	--	--	--
3	592.9	767.5	718.0	--	--	--
6	357.0	729.5	780.5	--	--	--
10	393.8	504.5	501.9	--	--	2.5
16	277.7	319.1	485.9	4.8	2.8	11.0
28	449.8	422.7	166.2	24.8	11.1	12.9
59	110.6	67.5	56.6	30.7	39.2	34.S
85	44.5	50.6	44.9	21.5	24.1	1S.0
120	21.6	37.8	33.8	4.9	5.1	2.7
150	21.5	30.8	19.9	--	--	--
175	15.3	29.6	23.5	--	--	--
233	18.4	24.0	14.4	--	--	--
366	2.6	2.6	2.6	--	--	--

Table B.8.1.2-84: Total residues of dimethenamid-P and its metabolites under field conditions in soil processed for kinetic evaluation (trial L110062)

Trial Country	dimethenamid-P			M656PH027		
DAT	Replicate A [g/ha]	Replicate B [g/ha]	Replicate C [g/ha]	Replicate A [g/ha]	Replicate B [g/ha]	Replicate C [g/ha]
0	531.5	625.2	890.4	--	--	--
3	741.8	808.5	886.6	--	--	--
6	735.5	834.2	850.5	--	--	--
10	769.4	647.8	625.7	1.9	2.0	1.9
16	460.2	400.6	539.2	8.7	9.0	9.9
28	226.3	158.1	152.3	33.S	35.5	32.0
58	9.9	10.1	8.5	4.8	14.8	4.5
92	1.6	1.5	1.S	--	3.0	--

DAT	M656PH023		
	Replicate A [g/ha]	Replicate B [g/ha]	Replicate C [g/ha]
0	--	--	--
3	--	--	--
6	2.1	--	2.3
10	7.5	4.2	9.0
16	9.7	17.9	15.1
28	13.4	11.0	13.3
58	2.1	2.1	1.9
92	--	--	--

Table B.8.1.2-85: Total residues of dimethenamid-P and its metabolites under field conditions in soil processed for kinetic evaluation (trial L110063)

Trial Country	dimethenamid-P			M656PH027		
DAT	Replicate A [g/ha]	Replicate B [g/ha]	Replicate C [g/ha]	Replicate A [g/ha]	Replicate B [g/ha]	Replicate C [g/ha]
0	860.5	721.2	807.0	--	--	--
3	749.6	763.7	763.1	--	--	--
6	761.1	759.8	605.8	--	--	--
10	540.7	781.8	765.3	5.1	5.2	2.S
19	340.4	373.9	219.9	24.4	24.2	14.0
28	125.1	160.9	125.4	28.6	47.7	33.3
59	10.4	17.9	11.1	17.0	5.7	15.5
94	2.4	2.4	2.5	2.2	--	2.7

Table B.8.1.2-86: Total residues of dimethenamid-P and its metabolites under field conditions in soil processed for kinetic evaluation (trial L110064)

Trial Country	dimethenamid-P			M656PH027		
DAT	Replicate A [g/ha]	Replicate B [g/ha]	Replicate C [g/ha]	Replicate A [g/ha]	Replicate B [g/ha]	Replicate C [g/ha]
0	939.5	887.2	999.4	--	--	--
3	586.0	898.8	631.4	--	--	--
6	693.5	684.0	879.3	--	--	--
10	350.8	760.6	684.2	3.3	3.4	--
17	613.6	508.3	459.5	13.0	18.0	3.7
31	286.7	157.4	177.0	50.7	39.7	31.0
60	19.3	20.5	21.8	43.4	35.5	26.2
95	2.9	3.0	2.9	5.8	23.7	21.7
116	--	--	--	16.2	30.0	5.8
151	--	--	--	3.0	5.8	--

DAT	M656PH023		
	Replicate A [g/ha]	Replicate B [g/ha]	Replicate C [g/ha]
0	--	--	--
3	--	--	--
6	--	--	--
10	3.3	3.4	3.5
17	14.8	19.9	17.5
31	43.4	36.2	29.2
60	19.3	19.0	17.5
95	2.9	3.0	2.9
116	--	--	--
151	--	--	--

Table B.8.1.2-87: Total residues of dimethenamid-P and its metabolites under field conditions in soil processed for kinetic evaluation (trial L110481)

Trial Country	dimethenamid-P			M656PH027		
DAT	Replicate A [g/ha]	Replicate B [g/ha]	Replicate C [g/ha]	Replicate A [g/ha]	Replicate B [g/ha]	Replicate C [g/ha]
0	710.6	572.3	498.0	--	--	--
3	532.2	253.4	487.4	--	--	--
6	590.2	417.9	223.6	--	--	--
10	288.9	343.0	397.9	1.9	1.9	1.S
17	420.3	350.0	193.3	16.2	15.2	9.9
29	255.2	177.0	214.1	22.7	14.2	25.8
62	127.4	138.2	160.2	40.3	37.S	51.1
85	95.0	149.3	79.9	45.0	32.9	39.3
122	54.8	81.4	51.4	27.6	32.8	14.6
154	60.9	71.7	50.6	42.8	33.7	27.0
182	71.9	32.0	45.0	55.7	31.3	28.8
246	2.2	10.8	15.4	7.6	7.3	7.7
367	--	3.2	2.9	--	--	--

DAT	M656PH023		
	Replicate A [g/ha]	Replicate B [g/ha]	Replicate C [g/ha]
0	--	--	--
3	--	--	--
6	--	--	--
10	1.9	1.9	1.9
17	13.0	8.6	9.9
29	14.9	8.1	17.1
62	9.4	9.0	17.S
85	2.0	1.9	2.1
122	--	--	--
154	--	--	--
182	--	--	--
246	--	--	--
367	--	--	--

Table B.8.1.2-88: Total residues of dimethenamid-P and its metabolites under field conditions in soil processed for kinetic evaluation (trial L110482)

Trial Country	dimethenamid-P		
DAT	Replicate A [g/ha]	Replicate B [g/ha]	Replicate C [g/ha]
0	459.2	461.9	419.4
3	356.2	295.8	329.0
6	285.9	298.5	251.7
10	219.5	239.4	308.2
17	153.4	156.1	172.8
27	80.4	89.2	83.5
59	53.3	53.1	38.3
87	34.2	45.4	27.0
123	43.2	41.0	33.8
185	24.3	18.2	16.3
242	3.1	3.0	3.1

Table B.8.1.2-89: Total residues of the metabolite M656PH027 under field conditions in soil (direct application) processed for kinetic evaluation (trial L110330)

Trial Country	M656PH027		
DAT	Replicate A [g/ha]	Replicate B [g/ha]	Replicate C [g/ha]
0	160.7	143.3	174.0
3	158.0	151.4	214.8
6	184.9	150.8	214.2
10	256.8	138.9	134.0
17	166.3	104.0	115.3
31	110.8	54.5	78.0
60	58.7	54.2	41.0
85	41.6	26.6	5.9
120	6.2	2.9	--

Table B.8.1.2-90: Total residues of the metabolite M656PH027 under field conditions in soil (direct application) processed for kinetic evaluation (trial L110331)

Trial Country	M656PH027		
DAT	Replicate A [g/ha]	Replicate B [g/ha]	Replicate C [g/ha]
0	178.5	178.5	195.2
3	147.0	152.2	143.3
6	113.6	105.0	163.1
10	74.6	93.3	111.9
16	74.6	67.7	79.7
28	39.4	46.3	41.1
58	4.6	4.9	4.7

Table B.8.1.2-91: Total residues of the metabolite M656PH027 under field conditions in soil (direct application) processed for kinetic evaluation (trial L110332)

Trial Country	M656PH027		
DAT	Replicate A [g/ha]	Replicate B [g/ha]	Replicate C [g/ha]
0	166.6	174.0	218.3
3	182.7	203.3	153.5
6	197.1	134.5	151.3
10	188.0	192.4	130.5
16	144.2	180.0	128.1
29	36.6	33.8	46.7
59	5.3	5.5	5.4

Table B.8.1.2-92: Total residues of the metabolite M656PH027 under field conditions in soil (direct application) processed for kinetic evaluation (trial L110333)

Trial Country	M656PH027		
DAT	Replicate A [g/ha]	Replicate B [g/ha]	Replicate C [g/ha]
0	186.8	165.7	129.6
3	166.6	170.0	188.1
6	173.3	123.5	222.8
10	151.2	162.6	139.9
16	155.8	94.0	88.7
29	69.0	65.5	71.9
59	28.9	46.1	5.3
91	5.6	22.3	--
120	--	5.8	--

The processed residue data were evaluated according to recommended procedures as given in the guideline of the FOCUS Work Group on Degradation Kinetics (2011) using the software package KinGUI (version 2).
In trials with dimethenamid-P and metabolites, the parent parameters were fitted in a first step with SFO and FOMC kinetics. The parameters of this SFO or FOMC model (depending on which model gave a better fit) were considered as relevant for the parent substance. In a second step, all parameters for parent and metabolites were fitted simultaneously using the best-fit model for the parent and SFO kinetics for the metabolites.
Additionally, the trials were evaluated according to criteria compiled by the Dutch regulatory authority (CTB) in order to ensure that the field study is adequately performed, and that samples are adequately taken and analysed.

Results and Discussion

The degradation of dimethenamid-P under field conditions was analysed in six trials. Only SFO and FOMC kinetics were tested since these already provided good fits. No outliers were identified in any of the trials. Details for each location are presented in the following tables. The graphs show the results of the best fit model. The following results are taken from the fits for dimethenamid-P without metabolites.
The statistical and visual assessment of the kinetic models for dimethenamid-P applied in the six field trials L110060, L110061, L110062, L110063, L110064, L110481 and L110482 is given in Table B.8.1.2-93 to Table B.8.1.2-98. The visual fits of the finally chosen model for dimethenamid-P is presented in Figure B.8.1.2-21 to Figure B.8.1.2-23.
The degradation of M656PH027 as a metabolite of dimethenamid-P was evaluated for trials L110061, L110062, L110063, L110064 and L110481; for metabolite M656PH023, trials L110062, L110064 and L110481 were considered. The fitted curves for M656PH027 and M656PH023 in all these trials are visually poor, and the χ^2 are always > 30 %. Therefore, the resulting parameters are not considered acceptable as persistence endpoints for environmental risk assessments.
The statistical and visual assessment of the kinetic models for M656PH027 applied four field trials L110330 to L110334 is given in Table B.8.1.2-99 to Table B.8.1.2-102. The visual fits of the finally chosen model for M656PH027 is presented in Figure B.8.1.2-24 and Figure B.8.1.2-25.

Table B.8.1.2-93: Statistical and visual assessment of kinetic models for dimethenamid-P in trial L110061 – persistence endpoints

Kinetic Model	Fitted parameters	χ^2 error	p (t-test)*	Visual assessment	$DegT_{50}$ [d]	$DegT_{90}$ [d]
SFO	M_0: 726 k: 0.0340 d^{-1}	10.5	k: < 0.001	Good	20.4	67.7
FOMC	M_0: 746 Alpha: 523 Beta: 13550	11.5	Alpha: 0.369 Beta: 0.370	Good	18.0	59.8
→ SFO fit visually and statistically good. FOMC visually good, but t-test fails.						
→ **Conclusion: The degradation of dimethenamid-P is well described using SFO kinetics.**						

* Type I error rate

Table B.8.1.2-94: Statistical and visual assessment of kinetic models for dimethenamid-P in trial L110062 – persistence endpoints

Kinetic Model	Fitted parameters	χ^2 error	p (t-test)*	Visual assessment	$DegT_{50}$ [d]	$DegT_{90}$ [d]
SFO	M_0: 858 k: 0.0393 d^{-1}	17.3	k: < 0.001	Good	17.6	58.6
FOMC	M_0: 915 Alpha: 1047 Beta: 19956	21.0	Alpha: 0.126 Beta: 0.126	Good	13.2	43.9
→ SFO fit visually and statistically good. FOMC visually good, but t-test fails.						
→ **Conclusion: The degradation of dimethenamid-P is well described using SFO kinetics**.						

* Type I error rate

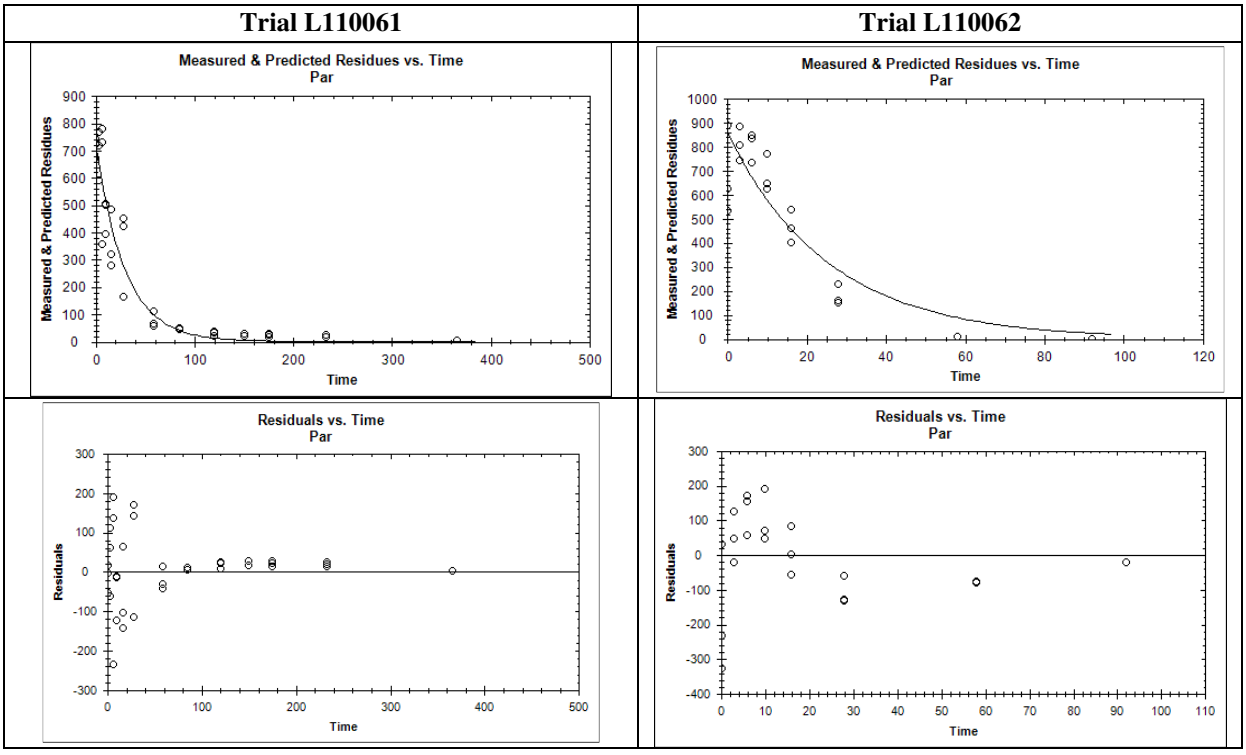


Figure B.8.1.2-21: SFO fit for dimethenamid-P in the trials L110061 and L110062– persistence endpoints

Table B.8.1.2-95: Statistical and visual assessment of kinetic models for dimethenamid-P in trial L110063 – persistence endpoints

Kinetic Model	Fitted parameters	χ^2 error	p (t-test)*	Visual assessment	$DegT_{50}$ [d]	$DegT_{90}$ [d]
SFO	M_0: 880 k: 0.0 479d^{-1}	13.8	k: < 0.001	Good	14.5	48.1
FOMC	M_0: 960 Alpha: 861 Beta: 12179	20.7	Alpha: 0.363 Beta: 0.363	Good	9.8	32.6
→ SFO fit visually and statistically good. FOMC visually good, but t-test fails.						
→ **Conclusion: The degradation of dimethenamid-P is well described using SFO kinetics**.						

* Type I error rate

Table B.8.1.2-96: Statistical and visual assessment of kinetic models for dimethenamid-P in trial L110064 – persistence endpoints

Kinetic Model	Fitted parameters	χ^2 error	p (t-test)*	Visual assessment	$DegT_{50}$ [d]	$DegT_{90}$ [d]
SFO	M_0: 913 k: 0.0421 d^{-1}	9.2	k: < 0.001	Good	16.5	54.7
FOMC	M_0: 955 Alpha: 1112 Beta: 21617	11.7	Alpha: 0.338 Beta: 0.338	Good	13.5	44.8
→ SFO fit visually and statistically good. FOMC visually good, but t-test fails.						
→ **Conclusion: The degradation of dimethenamid-P is well described using SFO kinetics**.						

* Type I error rate

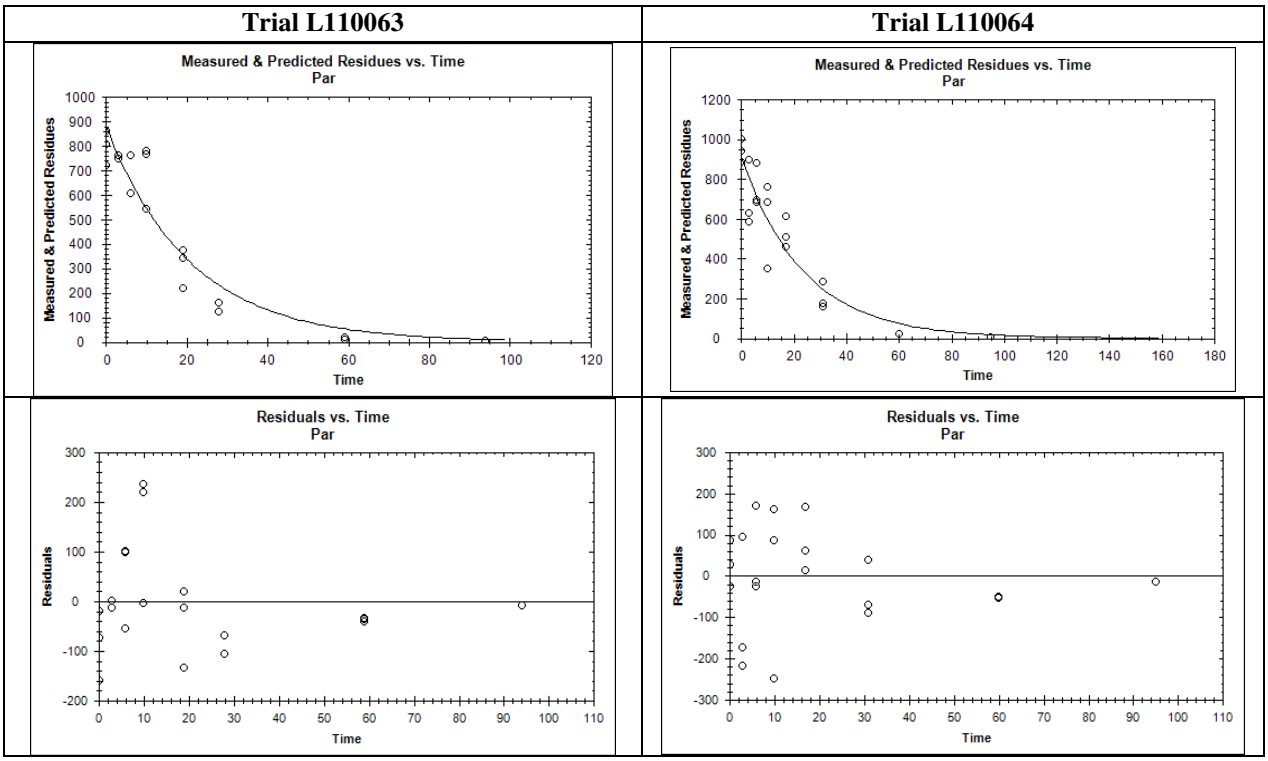


Figure B.8.1.2-22: SFO fit for dimethenamid-P in the trials L110063 and L110064 – persistence endpoints

Table B.8.1.2-97: Statistical and visual assessment of kinetic models for dimethenamid-P in trial L110481 – persistence endpoints

Kinetic Model	Fitted parameters	χ^2 error	p (t-test)*	Visual assessment	$DegT_{50}$ [d]	$DegT_{90}$ [d]
SFO	M_0: 490 k: 0.0224 d^{-1}	16.2	k: < 0.001	Good	31.0	103
FOMC	M_0: 559 Alpha: 0.955 Beta: 16.5	9.3	Alpha: 0.005 Beta: 0.089	Good	17.6	167
→ SFO and FOMC fits both statistically good, FOMC visually better than SFO						
→ **Conclusion: The degradation of dimethenamid-P is well described using FOMC kinetics**.						

* Type I error rate

Table B.8.1.2-98: Statistical and visual assessment of kinetic models for dimethenamid-P in trial L110482 – persistence endpoints

Kinetic Model	Fitted parameters	χ^2 error	p (t-test)*	Visual assessment	$DegT_{50}$ [d]	$DegT_{90}$ [d]
SFO	M_0: 420 k: 0.0565 d^{-1}	12.5	k: < 0.001	Acceptable	12.3	40.8
FOMC	M_0: 441 Alpha: 1.36 Beta: 15.4	8.3	Alpha: < 0.001 Beta: 0.003	Good	10.2	68.2
→ SFO and FOMC fits both statistically good, FOMC visually better than SFO						
→ **Conclusion: The degradation of dimethenamid-P is well described using FOMC kinetics**.						

* Type I error rate

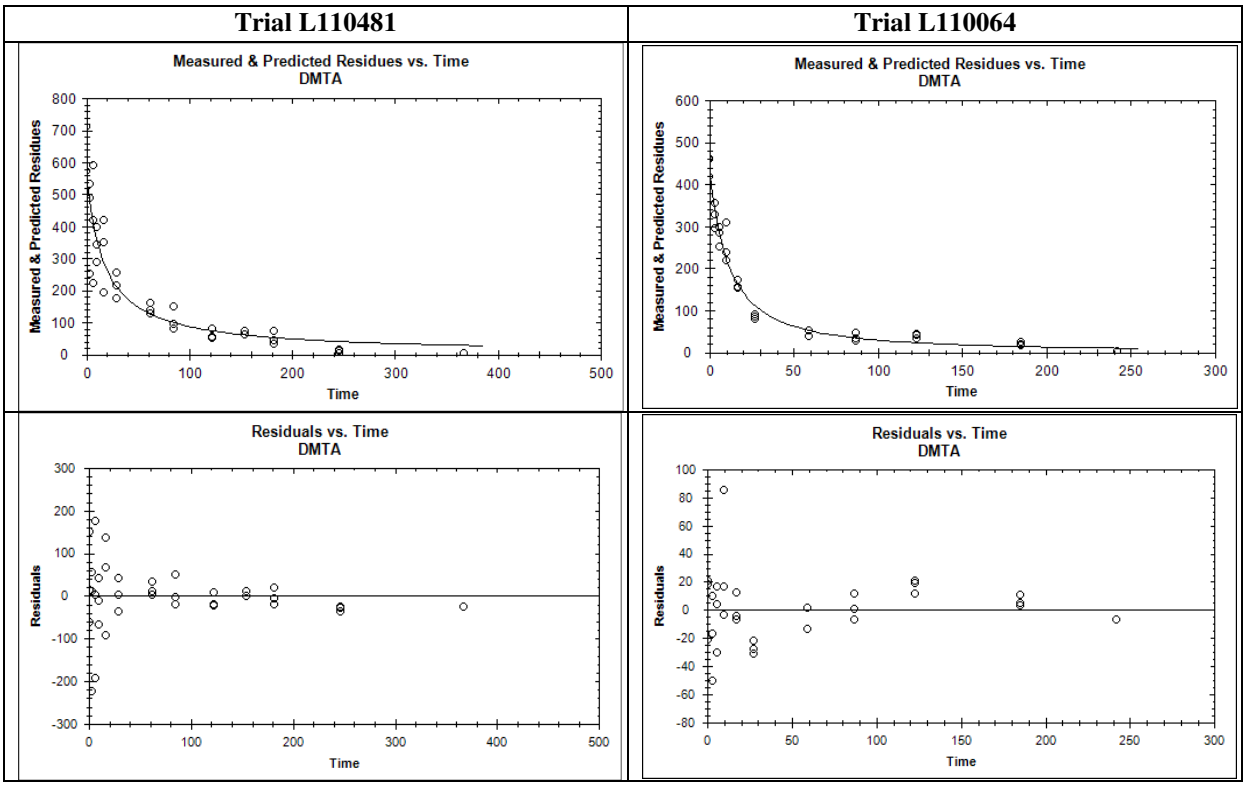


Figure B.8.1.2-23: FOMC fit for dimethenamid-P in the trials L110481 and L110482 – persistence endpoints

Table B.8.1.2-99: Statistical and visual assessment of kinetic models for the metabolite M656PH027 in trial L110330 – persistence endpoints

Kinetic Model	Fitted parameters	χ^2 error	p (t-test)*	Visual assessment	$DegT_{50}$ [d]	$DegT_{90}$ [d]
SFO	M_0: 188 k: 0.0220 d^{-1}	11.2	k: < 0.001	Good	31.4	104
FOMC	M_0: 197 Alpha: 953 Beta: 33663	13.8	Alpha: 0.415 Beta: 0.416	Good	24.5	81.4
→ SFO fit visually and statistically good. FOMC visually good, but t-test fails.						
→ **Conclusion: The degradation of M656PH027 is well described using SFO kinetics.**						

* Type I error rate

Table B.8.1.2-100: Statistical and visual assessment of kinetic models for the metabolite M656PH027 in trial L110331 – persistence endpoints

Kinetic Model	Fitted parameters	χ^2 error	p (t-test)*	Visual assessment	$DegT_{50}$ [d]	$DegT_{90}$ [d]
SFO	M_0: 179 k: 0.0576 d^{-1}	3.7	k: < 0.001	Good	12.0	40.0
FOMC	M_0: 182 Alpha: 5.78 Beta: 90.0	3.5	Alpha: 0.232 Beta: 0.255	Good	11.5	44.0
→ SFO fit visually and statistically good. FOMC visually good, but t-test fails.						
→ **Conclusion: The degradation of M656PH027 is well described using SFO kinetics.**						

* Type I error rate

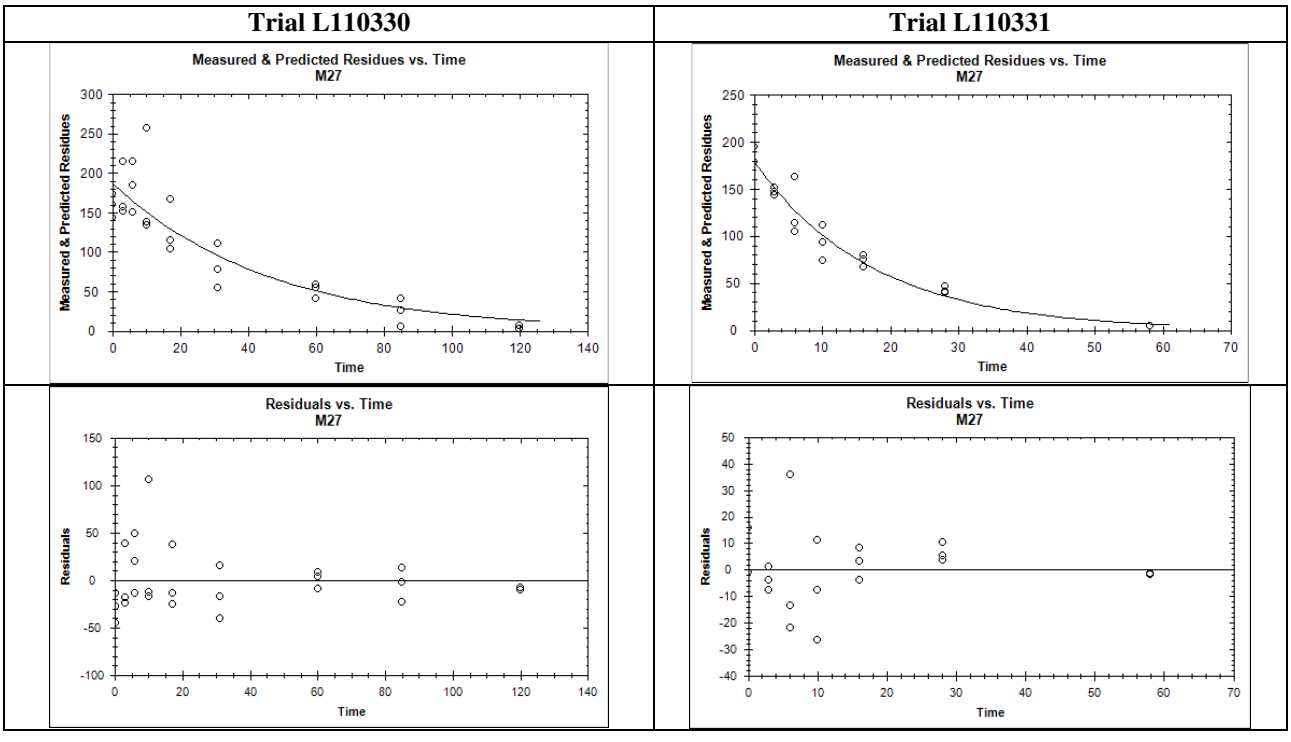


Figure B.8.1.2-24: SFO fit for M656PH027 in the trials L110330 and L110331 – persistence endpoints

Table B.8.1.2-101: Statistical and visual assessment of kinetic models for the metabolite M656PH027 in trial L110332 – persistence endpoints

Kinetic Model	Fitted parameters	χ^2 error	p (t-test)*	Visual assessment	$DegT_{50}$ [d]	$DegT_{90}$ [d]
SFO	M_0: 205 k: 0.0358 d^{-1}	14.6	k: < 0.001	Good	19.4	64.3
FOMC	M_0: 218 Alpha: 508 Beta: 10458	18.4	Alpha: 0.393 Beta: 0.393	Good	14.3	47.5
→ SFO fit visually and statistically good. FOMC visually good, but t-test fails.						
→ **Conclusion: The degradation of M656PH027 is well described using SFO kinetics.**						

* Type I error rate

Table B.8.1.2-102: Statistical and visual assessment of kinetic models for the metabolite M656PH027 in trial L110333 – persistence endpoints

Kinetic Model	Fitted parameters	χ^2 error	p (t-test)*	Visual assessment	$DegT_{50}$ [d]	$DegT_{90}$ [d]
SFO	M_0: 185 k: 0.0293 d^{-1}	9.6	k: < 0.001	Good	23.7	78.6
FOMC	M_0: 195 Alpha: 1029 Beta: 26530	13.1	Alpha: 0.409 Beta: 0.409	Good	17.9	59.4
→ SFO fit visually and statistically good. FOMC visually good, but t-test fails.						
→ **Conclusion: The degradation of M656PH027 is well described using SFO kinetics.**						

* Type I error rate

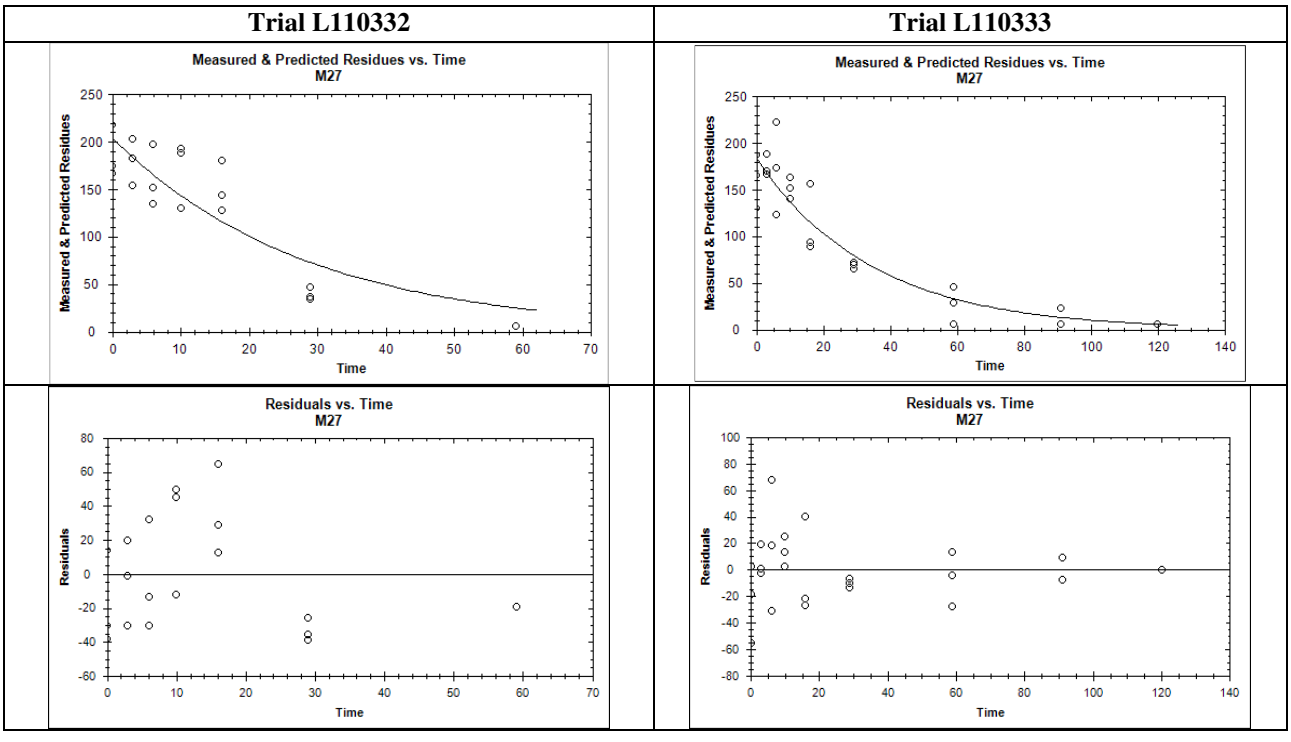


Figure B.8.1.2-25: SFO fit for M656PH027 in the trials L110332 and L110333 – persistence endpoints

The final DT_{50} and DT_{90} values for dimethenamid-P to be used as persistence endpoints are summarised in Table B.8.1.2-103. The final DT_{50} and DT_{90} values for M656PH027 to be used as persistence endpoints are summarised in Table B.8.1.2-104.

Table B.8.1.2-103: $DegT_{50}$ and $DegT_{90}$ values of dimethenamid-P– persistence endpoints

Field trial	Kinetic model	$DegT_{50}$ [d]	$DegT_{90}$ [d]	Reference
L110061	SFO	20.4	67.7	Bayer & Marwitz (2014a)
L110062	SFO	17.6	58.6	
L110063	SFO	14.5	48.1	
L110064	SFO	16.5	54.7	
L110481	FOMC	17.6	167	Bayer & Marwitz (2014b)
L110482	FOMC	10.2	68.2	

Table B.8.1.2-104: $DegT_{50}$ and $DegT_{90}$ values of M656PH027– persistence endpoints

Field trial	Kinetic model	$DegT_{50}$ [d]	$DegT_{90}$ [d]	Reference
L110330	SFO	31.4	104	Bayer & Marwitz (2014c)
L110331	SFO	12.0	40.0	
L110332	SFO	19.4	64.3	
L110333	SFO	23.7	78.6	

Conclusion

The study is considered acceptable by the RMS and the resulting persistence endpoints are considered suitable for environmental risk assessment.
Under field conditions (not temperature or moisture normalised), dimethenamid-P degrades in different European regions with DT_{50} values of 10.2 - 20.4 d and DT_{90} values of 48.1 – 167 d.
The soil metabolite M656PH027 degrades under field conditions (not temperature or moisture normalised) in different European regions with DT_{50} values of 12.0 - 31.4 d and DT_{90} values of 40.0 – 104 d.
All acceptable persistence and modelling endpoints of dimethenamid-P and its metabolites in soil are summarised in Volume 1 under 2.8.2.

KCA 7.1.2.2.1/ 9–Wiedemann, 2014b (new study)

Author: Wiedemann, G.
Title: Calculation of normalised modelling half-lives from terrestrial field dissipation studies with dimethenamid-P and its metabolite M27 according to Focus kinetics
Date: 02/12/2014
Doc ID: BASF DocID 2014/1031648, study code CALC-1832
Guidelines: FOCUS Degradation Kinetics (2011) Sanco/10058/2005 version 2.0
GLP: No (not applicable)
Validity: Acceptable

Aim of the study

Two field dissipation studies Bayer & Marwitz, 2014a & c (six trials) with the active substance dimethenamid-P and one study Bayer & Marwitz, 2014b (four trials) with the dimethenamid-P soil metabolite M656H027 (= M27 in this study) were evaluated to derive normalised modelling endpoints following the recommendations of the guidelines by the FOCUS work group on degradation kinetics (FOCUS, 2011).

Material and Methods

First the residue data were processed according to the procedure described under KCA 7.1.2.2.1/ 8–Wiedemann, 2014a. The processed residues for dimethenamid-P and its metabolites used for kinetic evaluation are presented in Table B.8.1.2-83 to Table B.8.1.2-92.

Afterwards, the data of the field trials were normalised to reference conditions (20 °C soil temperature,

soil moisture at pF 2). The day length normalisation was carried out by reducing or increasing day lengths depending on soil temperature and moisture by means of correction factors. Actual soil temperature and moisture were derived employing the FOCUS-PEARL 4.4.4 groundwater model which was run with individual climate and soil data corresponding to each trial location.
The soil moisture correction was conducted using the modified Walker equation (exponent of the moisture response function = 0.7), as recommended by the FOCUS Kinetics (2011). Day lengths were normalised if the soil moisture calculated with FOCUS-PEARL 4.4.4 was lower than the reference soil moisture at pF 2. If the actual soil moisture was higher than the reference value, the moisture correction factor was set to 1 since wetter conditions do not accelerate the degradation processes. Reference moisture at pF 2 was taken from the soil certificates of the field phase reports converted to volumetric moisture using the measured bulk density.
Temperature correction factors were derived using the Arrhenius equation (Q_{10} value = 2.58) as described in the report of the FOCUS Work Group on Degradation Kinetics (2011). If the soil temperature was ≤ 0 °C, the correction factor had to be set to 0.
Afterwards, the day length normalised for soil temperature and soil moisture was calculated according to FOCUS (2011).
Cumulative corrected day lengths values were calculated for each sampling interval. These "normalised days after applications" were assigned to the residue data of the different field trials and used as input model data for the calculation of modelling endpoints.

The actual sampling days and the corrected day lengths for all trials are presented in Table B.8.1.2-105, Table B.8.1.2-106 and Table B.8.1.2-107.

Table B.8.1.2-105: Actual sampling days and the soil moisture and temperature corrected day lengths for the field trials with dimethenamid-P - L110061 to L110064

Trial L110061		Trial L110062		Trial L110063		Trial L110064	
Time (DAT)							
actual	corrected	actual	corrected	actual	corrected	actual	corrected
0	0.0	0	0.0	0	0.0	0	0.0
3	1.5	3	1.8	3	2.4	3	1.6
6	3.0	6	3.2	6	4.8	6	3.3
10	5.4	10	5.4	10	7.4	10	5.3
16	10.0	16	9.7	19	13.8	17	9.1
28	16.6	28	16.5	28	20.9	31	18.8
59	38,8	58	35,5	59	50.1	60	41.1
85	57.7	92	59.4	94	86.9	95	70.7
120	82.8					116	88.0
150	99.4					151	117.7
175	109.3						
233	124.6						
366	165.9						

Table B.8.1.2-106: Actual sampling days and the soil moisture and temperature corrected day lengths for the field trials with dimethenamid-P - L110481 to L110482

Trial L110481		Trial L110482	
Time (DAT)			
actual	corrected	actual	corrected
0	0.0	0	0.0
3	2.2	3	2.1
6	4.5	6	3.9
10	7.2	10	5.9
17	11.4	17	9.1
29	15.9	27	14.9
62	27.9	59	24.4
85	33.6	87	29.0
122	43.9	123	35.9
154	49.5	185	43,1
182	57.3	242	63.4
246	19.7		
367	150.1		

Table B.8.1.2-107: Actual sampling days and the soil moisture and temperature corrected day lengths for the field trials with M656PH027 - L110330 to L110333

Trial L110330		Trial L110331		Trial L110332		Trial L110333	
Time (DAT)							
actual	corrected	actual	corrected	actual	corrected	actual	corrected
0	0.0	0	0.0	0	0.0	0	0.0
3	1 .1	3	2.1	3	2.0	3	2.7
6	2.2	6	3.9	6	3.6	6	6.0
10	3.9	10	7.2	10	5.8	10	10.1
17	7.5	16	11.6	16	9.8	16	16.2
31	13.4	28	21.1	29	19.3	29	30.7
60	28.6	58	43.5	59	45.3	59	69.1
85	42.4					91	112.8
120	61.5					120	154.0

The processed residue data were evaluated according to recommended procedures as given in the guideline of the FOCUS Work Group on Degradation Kinetics (2011) using the software package KinGUI (version 2). In trials with dimethenamid-P and metabolites, the parent parameters were fitted in a first step. The parameters of this fit were considered as relevant for the parent substance. In a second step, all parameters for parent and metabolites were fitted simultaneously. Only SFO kinetics were applied in the current modelling.

Additionally, the trials were evaluated according to criteria compiled by the Dutch regulatory authority (CTB) in order to ensure that the field study is adequately performed, and that samples are adequately taken and analysed.

Results and Discussion

The degradation of dimethenamid p under field conditions was analysed in six trials in order to derive appropriate degradation kinetics and modelling $DegT_{50}$. Only SFO kinetics in combination with time-step normalisation (i.e. with corrected sampling time) were tested since these already provided good fits. No outliers were identified in any of the trials.
The statistical and visual assessment of the kinetic models for dimethenamid-P applied in the six field trials L110060, L110061, L110062, L110063, L110064, L110481 and L110482 is given in Table B.8.1.2-108. The visual fits of the finally chosen kinetic model for dimethenamid-P is presented in Figure B.8.1.2-26 to Figure B.8.1.2-28.

The degradation of M656PH027 as a metabolite of dimethenamid-P was evaluated for trials L110061, L110062, L110063, L110064 and L110481; for metabolite M656PH023, trials L110062, L110064 and L110481 were considered. The fitted curves for M656PH027 and M656PH023 in all these trials are visually poor, and the χ^2 are always > 30 %. Therefore, the resulting parameters are not considered acceptable for modelling in environmental risk assessments.
The statistical and visual assessment of the kinetic models for M656PH027 applied for field trials L110330 to L110334 is given in Table B.8.1.2-109. The visual fits of the finally chosen model for M656PH027 is presented in Figure B.8.1.2-29 and Figure B.8.1.2-30.

Table B.8.1.2-108: Statistical and visual assessment of kinetic models for dimethenamid-P – modelling endpoints

Field trial	Kinetic Model	Fitted parameters	χ^2 error	p (t-test)*	Visual assessment	$DegT_{50}$ [d]	$DegT_{90}$ [d]
L110061	SFO	M_0: 712 k: 0.0548 d^{-1}	10.1	k: < 0.001	Good	12.6	42.0
L110062	SFO	M_0: 855 k: 0.0670 d^{-1}	16.4	k: < 0.001	Good	10.4	34.4
L110063	SFO	M_0: 883 k: 0.0638 d^{-1}	13.9	k: < 0.001	Good	10.9	36.1
L110064	SFO	M_0: 899 k: 0.0716 d^{-1}	8.0	k: < 0.001	Good	9.7	32.2
L110481	SFO	M_0: 530 k: 0.0501 d^{-1}	10.4	k: < 0.001	Good	13.8	45.9
L110482	SFO	M_0: 429 k: 0.101 d^{-1}	8.2	k: < 0.001	Good	6.9	22.8
→ SFO fits visually and statistically good							
→ **Conclusion: The degradation of dimethenamid-P is well described using SFO kinetics.**							

* Type I error rate

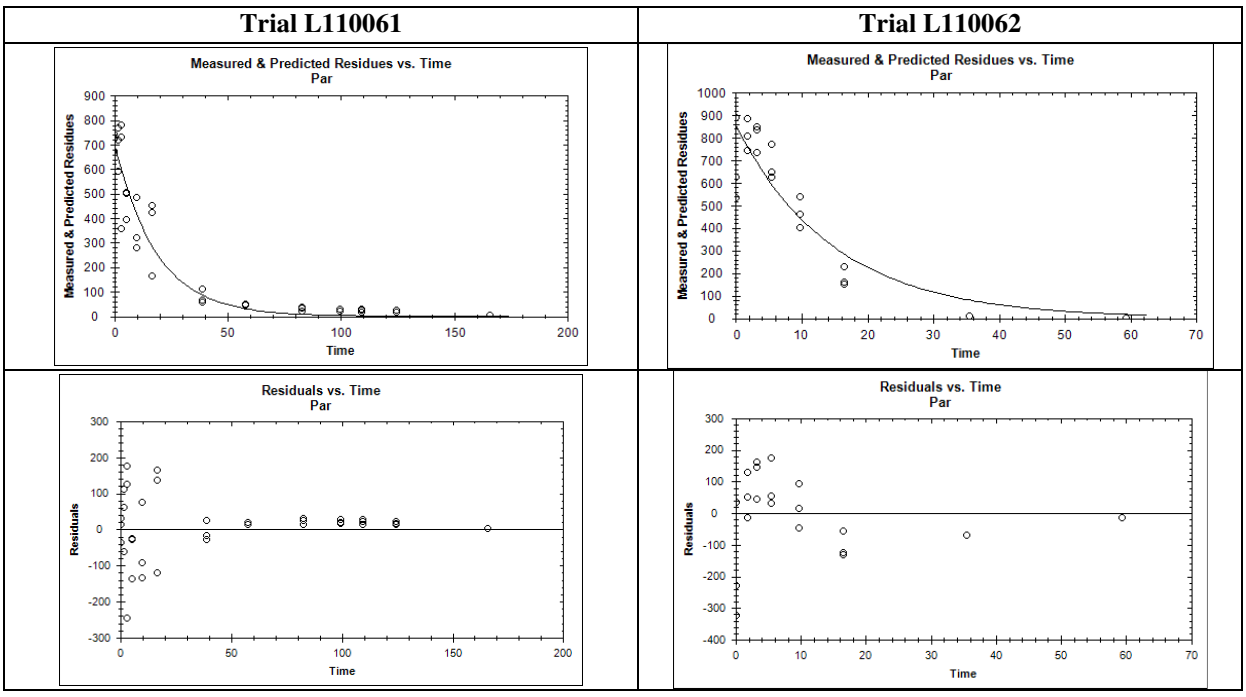


Figure B.8.1.2-26: SFO fit for dimethenamid-P in the trials L110061 and L110062– modelling endpoints

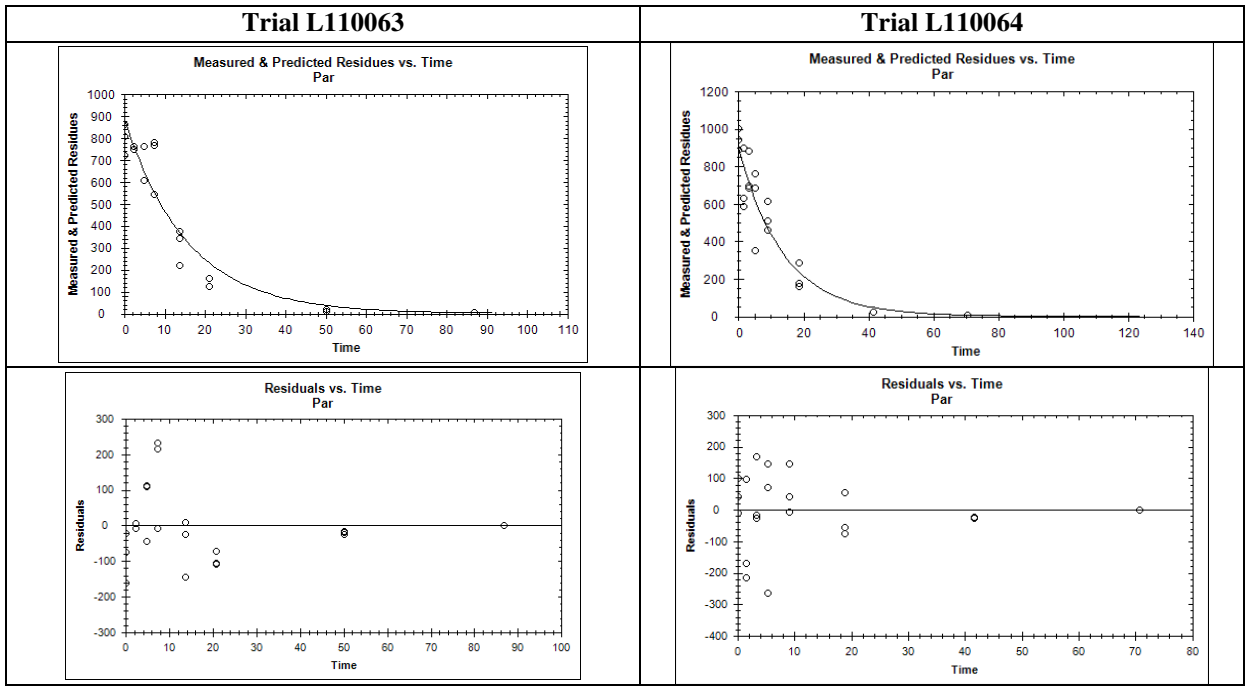


Figure B.8.1.2-27: SFO fit for dimethenamid-P in the trials L110063 and L110064– modelling endpoints

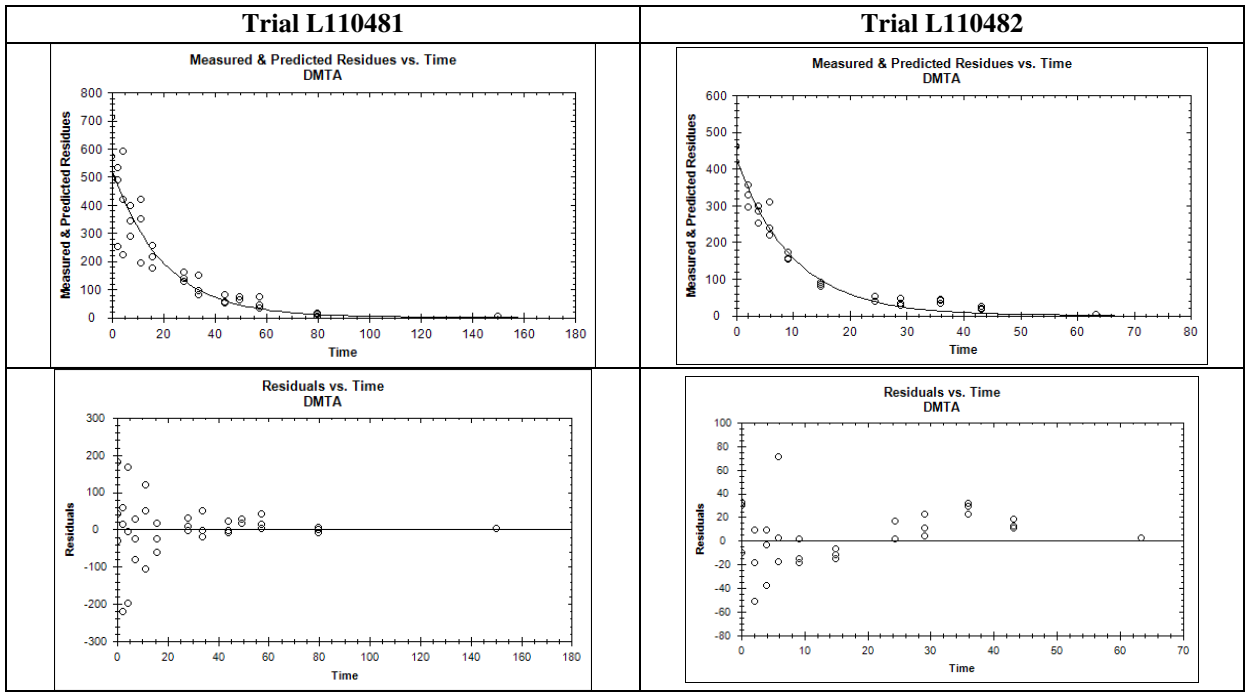


Figure B.8.1.2-28: SFO fit for dimethenamid-P in the trials L110481 and L110482– modelling endpoints

Table B.8.1.2-109: Statistical and visual assessment of kinetic models for M656PH027 – modelling endpoints

Field trial	Kinetic Model	Fitted parameters	χ^2 error	p (t-test)*	Visual assessment	DegT$_{50}$ [d]	DegT$_{90}$ [d]
L110330	SFO	M_0: 185 k: 0.0474 d^{-1}	10.3	k: < 0.001	Good	14.6	48.6
L110331	SFO	M_0: 178 k: 0.0787 d^{-1}	4.4	k: < 0.001	Good	8.8	29.3
L110332	SFO	M_0: 203 k: 0.0546 d^{-1}	12.9	k: < 0.001	Acceptable	12.7	42.2
L110333	SFO	M_0: 182 k: 0.0268 d^{-1}	9.2	k: < 0.001	Good	25.9	86.0
→ SFO fits visually and statistically good							
→ **Conclusion: The degradation of M656PH027 is well described using SFO kinetics.**							

* Type I error rate

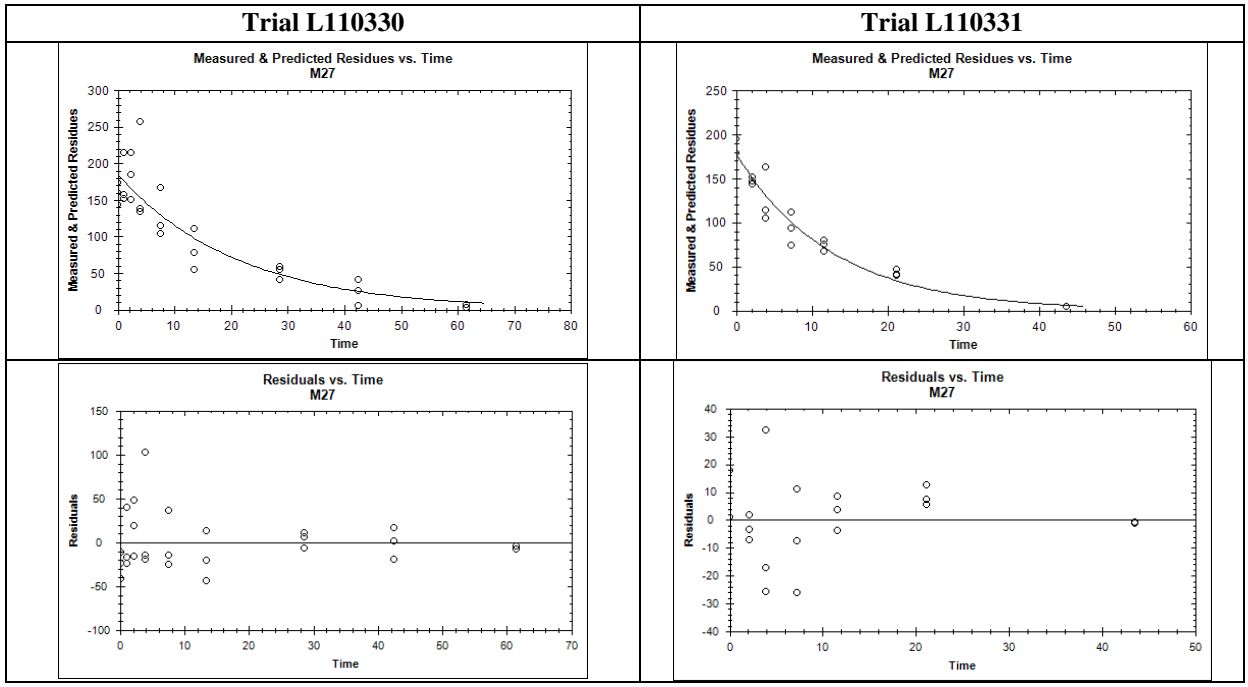


Figure B.8.1.2-29: SFO fit for the metabolite M656PH027 in the trials L110330 and L110331– modelling endpoints

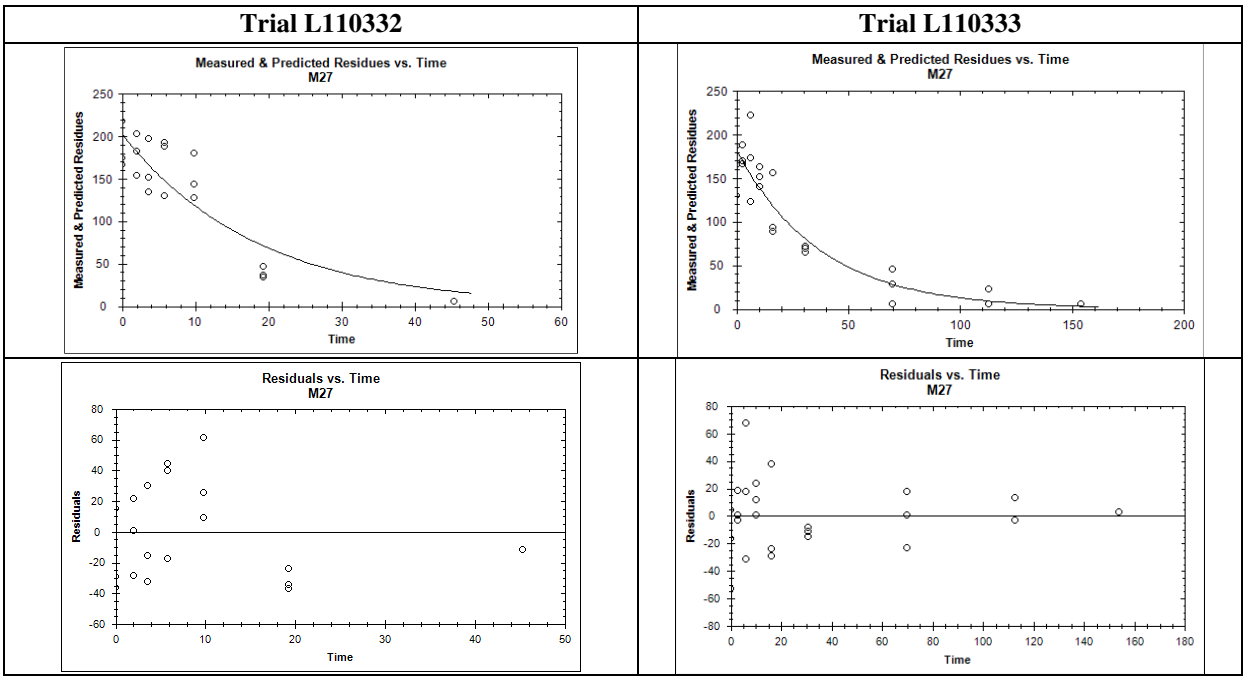


Figure B.8.1.2-30: SFO fit for the metabolite M656PH027 in the trials L110332 and L110333– modelling endpoints

The final DT_{50} and DT_{90} values for dimethenamid-P to be used for modelling are summarised in Table B.8.1.2-110. The final DT_{50} and DT_{90} values for M656PH027 to be used for modelling are summarised in Table B.8.1.2-111.

Table B.8.1.2-110: $DegT_{50}$ and $DegT_{90}$ values normalised to 20 °C and pF2 of dimethenamid-P– modelling endpoints

Field trial	Kinetic model	$DegT_{50}$ [d]	$DegT_{90}$ [d]	Reference
L110061	SFO	12.6	42.0	Bayer & Marwitz (2014a)
L110062	SFO	10.4	34.4	
L110063	SFO	10.9	36.1	
L110064	SFO	9.7	32.2	
L110481	SFO	13.8	45.9	Bayer & Marwitz (2014b)
L110482	SFO	6.9	22.8	

Table B.8.1.2-111: $DegT_{50}$ and $DegT_{90}$ values normalised to 20 °C and pF2 of M656PH027– modelling endpoints

Field trial	Kinetic model	$DegT_{50}$ [d]	$DegT_{90}$ [d]	Reference
L110330	SFO	14.6	48.6	Bayer & Marwitz (2014c)
L110331	SFO	8.8	29.3	
L110332	SFO	12.7	42.2	
L110333	SFO	25.9	86.0	

Conclusion

The study is considered acceptable by the RMS and the resulting modelling endpoints are considered suitable for environmental risk assessment.
Under field conditions, dimethenamid-P degrades with DT_{50} values normalised to reference conditions of 20 °C and pF2 between 6.9 – 13.8 d.
The soil metabolite M656PH027 degrades under field conditions with DT_{50} values normalised to reference conditions of 20 °C and pF2 between 8.8 – 25.9 d.

Soil accumulation studies

No soil accumulation studies with dimethenamid-P were submitted for the first Annex I inclusion. They are not required since dimethenamid-P degrades sufficiently fast in soil.

B.8.1.3 Adsorption and desorption in soil

Adsorption and desorption of the active substance

KCA 7.1.3.1.1/1 – Tong & Su, 1997 (study evaluated in the monograph, 2000) with addendum Paulick, 2007 (new study)

Author:	Tong, T.M. Su, L.Y.
Title:	Soil adsorption and desorption of SAN-1289H, unaged, by the batch equilibrium method
Date:	29/04/1997
Doc ID:	BASF RegDoc.# 97/5180
Guidelines:	US-EPA, Subdivision N, 163-1
GLP:	Yes
Validity:	Acceptable

Author:	Paulick, R.C.
Title:	Soil Adsorption and Desorption of SAN-1289H, Unaged, by the Batch Equilibrium Method – Report Amendment Number 1
Date:	04/06/2007
Doc ID:	BASF RegDoc.# 2007/7003537
Guidelines:	US-EPA, Subdivision N, 163-1
GLP:	Yes
Validity:	Acceptable

Material and Methods

Adsorption and desorption characteristics of ^{14}C-dimethenamid-P (3-^{14}C-thienyl dimethenamid-P, radiochemical purity 96.0 %; dimethenamid-P, purity 94.0 %) were determined on 5 European and 5 U.S. soils by the batch equilibrium method. The addendum Paulick (2007) corrects some errors and calculations of adsorption and desorption parameters for the US soils.
The properties of the soils used are summarised in Table B.8.1.3-1.

Table B.8.1.3-1: Characterisation of European and U.S. soils used for batch soil adsorption/ desorption study with dimethenamid-P

Source (code)	**Italy (Eu-1)**	**Greece (Eu-2)**	**Great Britain (Eu-3)**	**France (Eu-4)**	**Germany (Eu-5)**
Texture class	Sandy clay loam	Clay loam	Sandy loam	Silt loam	Sand
Organic carbon[1)] (%)	1.40	2.03	2.38	1.22	3.43
Organic matter (%)	2.4	3.5	4.1	2.1	5.9
CEC (meq/100 g)	35.6	25.6	14.9	18.6	3.3
pH	5.6	8.0	5.5	6.6	3.9
Field capacity (g/100g)	27.51	32.07	20.01	24.64	13.32
Sand (%)	50	38	68	18	88
Silt (%)	22	34	20	60	8
Clay (%)	28	28	12	22	4
Source	**Arizona (US-1)**	**Illinois (US-2)**	**California (US-3)**	**California (US-4)**	**Illinois (US-5)**
Texture class	Clay	Clay loam	Loam	Sandy loam	Silt loam
Organic carbon[1)] (%)	0.99	2.38	1.22	0.35	1.51
Organic matter (%)	1.70	4.10	2.10	0.60	2.60
CEC (meq/100 g)	32.80	15.60	16.90	4.00	11.80
pH	8.0	6.4	7.3	7.0	6.7
Field capacity (g/100g)	37.34	33.37	31.42	6.42	28.62
Sand (%)	12	24	32	74	26
Silt (%)	40	44	46	20	56
Clay (%)	48	32	22	6	18

1) % Organic Carbon = % Organic Matter/1.72

In preliminary experiments the appropriate equilibrium time was determined (24 h) and stability of dimethenamid-P was demonstrated. Definitive equilibrations were conducted with ^{14}C-dimethenamid-P in 0.01 M $CaCl_2$ at nominal concentrations of 0.04, 0.2, 1 and 5 µg/mL at 23 °C. Analysis was done using LSC, TLC and HPLC.

Results and Discussion

Total recoveries ranged from 90.7 to 111.8 % AR for the single adsorption/desorption experiments. Mean values of the mass balance for each soil were in the range from 96.9 to 105.0 % AR. Dimethenamid-P was stable in 0.01 M $CaCl_2$ solution during the adsorption and desorption study in both European and U.S. soils. Both linear and Freundlich isotherm models were constructed and the results were similar. Freundlich K_d and K_{oc} values are summarised in

Table B.8.1.3-2: Freundlich adsorption and desorption coefficients of dimethenamid-P

European Soils							
		Adsorption			Desorption		
Soil	**Soil type**	**K_F**	**1/n**	**K_{OC}**	**K_F**	**1/n**	**K_{OC}**
Eu-1	Sandy clay loam	6.61	0.92	474	8.32	0.91	596
Eu-2	Clay loam	2.51	0.96	123	2.40	0.85	118
Eu-3	Sandy loam	2.14	1.00	90	2.63	1.11	110
Eu-4	Silt loam	1.23	1.07	101	2.63	1.15	215
Eu-5	Sand	13.49	0.94	393	20.89	1.06	609

U.S. Soils							
		Adsorption			Desorption		
Soil	**Soil type**	**K_F**	**1/n**	**K_{OC}**	**K_F**	**1/n**	**K_{OC}**
US-1	Clay	2.09	1.05	211	3.24	1.18	328
US-2	Clay loam	2.51	0.97	105	3.31	0.90	139
US-3	Loam	3.02	1.03*	247	3.89	0.98	319
US-4	Sandy loam	0.72*	1.04	205.71*	1.25*	1.4*	357.14*
US-5	Silt loam	1.95	0.96	129	2.09	0.87	138

* corrected by Paulick, 2007

The K_{oc} (adsorption) and K_{oc} (desorption) ranges for European soils were 90 – 474 and 110 – 609, respectively. Ranges for the U.S. soils were 105 – 396 and 138 – 401, respectively.

Conclusion

The study is acceptable.
Taking into account K_{OC} values of 90 – 474, dimethenamid-P can be predicted to have a medium to high mobility in soil.

Adsorption and desorption of metabolites, breakdown and reaction products

KCA 7.1.3.1.2/1 – Mamouni, 1995 with addendum Tong, 1999 (study evaluated in the monograph, 2000)

Author: Mamouni, A.
Title: Adsorption/desorption of dimethenamid oxalamide (M23) and dimethenamid sulfonate sodium salt (M27) in six soils
Date: 10/02/1995
Doc ID: BASF RegDoc.# 95/10121
Guidelines: OECD 106 (May 1981)
GLP: Yes
Validity: Not acceptable

Author: Tong, T.M.R-
Title: Addendum to the report titled "adsorption/desorption of dimethenamid oxalamide (M23) and dimethenamid sulfonate sodium salt (M27) in six soils
Date: 02/03/1999
Doc ID: BASF RegDoc.# 99/5014
Guidelines: Not applicable (calculation of adsorption coefficients from existing data)
GLP: Yes
Validity: Not acceptable

Material and Methods

The adsorption and desorption of metabolites M656H023 (oxalamide or M23 in this study, purity 99.8 %) and M656H027 (sulfonate sodium salt or M27 in this study, purity 97.2 %) were determined in six different European soils. In the addendum Tong, 1999, K_d values were calculated for both

metabolites. The properties of the soils used are summarised in Table B.8.1.3-3. Equilibrium time was 24 h. For all except the Vetroz soil, the soil to water ratio was 1:5 (w/w); for the Vetroz soil this ratio was 1:2 (w/w). Analysis was done using HPLC.

Table B.8.1.3-3: Characterisation of European soils used for batch soil adsorption/ desorption study with dimethenamid metabolites M656PH023 and M656PH027

Designation	BBA 2.2	Duering/ Horneburg	Witterswill	Flaach	BBA 2.3	Vetroz
Texture class	Loamy sand	Loamy sand	Silty clay	Loam	Sandy loam	Silt loam
Organic carbon[1)] (%)	1.60	1.40	2.90	1.10	0.90	4.39
Organic matter (%)	2.76	2.41	5.00	1.90	1.55	7.57
CEC (meq/100 g)	6.7	2.7	34.4	14.3	8.7	30.7
pH (H_2O)	6.4	4.2	7.8	7.9	7.5	
pH ($CaCl_2$)	6.0	3.6	7.4	7.4	7.0	7.1
Sand (%)	83.7	77.2	2.5	45.6	65.4	18.4
Silt (%)	8.4	16.0	50.9	29.4	22.2	56.8
Clay (%)	7.9	6.6	46.6	25.0	12.4	24.8

1) % Organic carbon = % Organic matter/1.72

Results and Discussion

After 24 hours of equilibration, no significant adsorption (< 5 %) occurred with five of the soils tested. Only in the case of the Vetroz silt loam being the soil with the highest organic carbon content (4.39 %) adsorption of 23.1 % and 20.6 % of the initially applied amount were found for M656H023 and M656H027, respectively. No adsorption of M656H023 and M656H027 on the Teflon tubes and no degradation of the test substance in the aqueous solution were observed under the experimental conditions. Due to the results of the pre-tests no advanced test using different concentrations was performed. The K_d values for both M656H023 and M656H027 were estimated to range from 0 to 0.43 and the respective K_{OC} values ranged from 0 to 17.2 (see Table B.8.1.3-4). There was no clear relationship between the K_{OC} values and the soil parameters.

Table B.8.1.3-4: K_d and K_{OC} values (adsorption) for M656H023 and M656H027 in 6 soils

Soil	Metabolite M656H023		Metabolite M656H027	
	K_d	K_{OC}	K_d	K_{OC}
BBA 2.2 Loamy sand	0.06	3.5	0.23	14.4
Duerring/ Horneburg Loamy sand	0.24	17.2	0.14	10.3
Witterswill Silty clay	0.11	3.9	0.10	3.5
Flaach Loam	0.05	4.1	0.00	0.0
BBA 2.3 Sandy loam	0.09	9.6	0.02	2.2
Vetroz Silt loam	0.35	7.9	0.43	9.9

Conclusion

The study was considered acceptable for first Annex I inclusion of dimethenamid-P. However, after re-evalution for the renewed approval for dimethenamid-P, the RMS considers the study as not acceptable anymore. The following shortcomings in the study were found by the RMS:
No preliminary study was performed to determine the optimum soil/solution ratio and equilibration time for the test substances. As a consequence, the adsorption experiments were performed at soil solution ratios of 1:5 and 1:2 which is too low for poorly absorbable substances like M656H023 and M656H027. As a consequence of the unfavourable experimental conditions and the poor adsorption properties of M656H023 and M656H027, the adsorption was below 20 % for all soils except Vertroz and the determined K_d values x soil/solution ratio were <0.1 for most samples, thus making accurate

K_d determination not possible.
Finally, the soil Vetroz was stored for more than three years without re-analysis before the start of the experiment and the overall mass balance after adsorption and subsequent desorption for this soil was with 79.4 % for M656H023 and 84.7 % for M656H027 below the required 90 %.

KCA 7.1.3.1.2/2 – Class & Dorn, 2004 (new study)

Author:	Class, T. Dorn, U.
Title:	Dimethenamid Metabolite M27 (Sulfonate): Adsorption - Desorption on Different Soils
Date:	01/28/2004
Doc ID:	BASF DocID 2004/1015224
Guidelines:	OECD 106
GLP:	Yes
Validity:	Acceptable

Material and Methods

The adsorption behaviour of M656H027 (M27 or sulfonate in this study, 97.4 % purity), metabolite of dimethenamid-P was investigated in four different soils. The soils covered a range of pH from 6.1 to 7.3, a range of organic carbon content from 0.8 % to 2.72 % and different textural classes. The physico-chemical characterisation of the soils is provided in Table B.8.1.3-5.

Table B.8.1.3-5: Characterisation of soils used to investigate the adsorption and desorption of M656H027

Soil designation Origin	**Sora (Field preparation August 2000)**	**LUFA 3A**	**Birnbaum (Henninger)**	**Bruch West**
Textural class (USDA scheme)	Silt loam	Loam	Loamy sand	Sandy loam
Soil texture [%], (USDA scheme)				
Sand	10.8	48.8	83	60.3
Silt	77.8	35.7	6	26.6
Clay	11.2	15.5	11	13.1
Organic carbon [%]	1.91	2.44	0.8	2.72
Organic matter[1)] [%]	3.29	4.20	1.38	4.68
CEC [meq/100g]	16.6	18.8	13	14.0
pH ($CaCl_2$)	6.4	7.2	6.1	7.3
pH (water)	-	7.7	-	8.2

1) organic matter = organic carbon x 1.724

To determine adsorption kinetics 10 g of soil were equilibrated with 9.5 mL of 0.01 M $CaCl_2$ overnight by shaking. Then M656H027 was added to the soil water to obtain a nominal concentration of 5 µg/mL in the aqueous phases. The soil/solution ratio chosen was ≈1/1, as the adsorption of the test item was assumed to be low. Duplicate specimens were dosed per soil type. Two blank controls per soil type were prepared without M656H027 and two specimens with no soil were dosed with M656H027 at a nominal concentration of 5 µg/mL. The specimens were shaken at 22-24 °C for 2, 4, 6, 8, 24 and 48 h. After each interval an aliquot of the water phase was taken for analysis of M656H027 by LC/MS/MS. After final sampling the soil pellets were washed with 0.01 M $CaCl_2$ and adsorbed M656H027 was extracted with methanol/water (6/4, v/v). Combined washes and soil extracts were analysed by LC/MS/MS.
To determine adsorption isotherms, standard solutions of the test item in 0.01 M $CaCl_2$ were prepared with five concentrations ranging from 0.05 to 5.0 µg/mL. For all experiments, the soil was pre-equilibrated with aqueous 0.01 M $CaCl_2$ overnight, before addition of the test solution. All experiments were performed in glass centrifuge tubes. Per soil type a total of 10 soil samples were dosed (duplicates per amount/concentration level dosed), plus two blank controls without M656H027

per soil and two specimens dosed with 0.05 µg/mL M656H027 without soil (adsorption controls).
Aliquots of 2 mL of the test solution were shaken with 2 g of the test soil at 23-25 °C. The appropriate time for reaching equilibrium conditions was 22 h for Sora and LUFA 3A and 2 h for Birnbaum and Bruch West as determined in preliminary adsorption kinetics tests (see above).
The adsorbed test item was determined by analysing the aqueous phase (indirect method) and the solvent phase obtained by soil extraction (direct method).
Control specimens with only the test item in aqueous 0.01 M $CaCl_2$ solution (adsorption controls) were used to show that no significant adsorption on the surface of the test vessels occurred.

Aliquots of the supernatant of soil water obtained after equilibrating soil for several hours in fortified 0.01 M aqueous $CaCI_2$ solution were centrifuged, filtered (0.2 µm pore width), diluted (dilution factors DF: 4, 10, and 25) and finally analysed for M656H027 by LC-MS/MS. The analytical procedure was assessed and pre-validated for soil water at M656H027 concentrations of 5.0, 0.20 and 0.005 µg/mL.
Soil pellets (2 g) were washed with 0.01 M $CaCl_2$ and the soil/water phases were separated by filtration (paper filters using Buchner funnels and vacuum suction) or centrifugation. The washed fractions were combined and the total volume noted. The washed soil pellets were extracted repeatedly with methanol/water (6/4, v/v) and then the extracts were combined. Aliquots of the washes and soil extracts were filtered, diluted and subjected to LC/MS/MS analysis. The applicability of the soil extraction method was demonstrated by fortifying soil pellets of control specimens at 0.050 µg/g with M656H027 (10 g soil) and 0.025 µg/g with M656H027 (2 g soil) prior to extraction with methanol/water.

Results and Discussion

Mass balances were complete and ranged from 95 % to 101 %, thus indicating that no degradation of the test substance or adsorption on the test vessels occurred.
The resulting adsorption and the derived adsorption coefficients are summarised in Table B.8.1.3-6.

Table B.8.1.3-6: Summary of Adsorption (A) at equilibrium (eq), adsorption kinetics and isotherms for M656H027

Soil	A(eq) indirect	A(eq) direct	A(eq) Average Indirect/direct	K_d [cm^3/g]	K_{OC} [cm^3/g]	K_F [$\mu g^{1-1/n} (cm^3)^{1/n} g^{-1}$]	1/n
Sora	11.1	12.1	11.6	0.15	7.8	0.076	0.992
LUFA 3A	13.3	9.3	11.3	0.16	6.5	0.120	0.940
Birnbaum	7.2	8.3	7.7	0.087	10.9	0.036	0.937
Bruch West	7.7	5.8	6.8	0.092	3.4	0.030	0.910

M656H027 showed weak adsorption (A(eq) <15 %) on all four soils, resulting in little depletion in the aqueous solutions. Adsorption found after 48 to 50 h of equilibration was 11.1 % for Sora soil, 13.3 % for LUFA 3A soil, 7.2 % for Birnbaum soil and 7.7 % for Bruch West soil determined by the indirect method. The direct method obtained 12.1 % for Sora soils, 9.3 % for LUFA 3A soils, 7.2 % for Birnbaum soils and 5.8 % for Bruch West soils.
The results for adsorption at equilibrium A(eq) obtained from adsorption kinetics tests by direct and indirect method were averaged and used to calculate the distribution coefficients K_d. The K_d values were further used to obtain the organic carbon normalised adsorption coefficients K_{OC}.
K_d values ranged between 0.087 to 0.16 cm^3/g and resulted in K_{OC} values between 3.4 and 10.9 cm^3/g.

The adsorption coefficients K_F derived from Freundlich adsorption isotherms ranged from 0.030 to 0.12 with 1/n ranging from 0.910 to 0.992. The significance of these results is limited as an accurate determination of K_d is problematic, if the $K_d \times m_{soil} / V_{solution}$ ratio is not >0.1 (for direct determination of sorption, for an indirect measurement the ratio must be above 0.3). Based on the methods of determination only the soil LUFA 3A with a $K_F > 0.1$ shows reliable sorption.

Conclusion

The study is considered acceptable by the RMS. As stated by the study author, the K_{foc} values of the soil LUFA 3A fulfil the criteria K_d x m_{soil} /$V_{solution}$ ratio >0.1 and are thus considered reliable. However, for the soil Sora only the K_d value of the lowest soil concentration (0.1 µg M656PH027) does not fulfil the criteria K_d x m_{soil} /$V_{solution}$ ratio > 0.1. The K_d values for the remaining concentrations (0.4, 1, 5 and 10 µg/g M656PH027) fulfil the criteria. Thus, also the K_{foc} and Freundlich exponents of the soil Sora are considered sufficiently reliable by the RMS.
The adsorption of M656PH027 to the soils Birnbaum and Bruch West is significantly lower. Thus, the criteria K_d x m_{soil} /$V_{solution}$ ratio > 0.1 is not fulfilled for any of the used concentrations. However, the determined K_{foc} values are in a similar range to the more reliable K_{foc} values of the soils LUFA 3A and Sora and also to the K_{foc} values determined in the study KCA 7.1.3.1.2/4 – Sacchi, 2013, where a slightly altered method following OECD 106 was used. Besides, the Freundlich exponents of all soils indicated only a small influence of the substance concentration on the adsorption of M656PH027. Since excluding the slightly lower K_{foc} values of the soils Birnbaum and Bruch West would be a best case for endpoint derivation of M656H027 and replacing them by default values of 1 does not appear justified in view of all available K_{foc} values for this metabolite, the RMS decided to also include these slightly less reliable K_{foc} values of M656H027 for endpoint derivation.
Adsorption parameters of M656H027 were determined in 4 soils. The resulting K_d values ranged from 0.087 to 0.16 cm^3/g and resulted in K_{OC} values between 3.4 and 10.9 cm^3/g. The adsorption coefficients K_F derived from Freundlich adsorption isotherms ranged from 0.030 to 0.12 with 1/n ranging from 0.910 to 0.992.

KCA 7.1.3.1.2/3 – Class, 2011a (new study)

Author:	Class, T.
Title:	Determination of the Adsorption / Desorption Behavior of Reg.No. 360712 (Metabolite M31 of BAS 656 H, Dimethenamid-P) on Soils
Date:	24/11/2011
Doc ID:	BASFDocID 2011/1277426
Guidelines:	OECD 106 (January 2000)
GLP:	Yes
Validity:	Acceptable

Material and Methods

The aim of this study was to determine the adsorption and desorption behaviour of the metabolite M656PH031 (M31 in this study, purity 98.7 %) on five soils with different chemical and physical properties.
The soils covered a range of pH from 5.2 to 7.5, and a range of organic carbon content from 0.52 % to 3.84 %. The physico-chemical properties of the soils are provided in Table B.8.1.3-7.

Table B.8.1.3-7: Characterisation of soils used to determine the adsorption / desorption behaviour of M656PH031

Soil designation Origin	LUFA 2.1	Nierswalde (Wildacker)	Li 10	LUFA 2.3	La Gironda (Arahal)
Textural class (DIN 4220)	Sand	Clay silt	Loamy sand	Loamy sand	Silty clay
Soil texture [%], (ISO 11277)					
Sand	88.2	17.6	80.3	54.8	10.2
Silt	8.9	73.1	13.8	34.0	50.8
Clay	2.9	9.3	6.0	11.2	39.0
Textural class (USDA)	Sand	Silt loam	Loamy sand	Sandy loam	Silty clay loam
Soil texture [%], (USDA)					
Sand	89.1	24.1	81.1	56.8	12.7
Silt	8.0	66.6	13.0	32.0	48.3
Clay	2.9	9.3	6.0	11.2	39.0
Organic carbon [%] (ISO 10694)	0.52	1.63	0.88	1.09	3.84
Effective CEC [cmol$^+$/kg]	2.0	7.4	5.4	10.4	29.0
pH ($CaCl_2$)	5.2	6.5	5.9	6.9	7.5
pH (H_2O)	6.3	7.1	6.8	7.9	8.1
MWHC [g/100g dry soil]	24.5	39.8	24.2	27.7	36.6
Bulk density [g/L]	1354	1230	1406	1278	1342

The Tier 1 adsorption kinetics preliminary test was performed with two soils, LUFA 2.1 with the lowest pH value and organic carbon content, and La Gironda with the highest pH and organic carbon content. Duplicate portions of 5 g dry soil were equilibrated on a horizontal shaker with slightly less than 5 mL $CaCl_2$ solution (1:1 soil/solution ratio, based on actual soil water content determined in the lab) in a centrifuge tube overnight. A 0.25 mL of the 100 µg/mL application solution was added to the mixture to obtain a nominal initial concentration of 25 µg in a total volume of 4.8 mL for LUFA 2.1 and 5 mL for La Gironda Arahal. Test systems were equilibrated on a horizontal shaker for various equilibration times (0.5, 2, 4, 6, and 24 hours) at room temperature (23 – 25 °C). Samples were pre-centrifuged at 4000 rpm for 5 minutes, and the aqueous phases were removed. The supernatants were subsequently centrifuged at 15000 rpm for 30 minutes. The liquid phases obtained after the second centrifugation step were diluted in 1:1 (v/v) methanol/water solution containing 0.1 % formic acid by a factor of 1000. Soil pellets were extracted and diluted to a factor of 10 (controls) or 100 (all dosed samples). All aqueous phases and extracts were analysed for M656PH031 by LC-MS/MS.

Adsorption isotherms were determined for all soils using an equilibration time of 48 hours and 1:1 soil/solution ratio. Soil samples (5 g) were equilibrated overnight with < 5.0 mL 0.01 M $CaCl_2$ solution. The test substance was added to the mixture to achieve the following amounts: 0.05, 0.25, 1.25, 5 and 25 µg in 5 mL total aqueous volume. Duplicate samples were used for each concentration and for each soil. The test systems were equilibrated by shaking for 48 hours on a horizontal shaker in the dark at room temperature (21 – 25 °C). Samples were pre-centrifuged for 5 minutes at 4000 rpm. An aliquot of the supernatant was transferred into a 1.8 mL centrifuge vial and centrifuged at 15000 rpm for 30 minutes. A portion of the supernatant was diluted with 1:1 methanol/water solution containing 0.1 % formic acid. The total volume of the complete aqueous phase was determined gravimetrically. Soil pellets were extracted and diluted. The amount of M656PH031 was determined in all aqueous phases and extracts by LC-MS/MS.

Aqueous phase and solid phases (soil pellets) were analysed separately by means of LC-MS/MS. Determination of M656PH031 in 0.01 M $CaCl_2$ aqueous solution ("soil water") involved volumetric dilution (dilution factors DF of 10, 100, or 1000) with subsequent LC/MS/MS analyses.

Determination of M656PH031 in the soil involved three times extraction of the soil pellets with 5 mL of with acetone/water (1/1 v/v). First the soil pellet was loosened by brief, intensive shaking by hand and sonication (10 min) then by horizontal shaking (30 min). The soil/solvent phases were separated by centrifugation (5 min at 4000 rpm), then the extracts were combined, filled up to volume (V Ex= 20 mL) with the extraction mixture and diluted (dilution factors DF of 5, 10, 50, 100, 200, or 500) for

LC/MS/MS determination of M656PH031. The applicability of the soil extraction method was investigated by fortifying soil pellets of control specimens with M656PH031 at different concentration levels, extraction and analysis during Tier 1 and Tier 3 testing performance

Results and Discussion

LC/MS/MS analysis of diluted soil water resulted in excellent average recoveries (Tier 1: 93 % and 99 %, Tier 3: 95 % to 101 %) and standard deviations (≤ 9 %) for the dose levels (0.01, 0.050, 0.25, 1.0, and 5.0 µg/rnL) used during Tier 1 and Tier 3 tests. LC/MS/MS analysis of soil extracts resulted in excellent average recoveries (Tier 1: 100 % and 93 %, Tier 3: 94 % to 98 %) and standard deviations (≤ 6 %) for the dose levels (0.01, 0.05, 0.25, 1.0, and 5.0 µg/g) used during Tier 3 tests.
The adsorption kinetics on two soils revealed that reaching adsorption equilibrium requires two days (48 h). Using control specimens with only M656PH031 in 0.01 $CaCL_2$ without soil demonstrated the absence of M656PH031 adsorption on the surface of the test vessels.

The resulting adsorption and the derived adsorption coefficients are summarised in Table B.8.1.3-8.

Table B.8.1.3-8: Summary of Adsorption (A) at equilibrium (eq), adsorption kinetics and isotherms for M656PH031

Soil	Soil Type (USDA)	Org. C [%]	pH ($CaCl_2$)	Adsorption at equilibrium [%]*	K_d [mL/g]	K_{OC} [mL/g]	K_F [$\mu L^{1-1/n}$ $mL^{1/n}$ g^{-1}]	K_{FOC} [$\mu L^{1-1/n}$ $mL^{1/n}$ g^{-1}]	1/n
LUFA 2.1 (2^{nd} trial)	Sand	0.52	5.2	2	0.027	5.1	0.031	6.0	0.69
Li 10	Loamy sand	0.88	5.9	1	0.010	1.1	0.016	1.8	0.73
Nierswalde Wildacker	Silt loam	1.63	6.5	9	0.087	5.3	0.078	4.8	1.02
LUFA 2.3	Sandy loam	1.09	6.9	5	0.047	4.3	0.046	4.2	0.96
La Gironda Arahal	Silty clay loam	3.84	7.5	3	0.036	0.9	0.037	1.0	0.92
LUFA 2.1 (1^{st} trial)	Sand	0.52	5.2	2	0.023	4.3	Not evaluated-		

* Values for adsorption at equilibrium, K_d and K_{oc} are obtained from nominal dose level 5 µg/mL

The adsorption of M656PH031 on soil at a nominal concentration 5 µg/mL ranged from 1 % to 9 %. Control specimens demonstrated stability of the test item in $CaCl_2$ solution and absence of adsorption on the surface of test vessels.
The distribution coefficient K_d and K_{oc} values were calculated at nominal concentration of 5 µg/mL K_d values ranged from 0.010 to 0.087 mL/g, K_{oc} values from 0.9 to 5.3 mL/g.
The Freundlich adsorption coefficients K_F ranged from 0.016 to 0.078 $\mu L^{1-1/n}$ $mL^{1/n}$ g^{-1} with the Freundlich exponent 1/n ranging from 0.69 to 1.02. The organic carbon normalised Freundlich coefficient K_{Foc} ranged from 1.0 to 6.0 $\mu L^{1-1/n}$ $mL^{1/n}$ g^{-1}. Evaluation of the significance of sorption (K_d x m_{soil} /$V_{solution}$ should be larger than 0.1 due to direct determination of sorption) shows no reliable sorption since all K_d are < 0.1 (using a soil/solution ratio of 5:5).

Conclusion

The study is considered acceptable in the way that it was performed in line with the guideline OECD 106. Thus, there is no data gap regarding the adsorption properties of M656PH031, although the adsorption of the metabolite proved to be so poor to obtain reliable parameters.
The adsorption of M656H031 at nominal concentration 5 µg/mL on the five investigated soils ranged from 1 % to 9 %. Distribution coefficients Kd values of M656PH031 remained < 0.1 for all soils. These results in K_{oc} values ranging from < 3 to < 19 mL/g. M656PH031 is be considered as qualitatively mobile.

KCA 7.1.3.1.2/4 – Sacchi, 2013 (new study)

Author: Sacchi, R. R.
Title: Adsorption behavior of M23, M27 and M31 (metabolites of dimethenamid-P) on different European soils
Date: 2418/11/2013
Doc ID: BASF DocID 2013/3012762
Guidelines: Altered method following OECD 106 (January 2000)
GLP: Yes
Validity: Acceptable

Material and Methods

The adsorption behaviour of the dimethenamid-P metabolites M656PH023 (M23 in this study, purity 100 %), M656PH027 (M27 in this study, purity 97.4 %), and M656H031 (M31 in this study, purity 98.7 %) were investigated on five different European soils. The five soils covered a range of pH (in $CaCl_2$) from 5.6 to 7.4, a range of organic carbon content from 0.60 % to 1.85 % and different textural classes. Soils physico-chemical properties are provided in Table B.8.1.3-9.

Table B.8.1.3-9: Characterisation of soils used to investigate the adsorption and desorption of M656PH023, M656PH027 and M656H031

Soil designation Origin	LUFA 2.1	Nierswalder Wildacker	Li 10	LUFA 2.3	LUFA 5M
Textural class (USDA scheme)	Sand	Silt loam	Loamy sand	Sandy loam	Sandy loam
Soil texture [%], (USDA scheme) **Sand** **Silt** **Clay**	 90.8 6.9 2.3	 17.7 73.5 8.8	 84.6 11.3 4.1	 68.6 23.1 8.3	 58.1 29.7 12.1
Organic carbon [%] **Organic matter[1)] [%]**	0.60 1.03	1.85 3.19	0.93 1.60	0.99 1.71	1.07 1.84
CEC [cmol+/kg]	-0.7	3.1	5.3	7.5	10.1
pH ($CaCl_2$)	5.6	5.7	6.0	6.7	7.4

1) organic matter =organic carbon x 1.724

For low sorbing compounds it is important to have full separation of the phases (water and soil) to utilise the direct method. When a small amount of water remains after centrifugation and subsequent partitioning, results for low sorbing compounds may be inaccurate. To circumvent this problem, a "syringe" method was developed in which after shaking the soil and water mixture inside the syringe, the syringe is then centrifuged and the centripetal force is used to fully separate the phases through a frit. The water is collected for analysis. This method improves the accuracy for low sorbing compounds and was used in these studies. This method allows for more adequate separation of the phases and therefore this enables a more precise determination of the amount of test substance adsorbed on soil.

The adsorption equilibrium was determined in Tier 1 testing using standard solutions of the test items with a concentration of 1.0 µg/mL in 0.01 M $CaCl_2$ A soil/solution ratio of 1:1 was chosen. Series of duplicate samples (one duplicate for each sampling) of each soil were prepared. For each sample 3 g of soil were weighed in glass tubes and 3 mL of standard solution were added. The samples were agitated in a temperature controlled dark room at 20 ± 2 °C for 4, 8, 24, 32 and 48 h and then the suspensions were separated by centrifugation. The aqueous phase was analysed (after appropriate dilution) by LC-MS/MS and the amount of analyte adsorbed on the soil was calculated as difference between the amount initially dosed and the amount remaining at the end of the experiment in the

aqueous phase (indirect method). Subsequently the soil was extracted to analyse the test item adsorbed to the soil (direct method).
The adsorption isotherm determination was performed with all five concentration levels (nominal concentrations: 1.0, 0.5, 0.1, 0.05 and 0.01 µg/mL) and the five soils. All Tier 3 experiments were performed using a constant soil/solution ratio of 1/1. For all samples 1 g of soil was weighed into syringes, and then 1 mL solution of each concentration level was added. Each experiment (one soil and one solution) was done in duplicate. All samples were shaken on a horizontal shaker at 20 ± 2 °C until adsorption equilibrium was reached. The appropriate time for adsorption equilibrium was 48 hours for the test item M656PH023 and M656PH027 and 24 hours for test item M656H031. The soil / solution suspension was then centrifuged and the filtrate was collected for analysis. Syringes were used for the experiment as this allowed the reduction of the remaining volume of test solution in soil after equilibration time by centrifugation at high speed over a frit.
Aliquots of both suspensions and initial solution applied (after dilution) were analysed in order to determine the initial concentration as well as the concentration of the test item in the aqueous solution after adsorption. This information provides data for indirect determination of adsorption.
Since adsorption of the test item was very low, adsorption was also determined by the direct method. The remaining soil in the syringe was extracted with methanol / water (60/40, v/v) solution for M656PH023 and M656PH027 and with acetone/water (1/1, v/v) for M656PH031.

The test item concentrations in aqueous phase and soil extracts were determined by HPLC-MS/MS. The analytical methods for the determination of M656PH023, M656PH027 and M656PH031 were developed and validated within this study. For HPLC-MS/MS quantitation purposes, calibration standard solutions from 0.01 ng/mL up to 1.0 ng/mL in methanol (M656PH023 and M656PH027) and methanol/water (50/50, v/v) (M656PH031), including at least six levels, were used for all the samples.
For validation of analysis of the test substances M656PH023, M656PH027 and M656PH031 in aqueous solution, aqueous solutions were fortified with the test item at the LOQ (0.5 ng/mL) and at a level of 1000 ng/mL, the highest nominal test concentration. In addition, an aliquot of the aqueous solution (untreated) was analysed to demonstrate that matrix components do not interfere with the detection and quantification of M656PH023, M656PH027 or M656PH031. The fortified aqueous solutions were diluted with methanol / water (20 / 80, v/v) solution, when appropriate, and analysed by HPLC-MS/MS.
For validation of analysis of the test substance M656PH023 and M656PH027 in soil, soil samples were fortified with the test item at the LOQ (0.0005 mg/kg) and at a level of 1.0 mg/kg, the highest nominal test concentration. In addition, a soil sample (untreated) was analysed to demonstrate that matrix components do not interfere with the detection and quantification of M656PH023 and M656PH027. The soil samples fortified were extracted twice with methanol / water (60/40, v/v) solution. Samples were diluted with methanol / water (60/40, v/v) solution, when appropriate, and then analysed by HPLC-MS/MS. The LUFA 2.1 soil was used for validation. The analytical method for M656H031 was the same, however the soil samples were extracted three times with acetone / water (1/1, v/v) solution instead of methanol / water (60/40, v/v) solution.

Results and Discussion

Overall recoveries ranged from 78.4 % to 102.6 % for M656PH023, 75.4 % to 101.9 % for M656PH027 and 90.0 % to 110.0 % for M656PH031 for the equilibrium test. For the isotherm determinations overall recoveries ranged from 90.4 % to 119.8 % for M656PH023, 71.1 % to 116.2 % for M656PH027 and 92.6 % to 133.4 % for M656H031.
The validation results of the analytical methods are given in Table B.8.1.3-10. For a fortification level of 0.5 ng/mL they range from 80.7 % to 97.3 % and from 84.4 % to 115.4 % for $CaCl_2$ solution and soil, respectively. For a fortification level of 1000 ng/mL they range from 87.4 % to 103 % and from 72.5 % to 100.9 % for $CaCl_2$ solution and soil, respectively.

Table B.8.1.3-10: Summary of validation results – mean recoveries obtained for fortified $CaCl_2$ solution and soil LUFA 2.1

		$CaCl_2$ solution		Soil	
		Fortification level:		Fortification level:	
		0.5 ng/mL	1000.0 ng/mL	0.5 ng/mL	1000.0 ng/mL
M656PH023		97.3 (n = 7)	87.4 (n = 6)	84.4 (n = 6)	72.5 (n = 5)
M656PH027	Quantitation transition	80.7 (n = 6)	100.7 (n = 5)	115.4 (n = 7)	85.7 (n = 7)
	Confirmation transition	80.5 (n = 6)	103.0 (n = 5)	114.4 (n = 7)	82.8 (n = 7)
M656H031	Quantitation transition	96.3 (n = 7)	96.8 (n = 7	97.8 (n = 7)	95.3 (n = 7)
	Confirmation transition	94.4 (n = 7)	93.8 (n = 7)	92.5 (n = 7)	100.9 (n = 7)

In the soil equilibrium test, M656PH023 showed constant adsorption throughout the test period in the soils Nierswalder Wildacker and LUFA 5M. For the other soils the adsorption values fluctuated throughout the test period, but the percentage of active substance adsorbed at 48 h did not increase significantly from sampling 8 h. The time chosen for conduction of isotherm tests was 48 hours.
The metabolite M656PH027 showed constant adsorption throughout the soil equilibrium test with the soil Li10. In the other soils the adsorption increased throughout the test period. The time chosen for conduction of isotherm tests was 48 hours.
The metabolite M656H031 showed constant adsorption throughout the soil equilibrium test. The time chosen for conduction of isotherms test was 24 hours.

The derived adsorption coefficients of the Freundlich adsorption isotherm determination are summarised in Table B.8.1.3-11, Table B.8.1.3-12 and Table B.8.1.3-13.

Table B.8.1.3-11: Adsorption of M656PH023 based on Freundlich isotherms in five soils

Soil	Soil Type (USDA)	Org. C [%]	pH ($CaCl_2$)	K_F [mL/g]	1/n	K_{FOC} [mL/g]
Nierswalder Wildacker	Silt Loam	1.85	5.7	0.14	0.68	7.62
Li10	Loamy Sand	0.93	6.0	0.10	0.76	10.53
LUFA 2.1	Sand	0.60	5.6	0.13	0.87	22.39
LUFA 2.3	Sandy Loam	0.99	6.7	0.12	0.70	12.46
LUFA 5M	Sandy Loam	1.07	7.4	0.07	0.60	6.29

Table B.8.1.3-12: Adsorption of M656PH027 based on Freundlich isotherms in five soils

Soil	Soil Type (USDA)	Org. C [%]	pH ($CaCl_2$)	K_F [mL/g]	1/n	K_{FOC} [mL/g]
Nierswalder Wildacker	Silt Loam	1.85	5.7	0.16	1.14	8.55
Li10	Loamy Sand	0.93	6.0	0.09	0.97	9.89
LUFA 2.1	Sand	0.60	5.6	0.05	1.00	7.73
LUFA 2.3	Sandy Loam	0.99	6.7	0.11	0.98	10.96
LUFA 5M	Sandy Loam	1.07	7.4	0.14	0.94	13.54

Table B.8.1.3-13: Adsorption of M656H031 based on Freundlich isotherms in five soils

Soil	Soil Type (USDA)	Org. C [%]	pH ($CaCl_2$)	K_F [mL/g]	1/n	K_{FOC} [mL/g]
Nierswalder Wildacker	Silt Loam	1.85	5.7	0.04	0.98	2.11
Li10	Loamy Sand	0.93	6.0	0.04	1.01	4.58
LUFA 2.1	Sand	0.60	5.6	0.06	0.77	9.20
LUFA 2.3	Sandy Loam	0.99	6.7	0.04	0.96	4.28
LUFA 5M	Sandy Loam	1.07	7.4	0.02	0.93	1.72

The Freundlich adsorption coefficient K_F covered a range from 0.07 mL/g to 0.14 mL/g for M656PH023, 0.05 mL/g to 0.16 mL/g for M656PH027 and 0.02 mL/g to 0.06 mL/g for M656PH031. The K_{FOC} values ranged from 6.29 mL/g to 22.39 mL/g for M656PH023, 7.73 mL/g to 13.54 mL/g for M656PH027 and 1.72 mL/g to 9.20 mL/g for M656H031. The 1/n values ranged from 0.60 to 0.87 for M656PH023, 0.94 to 1.14 for M656PH027 and 0.77 to 1.01 for M656PH031.

Conclusion

The study was not performed according to OECD 106, although it followed the guidance in all aspects but the used incubation vessels and the separation of the $CaCl_2$ solution and the soil phase. In order to allow a more accurate determination of the adsorption properties for the poorly absorbable metabolites M656PH027, M656PH023 and M656PH031, a new method was developed where the two phases were separated through the frit of a syringe. The syringe method was introduced in order to reduce the remaining volume of test solution in soil after equilibration time by centrifugation at high speed over the frit. This method allows for more adequate separation of the phases and thus enables a more precise determination of the amount of test substance adsorbed on soil. The study author therefore claims that the significance criteria of sorption (K_d x m_{soil} /$V_{solution}$ should be larger than 0.1) does not apply for this method.
While the RMS agrees that the separation of the two phases via high speed centrifugation over a frit is likely to be more thorough, in the opinion of the RMS there surely is also a limit after which the adsorption cannot be determined reliably anymore, even when using a more efficient separation technique. However, no 'adapted' significance criterion is available to test the determined adsorption parameters for the three metabolites. Besides, while the separation is likely to be more accurate, the overall recoveries of the adsorption experiments clearly suffer and are out off the range of 90 % to 110 % which is considered acceptable according to OECD 106. This is possibly due to the smaller soil and solution volumes used in the experiments and the resulting higher measurement variability. Since the greater variability might counterbalance some of the positive effects of the better separation and since no 'adapted' significance criterion is available, the RMS decided to still test the determined adsorption parameters against the significance criteria 'K_d x m_{soil} /$V_{solution}$ should be larger than 0.1' nevertheless.
For M656H023, the significance criteriion of the K_d values derived for each concentration was fulfilled for all soils except the two highest concentrations of the soil LUFA 5M. However, excluding this two highest concentrations did not lead to any major changes in the adsorption parameters. Thus the derived adsorption parameters of M656H023 are considered acceptable by the RMS and will be used for endpoint derivation. Adsorption parameters of M656H023 were determined in five soils. The resulting K_f values ranged from 0.07 to 0.14 cm^3/g and resulted in K_{FOC} values between 6.29 and 22.39 cm^3/g. Freundlich exponents ranged from 0.68 to 0.872.
For M656PH027, acceptable K_f and 1/n values could mostly be determined for the soils NW and Li10 although some of the concentrations did not fulfil the criteria K_d x soil/solution ratio < 0.1. For soil LUFA 2.1, the K_f values were far below K_d x soil/solution ratio < 0.1 and thus are expected to be unreliable. However the more reliable K_f values of this study and the study KCA 7.1.3.1.2/2 – Class & Dorn, 2004 are in a similar range and excluding this lower K_f values from endpoint derivation would be a best case (soils of poor adsorption would not be considered). Thus, they will also be included for endpoint derivation. Adsorption parameters of M656PH027 were determined in five soils. The resulting K_f values ranged from 0.05 - 0.16 cm^3/g and resulted in K_{FOC} values between 7.73 and 13.54 cm^3/g. Freundlich adsorption isotherms ranged from 0.68 to 0.872.

For M656H031, the significance criterion is not fulfilled for any of the soils. Besides, variations between the K_f values determined by Sacchi, 2013 and by Class, 2011 show that the variations in K_f values is very high for soils from the same origin and very similar soil properties (soil Nierswalde Wildacker, soil Li10, soil LUFA 2.1 and LUFA 2.3). Thus, the determined K_f and K_{foc} values are not considered acceptable by the RMS. However, they allow an estimation of the likely adsorption of M656PH031 which is poor in most soils. The adsorption of M656PH031 was investigated in five soils. Distribution coefficients K_d values of M656PH031 remained < 0.1 for all soils. This results in K_{oc} values ranging from < 5 to < 17 mL/g. M656PH031 is considered as qualitatively mobile in these five soils.

KCA 7.1.3.1.2/5 – Class & Walter, 2014a (new study)

Author:	Class, T. Walter, W.
Title:	Determination of Adsorption and Desorption Behavior of M656PH043 (Reg No. 5917262, Metabolite of Dimethenamid-P) in 5 Soils
Date:	04/02/2014
Doc ID:	BASF DocID 2013/1348092
Guidelines:	OECD 106 (January 2000)
GLP:	Yes
Validity:	Acceptable

Material and Methods

The adsorption behaviour of M656PH043 (purity: 94.6 %), metabolite of dimethenamid-P, was investigated in five different soils. The soils covered a range of pH from 4.1 to 7.4 and a range of organic carbon content from 0.75 % to 2.03 %. The physico-chemical properties of the soils are provided in Table B.8.1.3-14.

Table B.8.1.3-14: Characterisation of soils used to determine the adsorption / desorption behaviour of M656PH043

Soil designation **Origin**	**LUFA 2.2**	**LUFA 5M**	**Li 10**	**La Gironda (Arahal)**	**Schifferstadt**
Textural class (DIN 4220)	Loamy sand (SI4)	Loamy sand (SI2)	Loamy sand (SI2)	Sandy clay loam	Sand
Soil texture [%], (ISO 11277)					
Sand	55.9	80.0	81.2	48.0	88.1
Silt	32.1	13.9	13.2	24.3	7.7
Clay	12.0	6.1	5.6	27.7	4.3
Textural class (USDA)	Sandy loam	Loamy sand	Loamy sand	Sandy clay loam	Sand
Soil texture [%], (USDA)					
Sand	60.3	82.8	82.8	49.2	88.5
Silt	27.7	11.1	11.6	23.0	7.2
Clay	12.0	6.1	5.6	27.7	4.3
Organic carbon [%] (ISO 10694)	1.47	2.03	0.84	1.22	0.75
Effective CEC [cmol⁺/kg]	7.6	11.4	5.3	26.3	0.3
pH ($CaCl_2$)	5.4	7.2	6.4	7.4	4.1
pH (H_2O)	5.9	7.9	6.9	8.3	5.0
MWHC [g/100g dry soil]	29.6	25.2	25.1	39.2	27.0
Bulk density [g/L]	1227	1367	1369	1308	1342

The Tier 1 adsorption kinetics preliminary test was performed exemplarily for two soils, one with low

pH and low organic carbon content (sand Schifferstadt: pH 4.1, 0.75 % organic carbon) and one with higher, neutral pH (loamy sand LUFA 5M: pH 7.2, 2.03 % organic carbon). Duplicate portions of 2 g dry soil were equilibrated on a horizontal shaker with slightly less than 2 mL $CaCl_2$ solution (1:1 soil/solution ratio) in a centrifuge tube overnight. Then the analyte dose solution was added to the soil water to obtain a nominal amount of 50 ng/mL in the aqueous phases. Test systems were then equilibrated on a horizontal shaker for various equilibration times (2, 4, 6, 24 and 48 hours) at 20-21°C. After shaking/equilibration and subsequent centrifugation, the supernatant aqueous phase was weighed to obtain the volume of the supernatant and to calculate the portion/volume of the aqueous phase remaining in the soil pellet. The liquid phases obtained after centrifugation were diluted and analysed by LC-MS/MS. Soil pellets were extracted and the extracts diluted and analysed by LC-MS/MS.
For the soils LUFA 2.2, Li 10 and La Gironda (Arahal), adsorption tests with a soil/solution ratio of 1/1 were performed for 48 hours of equilibration time using the same experimental conditions as described above for the adsorption kinetics preliminary test.

The Tier 1 test showed that the test item is expected to be stable in soils LUFA 5M and Li 10 but possibly disintegrates in the other three soils. However, the K_d values obtained by the direct method and the soil/solution ratio of 1/1 were rather low and thus the test item has to be considered “to be qualitatively mobile” (OECD Guideline 106 Section 69) or not significantly adsorbed. Therefore, Tier 3 testing was only considered to lead to accurate Freundlich adsorption isotherms for the acidic sand Schifferstadt.
The tier 3 adsorption isotherm test was performed using an equilibration time of 24 hours and 1/1 soil/solution ratio. Soil samples (2 g) were equilibrated overnight with < 2.0 mL of 0.01 M $CaCl_2$ solution. The test substance was added to the mixture to achieve the following amounts: 5, 25, 50, 250 and 500 ng/mL in the aqueous solution. Duplicate samples were used for each concentration. The test systems were equilibrated by shaking on a horizontal shaker at 20-21 °C. After equilibration the samples were analysed as described for the adsorption kinetics preliminary test.

Aqueous phase and solid phases (soil pellets) were analysed separately after centrifugation by means of LC-MS/MS. Aliquots of supernatant were diluted volumetrically by a dilution factor into methanol/water (1/1, v/v) for LC/MS/MS analysis. Determination of M656PH043 in the soil involved one extraction of soil pellets with 5 mL of methanol and two extractions with 5 mL of methanol/water (1/1, v/v). After separation via centrifugation, extracts were combined and diluted. An aliquot of the final extract was diluted with methanol/water (1/1) and subjected to LC-MS/MS analysis.
The soil extraction method was concurrently validated for all five soils at two fortification levels (5 and 50 ng/g).

Results and Discussion

Mass balances ranged from 84 - 86 % were found for sand Schifferstadt (pH 4.1) obtained after 2 to 48 hours of equilibration time with soil pellet extraction indicating limited stability or irreversibly bounding on the soil. For sandy loam LUFA 5M, mass balances ranged from 95 – 101 % after 2 to 48 hours of equilibration time with soil pellet extraction. Mass balances after soil extraction after 48 h were 97 % for soil Li 10, 89 % for soil LUFA 2.2 and 79 % for soil La Gironda (Arahal), indicating the stability of the test item during the experiments for LUFA 2.2 but limited stability on the other two soils. For the adsorption isotherm testing in soil Schifferstadt the mass balances obtained after 24 hours of equilibration time were 84 – 90 % (25 to 500 ng/mL) with the exception of 77 % for the 5 ng/mL samples.

A summary of the Tier 1 results is given in Table B.8.1.3-15.

Table B.8.1.3-15: Summary of Tier 1 results for M656PH043 (48 h equilibration, 1/1 ratio)

Soil	Soil Type (USDA)	Org. C [%]	pH ($CaCl_2$)	Adsorption at equilibrium [%]	K_d [mL/g]	K_{OC} [mL/g]
Schifferstadt	Sand	0.75	4.1	16	0.229	30.5
LUFA 5M	Loamy sand	2.03	7.2	6	0.062	3.06
LUFA 2.2	Sandy Loam	1.47	5.4	8	0.097	6.60
Li 10	Loamy sand	0.84	6.4	5	0.055	6.52
La Gironda (Arahal)	Sandy clay loam	1.22	7.4	5	0.074	6.07

The percentage of adsorption for the soil Schifferstadt reached a plateau (adsorption measured directly ≈ 15 % to ≈ 17 %) after 6 to 48 hours of equilibration time. K_d calculated by the direct method reached about 0.2 mL/g after 48 hours of equilibration time. This result allows considering the test item to be significantly adsorbed and as "to be qualitatively mobile". Besides, the K_d of about 0.2 mL/g (direct method) multiplied by the soil/solution ratio of 1/1 (= 1) is > 0.1. Thus, for this soil the experiments to study the adsorptive behaviour of the chemical in soil and its potential mobility were continued by determining Freundlich adsorption isotherms in Tier 3.
The percentage of adsorption for the soil LUFA 5M was observed to reach a plateau (adsorption measured directly ≈ 4 %) after 2 hours of equilibration time. K_d calculated by the direct method reached only about 0.06 mL/g after 48 hours of equilibration time. This result allows considering the test item as "to be qualitatively mobile". A K_d of about 0.06 mL/g (direct method) multiplied by the soil/solution ratio of 1/1 (= 1) obviously is < 0.1. As a result, the compound can be considered to be not significantly adsorbed. Thus (as recommended in Section 71) for this neutral loamy sand LUFA 5M experiments to determine Freundlich adsorption isotherms in Tier 3 were expected not to yield accurate results and were therefore not performed.
For the three remaining soils LUFA 2.2, Li 10 and La Gironda, the adsorption after 48 hours equilibration (adsorption measured directly) was always < 10 %. Mean K_d calculated by the direct method reached for all three soils 0.055 mL/g to 0.097 mL/g after 48 hours of equilibration time. These allow considering the test item as "to be qualitatively mobile" as especially for Li 10 and La Gironda soil test item is not significantly adsorbed. When the results for K_d of 0.055 mL/g to 0.097 mL/g obtained with the direct method are multiplied by the soil/solution ratio of 1/1 (= 1) results for these two soils are significantly < 0.1. The K_d value for LUFA 2.2 soil is around 0.1 and due to low variability between individual experimental replicates and of still well determinable soil residue levels, K_d for this soil can be considered valid, despite it is formally below 0.1.
Thus no Freundlich isotherms were determined for the soils LUFA 2.2, LUFA 5M, Li 10 and La Gironda.

The adsorption isotherms of M656PH043 on the soil Schifferstadt is given in Table B.8.1.3-16.

Table B.8.1.3-16: Summary of adsorption isotherm test of M656PH043 on soil Schifferstadt

Soil Type (USDA)	Org. C [%]	pH ($CaCl_2$)	Equilibration time [%]	K_F [$ng^{1-1/n}$ $mL^{1/n}$ g^{-1}]	K_{FOC} [$ng^{1-1/n}$ $mL^{1/n}$ g^{-1}]	1/n
Sand	0.75	4.1	24	0.702	94	0.51

The adsorption coefficient K_F of M656PH043 on the soil Schifferstadt derived from Freundlich adsorption isotherms is 0.702 with a Freundlich exponent of 0.51.

Conclusion

The study is considered acceptable in the way that it was performed in line with the guideline OECD 106. Thus, there is no data gap regarding the adsorption properties of M656PH043, although the adsorption of the metabolite proved to be too poor to obtain reliable parameters for a sufficient number of soils.
Distribution coefficients K_d values of M656PH043 remained < 0.1 for the four of the five investigated soils. Thus, the resulting K_{oc} values ranged from < 5 to < 12 mL/g. M656PH043 is considered as

qualitatively mobile in these four soils.
For the soil Schifferstadt, a reliable K_d of 0.229 could be obtained resulting in a K_{oc} of 30.5. However, in the opinion of the RMS the subsequently derived K_f value together with the 1/n value should be considered with caution. For 3 of the measured 5 concentrations the criteria Kd x soil/solution ratio was >0.1 and thus not fulfilled leaving only reliable Kd values for two concentrations. This is not considered sufficient for K_f and Freundlich exponent derivation.

KCA 7.1.3.1.2/6 – Class & Walter, 2014b (new study)

Author:	Class, T. Walter, W.
Title:	Determination of Adsorption and Desorption Behavior of M656PH047 (Reg No. 5917260, Metabolite of Dimethenamid-P) in 5 Soils
Date:	17/02/2014
Doc ID:	BASF DocID 2013/1348093
Guidelines:	OECD 106 (January 2000)
GLP:	Yes
Validity:	Acceptable

Material and Methods

The adsorption behaviour of M656PH047 (90.7 % purity), metabolite of dimethenamid-P was investigated in five different soils. The soils covered a range of pH from 4.1 to 7.4 and a range of organic carbon content from 0.75 % to 2.03 %. The physico-chemical properties of the soils are provided in Table B.8.1.3-17.

Table B.8.1.3-17: Characterisation of soils used to determine the adsorption / desorption behaviour of M656PH047

Soil designation Origin	**LUFA 2.2**	**LUFA 5M**	**Li 10**	**La Gironda (Arahal)**	**Schifferstadt**
Textural class (DIN 4220)	Loamy sand (SI4)	Loamy sand (SI2)	Loamy sand (SI2)	Sandy clay loam	Sand
Soil texture [%], (ISO 11277)					
Sand	55.9	80.0	81.2	48.0	88.1
Silt	32.1	13.9	13.2	24.3	7.7
Clay	12.0	6.1	5.6	27.7	4.3
Textural class (USDA)	Sandy loam	Loamy sand	Loamy sand	Sandy clay loam	Sand
Soil texture [%], (USDA)					
Sand	60.3	82.8	82.8	49.2	88.5
Silt	27.7	11.1	11.6	23.0	7.2
Clay	12.0	6.1	5.6	27.7	4.3
Organic carbon [%] (ISO 10694)	1.47	2.03	0.84	1.22	0.75
Effective CEC [cmol⁺/kg]	7.6	11.4	5.3	26.3	0.3
pH ($CaCl_2$)	5.4	7.2	6.4	7.4	4.1
pH (H_2O)	5.9	7.9	6.9	8.3	5.0
MWHC [g/100g dry soil]	29.6	25.2	25.1	39.2	27.0
Bulk density [g/L]	1227	1367	1369	1308	1342

The Tier 1 adsorption kinetics preliminary test was performed exemplarily for two soils, one with low pH and low organic carbon content (sand Schifferstadt: pH 4.1, 0.75 % organic carbon) and one with higher, neutral pH (sandy loam LUFA 5M: pH 7.2, 2.03 % organic carbon). Duplicate portions of 2 g

dry soil were equilibrated on a horizontal shaker with slightly less than 2 mL $CaCl_2$ solution (1:1 soil/solution ratio) in a centrifuge tube overnight. Then the analyte dose solution was added to the soil water to obtain a nominal amount of 50 ng/mL in the aqueous phases. Test systems were then equilibrated on a horizontal shaker for various equilibration times (2, 4, 6, 24 and 48 hours) at 20-21 °C. After shaking/equilibration and subsequent centrifugation, the supernatant aqueous phase was weighed to obtain the volume of the supernatant and to calculate the portion/volume of the aqueous phase remaining in the soil pellet. The liquid phases obtained after centrifugation were diluted and analysed by LC-MS/MS. Soil pellets were extracted and the extracts diluted and analysed by LC-MS/MS.
For the soils LUFA 2.2, Li 10 and La Gironda (Arahal), adsorption tests with a soil/solution ratio of 1/1 were performed for 48 hours of equilibration time using the same experimental conditions as described above for the adsorption kinetics preliminary test.

Aqueous phase and solid phases (soil pellets) were analysed separately after centrifugation by means of LC-MS/MS. Aliquots of supernatant were diluted volumetrically by a dilution factor into methanol/water (1/1, v/v) for LC/MS/MS analysis. Determination of M656PH047 in the soil involved one extraction of soil pellets with 5 mL of methanol and two extractions with 5 mL of methanol/water (1/1, v/v). After separation via centrifugation, extracts were combined and diluted. An aliquot of the final extract was diluted with methanol/water (1/1) and subjected to LC-MS/MS analysis.
The soil extraction method was concurrently validated for all five soils at two fortification levels (5 and 50 ng/g) resulting in an overall average recovery of 94 % (RSD 3 %).

Results and Discussion

For acidic sand Schifferstadt (pH 4.1) soil mass balance decreased from 87 % after 2 hours to 67 % for the 48 hours equilibration time, indicating limited stability with prolonged equilibration. For neutral loamy sand LUFA 5M (pH 7.2), a mass balance 100 % was obtained with soil pellet extraction after 2 h decreasing to 92 % after 48 h. For the adsorption testing of soils LUFA 2.2, Li 10 and La Gironda mass balances were 79 %, 88 % and 86 % after 48 h of equilibration time, indicating degradation or formation of bound residues.
A summary of the Tier 1 results is given in Table B.8.1.3-18.

Table B.8.1.3-18: Summary of Tier 1 results for M656PH047 (48 h equilibration, 1/1 ratio)

Soil	Soil Type (USDA)	Org. C [%]	pH ($CaCl_2$)	Adsorption at equilibrium [%]	K_d [mL/g]	K_{OC} [mL/g]
Schifferstadt	Sand	0.75	4.1	1.2	0.019	2.48
LUFA 5M	Loamy sand	2.03	7.2	1.5	0.016	0.79
LUFA 2.2	Sandy Loam	1.47	5.4	0.5	0.006	0.42
Li 10	Loamy sand	0.84	6.4	1.0	0.012	1.37
La Gironda (Arahal)	Sandy clay loam	1.22	7.4	0.7	0.009	0.72

The percentage of adsorption of M656PH047 on the soil Schifferstadt did not change significantly with prolonged equilibration time, and was about (adsorption measured directly) 1 % after 48 hours of equilibration time. K_d calculated by the direct method reached only about 0.02 mL/g after 48 hours of equilibration time. This result allowed considering the test item as “to be qualitatively mobile”. A K_d of maximal 0.02 mL/g (direct method) multiplied by the soil/solution ratio of 1/1 (= 1) is < 0.1. As a consequence, following the reported procedures, adsorption has to be considered not to be significant. Thus for this acidic sand Schifferstadt experiments to determine Freundlich adsorption isotherms in Tier 3 were expected not to yield accurate results and were, therefore, not performed.
The percentage of adsorption of M656PH047 on the soil LUFA 5M did not change significantly with prolonged equilibration time, and was about (adsorption measured directly) 2 % after 48 hours of equilibration time. K_d calculated by the direct method reached only about 0.02 mL/g after 48 hours of equilibration time. This result allowed considering the test item as “to be qualitatively mobile”. A K_d of about 0.02 mL/g (direct method) multiplied by the soil/solution ratio of 1/1 (= 1) is < 0.1. If K_d is below this value, adsorption is supposed to be not significant according to OECD Guideline 106. Thus for this neutral loamy sand LUFA 5M experiments to determine Freundlich adsorption isotherms in

Tier 3 were expected not to yield accurate results and were, therefore, not performed.
Adsorption of M656PH047 on the soils LUFA 2.2, Li 10 and La Gironda (Arahal) after 48 hours equilibration (adsorption measured directly) was always ≤ 1 %. Mean K_d calculated by the direct method were for all three soils 0.01 mL/g. These results allowed considering the test item as "to be qualitatively mobile". When these results for K_d obtained with the direct method are multiplied by the soil/solution ratio of 1/1 (= 1) the results are all < 0.1. Thus for these soils experiments to determine Freundlich adsorption isotherms in Tier 3 were expected not to yield accurate results and were, therefore, not performed.

Conclusion

The study is considered acceptable in the way that it was performed in line with the guideline OECD 106. Thus, there is no data gap regarding the adsorption properties of M656PH047, although the adsorption of the metabolite proved to be too poor to obtain reliable adsorption parameters for the investigated soils.
Distribution coefficients K_d values of M656PH047 remained < 0.1 for all five investigated soils. The resulting K_{oc} values ranged from < 5 to < 13 mL/g. M656PH047 is considered as qualitatively mobile in all five investigated soils.

KCA 7.1.3.1.2/7 – Class & Walter, 2014c (new study)

Author:	Class, T. Walter, W.
Title:	Determination of Adsorption and Desorption Behavior of M656PH054 (Reg No. 5920718, lVletabolite of Dimethenamid-P) in 5 Soils
Date:	30/01/2014
Doc ID:	BASF DocID 2013/1348094
Guidelines:	OECD 106 (January 2000)
GLP:	Yes
Validity:	Acceptable

Material and Methods

The adsorption behaviour of M656PH054 (purity 85.1 %, (tolerance ±1.0 %)), metabolite of dimethenamid-P was investigated in five different soils. The soils covered a range of pH from 4.1 to 7.4 and a range of organic carbon content from 0.75 % to 2.03 %. The physico-chemical properties of the soils are provided in Table B.8.1.3-19.

Table B.8.1.3-19: Characterisation of soils used to determine the adsorption/ desorption behaviour of M656PH054

Soil designation Origin	LUFA 2.2	LUFA 5M	Li 10	La Gironda (Arahal)	Schifferstadt
Textural class (DIN 4220)	Loamy sand (SI4)	Loamy sand (SI2)	Loamy sand (SI2)	Sandy clay loam	Sand
Soil texture [%], (ISO 11277) **Sand** **Silt** **Clay**	 55.9 32.1 12.0	 80.0 13.9 6.1	 81.2 13.2 5.6	 48.0 24.3 27.7	 88.1 7.7 4.3
Textural class (USDA)	Sandy loam	Loamy sand	Loamy sand	Sandy clay loam	Sand
Soil texture [%], (USDA) **Sand** **Silt** **Clay**	 60.3 27.7 12.0	 82.8 11.1 6.1	 82.8 11.6 5.6	 49.2 23.0 27.7	 88.5 7.2 4.3
Organic carbon [%] (ISO 10694)	1.47	2.03	0.84	1.22	0.75
Effective CEC [cmol$^+$/kg]	7.6	11.4	5.3	26.3	0.3
pH ($CaCl_2$) **pH (H_2O)**	5.4 5.9	7.2 7.9	6.4 6.9	7.4 8.3	4.1 5.0
MWHC [g/100g dry soil]	29.6	25.2	25.1	39.2	27.0
Bulk density [g/L]	1227	1367	1369	1308	1342

The Tier 1 adsorption kinetics preliminary test was performed exemplarily for two soils, one with low pH and low organic carbon content (sand Schifferstadt: pH 4.1, 0.75 % organic carbon) and one with higher, neutral pH (loamy sand LUFA 5M: pH 7.2, 2.03 % organic carbon). Duplicate portions of 2 g dry soil were equilibrated on a horizontal shaker with slightly less than 2 mL $CaCl_2$ solution (1:1 soil/solution ratio) in a centrifuge tube overnight. Then the analyte dose solution was added to the soil water to obtain a nominal amount of 50 ng/mL in the aqueous phases. Test systems were then equilibrated on a horizontal shaker for various equilibration times (2, 4, 6, 24 and 48 hours) at 20-21°C. After shaking/equilibration and subsequent centrifugation, the supernatant aqueous phase was weighed to obtain the volume of the supernatant and to calculate the portion/volume of the aqueous phase remaining in the soil pellet. The liquid phases obtained after centrifugation were diluted and analysed by LC-MS/MS. Soil pellets were extracted and the extracts diluted and analysed by LC-MS/MS.
For the soils LUFA 2.2, Li 10 and La Gironda, adsorption tests with a soil/solution ratio of 1/1 were performed for 48 hours of equilibration time using the same experimental conditions as described above for the adsorption kinetics preliminary test.

The Tier 1 tests showed that the test item is expected to be stable in soils. However, the K_d values obtained by the direct method and the soil/solution ratio of 1/1 were rather low and thus the test item has to be considered "to be qualitatively mobile". Therefore, based on OECD 106, Tier 3 testing was only considered to lead to accurate Freundlich adsorption isotherms for the acidic sand Schifferstadt.
The tier 3 test was performed using an equilibration time of 24 hours (not reported) and 48 hours and 1/1 soil/solution ratio. Soil samples (2 g) were equilibrated overnight with < 2.0 mL of 0.01 M $CaCl_2$ solution. The test substance was added to the mixture to achieve the following amounts: 5.0, 25, 50, 250 and 500 ng/mL in the aqueous solution. Duplicate samples were used for each concentration. The test systems were equilibrated by shaking on a horizontal shaker at 20-21 °C.

Aqueous phase and solid phases (soil pellets) were analysed separately after centrifugation by means of LC-MS/MS. Aliquots of supernatant were diluted volumetrically by a dilution factor into methanol/ water (1/1, v/v) for LC/MS/MS analysis. Determination of M656PH054 in the soil involved one extraction of soil pellets with 5 mL of methanol and two extractions with 5 mL of methanol/water

(1/1, v/v). After separation via centrifugation, extracts were combined and diluted. An aliquot of the final extract was diluted with methanol/water (1/1) and subjected to LC-MS/MS analysis.
The soil extraction method was concurrently validated for all five soils at two fortification levels (5 and 50 ng/g).

Results and Discussion

In the adsorption kinetics testing mass balances between 85 % (for 48 hours equilibration) and 102 % were obtained for acidic sand Schifferstadt. For sandy loam LUFA 5M mass balances between 96 % and 103 % were obtained after soil pellet extraction. For the adsorption testing of soils LUFA 2.2, Li 10 and La Gironda mass balances were between 93 % and 98 % considering individual samples.
For the adsorption isotherm testing in soil Schifferstadt, the mass balances obtained after 48 hours of equilibration time were between 63 and 91 %.

A summary of the Tier 1 results is given in Table B.8.1.3-20.

Table B.8.1.3-20: Summary of Tier 1 results for M656PH054 (48 h equilibration, 1/1 ratio)

Soil	Soil Type (USDA)	Org. C [%]	pH ($CaCl_2$)	Adsorption at equilibrium [%]	K_d [mL/g]	K_{OC} [mL/g]
Schifferstadt	Sand	0.75	4.1	15	0.217	28.90
LUFA 5M	Loamy sand	2.03	7.2	7	0.078	3.84
LUFA 2.2	Sandy Loam	1.47	5.4	8	0.087	5.93
Li 10	Loamy sand	0.84	6.4	7	0.080	9.53
La Gironda Arahal	Sandy clay loam	1.22	7.4	5	0.052	4.30

The percentage of adsorption of M656PH054 on the soil Schifferstadt increased with prolonged equilibration time, reaching a plateau (adsorption measured directly ≈ 10 % to 15 %) after 24 to 48 hours of equilibration time. K_d calculated by the direct method reached about 0.2 mL/g after 48 hours of equilibration time. This result allows to consider the test item as "to be qualitatively mobile", with the results for K_d of about 0.2 mL/g obtained with the direct method and multiplied by the soil/solution ratio of 1/1 (= 1) obviously being > 0.1. Thus for this soil the experiments to study the adsorptive behaviour of the chemical in soil and its potential mobility were continued by determining Freundlich adsorption isotherms in Tier 3.
The percentage of adsorption of M656PH054 on the soil LUFA 5M increased with prolonged equilibration time, reaching a plateau (adsorption measured directly ≈ 6 % to 8 %) after 24 to 48 hours of equilibration time. K_d calculated by the direct method reached only about 0.08 mL/g after 48 hours of equilibration time. This result allows to consider the test item as "to be qualitatively mobile", with the results for K_d of about 0.08 mL/g obtained with the direct method and multiplied by the soil/solution ratio of 1/1 (= 1) obviously being < 0.1. Thus (as recommended in Section 71) for this soil the experiments to study the adsorptive behaviour of the chemical in soil and its potential mobility by determining Freundlich adsorption isotherms in Tier 3 were considered not to result in accurate results and therefore were not performed.

The percentage of adsorption of M656PH054 on the soils LUFA 2.2, Li 10 and La Gironda after 48 hours equilibration (adsorption measured directly) were always < 10 %, indicating results obtained by the indirect method are considered inaccurate. K_d calculated by the direct method reached for all three soil only between 0.05 and 0.09 mL/g after 48 hours of equilibration time. These results allow considering the test item as "to be qualitatively mobile". When these results for K_d obtained with the direct method are multiplied by the soil/solution ratio of 1/1 (= 1) the results are still < 0.1. Thus for these soils the experiments to determining Freundlich adsorption isotherms in Tier 3 were considered not to result in accurate results and therefore were not performed.

Tier 3 tests resulted for soil Schifferstadt in Freundlich adsorption isotherms based on the direct method. The experimental results are given in Table B.8.1.3-21.

Table B.8.1.3-21: Summary of adsorption isotherm test of M656PH054 on soil Schifferstadt

Soil Type (USDA)	Org. C [%]	pH ($CaCl_2$)	Equilibration time [%]	K_F [$ng^{1-1/n}$ $mL^{1/n}$ g^{-1}]	K_{FOC} [$ng^{1-1/n}$ $mL^{1/n}$ g^{-1}]	1/n
Sand	0.75	4.1	48	0.196	26.2	0.81

The adsorption coefficient K_F of M656PH054 on the soil Schifferstadt derived from Freundlich adsorption isotherms is 0.196 with a Freundlich exponent of 0.81.

Conclusion

The study is considered acceptable in the way that it was performed in line with the guideline OECD 106. Thus, there is no data gap regarding the adsorption properties of M656PH054, although the adsorption of the metabolite proved to be too poor to obtain reliable parameters for a sufficient number of soils.
Distribution coefficients K_d values of M656PH054 remained < 0.1 for the four of the five investigated soils. Thus, the resulting K_{oc} values ranged from < 5 to < 12 mL/g. M656PH54 is considered as qualitatively mobile in these four soils.
For the soil Schifferstadt, a reliable K_d of 0.217 could be obtained resulting in a K_{oc} of 28.9. However, in the opinion of the RMS, the subsequently derived K_f value together with the 1/n value should be considered with caution. For 4 of the measured 5 concentrations the criteria Kd x soil/solution ratio was >0.1 and thus not fulfilled leaving only reliable K_d values for two concentrations. This is not considered sufficient for K_f and Freundlich exponent derivation.

B.8.1.4 Mobility in soil

B.8.1.4.1 Column leaching studies

KCA 7.1.4.1.1/1 – Koenig, 1995a (study evaluated in the monograph, 2000)

Author: Koenig, M.
Title: Leaching behaviour of [3-^{14}C-thienyl]-dimethenamid in five soils under laboratory conditions
Date: 13/02/1995
Doc ID: BASF RegDoc.# 95/10122
Guidelines: BBA Guidelines for the official examination of pesticides; Part IV, 4-2, Leaching of Pesticides; December 1986
GLP: Yes
Validity: Acceptable

Material and Methods

The leaching behaviour of ^{14}C-dimethenamid (3-^{14}C-thienyl dimethenamid, radiochemical purity > 98 %; dimethenamid formulation (Frontier), content test substance 78.3 % w/w) was investigated in five soils. Chemical and physical properties of the soils are shown in Table B.8.1.4-1.

Table B.8.1.4-1: Characterisation of soils used to investigate the column leaching potential of dimethenamid

Designation	BBA 2.1	BBA 2.2	BBA 2.3	Möhlin	Flaach
Texture class	Sand	Sandy loam	Loamy sand	Silt loam	Sandy clay loam
Organic carbon (%)[1)]	0.2	1.5	0.7	0.9	0.8
Organic matter (%)	0.3	2.5	1.2	1.6	1.3
CEC (meq/100 g)	3.8	7.0	9.5	8.9	12.7
pH (H_2O)	7.6	7.0	7.9	7.0	8.3
Sand (%) 0.063 – 2.0 mm	89	86	66	21	48
Silt (%) 0.002 – 0.063	7	7	22	63	27
Clay (%) < 0.002 mm	4	7	12	16	25

1) % Organic carbon = % Organic matter/1.72

Soils were added to glass columns (5 cm inner diameter, 39 cm length) to reach a uniformly packed soil core of 30 cm height. After saturation with water, 2 columns for each soil type were treated once with the radio-labelled test substance mixed with formulated product at the maximum recommended label rate equivalent to 1440 g/ha of dimethenamid. The leaching experiment was done at room temperature in the dark by adding totally 393 mL of demineralised water over two days, which is equivalent to 200 mm of precipitation over the surface of the column. The leachates of the treated columns were quantitatively collected and analysed for radiocarbon content. After extraction with dichloromethane the resulting organic and aqueous phases were analysed for radiocarbon, parent compound and metabolites by radio TLC and radio HPLC. After the leaching step the soil cores were sectioned into 6 layers of about 5 cm each. Radiocarbon in each section was determined by extraction and bound residues were determined using combustion techniques.

Results and Discussion

The results of the column leaching experiment are presented in Table B.8.1.4-2 and Table B.8.1.4-3.

Table B.8.1.4-2: Distribution of radioactivity in the soil column and leachate following column leaching of [^{14}C]-dimethenamid (% AR, mean of two column leaching experiments with each soil)

Fraction	**BBA 2.1**	**BBA 2.2**	**BBA 2.3**	**Möhlin**	**Flaach**
Soil segment 0-5 cm (extractable)	1.3	3.1	2.7	1.5	4.0
Soil Segment 5-10 cm (extractable)	1.7	11.9	3.9	3.1	10.2
Soil Segment 10-15 cm (extractable)	2.8	36.2	9.2	8.8	18.3
Soil Segment 15-20 cm (extractable)	5.0	29.4	17.7	18.5	18.4
Soil Segment 20-25 cm (extractable)	10.4	2.5	26.3	34.0	20.3
Soil Segment 25-30 cm (extractable)	24.0	1.7	18.9	18.3	13.5
Sea sand	4.9	0.5	1.2	1.4	0.4
all soil segments (bound residues)	9.8	8.9	11.1	10.5	13.4
Leachate	40.2	4.9	8.7	5.2	3.3
Total radioactivity	100.0	98.9	99.7	101.2	101.8

Table B.8.1.4-3: Amount of [^{14}C]-dimethenamid in the leachate (% AR, mean of two column leaching experiments with each soil)

	BBA 2.1	**BBA 2.2**	**BBA 2.3**	**Möhlin**	**Flaach**
Dimethenamid in leachate	33.4	ND*	3.3	0.6	1.7

* Not detected

Total recoveries were found to range from 98.9 to 101.8 % AR. Radioactivity was mainly distributed in the middle to lower sections of the columns for all soils. For the 5 soils, the amounts of radioactivity

in the 15-20 cm layer ranged from 5 % to 29.4 % AR, while extractable radioactivity in the 20-25 and 25-30 cm sections accounted for up to 34 % and 24 % AR, respectively. Cumulative bound residues from each column section accounted for approximately 9 to 13 % AR for the five soils.
Dimethenamid was detected in the leachates of four soils up to 33.4 % AR in the case of soil 2.1 (sand). Metabolites M656H023 (M23 in this study), M656H027 (M27 in this study) and M656H031 (M31 in this study) were found in the leachates, but none of these residues exceeded 2.8 % AR, which implies that limited degradation of the parent molecule occurred during the leaching experiment.

Conclusion

The study is considered acceptable by the RMS. Dimethenamid was found to be mobile in soil columns.

KCA 7.1.4.1.1/2 – Koenig, 1994 & 1995b (study evaluated in the monograph, 2000)

Author:	Koenig, M.
Title:	Leaching behaviour of [3-14C-thienyl]-dimethenamid in aged BBA 2.2 soil under laboratory conditions
Date:	15/08/1994
Doc ID:	BASF RegDoc.# 94/10635
Guidelines:	BBA Guidelines for the official examination of pesticides; Part IV, 4-2, Leaching of Pesticides; December 1986
GLP:	Yes
Validity:	Acceptable

Author:	Koenig, M.
Title:	Leaching behaviour of [3-^{14}C-thienyl]-dimethenamid in aged BBA 2.1 soil under laboratory conditions
Date:	21/02/1995
Doc ID:	BASF RegDoc.# 95/10101
Guidelines:	BBA Guidelines for the official examination of pesticides; Part IV, 4-2, Leaching of Pesticides; December 1986
GLP:	Yes
Validity:	Acceptable

Material and Methods

Samples of the German standard soils BBA 2.1 were treated with ^{14}C-dimethenamid (3-^{14}C-thienyl dimethenamid, radiochemical purity 98 %; dimethenamid, purity 99.8 %) at a concentration of 2.82 mg/kg. Samples of German standard soil BBA 2.2 were treated with ^{14}C-dimethenamid (3-^{14}C-thienyl dimethenamid, radiochemical purity 98 %; dimethenamid, purity 99.8 %) at a concentration of 2.82 mg/kg. The soil characteristics are given in Table B.8.1.4-4.

Table B.8.1.4-4: Characterisation of soils used to investigate the column leaching potential of dimethenamid aged residues (Koenig, 1994)

Designation	**BBA 2.2**
Texture class	Sandy loam
Organic carbon (%)	2.29
CEC (meq/100 g)	9.7
pH	5.8
Sand (%) **0.063 – 2.000 mm**	82
Silt (%) **0.002 – 0.063 mm**	13
Clay (%) **< 0.002 mm**	5.1
MWC (g H_2O/100g dry soil)	56.44
Designation	**BBA 2.1**
Texture class	Sand
Organic carbon (%)	0.50
CEC (meq/100 g)	3.00
pH (water)	6.90
pH ($CaCl_2$)	6.30
Sand (%)	86.9
Silt (%)	7.3
Clay (%)	5.8
MWC (g H_2O/100g dry soil)	33.31

Dimethenamid on the soil BBA 2.1 was aged in the dark at 20 °C aged in the dark at 20 °C for 22 and 31 days o ensure a degradation of about 50 % of the applied dimethenamid, respectively. The moisture content was maintained at 40 % of the maximum water holding capacity. Aged soil samples (31 d) of the soil BBA 2.1 were quantitatively transferred onto glass columns of 5-cm diameter containing a core of 28 cm of the water-saturated German standard soil 2.1. A volume of 393 mL of deionised water (equivalent to 200 mm precipitation) was applied dropwise on top of the soil over 2 days. Aliquots of the leachate and of soil extracts (5 cm segments) were analysed by HPLC to determine the amount of parent and metabolites in each fraction. Non-extractable residues in the soil layers were determined using combustion techniques.
Dimethenamid on the soil BBA 2.2 was aged in the dark at 20 °C for 22 days. The moisture content was maintained at 40 % of the maximum water holding capacity. Aged soil samples of the soil BBA 2.2 were quantitatively transferred onto glass columns of 5 cm diameter containing a core of 28 cm of the water-saturated German standard soil 2.2. A volume of 393 mL of deionised water (equivalent to 200 mm precipitation) was applied dropwise on top of the soil over 2 days. Aliquots of the leachate and of soil extracts (5 cm segments) were analysed by HPLC to determine the amount of parent and metabolites in each fraction. Non-extractable residues in the soil layers were determined using combustion techniques.

Results and Discussion

The nature of the residues after 22 days of incubation in both soils is summarised in Table B.8.1.4-5. The distribution of radioactivity in soil and leachate after leaching is presented in Table B.8.1.4-6.

Table B.8.1.4-5: Analysis of ^{14}C-dimethenamid residues in soil after ageing for 22 days (mean of two experiments)

Soil	**BBA 2.1**	**BBA 2.2**
	% AR	
Extractable	82.6	70.1
Dimethenamid	60.0	35.5
M23	10.0	14.0

Table B.8.1.4-6: Distribution of radioactivity following aged residue column leaching of ^{14}C-dimethenamid (% AR, mean of two column leaching experiments with each soil)

Fraction	BBA 2.1	BBA 2.2
Soil (extractable)	**%TAR**	
Soil Segment 0-5 cm	14.7	21.9
Soil Segment 5-10 cm	3.7	11.3
Soil Segment 10-15 cm	4.8	8.4
Soil Segment 15-20 cm	8.1	1.6
Soil Segment 20-25 cm	9.3	1.1
Soil Segment 25-30 cm	3.2	2.3
all soil segments (bound residues)	24.8	29.9
Leachate	23.8	22.7
Total radioactivity	92.4	99.2

The total recovered radioactive residues were in the range of 91.9 to 100.2 % AR. On average, the leachates contained 23.8 % AR and 22.7 % AR for the soils 2.1 and 2.2, respectively. Analysis of the soil cores after percolation indicated that 35 – 60 % AR remained in the upper 10 cm of the columns about half of which was extractable with methanol:water.
The highest concentration of dimethenamid was found in the top 5 cm layer, 11.1 % AR and 15.7 % AR, respectively, for BBA 2.1 and BBA 2.2 soil, and decreased moderately with increasing soil depth. The average level of dimethenamid found in the deepest soil horizon was 2.1 % AR (BBA 2.1). Cumulative residues of individual metabolites in the soil extracts of both studies were < 3 % AR. Non-extractable residues amounted to 24.8 % AR and 29.9 % AR, respectively, most of which was found in the upper 5 cm layer.
Distribution of dimethenamid and the metabolites M656H023 (M23 in this study), M656H027 (M27 in this study) and M656H031 (M31 in this study) in soil sections and leachate are specified in Table B.8.1.4-7.

Table B.8.1.4-7: Composition of recovered radioactivity in soil extracts and leachates following aged residue column leaching of ^{14}C-dimethenamid (% AR, mean of two column leaching experiments with each soil)

Soil fraction	BBA 2.1				BBA 2.2			
	as	M23	M27	M31	as	M23	M27	M31
0-5 cm	11.1	0.5	0.25	0.18	15.7	1.1	0.43	0.64
5-10 cm	3.2	0.13	0.08	0.09	9.3	0.37	0.44	0.35
10-15 cm	4.1	0.13	0.11	0.14	5.7	0.25	0.27	0.22
15-20 cm	6.7	0.2	0.13	0.19	0.45	0.15	0.1	0.1
20-25 cm	8.4	0.21	0.14	0.24	0.13	0.21	0.1	0.1
25-30 cm	2.1	0.22	0.11	0.23	0.2	0.69	0.22	0.2
Leachate	< 0.1	16.7	0.7	1.0	< 0.1	10.9	2.4	2.3

M23 = M656H023, M27 = M656H027, M31 = M656H031

Analysis of the leachate indicated the presence of metabolite M656H023 and minor amounts of M656H027 and M656H031, whereas levels of dimethenamid were below the LOD (0.1 % TAR).

Conclusion

The study is considered acceptable by the RMS.
Following column leaching of dimethenamid after ageing of the substance for 22 and 31 d, <0.1 % dimethenamid was found in the leachate of the soils BBA 2.1 and BBA 2.2. The metabolites M656H023, M656H027 and M656H031 showed a tendency to move through soil. M656H023 was found in concentrations of 16.7 % and 10.9 % AR in the leachate. M656H027 and M656H031 were only found in the leachate in concentrations below 2.5 % AR.

B.8.1.4.2 Lysimeter studies

KCA 7.1.4.2/1 – Burgener, 1996 (study evaluated in the monograph, 2000)

Author: Burgener, A.
Title: [3-^{14}C-thienyl]dimethenamid: Mobility and degradation in soil in outdoor lysimeters
Date: 03/01/1996
Doc ID: BASF Doc ID 96/10707
Guidelines: BBA Guideline Part IV, 4-3 and Modification of the Lysimeter Guideline
GLP: Yes
Validity: Acceptable

Material and Methods

The fate and mobility of dimethenamid was studied in two lysimeters with undisturbed soil monoliths (depth 1.2 m, surface area 1.0 m^2) taken from agricultural land with a sandy soil and low organic carbon content (Borstel near Neustadt a. R., Lower Saxony/Germany). The characteristics of the soil are given in Table B.8.1.4-8.

Table B.8.1.4-8: Characterisation of the soil used in the ^{14}C-dimethenamid lysimeter study

Soil designation	Borstel Sand			
Textural class (USDA scheme)	Sand			
Origin	Borstel, Lower Saxony, Germany			
Soil horizon (cm)	0-30	30-60	60-90	90-120
Particle size distribution (%):				
sand (> 0.05 mm)	83.5	89.0	91.0	99.6
silt (0.002 – 0.05 mm)	10.9	8.4	5.8	0.1
clay (< 0.002 mm)	5.6	2.6	3.2	0.3
Organic C (%)	1.05	0.49	0.14	0.00
CEC (meq/100 g; cation exchange capacity)	5.62	4.06	2.51	0.94
pH (KCl)	6.1	5.9	6.1	7.3
FC (g H_2O/100 g dry soil; field capacity)*	17.9	15.5	11.6	7.4
MWC (g H_2O/100 g dry soil)	34.5	28.6	23.2	23.6
Soil Density (g/cm^3)	1.34	1.50	1.62	1.41

After excavation, the lysimeters transported to the lysimeter facility at RCC Itingen, Switzerland. The lysimeters were embedded into the ground to soil level. Each pair of lysimeters was surrounded by a small untreated field plot of about 2.2 to 4 meters which was cultivated with the same crops as used for the lysimeter.
The radio-labelled test substance (3-^{14}C-thienyl dimethenamid, radiochemical purity 100 %/99.1 %; dimethenamid, purity 99.8 %), formulated as FRONTIER (SAN 582H 900 EC 408 DP; 900 g as/L)), was applied to the bare soil of both lysimeters. An overview over the application rates and the cultivated crops during the experiment is given in Table B.8.1.4-9.

Table B.8.1.4-9: Application rates and cultivated crops in the ^{14}C-dimethenamid lysimeter study

Application rate of dimethenamid-P (kg/ha)		Application date
Lysimeter 1	**Lysimeter 2**	
1.44	1.44	21st of May 1992
-	1.44	14th of May 1993
Cultivated Crops	**Sowing**	**Harvest**
Maize	20th of May 1992	13th October 1992
Winter rye	28th of Oct 1992	23rd of April 1993 (the rye was cut and spaded into top soil)
Maize	13th of May 1993	11th Oct 1993
Winter wheat	26th of Oct 1993	21st of July 1994
Winter rape	15th of August 1994	17th of May 1995 (the total plant head was cut off)

^{14}C dimethenamid-P was applied pre-emergence to maize in May 1992 and again in May 1993 to lysimeter 2. The application rate was equivalent to the intended maximum field rate of 1.44 kg as/ha. The total amount of dimethenamid applied to the soil was 138 and 275 mg for lysimeters 1 and 2, respectively. Immediately after application of ^{14}C-dimethenamid, maize was sawn onto the lysimeters. Winter rye and winter wheat were sown after harvest of maize in October 1992 and 1993, respectively. As a final crop, winter rape was sown in autumn 1994. The experiment ended on the 17th of May. Planting, maintenance and harvest of the plots were done according to common agricultural practice.

During the entire duration of the study, the test system was exposed to outdoor climatic conditions, precipitation was amended by irrigation if necessary, and the cumulative precipitation reached 3140 mm in three years. The minimum amount of precipitation was 910 mm in year one, the years two and three had precipitation of 1159 and 1071 mm, respectively. The amount of precipitation and the volume of collected leachate throughout the lysimeter study are presented in Table B.8.1.4-10.

Table B.8.1.4-10: Amount of precipitation and leachate throughout the ^{14}C-dimethenamid lysimeter study

Year	Precipitation (mm)	Leachate Volume (l)	
		Lysimeter 1	**Lysimeter 2**
1	910	318	365
2	1159	491	533
3	1071	369	434
Total	3140	1178	1332

Lysimeter leachate was sampled at intervals depending on the rainfall and analysed for radioactivity. Samples containing > 0.05 µg/L parent compound equivalents were further examined for $^{14}CO_2$ (stripping, LSC) and active substance and metabolites (HPLC, TLC, GC-MS). In May 1995 the lysimeters were excavated and the soil monoliths were sectioned into 12 layers of about 8 – 10 cm each. Samples of each soil layer and the grain, straw and spindles of the cultivated crops were combusted for total radioactivity determination via LCS. Besides, the soil samples were extracted once with methanol, once with methanol water (8:2) and twice with a mixture of methanol/water/HCl (79/20/1) for HPLC analysis.

Results and Discussion

The distribution of the radioactivity in the lysimeter leachate of lysimeter 1 and 2 as dimethenamid-equivalents is presented in Table B.8.1.4-11. The distribution of the radioactivity in the lysimeter leachate of lysimeter 1 and 2 as percentage of applied radioactivity is presented in Table B.8.1.4-12.

Table B.8.1.4-11: Concentrations of HPLC chromatograms of radioactive fractions in leachate samples (annual average as dimethenamid-equivalents)

Radioactive fraction		Lysimeter 1	Lysimeter 2
		Annual average ^{14}C-concentration in leachate (µg/L)	
dimethenamid	1st year	< 0.05	< 0.05
	2nd year	< 0.05	< 0.05
	3rd year	< 0.05	< 0.05
Unknown Fraction U1	1st year	12.9	7.2
	2nd year	1.4	5.9
	3rd year	0.6	1.9
Unknown Fraction U2	1st year	2.2	3.2
	2nd year	0.8	3.9
	3rd year	0.5	1.4
Unknown Fraction U3	1st year	1.1	2.2
	2nd year	0.5	2.6
	3rd year	0.2	0.9
Unknown Fraction U4	1st year	0.9	1.3
	2nd year	0.4	2.0
	3rd year	0.4	1.4
Unknown Fraction U5	1st year	1.1	3.0
	2nd year	0.4	2.3
	3rd year	0.3	1.0
Unknown Fraction U6	1st year	2.4	3.4
	2nd year	1.0	3.3
	3rd year	0.3	0.9
Unknown Fraction U7	1st year	0.7	0.5
	2nd year	0.2	0.7
	3rd year	0.2	0.8
Unknown Fraction U8	1st year	3.2	2.1
	2nd year	0.4	1.4
	3rd year	0.4	1.0
Unknown Fraction U9	1st year	0.2	0.3
	2nd year	0.5	0.8
	3rd year	0.3	1.3
Unknown Fraction U10	1st year	0.7	1.2
	2nd year	1.3	2.5
	3rd year	0.5	1.9
Unknown Fraction U11	1st year	0.0	0.0
	2nd year	0.1	0.4
	3rd year	<0.05	<0.1
Unknown Fraction U12	1st year	0.5	1.2
	2nd year	0.2	0.6
	3rd year	0.1	0.4
Metabolit M656H027	1st year	1.7	2.7
	2nd year	0.7	4.0
	3rd year	0.2	0.8
Unknown Fraction U13	1st year	0.1	0.4
	2nd year	0.1	0.4
	3rd year	0.1	0.5
Metabolit M656H023	1st year	0.3	0.9
	2nd year	0.1	1.0
	3rd year	0.1	0.2
Unknown Fraction U14	1st year	0.3	0.1
	2nd year	0.3	1.1
	3rd year	<0.05	0.2

Radioactive fraction		Lysimeter 1	Lysimeter 2
		Annual average ^{14}C-concentration in leachate (µg/L)	
Unknown Fraction U15	1st year	0.1	<0.1
	2nd year	0.1	0.1
	3rd year	<0.05	0.2
Unknown Fraction U16	1st year	0.6	0.3
	2nd year	0.2	1.5
	3rd year	<0.05	0.3
Unknown Fraction U17	1st year	0.1	0.1
	2nd year	0.1	0.3
	3rd year	<0.05	0.1
Total unknown radioactivity	1st year	2.1	26.6
	2nd year	8.0	29.9
	3rd year	4.2	14.3
Total radioactivity (including volatiles)	1st year	30.3	31.5
	2nd year	8.9	35.3
	3rd year	4.5	15.4

Table B.8.1.4-12: Concentrations of HPLC chromatograms of radioactive fractions in leachate samples (% of applied radioactivity)

Radioactive fraction		Lysimeter 1	Lysimeter 2
		% AR per year	
dimethenamid	1st year	ND	ND
	2nd year	ND	ND
	3rd year	ND	ND
Unknown Fraction U1	1st year	2.97	1.87
	2nd year	0.50	1.16
	3rd year	0.16	0.31
Unknown Fraction U2	1st year	0.51	0.85
	2nd year	0.29	0.76
	3rd year	0.13	0.22
Unknown Fraction U3	1st year	0.25	0.56
	2nd year	0.17	0.51
	3rd year	0.07	0.15
Unknown Fraction U4	1st year	0.22	0.35
	2nd year	0.14	0.38
	3rd year	0.11	0.22
Unknown Fraction U5	1st year	0.24	0.79
	2nd year	0.13	0.44
	3rd year	0.09	0.16
Unknown Fraction U6	1st year	0.55	0.89
	2nd year	0.36	0.64
	3rd year	0.09	0.13
Unknown Fraction U7	1st year	0.29	0.27
	2nd year	0.10	0.15
	3rd year	0.06	0.13
Unknown Fraction U8	1st year	0.74	0.56
	2nd year	0.13	0.28
	3rd year	0.10	0.16
Unknown Fraction U9	1st year	0.04	0.09
	2nd year	0.15	0.15
	3rd year	0.09	0.21
Unknown Fraction U10	1st year	0.16	0.32
	2nd year	0.47	0.50
	3rd year	0.12	0.30
Unknown Fraction U11	1st year	0.00	0.00
	2nd year	0.03	0.08
	3rd year	0.01	0.01
Unknown Fraction U12	1st year	0.10	0.32
	2nd year	0.07	0.11
	3rd year	0.02	0.06
Metabolit M656H027	1st year	0.40	0.71
	2nd year	0.24	0.77
	3rd year	0.06	0.12
Unknown Fraction U13	1st year	0.03	0.12
	2nd year	0.03	0.08
	3rd year	0.01	0.08
Metabolit M656H023	1st year	0.08	0.24
	2nd year	0.04	0.20
	3rd year	0.02	0.04
Unknown Fraction U14	1st year	0.07	0.03
	2nd year	0.10	0.22
	3rd year	0.01	0.03
Unknown Fraction U15	1st year	0.01	0.00
	2nd year	0.02	0.03
	3rd year	0.01	0.03

Radioactive fraction		Lysimeter 1	Lysimeter 2
		% AR per year	
Unknown Fraction U16	1st year	0.01	0.08
	2nd year	0.02	0.29
	3rd year	0.01	0.05
Unknown Fraction U17	1st year	0.03	0.03
	2nd year	0.03	0.07
	3rd year	<0.01	0.01
Total unknown radioactivity	1st year	6.22	7.13
	2nd year	2.74	5.85
	3rd year	1.09	2.26
Total volatiles *	1st year	0.098	0.115
	2nd year	0.056	0.072+
	3rd year	0.025	0.040+
Total radioactivity (including volatiles)	1st year	6.96	4.19+ (8.24§)
	2nd year	3.16	6.86§
	3rd year	1.19	2.44§

* Only CO_2 was detected
\+ Percent of 1992 and 1993 applied radioactivity
§ percent of 1992 applied radioactivity
ND not detected

No dimethenamid was found in any of the leachate samples exceeding the limit of detection (0.05 µg/L; GC-MS). The radioactivity contained in the percolation water consisted of at least 19 radioactive fractions, and the chromatographic profile of the leachate changed during the course of the study indicating an increased formation of polar degradation products in course of time. Two metabolites exceeding 0.1 µg/L dimethenamid equivalents were identified as M656H023 (M23 in this study) and M656H027 (M27 in this study) by co-chromatography with reference substances. The other radioactive fractions were characterised, but remained unidentified and were mainly highly polar. They consisted partially of several further unknown sub-fractions. Attempts to identify the remaining fractions by comparison to 24 reference substances of known metabolites (M1, M2, M3, M7, M9, M10, M11, M12, M13, M14, M17, M19, M20, M25, M30, M31, M32, PL 14-88, PL-15-88, PL-16-88,PL 18-88, PL 20-88, PL 36-88, PL 76-88 and PL 77-88) were not successful.

The distribution of the radioactivity in the sections of the soil monoliths is presented in Table B.8.1.4-13.

Table B.8.1.4-13: Residues in soil (percentag of applied radioactivity, dimethenamid equivalent concentrations, non-extractable residues)

		Lysimeter 1				Lysimeter 2			
Layer	**Depth**	**Total ^{14}C**	**as**	**Total ^{14}C**	**NER**	**Total ^{14}C**	**as**	**Total ^{14}C**	**NER**
	cm	**µg/kg**		**% AR**	**%**	**µg/kg**		**% AR**	**%**
1	0-8	151	4.4	12.3	88.4	368	13.1	14.7	73.5
2	8-17	42	0.3	4.2	93.7	86	0.6	4.4	81.9
3	17-27	20		2.2	91.0	47		2.4	81.6
4	27-37	9		1.0	80.5	26		1.5	71.5
5	37-47	8		0.8	78.9	17		1.0	61.4
6	47-57	5		0.5	76.1	10		0.6	54.4
7	57-67	4	ND	0.5	71.9	7	ND	0.4	53.0
8	67-77	4		0.4	71.1	5		0.3	39.6
9	77-87	2		0.3	69.1	4		0.2	39.0
10	87-97	2		0.2	56.9	4		0.2	43.2
11	97-107	<1		0.1	65.9	3		0.2	40.6
12	107-118	<1		0.1	51.6	3		0.2	39.0

as = active substance, ND = not detected

22.7 and 26.2 % AR were still present in the lysimeter monoliths 1 and 2, respectively. The majority of the total radiocarbon was found in the top 3 layers. In each layer, the majority of the radiocarbon was in the form of bound residues, the percentage of extractability increased in lower soil layers. The amount of active substance ranged from 4 to 13 µg/kg in the top 8 cm and from 0.4 to 0.6 µg/kg in the 8 – 17 cm layer. The active substance was not detected in any layer below 17 cm.
The soil bound residues of the top layers were further investigated by separation into fulvic acids, humic acids and the humin fraction. The distribution of radioactivity in soil bound residues is specified in Table B.8.1.4-14.

Table B.8.1.4-14: Distribution of radioactivity in bound soil residues

Soil Fraction	% of non-extractable radioactivity		
	Layer 1 (0-8 cm)	Layer 2 (8-17 cm)	Layer 3 (17-27 cm)
	Lysimeter 1		
Fulvic acids	34.4	35.0	37.8
Humic acids	39.8	38.8	39.9
Humins	25.8	26.2	22.4
	Lysimeter 2		
Fulvic acids	35.8	40.0	40.8
Humic acids	37.9	36.7	36.7
Humins	26.4	23.3	22.5

The radioactive distribution in the cultivated crops is provided in Table B.8.1.4-15.

Table B.8.1.4-15: Distribution of radioactivity in crops cultivated on the lysimeter surfaces

Crop Year	Crop Matrix	Residue (mg/kg)	% AR
Lysimeter 1			
1992	Maize grain	0.044	0.02
	Maize straw	0.656	0.61
	Maize spindles	0.059	0.01
1993	Maize grain	0.002	<0.01
	Maize straw/spindles	0.040	0.05
1994	Winter wheat grain	0.006	<0.01
	Winter wheat straw	0.016	0.01
	Winter wheat chaff	0.009	<0.01
Total Lysimeter 1			0.70
Lysimeter 2			
1992	Maize grain	0.052	0.002
	Maize straw	0.932	0.34
	Maize spindles	0.043	<0.01
1993	Maize grain	0.026	0.01
	Maize straw/spindles	0.312	0.14
1994	Winter wheat grain	0.019	<0.01
	Winter wheat straw	0.056	0.01
	Winter wheat chaff	0.046	<0.01
Total Lysimeter 2			0.050

Conclusion

The lysimeter study is considered acceptable by the RMS. The outdoor lysimeter study demonstrated that ^{14}C-dimethenamid does not leach into groundwater in concentrations > 0.1 µ/L for a maximum yearly application rate of 1.44 kg/ha in two subsequent years. The metabolites M656H023 and M656H027 were detected in amounts > 0.1 µg/L (dimethenamid equivalents) in the leachate of both

lysimeters with maximum concentrations of 1.0 µg/L M656H023 and 4.0 µg/L M656H027 in lysimeter 2 in the second year. 17 fractions of unidentified radioactivity were found in concentrations > 0.1 µg/L in the leachate with a maximum of 29.9 µg/L of unknown radioactivity in the leachate of lysimeter 2 in the second year.

KCA7.1.4.2/2 – Fent, 2008 (new study)

Author:	Fent, G.
Title:	Microlysimeterstudy (Soil „Borstel“) with ^{14}C-Deimethenamid-P for characterisation of the metabolite pattern in leachates
Date:	11/08/2008
Doc ID:	2008/1051489
Guidelines:	No guideline
GLP:	Yes
Validity:	Acceptable

Aim of study

The purpose of this study was the characterisation of the leachate metabolite pattern of ^{14}C-dimethenamid-P in undisturbed soil columns of an agricultural soil using a discontinuous irrigation system. The soil used in this study (”Borstel”) was the same as used in a previous outdoor lysimeter leaching study with ^{14}C-dimethenamid. The nature and amount of metabolites in the leachates of the mini-lysimeters of this study may be compared with the results of the outdoor lysimeter study in order to obtain more information about metabolites in the leachate water.

Material and Methods

The test was performed with thienyl-5-^{14}C-dimethenamid-P (puritiy 99.4 %) mixed with non labelled dimethenamid-P using the ratios 2+1 in the pre-test and 1+1 in the definitive test. The soil characteristics of the soil originating from Borstel, Lower Saxony, Germany used in the microlysimeters is given in Table 8.1.4-16.

Table 8.1.4-16 Soil characterstics of the the soil used in the microlysimeter study

Soil designation	Borstel (17/03/07)
Origin	Borstel, Germany
DIN Particle size distribution [%]	
sand 0.063 – 2 mm	90.0
silt 0.002 – 0.063 mm	7.3
clay < 0.002 mm	2.7
textural class	sand
USDA Particle size distribution [%]	
sand 0.050 – 2 mm	91.1
silt 0.002 – 0.050 mm	6.3
clay < 0.002 mm	2.7
textural class	sand
Organic C [%]	0.75
Organic matter [%] **	1.29*
pH [H_2O]	6.5
pH [$CaCl_2$]	5.9
Cation exchange capacity [$cmol^+$ / kg]	2.7
Maximum water holding capacity [g/100g dry soil]	23.0
Microbial biomass [mg C/100g dry soil]	14.5

Twelve undisturbed soil columns were sampled from an area without crop cover using stainless steel tubes of 211 mm in diameter and 300 mm length.
In the non-GLP pre-test five soil columns out of the twelve were used. The soil columns that were not used were stored in closed containers at temperatures between +1 - +10 °C in the dark. For the actual determination of the leachate metabolite pattern in the definitive test two soil columns (replicates Borstel-A and Borstel-B) out of the twelve were used.

For the microlysimeter study, a ceramic plate inserted in a stainless steel lid was mounted at the lower base of the soil columns. An outlet tube with an internal diameter of 3 mm was connected to the steel lid and was filled with a hanging water column of 300 mm to apply a constant tension to the lower end of the soil column to prevent the formation of a capillary fringe. On top of the column about 30 mm of the soil were replaced by 50 g of quartz sand ensuring a plain surface. Afterwards an irrigation head was placed on top of the column which is connected over a peristaltic pump with the water reservoir. Prior the application the soil columns were equilibrated under the actual irrigation conditions used for the test. This equilibration was conducted for at least 6 days. During this period the actual amount of leachate was determined and recorded. At the end of each irrigation cycle the actual volume of water applied to each column was measured and recorded.

Five different test variants were applied in the pre-test to determine the influence of application rate, sunlight after application and irrigation scheme on the leachate metabolite pattern. The experimental conditions of the pre-test are summarised in Table B.8.1.4-17.

Table B.8.1.4-17: Experimental conditions of the microlysimeter pre-test (nominal amount)

	Day after treatment	**Mini-lysimeter I**	**Mini-lysimeter II**	**Mini-lysimeter III**	**Mini-lysimeter IV**	**Mini-lysimeter V**
Amount applied	0	3 kg/ha	1 kg/ha	1 kg/ha	1 kg/ha	1 kg/ha
Solar radiation	0-2	No (laboratory)	Yes (outdoor)	No (laboratory)	No (laboratory)	No (laboratory)
Irrigation immediately after application	0	No	No	No	No	Yes corresponding to 5 mm
Irrigation Monday to Friday	3-30	Corresponding to 3 mm/day	Corresponding to 3 mm/day	Correspond-ing to 3 mm/day	Correspond-ing to 3 mm/day	None
Irrigation Day 31 after treatment	31	None	None	None	Correspond-ing to 12 mm followed by closing leachate valve	None
Irrigation after Day 32	32	Correspond-ing to 6 mm/day	Correspond-ing to 6 mm/day	Correspond-ing to 6 mm/day	None	Correspond-ing to 6 mm/day
Irrigation after Day 63	63	Corresponding to 6 mm/day	Corresponding to 6 mm/day	Correspond-ing to 6 mm/day	Correspond-ing to 6 mm/day	Correspond-ing to 6 mm/day
Sampling and analytical work						
Leachate volume and ^{14}C	0-31	Monday to Friday daily fractions and Saturday to Sunday one fraction				None
Leachate volume and ^{14}C	32-58	Weekly fractions			None	Weekly fractions
Leachate volume and ^{14}C	59-100	Weekly fractions				
Radio HPLC	> 28-93	Depending on ^{14}C-activity in the leachate				

The test conditions in the definitive test corresponded largely to those in mini-lysimeter 1 except for the nominal application rate which was slightly lower with 2.5 kg a.s./ha.
For the applications a mask with 20 holes was placed on top of the column. Through each hole equal

aliquots of the application solution were applied on the column surface using a pipette. Upon application, the soil cores were kept at room temperature (at about 20 °C) in darkness except for variant II which was exposed to sunlight for 3 days.
Upon the start of the irrigation, the leachate was collected according to the scheme described in Table B.8.1.4-17 and the amount of leachate was determined by weighing. The test duration was 100 days in the pre-test and 142 days in the definitive test.
The radioactivity in the liquid specimens was measured by liquid scintillation counting.
Leachate samples with sufficient amounts of radioactivity were subjected to radio HPLC investigation. Leachate was concentrated by means of a rotary evaporator. Depending on the radioactivity in the leachate samples were concentrated in order to achieve about 50,000 dpm in 500 µL injection volume for the HPLC analysis.
The identity of the ^{14}C-dimethenamid-P and of the metabolites M656PH023 (M23 in this study) and M656PH027 (M27 in this study) was confirmed by means of UV/VIS-radio HPLC co-chromatography with the non-radiolabelled reference items. Peaks were set manually and unknown peaks were named and characterised with their retention time.

Results and Discussion

Pre-test

The water balance of the soil columns is summarised in Table B.8.1.4-18.

Table B.8.1.4-18: Water balance of the soil-columns of the pre-test

Mini-lysimeter	Total irrigation [mL/mm]	Total leachate [mL/mm]	Total leachate [% of irrigation]
I	11,938/ 341	11,379/ 325	95.3
II	11,927/ 341	10,870/ 311	91.1
III	11,935/ 341	11,491/ 328	95.8
IV	7,471/ 214	7,469/ 213	99.9
V	10,111/ 289	9,743/ 278	96.4

Depending on the irrigation scheme of test variants, the soil columns were irrigated with a total amount between 214 and to 341 mm. With exception of the test variant II (3 days outdoor exposure) more than 95 % of the irrigation volume was sampled as leachate. The difference to the total applied amount of water can be explained by evaporation losses and by increase of the soil moisture close to saturation of the soil.
The amount of applied radioactivity found in the leachate of the soil columns is summarised in Table B.8.1.4-19.

Table B.8.1.4-19: Radioactivity in leachate of the individual mini-lysimeter used in the pre-test

Mini-lysimeter	Radioactivity applied	Radioactivity in leachate	
	[kBq]	[kBq]	[% applied]
I	35179	11799	33.5
II	11726	2538	21.6
III	11726	3823	32.6
IV	11726	2753	23.5
V	11726	4188	35.7

Between 21.6 % and 35.7 % of the applied radioactivity was found in the leachate.
About 18 days after application the radioactivity increased until reaching a maximum about 44 days after treatment. In the following the radioactivity in leachate decreased to a level < 50 µg/L a.s. equivalents indicating that most of the mobile radioactivity had leached through the soil cores. With the exception of the test variant V (irrigation and leachate formation started 32 days after application) all other test variants showed a similar breakthrough behaviour.
The metabolite patterns in the leachate of all test variants are summarised in Table B.8.1.4-20 to Table B.8.1.4-24.

Table B.8.1.4-20: Metabolite pattern of leachate radioactivity of mini-lysimeter I

	Metabolite fraction (Rt in min + 0.5 min) in % of total radioactivity in the leachate											
Rt	**2.8**	**9.4**	**11.7**	**13.1**	**19.2**	**21.2**	**22.3**	**23.3**	**25.6**	**28.5**	**30.7**	
DAT[1)]	**Start**	**A**	**B**	**C**	**C1**	**C2**	**D**	**E**	**M27**	**M23**	**F**	**n.c.[2)]**
31-38		3.3	5.8	5.7			2.9	3.4	24.3	29.9		24.7
39-44		2.0	4.1	4.7			2.8	4.1	25.9	29.3		27.0
45-51		2.8	3.4	3.7			4.9	6.3	26.4	22.6		30.0
52-58		2.4	3.5	3.4	3.5	2.4	5.6	7.7	27.5	16.8		27.1
59-65		2.3	4.1	3.5	3.7	2.7	6.0	7.0	26.9	14.5	1.1	28.3
66-72		2.6	3.2	3.7	3.9	3.3	5.7	6.8	24.9	13.8	1.8	30.2
73-79		4.3	2.7	3.9	3.9	4.1	5.2	6.2	22.9	12.4	2.9	31.7
80-86		3.2	3.2	4.7	3.4	3.2	5.2	6.6	22.3	12.3	2.7	33.3
87-93		3.2	2.8	3.8	4.8	3.2	4.7	5.6	22.0	13.9	3.7	32.2
Mean		**2.9**	**3.7**	**4.1**	**3.9**	**3.1**	**4.8**	**6.0**	**24.8**	**18.4**	**2.4**	**29.4**

[1)] Days after treatment
[2)] n.c.= not characterised by a retention time
M23 = M656PH023, M27 = M656PH027

Table B.8.1.4-21: Metabolite pattern of leachate radioactivity of mini-lysimeter II

	Metabolite fraction (Rt in min + 0.5 min) in % of total radioactivity in the leachate											
Rt	**2.8**	**9.4**	**11.7**	**13.1**	**19.2**	**21.2**	**22.3**	**23.3**	**25.6**	**28.5**	**30.7**	
DAT[1)]	**Start**	**A**	**B**	**C**	**C1**	**C2**	**D**	**E**	**M27**	**M23**	**F**	**n.c.[2)]**
31-38		7.4	6.7	8.1			2.3	2.4	16.5	11.6		45.0
39-44		3.0	3.5	4.9			3.8	5.2	26.8	14.6		38.1
45-51		3.6	2.9	4.1			6.8	8.9	26.5	11.7		35.5
52-58		3.7	3.2	3.1	3.2	3.0	6.9	9.4	26.5	9.5		31.4
59-65		2.6	3.8	4.4	3.5	3.7	5.7	7.2	27.5	8.6		32.9
66-72		4.0	3.7	4.3	3.5	3.3	5.1	6.1	22.8	8.8	1.4	36.9
73-79	6.9	4.3	3.0	4.4	3.3	3.5	4.9	6.2	23.1	7.3	2.6	37.5
80-86	6.0	4.2	3.6	5.7	2.3	2.6	4.4	6.2	22.5	8.8	3.4	36.2
87-93	5.5	3.5	4.0	4.2	3.9	3.0	4.8	6.6	21.0	9.4	4.0	35.6
Mean	**6.1**	**4.0**	**3.8**	**4.8**	**3.3**	**3.2**	**5.0**	**6.5**	**23.7**	**10.1**	**2.9**	**36.6**

[1)] Days after treatment
[2)] n.c.= not characterised by a retention time
M23 = M656PH023, M27 = M656PH027

Table B.8.1.4-22: Metabolite pattern of leachate radioactivity of mini-lysimeter III

	Metabolite fraction (Rt in min + 0.5 min) in % of total radioactivity in the leachate											
Rt	**2.8**	**9.4**	**11.7**	**13.1**	**19.2**	**21.2**	**22.3**	**23.3**	**25.6**	**28.5**	**30.7**	
DAT[1)]	**Start**	**A**	**B**	**C**	**C1**	**C2**	**D**	**E**	**M27**	**M23**	**F**	**n.c.[2)]**
31-38		3.1	4.2	5.7			2.1	3.8	29.0	24.0		28.1
39-44		3.2	4.3	4.1			3.2	5.1	32.4	19.2		28.6
45-51		2.4	3.9	3.3			4.4	5.9	31.5	17.4		31.2
52-58		3.0	3.6	3.3	2.8	2.2	5.4	7.1	31.5	12.9		28.3
59-65		2.8	3.6	3.5	3.2	3.5	5.9	8.3	28.2	11.3	1.0	28.7
66-72		3.2	3.1	3.6	3.2	3.0	5.1	7.1	27.2	10.2	2.6	31.9
73-79		3.2	3.4	4.9	2.6	2.9	5.7	6.3	25.6	8.8	2.7	33.8
80-86		4.8	4.0	4.0	3.2	3.0	5.3	6.6	23.2	9.6	3.6	32.8
87-93		4.2	2.9	3.8	3.6	2.3	5.8	6.4	24.6	9.2	4.4	33.0
Mean		**3.3**	**3.7**	**4.0**	**3.1**	**2.8**	**4.8**	**6.3**	**28.1**	**13.6**	**2.9**	**30.7**

[1)] Days after treatment
[2)] n.c.= not characterised by a retention time
M23 = M656PH023, M27 = M656PH027

Table B.8.1.4-23: Metabolite pattern of leachate radioactivity micro-lysimeter IV

	Metabolite fraction (Rt in min + 0.5 min) in % of total radioactivity in the leachate											
Rt	**2.8**	**9.4**	**11.7**	**13.1**	**19.2**	**21.2**	**22.3**	**23.3**	**25.6**	**28.5**	**30.7**	
DAT[1)]	**Start**	**A**	**B**	**C**	**C1**	**C2**	**D**	**E**	**M27**	**M23**	**F**	**n.c.[2)]**
28-30		4.6	4.7	4.3			2.9	4.4	25.2	28.9		24.9
31-38												
39-44												
45-51												
52-58												
59-65		4.1	5.0	7.0			2.9	4.8	24.3	19.8		32.1
66-72		5.1	5.3	8.0			3.0	4.3	22.9	13.6		37.9
73-79		3.8	3.9	4.8	3.2	2.3	4.6	6.6	24.1	15.7		31.1
80-86		3.7	3.0	2.9	2.9	4.1	7.5	9.5	19.0	13.6		33.8
87-93		3.0	3.1	3.8	6.5	4.0	8.5	10.6	17.8	10.1	2.2	30.2
Mean		**4.0**	**4.2**	**5.1**	**4.2**	**3.5**	**4.9**	**6.7**	**22.2**	**17.0**	**2.2**	**31.7**

[1)] Days after treatment
[2)] n.c.= not characterised by a retention time
M23 = M656PH023, M27 = M656PH027

Table B.8.1.4-24: Metabolite pattern of leachate radioactivity of mini-lysimeter V

	Metabolite fraction (Rt in min + 0.5 min) in % of total radioactivity in the leachate											
Rt	**2.8**	**9.4**	**11.7**	**13.1**	**19.2**	**21.2**	**22.3**	**23.3**	**25.6**	**28.5**	**30.7**	
DAT[1)]	**Start**	**A**	**B**	**C**	**C1**	**C2**	**D**	**E**	**M27**	**M23**	**F**	**n.c.[2)]**
39-44		3.7	4.0	6.9			0.0	0.0	19.2	34.9		31.3
45-51		1.3	3.1	3.8			4.0	6.1	20.6	32.0		29.1
52-58		2.2	3.1	3.7	3.7	3.3	6.3	8.5	24.3	20.5		24.5
59-65		2.1	3.4	3.2	3.4	3.1	6.1	6.7	27.3	15.3		29.5
66-72		2.6	3.3	3.9	4.0	3.6	5.1	6.3	25.9	12.7	2.3	30.3
73-79		2.5	2.3	4.0	3.6	3.3	5.6	5.9	24.3	11.7	3.7	33.1
80-86		3.1	2.4	4.5	2.7	2.5	4.3	6.0	22.7	11.8	4.7	35.5
87-93	4.9	3.6	3.2	5.0	2.3	2.8	5.4	6.6	23.6	12.6	5.8	24.2
Mean	**4.9**	**2.6**	**3.1**	**4.4**	**3.3**	**3.1**	**4.6**	**5.8**	**23.5**	**18.9**	**4.1**	**29.7**

[1)] Days after treatment
[2)] n.c.= not characterised by a retention time
M23 = M656PH023, M27 = M656PH027

The main known metabolite in the leachate was M656PH027 (in average 24.5 % of total leachate radioactivity) followed by metabolite M656PH023 (in average 15.6 % of total leachate radioactivity). Additionally, nine unknown metabolites L were found in the leachate of all soil columns in similar concentrations. All of the unknown metabolites except metabolite 'E' represented < 5 % of the total leachate radioactivity. Only the Metabolite "E" was detected in amounts slightly greater than 5 % of the total leachate radioactivity. Most of the radioactivity (about 32 %) represented unknown radioactivity showing an increased baseline without a specific retention time. With the exception of the metabolite M656PH023 (decreasing proportions in the course of the study) the leachate metabolite pattern did not change significantly in the course of the study.
It was concluded from the pre-test that the pattern of metabolites in the leachate is largely independent of the different conditions in the individual variants. For the definitive test, conditions similar to test variant I were chosen.

Definitive test

The water balance of the soil columns of the minilysimeters Borstel A and Borstel B is summarised in Table B.8.1.4-25. On average 95.3 % of the irrigation volume was sampled as leachate.

Table B.8.1.4-25: Water balance of the soil-columns of the definitve test

Mini-lysimeter	Total irrigation [mL/mm]	Total leachate [mL/mm]	Total leachate [% of irrigation]
Borstel-A	18,933/541	18,103/517	95.6
Borstel-B	18,920/541	17,983/514	95.0
Mean	18,927/541	18,043/516	95.3

The amount of applied radioactivity found in the leachate of the soil columns is summarised in Table B.8.1.4-26. On average, 39.2 % of the applied radioactivity was found in the leachate.

Table B.8.1.4-26: Radioactivity in leachate of the individual mini-lysimeter used in the definitive test

Mini-lysimeter	Radioactivity applied	Radioactivity in leachate	
	[kBq]	[kBq]	[% applied]
Borstel-A	37521	14696	39.2
Borstel-B	33769	13237	39.2
Mean	35645	13967	39.2

About 18 days after application the radioactivity increased by reaching a maximum about 44 days after treatment. In the following the radioactivity in leachate decreased to a level < 20 µg/L a.s. equivalents indicating that most of the mobile radioactivity had leached through the soil cores. Both replicates showed a similar breakthrough behaviour.

The metabolite patterns in the leachate of the two mini-lysimeters are summarised in Table B.8.1.4-27 and Table B.8.1.4-28.

Table B.8.1.4-27: Metabolite pattern of leachate radioactivity of mino-lysimeter Borstel A

	Metabolite fractions (Rt in min + 0.5 min) in % of total radioactivity in the leachate											
R_t[min]	**11.2**	**13.5**	**16.3**	**23.5**	**25.4**	**26.2**	**27.5**	**29.7**	**32.4**	**35.8**	**41.0**	
DAT[1)]	**A**	**B**	**C**	**C1**	**C2**	**D**	**E**	**360714 (M27)**	**360715 (M23)**	**F**	**G**	**n.c.[2)]**
31-37	1.91	3.86	4.62	1.88	0.94	3.77	5.67	26.50	29.53			21.32
38-44	1.77	2.31	3.08	3.00	2.27	5.15	5.73	25.74	27.90			23.05
45-51	1.99	2.64	2.90	3.47	2.49	5.41	5.47	26.34	22.11	0.82	8.26	18.10
52-58	2.17	2.16	2.44	2.55	2.47	5.10	7.41	25.19	18.70	1.34	0.55	29.92
59-65	1.45	2.93	3.40	4.40	2.77	4.91	6.10	25.75	18.18	2.27	0.54	27.30
66-72	3.60	2.55	4.36	3.59	1.55	3.27	4.43	29.27	15.01	3.98	0.77	27.62
73-79	2.20	2.08	2.51	2.83	2.40	5.50	5.36	27.53	14.18	2.96		32.45
80-86	1.34	2.41	3.03	5.21	2.13	5.36	5.31	24.02	14.25	3.31		33.63
87-93	2.03	2.11	2.94	2.62	2.64	4.45	5.53	26.20	13.70	4.09		33.69
94-100	2.40	2.34	4.38	4.58	2.54	4.03	5.79	22.73	10.93	5.07		35.21
101-107	2.77	2.47	4.13	4.06	2.55	5.18	3.97	22.46	11.82	4.16		36.43
108-114	3.32	2.91	4.43	4.14	1.54	4.14	5.21	24.78	12.24	3.94		33.35
115-121	3.19	3.42	4.69	3.01	2.55	5.44	5.85	21.70	13.67	3.44		33.04
122-128	2.95	3.63	4.91	4.12	1.84	4.85	4.94	22.16	13.14	3.51		33.95
129-135	3.45	2.24	4.12	3.53	2.44	4.91	4.80	20.24	13.59	3.56	2.17	34.95
136-142	2.69	3.00	3.59	3.68	2.70	4.70	4.44	21.84	12.44	3.20		37.72
Mean	**2.45**	**2.69**	**3.72**	**3.54**	**2.24**	**4.76**	**5.38**	**24.53**	**16.34**	**3.26**	**2.46**	**30.73**

[1)] Days after treatment
[2)] n.c.= not characterised by a retention time
M23 = M656PH023, M27 = M656PH027

Table B.8.1.4-28: Metabolite pattern of leachate radioactivity of mino-lysimeter Borstel B

	Metabolite fractions (Rt in min + 0.5 min) in % of total radioactivity in the leachate											
R_t[min]	**11.2**	**13.5**	**16.3**	**23.5**	**25.4**	**26.2**	**27.5**	**29.7**	**32.4**	**35.8**	**41.0**	
DAT[1)]	**A**	**B**	**C**	**C1**	**C2**	**D**	**E**	**360714 (M27)**	**360715 (M23)**	**F**	**G**	**n.c.[2)]**
31-37	2.75	3.67	4.54	2.06	1.13	4.93	5.06	23.57	30.43			21.86
38-44	1.95	2.80	2.66	2.61	2.15	6.65	6.53	24.96	29.22			20.47
45-51	2.08	2.66	3.58	4.11	2.00	5.53	5.68	26.65	23.36		2.00	22.35
52-58	1.79	2.55	2.81	3.27	2.30	4.54	6.33	29.04	16.89	2.81	0.79	26.88
59-65	1.69	2.29	2.66	3.23	1.92	4.35	7.15	28.19	18.51	1.81		28.20
66-72	3.85	2.60	4.16	3.13	2.07	4.56	5.49	28.04	16.19	3.00	0.57	26.34
73-79	1.87	1.81	3.22	3.14	1.98	4.49	5.84	26.45	14.49	2.67		34.04
80-86	2.26	2.79	3.68	2.63	2.67	4.37	5.96	23.66	14.16	2.94		34.88
87-93	2.01	2.29	2.93	2.41	2.69	5.03	5.19	24.48	14.57	3.97		34.43
94-100	2.64	2.80	3.86	4.49	2.99	4.39	5.84	22.58	13.90	4.18		32.33
101-107	2.95	2.17	4.02	4.84	2.02	4.10	4.27	20.85	14.13	3.65		37.00
108-114	2.76	2.45	4.42	4.17	2.00	4.17	3.67	22.43	12.80	3.60		37.56
115-121	3.03	2.93	4.19	4.93	2.53	4.05	5.74	22.81	12.43	3.74		33.62
122-128	2.63	3.18	4.75	4.40	2.21	6.40	3.50	21.96	14.32	6.39		30.26
129-135	3.35	1.66	4.75	6.93	1.99	4.78	4.99	21.22	13.45	3.46	2.65	30.77
136-142	3.32	3.2	3.82	4.08	2.07	4.99	4.8	19.39	14.02	3.42		37.07
Mean	**2.56**	**2.60**	**3.75**	**3.78**	**2.17**	**4.83**	**5.38**	**24.14**	**17.05**	**3.51**	**1.50**	**30.50**

[1)] Days after treatment
[2)] n.c.= not characterised by a retention time
M23 = M656PH023, M27 = M656PH027

Similar to the pre-test, the main known metabolite in the leachate was again M656PH027 (in average 24.3 % of total leachate radioactivity) followed by metabolite M656PH023 (in average 16.7 % of total leachate radioactivity). Additionally, nine unknown metabolites were found in the leachate of both soil columns in similar concentrations. All of the unknown metabolites except metabolite 'E' represented < 5 % of the total leachate radioactivity. Only the Metabolite 'E' was detected in amounts slightly greater than 5 % of the total leachate radioactivity. Again, most of the radioactivity (about 30.5 %) represented unknown radioactivity showing an increased baseline without a specific retention time.

Conclusion

The microlysimeter study Fent, 2008 is a non-guideline approach. Due to the fact that the experimental setup as well as the generated data are well documented and reasoned, the study is considered acceptable by the RMS as suitable approach to further investigate the leachate behaviour of dimethenamid-P through soil and to elucidate the unknown radioactive fractions of the lysimtere study Burgener, 1996.

In this mini-lysimeter study with ^{14}C-dimethenamid-P, a characteristic pattern of metabolites was observed in the leachate consisting of the known metabolites M656PH023 and M656PH027 and further up to 9 unknown metabolites. Additionally, unknown radioactivity showing an increased baseline without a specific retention time was observed. In between these peaks further small peaks were detected. The metabolite pattern was largely not affected by the application rate, sunlight after application and irrigation scheme.

KCA7.1.4.2/3 – Staudenmaier, 2009a with amendment no. 1 Staudenmaier, 2014a (new study)

Author:	Staudenmaier, H.
Title:	Structure elucidation of metabolites of Dimethenamid in lysimeter leachate
Date:	18/11/2009
Doc ID:	2009/1011362
Guidelines:	OECD 307, BBA IV 4-1, EPA Subdivision N, 162-1
GLP:	Yes
Validity:	Acceptable

Author:	Staudenmaier, H.
Title:	Structure elucidation of metabolites of Dimethenamid in lysimeter leachate – Amendment No 1
Date:	22/01/2014
Doc ID:	2014/1031599
Guidelines:	OECD 307, BBA IV 4-1, EPA Subdivision N, 162-1
GLP:	Yes
Validity:	Acceptable

Aim of study

In the leachate of a lysimeter study with dimethenamid, Burgener, 1996 also described under KCA 7.1.4.2/1 numerous fractions of unidentified radioactivity were observed. Since no lysimeter leachate was available any more, the material required for structure elucidation had to be newly generated. This was attempted by both, a soil study that used incubations of dimethenamid-P in soil under different conditions and a micro-lysimeter study Fent, 2008 also described KCA 7.1.4.2/2
In the present soil study the soil metabolism of dimethenamid-P was investigated under aerobic, anaerobic and photolytic conditions with the purpose to generate information about the formation of degradation products and to elucidate their structures as far as possible. During the conduct of the study, it turned out that the underlying task - the structure elucidation of metabolites in lysimeter leachate - may be supported by the analysis of the radioactive material detected in the leachate of the microlysimeter study. Therefore, it was decided to additionally use samples of leachate water of the latter study for structure elucidation.
The investigation and the results of the soil incubations with dimethenamid-P under aerobic, anaerobic and photolytic conditions are described under B.8.1.1.1 - Staudenmaier, 2009a with amendment no. 1 Staudenmaier, 2014a. Here the methodology and analysis of the leachate samples of the microlysimeter study as well as the structure elucidation of selected soil and leachate samples or isolated peaks are summarised
In the report amendment Staudenmaier, 2014a, also described here, two metabolite structures were revised because of new insights gained during the follow-up study Staudenmaier & Kuhnke, 2014. Additionally the new metabolite codes were introduced. Furthermore, one chapter of the original study report was revised because of new information on the identity of metabolite isomers. All changes introduced with the report amendment are included in the following summary.

Material and Methods

Leachate water from a laboratory mini-lysimeter study with dimethenamid-P in Borstel soil described by Fent G. 2008 became available and was known to contain substantial amounts of metabolites. Selected leachate water samples were further analysed in the present study by radio HPLC analysis.

Soil extracts from the aerobic, anaerobic soil incubations and the soil photolysis study described in more detail under under B.8.1.1.1 - Staudenmaier, 2009a with amendment no. 1 Staudenmaier, 2014a were reanalysed on the HPLC system used in the mini-lysimeter study in order to exactly compare their HPLC patterns with those of the mini-lysimeter leachate.

Suitable leachate samples of the micro-lysimeter study were worked up by solid phase extraction and were fractioned by semi-preparative HPLC. The fractions were then subjected to LC-MS and LC-

MS/MS analysis using an electrospray time-of-flight mass spectrometry (ESI-TOF MS) in positive- and negative-ion mode for structure elucidation. Selected fractions and/or samples of the soil extracts of the different soil incubations were also subjected to structure elucidation by LC-MS/MS.

Results and Discussion

The HPLC pattern of the leachate samples as determined in this study was in good agreement to that reported in the mini-lysimeter study Fent, 2008. Furthermore, the retention times of selected reference compounds (e.g. M656PH023, M66PH027) were comparable to those in the micro-lysimeter study.
The major peaks in the samples of the aerobic incubation, metabolites M656PH023, M656PH027 and M656PH031 corresponded well with prominent peaks in the micro-lysimeter leachate.
The sample of the anaerobic incubation showed also some major peaks that corresponded to major peaks in the micro-lysimeter leachate. These were presumably M656PH023 and M656PH027, but not M656PH031. Additional peaks were observed that either matched minor peaks in the mini-lysimeter leachate or were observed at retention times corresponding to unknown fractions of the lysimeter leachate of the study Burgener, 1996.
The complex pattern of HPLC peaks of the extract of the photolytic soil incubation showed only few matches to the peaks in the mini-lysimeter leachate. It was concluded that the metabolites that are formed under the conditions of photolysis on soil are mostly different from those observed in the mini-lysimeter leachate.

The identity of the prominent soil metabolites M656PH023, M656PH027 and M656PH031 in the aerobic soil studies was confirmed by LC-MS/MS investigation. This is in line with the previous knowledge and is not described in further detail here. The Metabolites M656PH023, M656PH027 and M656PH031were also positively identified in the mini-lysimeter leachate by LC-MS/MS.
Additionally to samples and HPLC fractions of the mini-lysimeter leachate samples, a few HPLC peaks/fractions of the anaerobic incubation were used for structure elucidation, that were not represented by samples of the mini-lysimeter leachate but were observed at retention times corresponding to unknown fractions of the lysimeter leachate described under Burgener, 1996.
The photolytic incubation led to a very complex pattern of HPLC peaks. Major efforts were undertaken to isolate individual peaks and to investigate these peaks by LC-MS/MS. However, it turned out later on that many of these peaks did not match exactly with the peaks in the mini-lysimeter leachate. Since there were doubts if the photolytical metabolites are identical to those in the leachate, it was decided not to rely on these for the assignment of structures to metabolites in the leachate.

Several of the identified metabolites appeared in isomeric forms for which no clear assignment to the type of isomerism can be given based on the spectral data of the ESI-TOF MS. Depending on the overall structure of a metabolite, the following isomeric variations – listed in order of falling chemical similarity - are possible:

a) Regioisomerism, in molecules where a methyl group on the thiophene ring has been oxidised (e.g., metabolite M656PH047)
b) Z/E isomerism, in molecules where the thiophene ring has been oxidatively opened (e.g., M656PH052)
c) Centrochiral diastereoisomerism with two or more chiral centers being present (e.g., M656PH059)
d) Axial-chiral diastereoisomerism, possible in all metabolites with an intact thiophene ring and two further substituents on the nitrogen atom (e.g. M656PH027)
e) Rotamerism about the amide N-CO bond, possible in all metabolites with carbonyl substituent on the nitrogen.

In cases d) and e), the isomeric forms are able to isomerise over a more or less high rotational barrier. Depending on the moieties in the vicinity, the barrier may easily be high enough to produce chromatographically separable entities. With these possibilities in mind, the forms with maximum chemical difference were assigned to double peaks in order to cover the whole chemical variety of possible isomers by the interpretation. If two or more indistinguishable isomers of a metabolite exist,

they were assigned different metabolite codes – usually in line with increasing retention time.

Numerous chemical structures were proposed upon LC-MS/MS investigation covering most of the peaks in the HPLC chromatograms of the mini-lysimeter leachate and additionally some peaks in the extracts of the anaerobic soil incubation. Many of these metabolite structures (M656PH043 to M656PH062) had not been observed previously in other studies.

For the following metabolites, unique structures could be proposed and assigned to specific peaks: M656PH003, M656PH010, M656PH023, M656PH027, M656PH031, M656PH032, M656PH043, M656PH045, M656PH047, M656PH050 (rota), M656PH051, M656PH054, M656H055, and M656PH062.

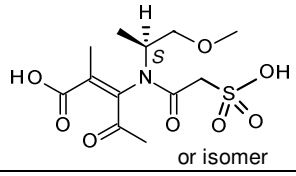
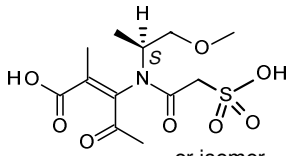
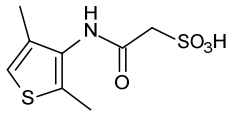
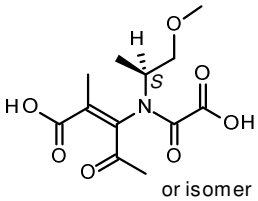
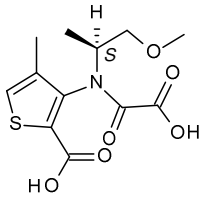
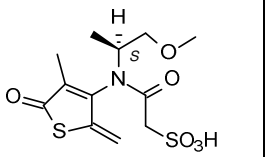
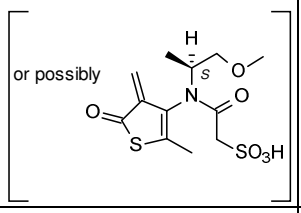
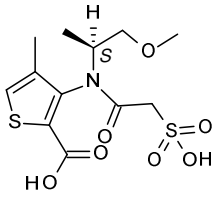
There were several pairs and one triplet of isomers of metabolites which are distinguishable by their retention time. Most of the metabolite pairs were shown to be rotamers which are in equilibrium: M656PH027 - two rotamers detected, M656PH043 - two rotamers detected, M656PH045 - two rotamers detected, M656PH047 - two rotamers detected, M656PH050 (rota) - one rotamer detected, M656PH054 - two rotamers detected.

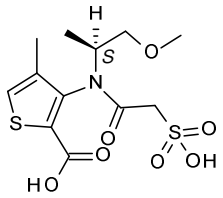
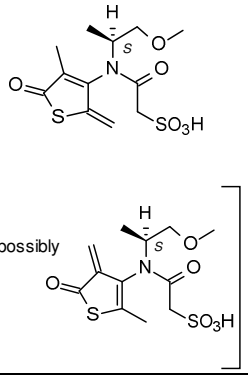
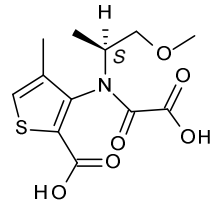
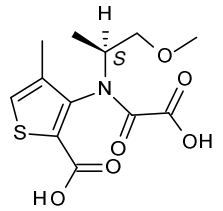
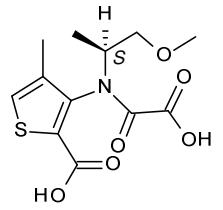
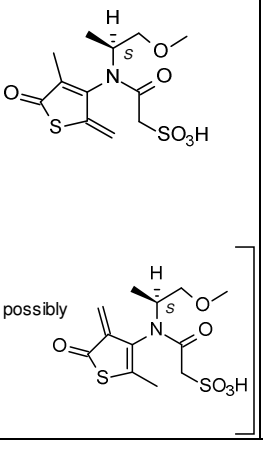
However, there are other metabolites which are marked with the suffix "(iso)" e.g. M656PH053 (iso) that have further stereochemical features (additional to rotamerism or without it) that give rise to multiple peaks for which no formation of an equilibrium was observed. Since it could not finally be decided from the MS results which of these isomeric forms is actually present in the respective HPLC peak, in these cases the same structures were given for each of the isomer peaks. This applies for the following isomeric pairs/triplet of metabolites: M656PH049 (iso) - one isomer detected, M656PH052 (iso) - two isomers detected, M656PH053 (iso) - two isomers detected, M656PH059 (iso) - three isomers detected.

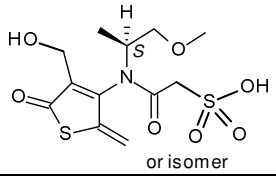
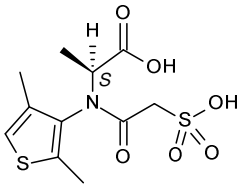
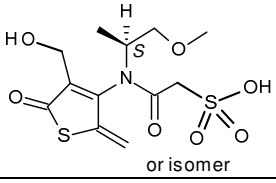
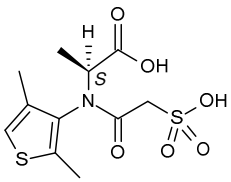
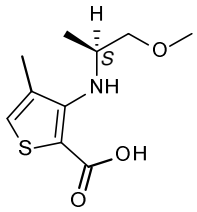
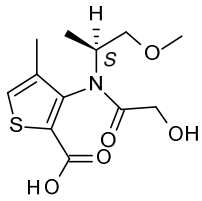
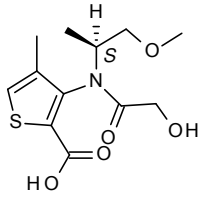
An overview on the results of the structure identification of all proposed metabolites is presented in Table B.8.1.4-29.

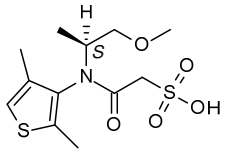
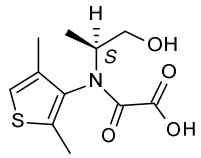
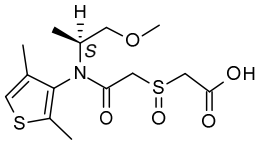
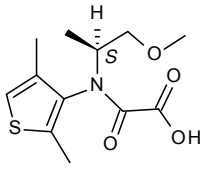
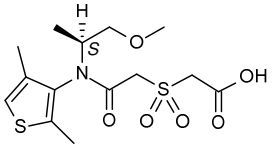
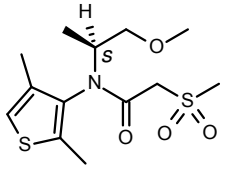
Due to the technical requirements of LC/MS, the isolation of HPLC fractions and LC-MS/MS investigation was done using a phosphate buffer free HPLC system.
Further HPLC analyses were performed in order to clearly assign the identified compounds to HPLC peaks in the original buffer-containing HPLC system used in the lysimeter and mini-lysimeter studies. Furthermore, some of the HPLC fractions were further fractioned by HPLC into subfractions containing single peaks in order to assist the assignment of individual peaks.
It turned out that reanalysis of the isolated single peaks with the phosphate buffer HPLC system resulted frequently in the separation into several peaks. This is in line with the observation during the LC-MS/MS investigation that often more than one compound is observed within one HPLC peaks. That means that the number of metabolites is even greater than expected from visual inspection of the HPLC chromatograms. Nevertheless, it was possible in most cases to assign the structure of the main peaks of the fractions to corresponding HPLC peaks in the total mini-lysimeter leachate. The results of this HPLC exercise are also shown in Table B.8.1.4-29 (last column).

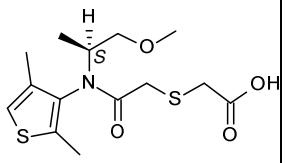
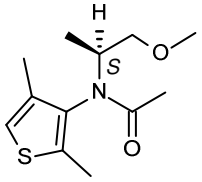
Table B.8.1.4-29: Overview on identified metabolites and their assignment to peaks in different HPLC systems

Source	t_R in LC/MS [min]	t_R in Acn/H_2O HPLC system [min]	Structure proposal	Molecular mass	Metabolite Code	t_R in phosphate buffer HPLC system [min]
mini-lysimeter leachate	8.5	10.3		337	M656PH052 (iso)	---
mini-lysimeter leachate	10.2	12.5		337	M656PH052 (iso)	13.2/14.5
	9.0	10.9				
mini-lysimeter leachate	14.0	16.4		249	M656H055	15.6/16.7
mini-lysimeter leachate	14.4	16.4		287	M656PH049	16.7
mini-lysimeter leachate	19.0	20.4		301	M656PH045 (one of two rotamers)	---
mini-lysimeter leachate	19.6	21.6	 	335	M656PH059 (one of three isomers)	**21.3**/22.7/ 23.6
mini-lysimeter leachate	19.6	21.6		351	M656PH047 (one of two rotamers)	**21.3**/22.7/ 23.6

Source	t_R in LC/MS [min]	t_R in Acn/H_2O HPLC system [min]	Structure proposal	Molecular mass	Metabolite Code	t_R in phosphate buffer HPLC system [min]
mini-lysimeter leachate	20.8	22.8		351	M656PH047 (one of two rotamers)	21.3/**22.7**/ **23.6/24.5**
mini-lysimeter leachate	21.4	23.3		335	M656PH059 (one of three isomers)	21.3/22.6/ 24.5
mini-lysimeter leachate	21.4	23.3		301	M656PH045 (one of two rotamers)	21.3/22.6/ 24.5
mini-lysimeter leachate	22.2	23.9		301	M656PH045 (one of two rotamers)	---
mini-lysimeter leachate	23 - 28	25.7		301	M656PH045 (one of two rotamers)	24.5/25.3/ 26.5/27.2
mini-lysimeter leachate	23.3	25.7		335	M656PH059 (one of three isomers)	**24.5**/25.3/ 26.5/27.2

Source	t_R in LC/MS [min]	t_R in Acn/H_2O HPLC system [min]	Structure proposal	Molecular mass	Metabolite Code	t_R in phosphate buffer HPLC system [min]
mini-lysimeter leachate	24.2	25.7	 or isomer	351	M656PH053 (one of two isomers)	**24.5**/25.3/ 26.5/27.2
mini-lysimeter leachate	24.3	25.7		321	M656PH054 (one of two rotamers)	**24.5**/25.3/ 26.5/27.2
mini-lysimeter leachate	24.9	26.9	 or isomer	351	M656PH053 (one of two isomers)	25.3/26.5/ **27.2**
mini-lysimeter leachate	25.1	26.9		321	M656PH054 (one of two rotamers)	25.3/26.5/ **27.2**
mini-lysimeter leachate	25.6	26.9		229	M656PH062	25.3/26.5/ **27.2**
anaerobic soil incubation	26.1	29.1		287	M656PH043 (one of two rotamers)	28.3
anaerobic soil incubation	27.4	30.2		287	M656PH043 (one of two rotamers)	28.9
mini-lysimeter leachate	27.7	30.1				

Source	t_R in LC/MS [min]	t_R in Acn/H_2O HPLC system [min]	Structure proposal	Molecular mass	Metabolite Code	t_R in phosphate buffer HPLC system [min]
mini-lysimeter leachate	29.8	30.9		321	M656PH027 (two rotamers)	30.3
	29.6	30.9				
anaerobic soil incubation	31.5	34.5		257	M656PH050 (rota)	31.8
anaerobic soil incubation	34.4	37.3		347	M656PH031	31.1
mini-lysimeter leachate	34.7	37.0				
mini-lysimeter leachate	35.2	37.9		271	M656PH023	32.5
anaerobic soil incubation	35.2	38.4				
mini-lysimeter leachate	35.6	38.4				
mini-lysimeter leachate	37.3	40.3		363	M656PH051	34.3
mini-lysimeter leachate	38.1	41.0		319	M656PH010	34.3
anaerobic soil incubation	38.0	41.2				

Source	t_R in LC/MS [min]	t_R in Acn/H_2O HPLC system [min]	Structure proposal	Molecular mass	Metabolite Code	t_R in phosphate buffer HPLC system [min]
anaerobic soil incubation	38.0	41.2		331	M656PH032	39.0
anaerobic soil incubation	38.9	42.0		241	M656PH003	39.4

Conclusion

The study is considered acceptable by the RMS.
The soil metabolism of dimethenamid-P was investigated under aerobic conditions (at low and high application rate) and under anaerobic conditions and in a soil photolysis study (at high application rate) in the sand soil Borstel that was earlier used in the lysimeter study Burgener, 1996 with the aim to elucidate the unknown radioactive fractions observed in the lysimeter study Burgener, 1996. The results of the soil incubations are summarised under KCA7.1.2.1.1/5.
Additionally, structure elucidations of selected HPLC peaks/ fractions of anaerobic soil samples and leachate samples of the mini-lysimeter study Fent, 2008 with dimethenamid-P were performed which are reported here. Due to the fact that many of the peaks found in the photolytic soil incubation did not match exactly with the peaks in the microlysimeter leachate, there were doubts if the photolytic metabolites are identical to those in the leachate. Therefore it was decided by the applicant not to rely on these for the assignment of structures to metabolites in the leachate. According to the "Guidance document on the assessment of the relevance of metabolites in groundwater of substances regulated under council directive 91/414/EEC" SANCO/221/2000 -rev.10- final (2003) all metabolites which are expected to occur in soil under normal use conditions on the basis of results from soil degradation and lysimeter studies should be subject to further assessments for their structure and environmental fate with the aim of quantitatively assessing their ability to contaminate groundwater. However, due to the fact that the photolytic metabolites do not seem to be identical to those in the leachate and the photolysis study was performed using an application rate three times higher than the one planned for the representative uses of dimethenamid-P, the decision of the applicant is accepted by the RMS.

Numerous chemical structures were proposed for 17 metabolites in total covering most of the peaks in the HPLC chromatograms of the mini-lysimeter leachate and additionally some peaks in the extracts of the anaerobic soil incubation. Many of these metabolite structures (M656PH043 to M656PH062) had not been observed previously in other studies.

KCA7.1.4.2/4 – Staudenmaier & Kuhnke, 2014 (new study)

Author:	Staudenmaier, H. Kuhnke, G.
Title:	Further investigations on structural identity of metabolites of dimethenamid-P in lysimeter leachate
Date:	15/01/2014
Doc ID:	BASF DocID 2013/1246087
Guidelines:	None (no guideline available)
GLP:	Yes
Validity:	Acceptable

Aim of study

The aim of this study was to investigate mini-lysimeter leachate samples and leachate extracts originating from preceding studies in order to generate further information on the structure of metabolites of dimethenamid-P. Leachate samples originating from this mini-lysimeter study Fent, 2008 and extracts thereof generated in the study Staudenmaier, 2009a with amendment no. 1 Staudenmaier, 2014a were further processed and investigated within the current study.

Material and Methods

Selected samples of the mini-lysimeter leachate samples were analysed by radio-HPLC directly or after concentration. For structure elucidation via mass spectroscopy, samples were further worked up in order to generate material for subsequent analyses. To generate samples for LC-MS/MS analyses, two different work-ups were performed which aimed at different fractions of the original leachate. In work-up I the eluates of a solid phase extraction (SPE) step were used whereas in work-up II the percolate of the SPE (containing highly polar components) was further processed and investigated.

Workup I: Leachate water sample, mini-lysimeter “Borstel A” (days 38-44):
The sample was subjected to clean-up on an NH_2-SPE (solid phase extraction) column. The column was loaded with leachate and the purified percolate was recovered for further workup. The percolate was further processed on a strata-X-CW-SPE column. The column was once eluted with methanol and once with methanol / 5 % ammonium hydroxide. The combined eluates were evaporated to dryness and dissolved in a small amount of methanol. The concentrated eluate was subjected to HPLC fractionation. Four fractions were collected. Fraction 2 (17-32 min) was concentrated, dissolved in acetonitrile / water (1/1, v/v) and further fractionated using HPLC. Thirteen fractions were sampled and aliquots of selected fractions were analysed by HPLC and LC-MS/MS.

Workup II: Leachate water sample, mini-lysimeter “Borstel A” (days 45-51):
The sample was filtered followed by a cleanup on NH_2-SPE columns. Three columns were loaded with aliquots of the filtered sample (985 mL). The percolate was further processed on strata-X-CW-SPE columns. The percolate of the strata-X-CW-SPE columns was concentrated and taken up in a small amount of methanol. The concentrated percolate was subjected to HPLC fractionation. Fifteen fractions were collected and aliquots of selected fractions were concentrated to dryness, taken up in water / acetonitrile (4/1, v/v) and analysed by HPLC and LC-MS/MS.

Further work-up of mini-lysimeter leachate was performed for NMR analyses. However, the NMR analyses did not significantly contribute to the overall structure assignments and are not presented here.

Samples were analysed with a Thermo Finnigan Linear-Ion-Trap (LTQ) Fourier-Transform (FT) Ultra mass spectrometer in ESI mode, which allows a very high resolution and precision of the accurate mass measurement.

Results and Discussion

Work up I included two subsequent HPLC fractionations on different HPLC systems. Fraction 2 out of 4 fractions of the first step contained the peaks of interest of the SPE eluate. About 5 larger and a

number of small peaks of medium retention time (i.e. ~20 - 35 min) were observed in this fraction. Fraction 2 was further fractioned in the second step into thirteen subfractions of which six were analysed by LC-MS/MS. All subfractions subjected to LC-MS/MS analysis contained more than one peak - even those that were isolated clearly as a single HPLC peak.

In work up II, concentrated SPE percolate was further worked up. At least 20 peaks were observed in the concentrated percolate. Numerous polar compounds of short retention time (~3 - 20 min) but also a number of compounds of medium retention time were present in the eluate fraction. Upon further analysis (including mass spectrometry) it became clear that some compounds of medium retention time were present in both, the eluate and the percolate whereas others were observed only in the percolate. Compounds in the concentrated percolate were strongly enriched during the work-up. Consequently the concentration of individual (mostly very polar) compounds that are found only in the percolate fraction is very low when related to the original total leachate. Due to their continuous sequence in HPLC chromatograms they give rise to the appearance of an elevated baseline in addition to small peaks. The concentrated percolate was fractioned by HPLC into fifteen fractions of which thirteen were analysed by LC-MS/MS. All fractions contained more than one peak although in most cases a single HPLC peak was isolated.

All extracts or fractions were re-chromatographed on an additional HPLC system for comparison and confirmation of results.

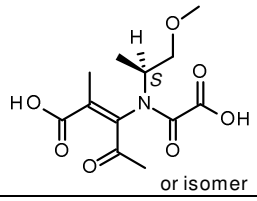
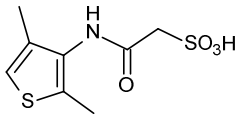
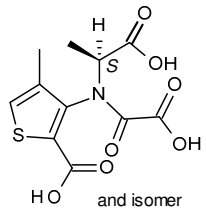
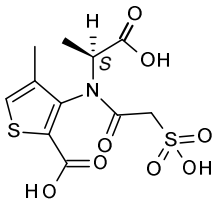
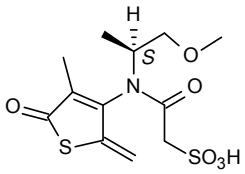
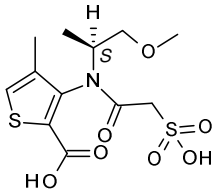
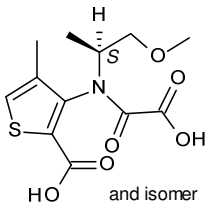
More peaks than expected were observed in the radio HPLC chromatograms in isolated metabolite fractions. In several cases additional peaks were obtained upon re-analysis of isolated peaks that clearly deviated from the original retention time. A more detailed investigation of this phenomenon revealed that there are several pairs of peaks that are in equilibrium to each other. This resulted in the effect that the same pair of HPLC peaks was observed if the one or the other of these peaks was isolated and then re-chromatographed. In such cases none of the two peaks could be isolated without formation the second peak.
Upon structure elucidation, the same structure and consequently the same metabolite code was assigned to each peak of the pairs. The two peaks are considered as rotamers, i.e. structures with hindered intramolecular rotation around a single bond that result in two peaks which however convert into each other.

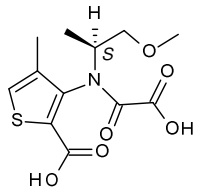
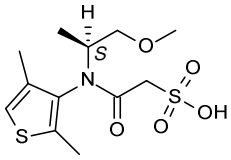
Subfractions of mini-lysimeter leachate were investigated by LC-MS/MS and numerous metabolite structures were proposed. The new coding system for metabolites of dimethenamid-P was used to assign metabolite codes to the identified structures. Additionally, the extensions "(rota)" and "(iso)" for the metabolite codes were introduced in order to account for the complex situation with different types of isomerism. Briefly, the suffix "(rota)" is added if rotamers but no other chirality elements appear besides those given by the parent compound. The suffix "(iso)" is added if additionally E/Z isomerism or additional chirality elements are present and the occurrence of the respective isomer species is possible. Further details may be taken from the original final report.

The following compounds were identified for which structures were proposed.
In the SPE eluates: M656PH027 (two rotamers), M656PH045 (two rotamers) and an isomer thereof (two rotamers), M656PH047, M656PH054 and M656PH059 (iso) [three isomers].
In the SPE percolates partly the same structures were identified: M656PH045 (two rotamers) and an isomer thereof (two rotamers), M656PH047 (two rotamers), M656PH054 (two rotamers) and M656PH059 (iso) [two isomers].
The following metabolites were found in the SPE percolate only: M656PH049 (iso), M656H055, M656PH109 (rota), M656PH110 (rota) [two rotamers] and an isomer thereof. Additionally, numerous further compounds were observed in mass spectrometry for which only the molecular mass could be determined.
The metabolites M656PH109 (rota), M656PH110 (rota) were identified for the first time in this study.

The identified metabolite structures and their attribution to HPLC peaks are shown in Table B.8.1.4-30.

Table B.8.1.4-30: Overview on identified metabolites and their assignment to peaks

t_R in LC/MS [min]	t_R in minilysimeter leachate [min]	Structure proposal	Molecular mass	Metabolite Code
8.5*	16.5	 or isomer	287	M656PH049 (iso)
8.5*	16.8		249	M656H055
11.8*	20.4, 22.0	 and isomer	301	M656PH110 (rota) (2 rotamers) and isomer
13.7* 15.0*	21.8, 22.4			
14.1*	21.8		351	M656PH109 (rota)
15.2* 18.4* 27.8** 31.0** 33.0**	21.8 23.6 24.3		335	M656PH059 (iso) (rota- and/or isomers)
16.4* 19.2* 28.9**	22.4, 23.6		351	M656PH047 (2 rotamers)
14.7* 19.3* 25.0** 29.9**	21.8, 24.3	 and isomer	301	M656PH045 (2 rotamers) and isomer (2 rotamers)
20.9* 25.2* 32.3** 35.8**	25.9, 27.4			

t_R in LC/MS [min]	t_R in minilysimeter leachate [min]	Structure proposal	Molecular mass	Metabolite Code
26.5*, 27.8* 37.8**	27.4, 28.4		321	M656PH054 (2 rotamers)
43.9**, 45.0**	32.6, 33.0		321	M656PH027 (2 rotamers)

* retention time in HPLC system used for SPE percolates
** retention time in HPLC system used for SPE eluates

Conclusion

The study is considered acceptable by the RMS.
Additional structure elucidations of worked-up leachate samples of the mini-lysimeter study Fent, 2008 with dimethenamid-P were performed. Additional information on the isomeric composition of the metabolites M656PH049, M656PH059 and M656PH045 could be gained. Besides, two metabolites M656PH109 and M656PH109 were identified.
For the metabolite M656PH054, a new chemical structure is proposed in Table B.8.1.4-30. However this is most likely a mistake, since in the summary table of all metabolites in the dossier of the applicant, the structure proposal of Staudenmaier, 2009 with amendment Staudenmaier, 2014a was used and the new structure proposal does not match with the proposed molecular mass of M656PH054.

KCA7.1.4.2/5 – Staudenmaier, 2014b (new study)

Author:	Staudenmaier, H.
Title:	Investigation of Metabolites in the Leachate of a Lysimeter Study with Dimethenamid –Updated version January 2014
Date:	10/02/2014
Doc ID:	BASF DocID 2013/1334938 (the document replaces the earlier version BASF DocID 2009/1007158)
Guidelines:	None (no guideline available)
GLP:	No (not applicable)
Validity:	Mostly acceptable

Aim of study

In this summary document, the HPLC results of the lysimeter study Burgener, 1996 are aligned to those of the new mini-lysimeter study Fent, 2008 with the aim to identify the unknown radioactive leachate fractions of the study Burgener, 1996. Therefore, numerous metabolite structures that were elucidated in the studies Staudenmaier, 2013 with addendum Staubenmaier, 2014a and Staudenmaier and Kuhnke, 2014 for HPLC leachate fractions of the mini-lysimeter study Fent, 2008 are assigned to the unknown lysimeter fractions of the lysimeter study Burgener, 1996. Concentrations of the individual metabolites in the leachate are estimated and limitations of the structure elucidation due to potential multiple isomerism of several metabolites are discussed.
The report is an updated version of the previous report Staudenmaier, 2010 and thus replaces Staudenmaier, 2010, which is therefore not summarised here anymore.

Material and Methods

Comparison of HPLC patterns of lysimeter and mini-lysimeter leachate

The lysimeter study which is described under Burgener, 1996 has been found to be in line with current study guidelines with respect to important parameters. Since the experimental conditions of the study were selected appropriately and the study was conducted in a scientifically sound way, it can be considered still valid as a whole according to current guidance.

However, looking more specifically at the HPLC analyses of the leachate water that led to the definition of the unidentified fractions in question, there are concerns about the evaluation of HPLC chromatograms with regard to metabolites. The main concerns with regard to HPLC analysis are

- the extreme complexity and variability of HPLC patterns
- the limitations to identify clear peaks (peak shape)
- the possibility that not only true substance peaks but also regions of background radioactivity were considered during the HPLC evaluation
- the low extent of structure identification by co-chromatography with known reference compounds

It was concluded that the interpretation of HPLC results with regard to the metabolites may be a subject for improvement. Thus, as a first step, a detailed investigation of the HPLC chromatograms was performed. The various fractions of identified and unidentified radioactivity in the leachate of the lysimeter study were described in detail and their potential for structure elucidation was discussed.

In order to reconstitute the metabolites in the lysimeter leachate, a laboratory mini-lysimeter study Fent, 2008 was conducted with dimethenamid-P, which is also described under B.8.1.4.2. In the mini-lysimeter study, the same soil as in the original lysimeter study ("Borstel", Lower Saxony, Germany) was used and several variants of incubation conditions were tested.
Additonally, the same HPLC system as in the original lysimeter study was used for the HPLC chromatograms of the mini-lysimeter, thus allowing direct comparison of the HPLC chromatograms of both studies within the range of the usual variability. Thus, the fractions defined in the HPLC chromatograms of the lysimeter study were aligned with the respective sections of chromatograms of the leachate sampled from the mini-lysimeter study.

Metabolite structure proposals for lysimeter HPLC fractions

In order to elucidate the structures of the metabolites in the leachate, different approaches were combined. In one approach, leachate of the mini-lysimeter study was worked up in order to isolate peaks directly out of the leachate. In a second approach, soil treated with ^{14}C-dimethenamid-P was incubated under aerobic and anaerobic conditions and in a soil photolysis study in order to produce sufficient amounts of metabolites. Details are described in Staudenmaier, 2009 with addendum Staudenmaier, 2014a under KCA7.1.1.1./5 and KCA7.1.4.2/3 and in Staudenmaier & Kuhnke, 2014 described under KCA7.1.4.2/4.

Further HPLC analysis and the LC-MS/MS investigation performed in these studies revealed that the number of metabolites and the complexity of the HPLC pattern is even higher than expected from the initial HPLC runs in the mini-lysimeter study. It is concluded that the complex HPLC results obtained in the original lysimeter study are indeed due to an extremely complex metabolism of (racemic) dimethenamid in the lysimeter leading to numerous metabolites which are further split into various isomers. Findings like the atypical peak shape and numerous fragmented peaks can be explained by this behaviour.

Taking together the results of the HPLC analyses and the LC-MS/MS investigations, metabolite structures could finally be proposed for most of the unidentified fractions. Most of the proposed structures were directly deduced from leachate peaks of the mini-lysimeter. Only few peaks from soil extracts of the anaerobic incubation had to be taken into account since corresponding peaks were not available from the leachate in sufficient amounts.

Estimation of metabolite concentrations in lysimeter leachate

Due to the limitations of the available HPLC analyses in the lysimeter study, distinct concentrations of individual compounds can hardly be derived directly from the study report. In order to provide a reasoned estimate of the concentration of the individual metabolites in the leachate, the compounds identified in fractions U3 - U17 were subjected to a step-wise calculation exercise. Fractions U1 and U2 were already previously excluded.
The calculation was based on the maximum annual average concentrations of the unidentified fractions from both lysimeters and all 3 experimental years, i.e. the derived concentrations for the identified metabolites are maximum annual average concentrations.
The calculation of concentrations of individual metabolites involves three steps:

As first step, an estimation of the annual average concentrations of the metabolites in the individual unidentified fractions was performed:
The calculation starts from the maximum annual average concentrations of the unidentified fractions U3 - U17 in the lysimeter study. In order to account for the uncertainties in the quantification in the lysimeter study, a conservative approach is proposed. For each identified peak a factor is attributed in order to account for its percentage within the respective HPLC fractions. These factors are selected in a conservative way, i.e. they are considered to result in an overestimation of the individual metabolites.
The assignment of factors (percentages) was performed according to the following rules:

- if there are no clear peaks within a HPLC fraction of the lysimeter study (like e.g. U3), one third (= **factor 0.33**) of the radioactivity of the fraction was attributed to the identified peak(s)
- if there are clear peaks within a HPLC fraction in only part of the analyses (like e.g. U7), two thirds (= **factor 0.66**) of the radioactivity of the fraction was attributed to the identified peak(s)
- if there are clear peaks within a HPLC fraction in the majority of the analyses (like e.g. U9), the entire radioactivity of the fraction (= **factor 1**) was attributed to the identified peak(s)
- if there is more than one identified compound per fraction, 3/4 (= **factor 0.75**) of the entire radioactivity as calculated in the previous steps is attributed to <u>each</u> of the compounds

In this way a substantial concentration is calculated even for those compounds that were identified within HPLC fractions that bear mainly an elevated HPLC baseline or scattered peaks rather than clear metabolite peaks. Furthermore, if there was more than one compound within one HPLC fraction, a major proportion was assumed for each of these compounds resulting overall in a significant overestimation of metabolite concentrations.

Since the concentrations of the metabolite fractions depend on the application rate, an adjustment is made for the application rate as a second calculation step. The application rate in the lysimeter study was 1440 g a.s./ha, but the maximum application rate in the representative uses for the renewal of approval is only 864 g a.s./ha. 864 g/ha / 1440 g/ha corresponds to a factor of 0.6. This factor is applied to the concentrations determined in the previous step.
Several of the metabolites appear in HPLC analyses as two rotamer peaks that are in equilibrium. Thus, in a final third calculation step the concentrations of the individual rotamers are summed up in order to end up with the overall concentration of the respective metabolite.

Results and Discussion

Comparison of HPLC patterns of lysimeter and mini-lysimeter leachate

The results of the alignment of the fractions defined in the HPLC chromatograms of the lysimeter leachate samples with the respective sections of HPLC chromatograms of the mini-lysimeter leachate summarised in Table B.8.1.4-31.

Table B.8.1.4-31: Comparison of HPLC chromatograms of the leachate samples originating from of the lysimeter study Burgener, 1996 and the mini-lysimeter study Fent, 2008

Guideline lysimeter Burgener, 1996			Mini-lysimeter Fent, 2008		
t_R [min]	Designation	Description/comment	t_R [min]	Designation	Description/comment
3	**U1**	artifact peak			
4-11	**U2**	unresolved radioactivity, no significant peaks	3-11		unresolved radioactivity/ minor peaks
11-13.5	**U3**	unresolved radioactivity, minor peaks	11-13.5	n.i.A	peak at t_R~11 min, additionally some unresolved radioactivity/minor peaks
13.5-16	**U4**	unresolved radioactivity, minor peaks	13.5-16	n.i.B	peak at t_R~13.5 min, additionally some unresolved radioactivity/minor peaks
16-18.5	**U5**	unresolved radioactivity, poorly reproducible peaks	16-18.5	n.i.C	peak at t_R~16.5 min, additionally unresolved radioactivity/minor peaks
18.5-24	**U6**	unresolved radioactivity, poorly reproducible peaks	18.5-23		unresolved radioactivity / minor peaks
23-24.5	**U7**	peak, partly split into insignificant peaks	23-24.5	n.i.C1	small peak at t_R~23.5 min, minor peaks
24-25.5	**U8**	peak, sometimes split into fragmented peaks	24-25.5	n.i.C2	small peak at t_R~25.5 min, additional minor peak
26	**U9**	large peak	26	n.i.D	peak
27.5	**U10**	large peak	27.5	n.i.E	peak
28	**U11**	small peak	~28		minor peak
29	**U12**	peak, frequently split	~29		minor peak
31	**M27**	peak, sometimes double peak	30	M27	double peak
33	**U13**	unresolved radioactivity/ minor peaks	31-32		unresolved radioactivity/minor peaks
33.5	**M23**	peak, may include other, minor peaks	32.5	M23	broad peak
35.5	**U14**	peak, may include other, minor peaks	33-35		radioactivity poorly separated from M23
36-37	**U15**	no reproducible peaks	36-40	n.i.F	peak at t_R~36 min, additionally minor peaks
39	**U16**	peak	41	n.i.G	small peak
40-42	**U17**	small peak, unresolved radioactivity	>41		low radioactivity
40.5		active substance (not detected)	42		active substance (not detected)

M23 = M656PH023, M27 = M656PH027

Despite differences of their relative percentages, it turned out that the principle distribution of definite peaks and sections of unresolved radioactivity or fragmented peaks is quite similar in both studies. Overall it can be stated that HPLC peaks in the lysimeter leachate correlate with peaks of the mini-lysimeter leachate. The metabolite pattern of the lysimeter leachate could largely be reproduced in the mini-lysimeter leachate. It is concluded that the metabolism is similar in both systems. This is further supported by the observation that the variation of experimental conditions in the mini-lysimeter study did not significantly affect the metabolite pattern in the leachate. It can be reasonably assumed that the HPLC peaks are caused by the same metabolites in both studies. This would mean that structure elucidation of lysimeter metabolites can be performed using mini-lysimeter leachate or soil extracts bearing the same HPLC peaks as the mini-lysimeter leachate.
In sum, definitive and reproducible peaks are observed in fraction U7, U8, U0, U10, U11, U12, U14 and U16. The same applies for the fractions containing metabolites M656PH023 and M656PH027.

Percentages as given in the report are expected to roughly represent the size of the actual peaks. However, in some cases peaks may be suspected to be caused by more than one compound or additional radioactivity may be present. Fractions U3, U4, U5 U6, U13, U15 and U17 exhibit only partly reproducible or small peaks but consist mainly of unresolved radioactivity or fragmented peaks. Percentages of the peaks in these fractions - and the compounds potentially identified behind these peaks - will only represent a small fraction of the respective entire 'unidentified fraction'. Fraction U1 is an artifact peak and fraction U2 does not contain significant peaks.

Metabolite structure proposals for lysimeter HPLC fractions

The metabolites identified the mini-lysimeter fractions and the aligned respective unknown radioactive fractions of the lysimeter study are presented in Table B.8.1.4-32. Some of the metabolites shown in Table B.8.1.4-30 do not appear in this table since there was no clear correlation to peaks in the original HPLC system or they were only observed in strongly enriched subfractions.

There were several pairs and one triplet of isomers of metabolites, which are distinguishable by their retention time. Most of the metabolite pairs were shown to be rotamers which are in equilibrium. Additionally, there are other metabolites which are marked with the suffix "(iso)" e.g. M656PH053 (iso) that have further stereochemical features (additional to rotamerism or without it) that give rise to multiple peaks for which no formation of an equilibrium was observed. Since it could not finally be decided from the MS results which of these isomeric forms is actually present in the respective HPLC peak, in these cases the same structures were proposed for each of the isomer peaks. The suggested structures of the metabolites can be found in Table B.8.1.4-29 and Table B.8.1.4-30.

Upon further investigation, a structural ambiguity resp. variability of certain metabolites became apparent. Some metabolites, e.g. M656PH049, may exist as an alternative structure to the original structure proposal or may be in equilibrium with isomeric structures (for more details see example in original study report to Staudenmaier, 2014b).

Table B.8.1.4-32: Metabolites identified in the mini-lysimeter study Fent, 2008 and/or samples of the anaerobic soil studies corresponding unknown radioactive fraction of the leachate of the lysimeter study Burgener, 1996

Guideline lysimeter			Mini-lysimeter			Identified Metabolites*
t_R [min]	Designation	Description/ comment	t_R [min]	Designation	Description/ comment	
3	**U1**	artifact peak				
4-11	**U2**	unresolved radioactivity, no significant peaks	3-11		unresolved radioactivity/ minor peaks	
11-13.5	**U3**	unresolved radioactivity, minor peaks	11-13.5	**n.i.A**	peak at 11 min, additionally some unresolved radioactivity/ minor peaks	M656PH052 (iso)
13.5-16	**U4**	unresolved radioactivity, minor peaks	13.5-16	**n.i.B**	peak at 13.5 min, additionally some unresolved radioactivity/ minor peaks	M656H055
16-18.5	**U5**	unresolved radioactivity, poorly reproducible peaks	16-18.5	**n.i.C**	peak at 16.5 min, additionally unresolved radioactivity/ minor peaks	M656PH049
18.5-24	**U6**	unresolved radioactivity, poorly reproducible peaks	18.5-23		unresolved radioactivity/ minor peaks	M656PH059 (iso) one of three isomers detected M656PH047 one of two rotamers
23-24.5	**U7**	peak, partly split into insignificant peaks	23-24.5	**n.i.C1**	small peak at 23.5 min, minor peaks	M656PH047 one of two rotamers M656PH059 (iso) one of three isomers detected M656PH045 one of two rotamers
24-25.5	**U8**	peak, sometimes split into fragmented peaks	24-25.5	**n.i.C2**	small peak at 25.5 min, additional minor peak	M656PH045 one of two rotamers M656PH059 (iso) one of three isomers detected M656PH053 (iso) one of two isomers detected
26	**U9**	large peak	26	**n.i.D**	peak	M656PH054 one of two rotamers
27.5	**U10**	large peak	27.5	**n.i.E**	peak	M656PH053 (iso)

Guideline lysimeter			Mini-lysimeter			Identified Metabolites*
t_R [min]	Designation	Description/ comment	t_R [min]	Designation	Description/ comment	
						one of two isomers detected M656PH054 one of two rotamers M656PH062
28	**U11**	small peak	~28		minor peak	M656PH043 one of two rotamers, isolated from t_R~31-32 min, isolated peaks showed different retention time
29	**U12**	peak, frequently split	~29		minor peak	M656PH043 one of two rotamers, isolated from t_R~31-32 min, isolated peaks showed different retention time
31	**M27**	peak, sometimes double peak	30	**M27**	double peak	M656PH027 double peak = two rotamers
33	**U13**	unresolved radioactivity/ minor peaks	31-32		unresolved radioactivity/ minor peaks	M656PH050 (rota) two rotamers expected but only this one detected structure derived from anaerobic sample
33.5	**M23**	peak, may include other, minor peaks	32.5	**M23**	broad peak	M656PH031 M656PH023
35.5	**U14**	peak, may include other, minor peaks	33-35		radioactivity poorly separated from M23	M656PH051
36-37	**U15**	no reproducible peaks	36-40	**n.i.F**	peak at 36 min, additionally minor peaks	M656PH010
39	**U16**	peak	41	**n.i.G**	small peak	M656PH032 isolated form anaerobic incubation, peak at this t_R in the leachate disappeared after storage
40-42	**U17**	small peak, unresolved radioactivity	>41		low radioactivity	M656PH003 isolated from anaerobic incubation

* in leachate samples of the lysimeter studie or in extracts of anaerobic soil samples

Many of the proposed metabolite structures had not been observed so far. This supports the finding in the lysimeter study that only few matches with known references were observed. Most of the new metabolites can however be regarded as derivatives of known metabolites like e.g. M656PH011,

M656PH023 and M656PH27 which have undergone further metabolic reactions (e.g. further oxidation or opening of the thiophene ring). The new metabolites are therefore considered to represent steps further downstream in the degradation process, which are not observed under other experimental conditions. In Figure B.8.1.4-1, the metabolites in the leachate are shown in their possible metabolic order.

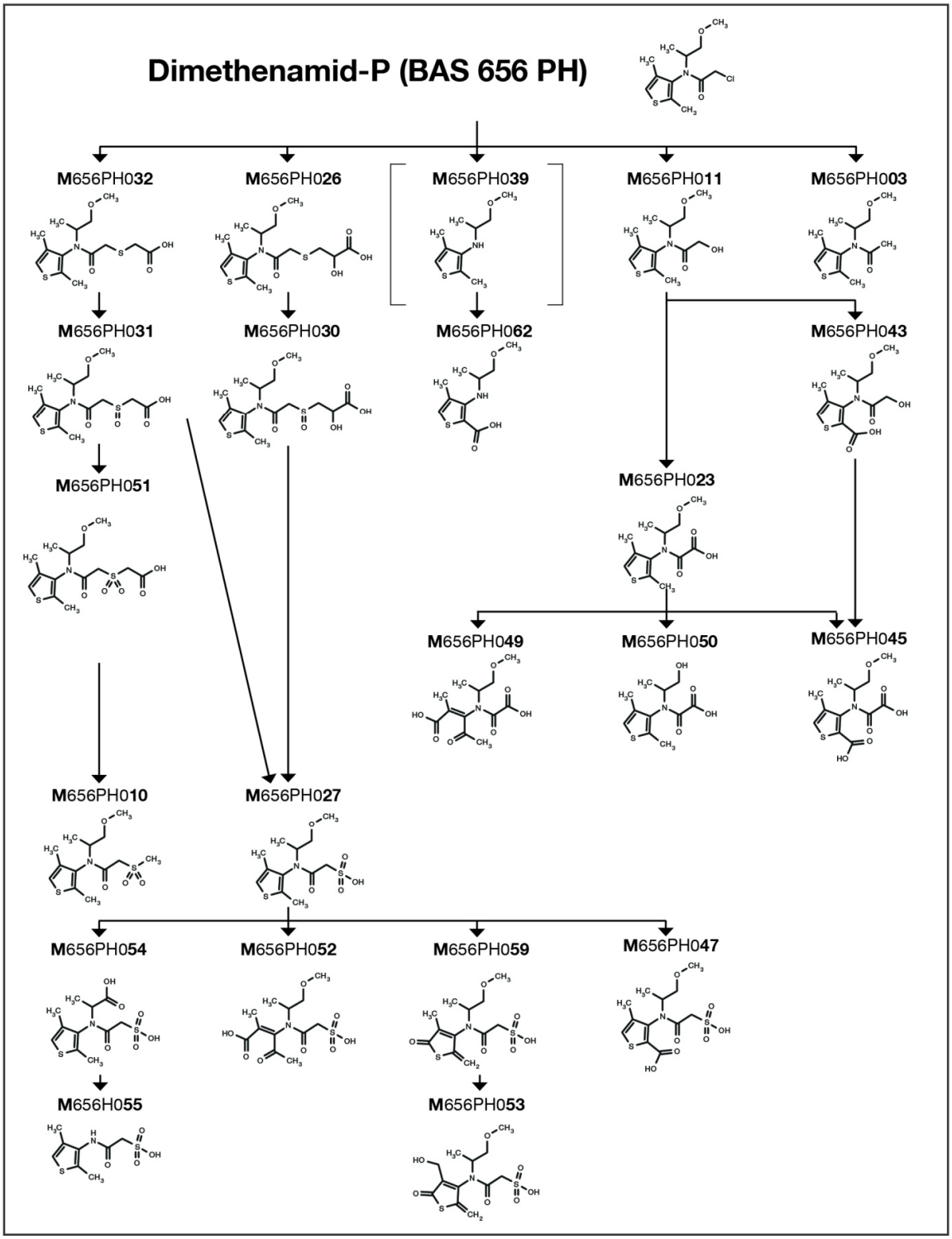


Figure B.8.1.4-1: Metabolic order of dimethenamid-P metabolites found in the leachate of the mini-lysimeter Fent, 2008 and the lysimeter Burgener, 1996

Estimation of metabolite concentrations in lysimeter leachate

The results of the step 1 calculation (= estimation of the annual average concentrations of the metabolites in the individual unidentified fractions) are shown in Table B.8.1.4-33.

Metabolite M656PH031 was present in the mini-lysimeter leachate in considerable amounts leading to a broad peak due to a partial overlap with M656PH023. In the lysimeter study Burgener 1996, where M656PH031, a similar broad peak shape is not observed leading to the conclusion that M656PH031 was not present in high amounts. This is in line with the finding that this metabolite was not identified by co-chromatography with its reference compound in the lysimeter stuy. It was thus concluded that under the conditions of the lysimeter study, the majority of the respective fration 'M23' indeed represents metabolite M656PH023 whereas metabolite M656PH031 is present only in small amounts if at all. Applying the precautionary principle, the entire fraction is attributed to the metabolite in order not to disregard it but set to 0.1 ug/L since it was detected under conditions of the lysimeter study.

Table B.8.1.4-33: Estimation of the concentration of individual metabolites in the leachate of the lysimeter study Burgener, 1996, step 1 calculation for individual peaks

R_t [min]	Unidentified fraction	Max. annual average conc. of HPLC fraction [µg/L]	Compound (new code)	Clear peak	Estimation of peaks in fraction		Estimation of individual peaks	
					factor A[(1)] (percentage of entire fraction)	all peaks in fraction [µg/L]	factor B[(2)]	individual peak [µg/L]
3	U1	12.9		no				
4-11	U2	3.9		no				
11-13.5	U3	2.6	M656PH052	no	0.33	0.9	1	0.9
13.5-16	U4	2.0	M656H055	no	0.33	0.7	1	0.7
16-18.5	U5	3.0	M656PH049	no	0.33	1.0	1	1.0
18.5-24	U6	3.4	M656PH059 Isomer 1	no	0.33	1.1	0.75	0.8
			M656PH047 Rotamer 1				0.75	0.8
23-24.5	U7	0.8	M656PH047 Rotamer 2	partly	0.66	0.5	0.75	0.4
			M656PH059 Isomer 2				0.75	0.4
			M656PH045 Rotamer 1				0.75	0.4
24-25.5	U8	3.2	M656PH045 Rotamer 2	partly	0.66	2.1	0.75	1.6
			M656PH059 Isomer 3				0.75	1.6
			M656PH053 Isomer 1				0.75	1.6
26	U9	1.3	M656PH054 rotamer 1	yes	1	1.3	1	1.3
27.5	U10	2.6	M656PH053 Isomer 2	yes	1	2.6	0.75	2.0
			M656PH054 Rotamer 2				0.75	2.0
			M656PH062				0.75	2.0
28	U11	0.4	M656PH043 Rotamer 1	yes	1	0.4	1	0.4
29	U12	1.2	M656PH043 Rotamer 2	partly	0.66	0.8	1	0.8
31	M27	4.0	M656PH027 Rotamer 1+2	yes	1	4.0	1	4.0
33	U13	0.5	M656PH050	yes	1	0.5	1	0.5
33.5	M23	1.0	M656PH031	yes	1	1	0.1[(3)]	0.1
			M656PH023				1[(3)]	1.0
35.5	U14	1.1	M656PH051	yes	1	1.1	1	1.1
36-37	U15	0.2	M656PH010	no	0.33	0.07	1	0.07
39	U16	1.5	M656PH032	yes	1	1.5	1	1.5
40-42	U17	0.3	M656PH003	no	0.33	0.1	1	0.1

(1) Factor A is defined depending on the occurrence of clear peaks in the respective HPLC fraction; further explanation see text.

(2) Factor B is defined depending on the occurrence of one or more compounds in the respective HPLC fraction, further explanation see text.
(3) Individually set; further explanation see text.

The result of the step 2 (adjustment of estimated metabolite concentrations in lysimeter to actual application rate) is presented in Table B.8.1.4-34.

Table B.8.1.4-34: Estimation of the concentration of individual metabolites in the leachate of the lysimeter study Burgener, 1996, step 2 adjustment on actual application rate of representative use

Unidentified fraction	Max. annual average conc. of HPLC fraction		Compound	Max. annual average conc. of individual compound	
	in original lysimeter [µg/L]	adjusted to 864 g/ha application rate [µg/L]		in original lysimeter [µg/L]	adjusted to 864 g/ha application rate [µg/L]
U1	12.9	7.7			
U2	3.9	2.3			
U3	2.6	1.6	M656PH052	0.9	0.5
U4	2.0	1.2	M656H055	0.7	0.4
U5	3.0	1.8	M656PH049	1.0	0.6
U6	3.4	2.0	M656PH059 Isomer 1	0.8	0.5
			M656PH047 Rotamer 1	0.8	0.5
U7	0.8	0.5	M656PH047 Rotamer 2	0.4	0.2
			M656PH059 Isomer 2	0.4	0.2
			M656PH045 Rotamer 1	0.4	0.2
U8	3.2	1.9	M656PH045 Rotamer 2	1.6	1.0
			M656PH059 Isomer 3	1.6	1.0
			M656PH053 Isomer 1	1.6	1.0
U9	1.3	0.8	M656PH054 rotamer 1	1.3	0.8
U10	2.6	1.6	M656PH053 Isomer 2	2.0	1.2
			M656PH054 Rotamer 2	2.0	1.2
			M656PH062	2.0	1.2
U11	0.4	0.2	M656PH043 Rotamer 1	0.4	0.2
U12	1.2	0.7	M656PH043 Rotamer 2	0.8	0.5
M27	4.0	2.4	M656PH027 Rotamer 1+2	4.0	2.4
U13	0.5	0.3	M656PH050	0.5	0.4
M23	1.0	0.6	M656PH031	0.1	0.06
			M656PH023	1.0	0.6
U14	1.1	0.7	M656PH051	1.1	0.7
U15	0.2	0.1	M656PH010	0.07	0.04
U16	1.5	0.9	M656PH032	1.5	0.9
U17	0.3	0.2	M656PH003	0.1	0.06

The overall concentrations of the metabolites after summing up the concentrations of the rotamers are presented in Table B.8.1.4-35.

Table B.8.1.4-35: Estimation of the concentration of individual metabolites in the leachate of the lysimeter study Burgener, 1996 after application adjustment to 864 g/ha, step 3 summing up of rotamer concentrations

Compound		Observed in fraction	Individual amounts [µg/L]	Sum [µg/L]
M656PH052		U3	0.5	0.5
M656H055		U4	0.4	0.4
M656PH049		U5	0.6	0.6
M656PH059	isomer 1	U6	0.5	0.5
M656PH047	rotamer 1+2	U6 + U7	0.5 + 0.2	0.7
M656PH059	isomer 2	U7	0.2	0.2
M656PH045	rotamer 1+2	U7 + U8	0.2 + 1.0	1.2
M656PH059	isomer 3	U8	1.0	1.0
M656PH053	isomer 1	U8	1.0	1.0
M656PH054	rotamer 1+2	U9 + U10	0.8 + 1.2	2.0
M656PH053	isomer 2	U10	1.2	1.2
M656PH062		U10	1.2	1.2
M656PH043	rotamer 1+2	U11 + U12	0.2 + 0.5	0.7
M656PH027	rotamer 1+2	M27	2.4	2.4
M656PH050		U13	0.3	0.3
M656PH031		M23	0.06	0.06
M656PH023		M23	0.6	0.6
M656PH051		U14	0.7	0.7
M656PH010		U15	0.04	0.04
M656PH032		U16	0.9	0.9
M656PH003		U17	0.06	0.06

Thus, according to the calculations, the estimated maximum annual average concentrations of the metabolites M656PH003, M656PH031 and M656PH010 in the lysimeter leachate remained < 0.1 µg/L.
The estimated maximum annual average concentrations of the metabolites M656PH023, M656PH051, M656PH043, M656PH052, M656PH047, M656H055, M656PH049, M656PH059 (2 isomers) and M656PH050 in the lysimeter leachate were between 0.1 – 0.75 µg/L.
The estimated maximum annual average concentrations of the metabolites M656PH027 , M656PH054, M656PH032, M656PH059 (1 isomer), M656PH045, M656PH062 and M656PH053 (2 isomers) in the lysimeter leachate were between 0.75 – 2.4 µg/L.

Conclusion

This report summarises the work that was done to elucidate the 17 unknown radioactive fractions with concentrations > 0.1 µg/L found in the lysimeter study Burgener, 1996 and provides a final estimation of annual average concentrations of the newly elucidated metabolites in the lysimeter leachate. The RMS wants to point out that a valid effort was performed to elucidate the unknown radioactive fractions of the lysimeter applying with the mini-lysimeter study a new approach that had never tried for elucidation of lysimeter leachate before and actually proved successful.
The alignment of the unknown leachate fractions of the lysimeter study with mini-lysimeter fractions is considered acceptable by the RMS. Also the estimated concentrations of individual metabolites in the fractions are considered acceptable. For the unknown fractions U3, U4, U5, U6, U12 and U17, part of the unknown radiaoactivity (between 0.13 – 1.8 µg/L, 7.53 ug/L in total) was not assigned to any metabolite. Since these fractions did not contain distinctive peaks but mostly unresolved radioactivity or minor peaks, it is considered unlikely that these remaining radioactivity contained any metabolites in concentrations > 0.1 ug/L. For the unknown fractions U7, U8 and U10 more radioactivity as

actually measured was assigned to the respective peaks (between 0.4 – 3.5 µg/L, 5.5 ug/L in total) thus providing an especially conservative approach for the metabolites found in these fractions.
The metabolites identified using the mini-lysimeter leachate fractions are already labelled to belong to dimethenamid-P, although the main lysimeter study Burgener, 1996 was performed using racemic dimethenamid (e.g. M656PH027 instead of M656H027). However, since it was shown that the degradation rate and route is the same for racemic dimethenamid and dimethenamid-P in soil and in water/sediment systems, this is also considered acceptable by the RMS.
However, the adjustment of the metabolite concentrations to the actual application rate of 864 g/ha by multiplying all estimated concentrations with a factor of 0.6 is considered oversimplified by the RMS. While it can be assumed that metabolite concentrations in the leachate will be smaller when reducing the application rate from 1440 g/ha to 864 g/ha dimethenamid-P, the experimental set-up is too complex to assume a simple reduction of 0.6.
Thus, the RMS repeated the final step 3 calculation (summing up of rotamers) using the metabolite concentrations initially estimated for the lysimeter leachate. The metabolite M656PH031 was excluded, since it was not found in the original lysimeter study though tested against reference substances and assuming annual average concentrations >0.1 µg/L for this metabolite appears therefore unrealistic. The results of the step 3 calculation (summing up of rotamers) using the metabolite concentrations initially estimated for the lysimeter leachate is presented in Table B.8.1.4-36.

Table B.8.1.4-36: Estimation of the concentration of individual metabolites in the leachate of the lysimeter study Burgener, 1996 for an annual application of 1440 g /ha dimethenamid (step 3 summing up of rotamer concentrations, recalculation by the RMS)

Compound		Observed in fraction	Individual amounts [µg/L]	Sum [µg/L]
M656PH052		U3	0.90	0.90
M656H055		U4	0.70	0.70
M656PH049		U5	1.00	1.00
M656PH059	isomer 1	U6	0.80	0.80
M656PH047	rotamer 1+2	U6 + U7	0.8+ 0.4	1.20
M656PH059	isomer 2	U7	0.40	0.40
M656PH045	rotamer 1+2	U7 + U8	2.00	2.00
M656PH059	isomer 3	U8	0.4 + 1.6	1.60
M656PH053	isomer 1	U8	1.60	1.60
M656PH054	rotamer 1+2	U9 + U10	2 + 1.3	3.30
M656PH053	isomer 2	U10	2.00	2.00
M656PH062		U10	2.00	2.00
M656PH043	rotamer 1+2	U11 + U12	0.4 + 0.8	1.20
M656PH027	rotamer 1+2	M27	4.00	4.00
M656PH050		U13	0.50	0.50
M656PH023		M23	1.00	1.00
M656PH051		U14	1.10	1.10
M656PH010		U15	0.07	0.07
M656PH032		U16	1.50	1.50
M656PH003		U17	0.10	0.10

For an annual application rate of 1440 g/ha dimethenamid to Borstel soil, the estimated maximum annual average concentrations of the metabolites M656PH010 and M656PH031 in the lysimeter leachate remained < 0.1 µg/L.
The estimated maximum annual average concentrations of the metabolites M656PH003, M656PH050,

M656PH055 and M656PH059 in the lysimeter leachate were between 0.1 – 0.75 µg/L.
The estimated maximum annual average concentrations of the metabolites M656PH023, M656PH027, M656PH032, M656PH043, M656PH045, M656PH047, M656PH049, M656PH051, M656PH052, M656PH053 (2 isomers), M656PH054, M656PH059 (1 isomer) and M656PH062 in the lysimeter leachate were between 0.75 – 4.0 µg/L.

KCA7.1.4.2/6 – Haering, 2013a (new study)

Author:	Haering, T.
Title:	Relevance assessment of lysimeter study for BAS 656 H - dimethenamid-P and its metabolites for agricultural areas of Europe as well as Germany, France, and UK
Date:	01/01/2013
Doc ID:	BASF DocID 2012/1262498
Guidelines:	None available
GLP:	No (modelling study)
Validity:	Partly acceptable as additional information provided further details on input parameter are provided

Aim of study

In this study, the relevance of the lysimeter study Burgener, 1996 with regard to its vulnerability regarding groundwater leaching for the agricultural areas of Europe has been analysed using spatial analysis and spatially distributed modeling in a Geographic Information System (GIS).

Material and Methods

In order to estimate the relevance of the dimethenamid-P lysimeter study for the European agricultural area, the "conservativeness" of the study site has to be set in context. The site characteristics of the study site have to be conservative regarding groundwater leaching in order to be vulnerable. Therefore, two different GIS-based approaches have been applied:
First, single site characteristics, which have an influence on the leaching behaviour of compounds, have been analysed - namely mean annual precipitation, soil organic matter content, and soil texture. European wide GIS maps of these parameters have been used to plot the cumulative empirical distribution. Information on environmental characteristics of the study area like soil properties or climate were derived from the latest version of the GIS data provided by the EFSA (EFSA Spatial Data Version 1.1).
Dimethenamid-P is applied to different arable and permanent crops. In order to include the entire potential use area of dimethenamid-P in this study, the latest version from 2006 of the CORINE (Coordination of Information on the Environment) land cover database has been used together with the 2000 version for Greece , since the country is excluded in the 2006 version.
In addition, the value of the variable at the study location is added to this distribution plot. By doing so, the relative agricultural area of Europe with a higher/lower value compared to the study location can be illustrated.

In addition to analysing single environmental conditions, MetaPEARL has been used to set the vulnerability of the study site in a spatial context.
MetaPEARL is a Metamodel of the process-based EuroPEARL model, a spatially distributed leaching model that may provide maps of the predicted leaching concentrations and allow for identification of high and low risk areas in terms of spatially varying environmental and land use properties on a European scale. Spatially distributed leaching models have been developed and were proposed by the Ground Water Work Group of FOCUS e.g. for higher-tier leaching assessments. Details on the derivation of EuroPEARL can be found in Tiktak, 2004[1].
The drawback of a spatially distributed, process based numerical models like EuroPEARL is their complexity and the need for a high number of scenarios (often more than 1000), which have to be

[1] Tiktak et al (2004). Assessment of the pesticide leaching risk at the Pan-Euopean level. The EuroPEARl approach. Journal of Hydrology 289, p. 222 -238

parameterised with overlaying environmental maps in a Geographic Information System (GIS). The delineation of a large number of parameters can be difficult, and some of the required environmental parameters are even unavailable at larger scales.
To overcome these problems, MetaPEARL has been developed. In MetaPEARL, the complex nature of EuroPEARL has been simplified by considering only those processes and parameters for which the considered simulation output is sensitive or for which input data are available. As such, a simpler model can be obtained which encompasses the behaviour of the complex model and which is more compatible with available geodatabases. The model was developed within the EU project "Harmonised environmental Indicators for pesticide Risk" (HAIR). Detailed description of the derivation of the model can be found in Tiktak (2006[2]) and FOCUS Generic Guidance for Groundwater (2011).
MetaPEARL is basically a regression model which predicts the 80th percentile of the leaching concentration at 1 m depth. The regression function is a process-based Metamodel of EuroPEARL. To account for climatic differences in Europe, e.g. seasonal dynamics in weather, model calibration was conducted with four subsets of the leaching sets, namely one for each climate zone. The definition of climate zones was adopted from FOCUS (2000), see Table B.8.1.4-37.

Table B.8.1.4-37: Major climate zones of the European Union

Zone	Mean annual rainfall [m yr^{-1}]	Mean annual temperature [°C]
Temperate, dry (TD)	<0.8	<12.5
Temperate, wet (TW)	>0.8	<12.5
Warm, dry (WD)	<0.8	>12.5
Warm, wet (WW)	>0.8	>12.5

MetaPEARL was calibrated with a leaching dataset for spring application as well as with a leaching dataset for autumn applications using EuroPEARL. The resulting spring and autumn regression coefficients α_0, α_1, and α_2 for autumn and spring application are presented in Table B.8.1.4-38.

Table B.8.1.4-38: MetaPEARL coefficients (spring / autumn application)

Climate Zone	α_0	α_1	α_2
Temperate, dry (TD)	5.09 / 5.3	0.44 / 0.16	0.46 / 0.46
Temperate, wet (TW)	4.72 / 4.95	0.39 / 0.16	0.58 / 0.6
Warm, dry (WD)	5.07 / 5.2	0.28 / 0.07	0.3 / 0.37
Warm, wet (WW)	4.81 / 5.02	0.58 / 0.23	0.46 / 0.57

Since the GAP for dimethenamid-P covers spring as well as autumn applications, the analysis in this study was performed for both, MetaPEARL with coefficients for spring application as well as for autumn application.

The map of organic matter content provided by EFSA describes only the topsoil (0-30 cm). However, the leaching dataset for calibration of MetaPEARL comprise average values for the top 1 m of organic matter. Therefore, leaching vulnerability would be underestimated when using the EFSA map for MetaPEARL calculations. Organic matter values are too high which leads to stronger sorption of the pesticide and therefore reduced groundwater leaching. Since information on organic matter of the subsoil is not at hand, it was assumed that the organic matter content in the subsoil is 0 as a conservative workaround. Consequently, the topsoil organic matter values were extrapolated to 1 m depth by multiplying the organic matter values of each grid cell in the map by 0.3.

MetaPEARL is a simplified approach for spatially distributed modelling. The only compound parameters for MetaPEARL calculation are the degradation half-life at reference temperature and the

[2] Tiktak et al (2006). ‚Mapping Groundwater vulnerability to pesticide leaching with a process-based Metamodel of EuroPEARL.' Journal of Environmental Qualitiy 35(4), pp. 1213-1226

organic matter-water partition coefficient. The parameters for dimethenamid-P and the metabolites M656PH023 (M23 in this study), M656PH027 (M27 in this study) and M656PH031 (M31 in this study) used in this study are shown in Table B.8.1.4-39.

Table B.8.1.4-39: Compound properties for MetaPEARL modelling

Substance	DT_{50} [d]	k_{om} [mL g^{-1}]
Dimethenamid-P	10.8*	98.7+
Metabolite M656PH023	19.7#	3.5~
Metabolite M656PH027	30.4#	3.9~
Metabolite M656PH031	30.8#	5.8~

* median of n=6
\# geometric mean of n=3
\+ median of n=10
~ arithmetic mean of n=6

As for the single environmental parameters, empirical cumulative distribution functions for the MetaPEARL maps have been plotted. In addition to the map of MetaPEARL concentrations also the MetaPEARL concentration for the lysimeter study has been calculated (Borstel soil + Itingen climate). This concentration has been added to the cumulative distribution plot to illustrate the relative agricultural area of Europe with a higher/lower MetaPEARL concentration compared to the lysimeter study, i.e. area with higher/lower vulnerability.

Results and Discussion

Results of single site characteristics analysis

The empirical cumulative distribution function for the annual average precipitation for the relative agricultural area of Europe as well as for the study site Itingen is illustrated in Figure B.8.1.4-2.

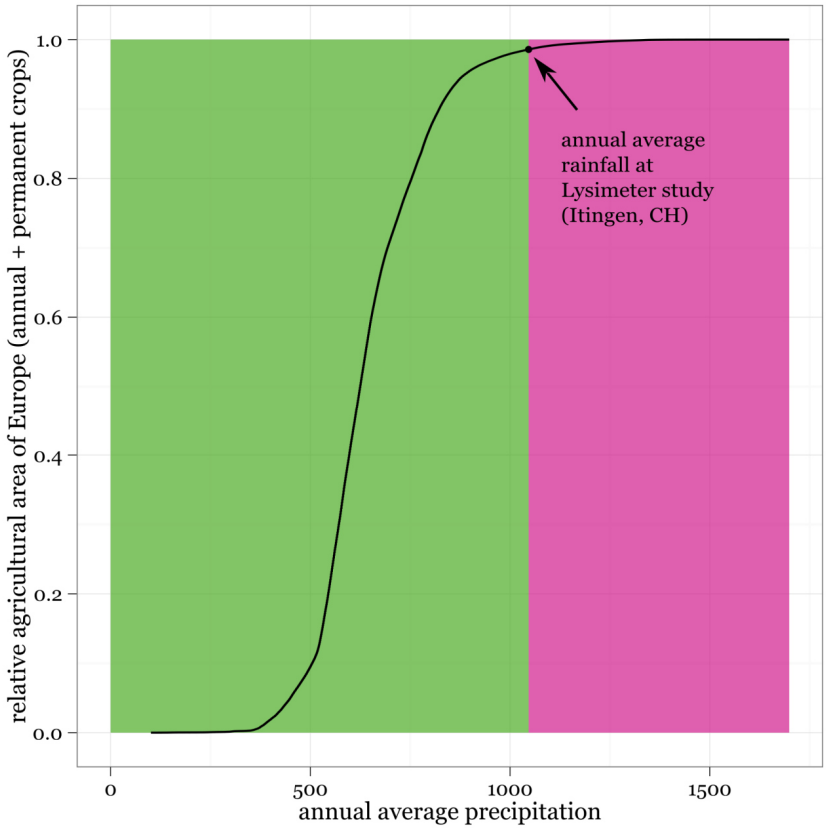


Figure B.8.1.4-2: Empirical cumulative distribution function of annual average precipitation for the relative agricultural area of Europe and the value for the lysimeter study

The plot indicates that the annual average precipitation at the lysimeter study location (1046.5 mm/a) is higher than 98.1 % of the agricultural area of Europe. Since higher rainfall amounts are directly linked to higher leaching to groundwater it can be concluded that the lysimeter study is characterised by vulnerable conditions regarding annual amount of rainfall.

The empirical cumulative distribution function for topsoil organic matter content for the relative agricultural area of Europe is illustrated in Figure B.8.1.4-3.

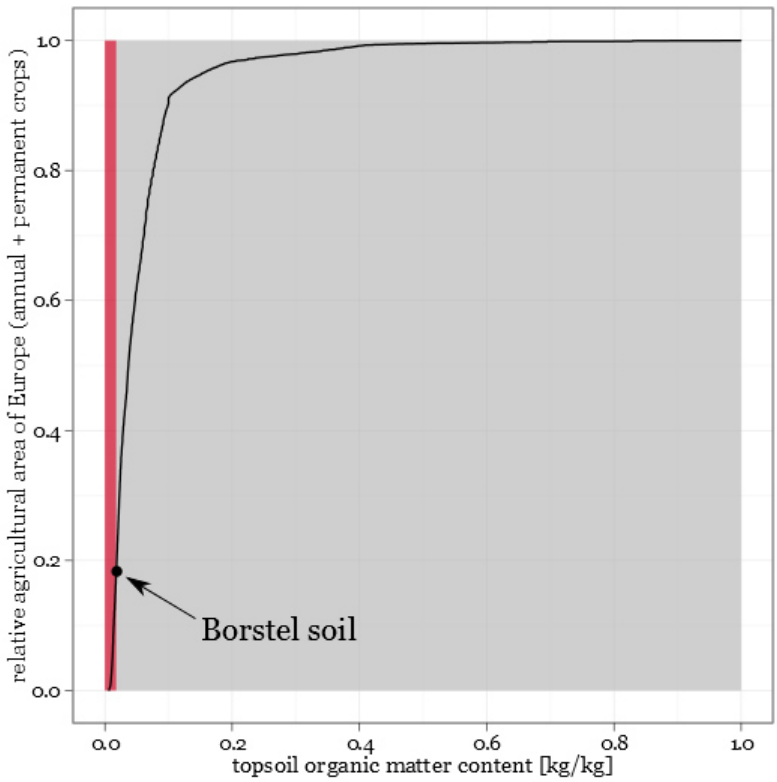


Figure B.8.1.4-3: Empirical cumulative distribution function of topsoil organic matter content for the relative agricultural area of Europe and the value for the lysimeter study

The plot indicates that the organic matter content in the top 30 cm at the lysimeter study location (0.0181 kg/kg) is higher than only 18.6 % of the agricultural area of Europe, i.e. 81.4 % of the agricultural area of Europe has a higher content of soil organic matter. Since lower soil organic matter content means less potential of sorption it can be concluded that the lysimeter study is characterised by vulnerable conditions regarding soil organic carbon content.

Soil texture properties could not be illustrated with cumulative distribution plots because of their level of measurement (nominal data). Typically, soil texture is plotted with a texture triangle, in which the soil texture class is plotted according to their particle size distribution (sand, silt, and clay content). To compare the texture properties of the European agricultural area with the Borstel soil the density over all raster cells of the soil texture map (topsoil, 1 km cell size) has been plotted into a texture triangle (see Figure B.8.1.4-4).

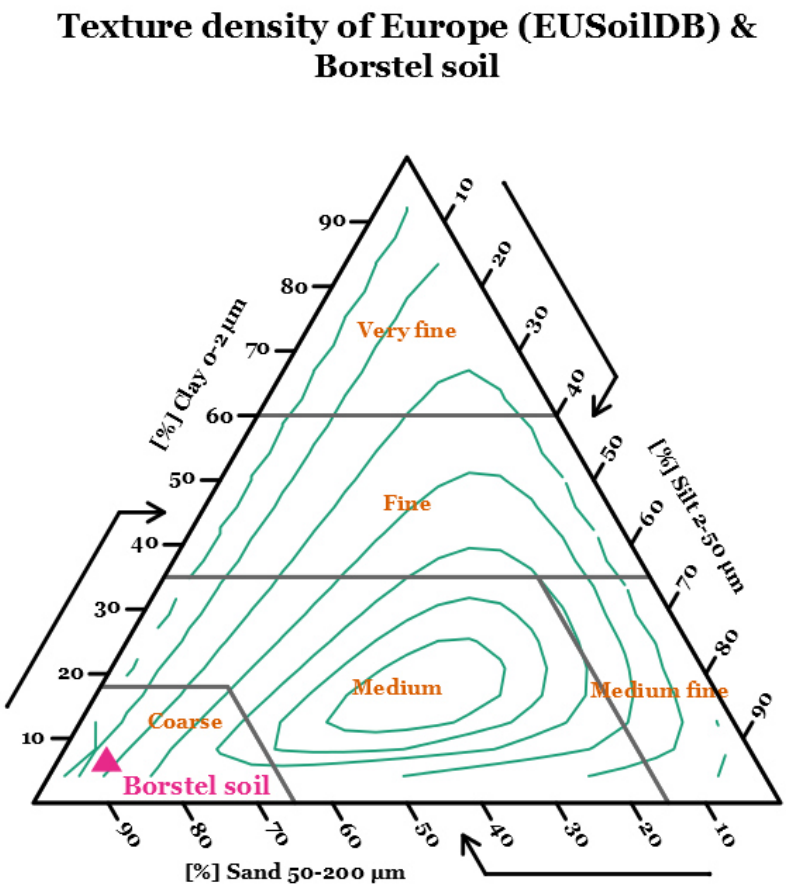


Figure B.8.1.4-4: Texture triangle according to the EUSoilDB indicating the distribution of topsoil texture in the agricultural area of Europe (isolines in green) and the texture properties of the Borstel soil

The plot indicates the highest texture density in the agricultural area in Europe in the Medium texture class whereas the texture properties of the Borstel soil show clear coarse texture. Since coarse textured soils have potentially higher infiltration rates and faster movement of water it can be concluded that the lysimeter study is characterised by vulnerable conditions regarding soil texture.

Results of the vulnerability analysis regarding groundwater leaching

For both the spring and autumn application relative MetaPEARL concentrations are depicted in Figure B.8.1.4-5 and Figure B.8.1.4-6.

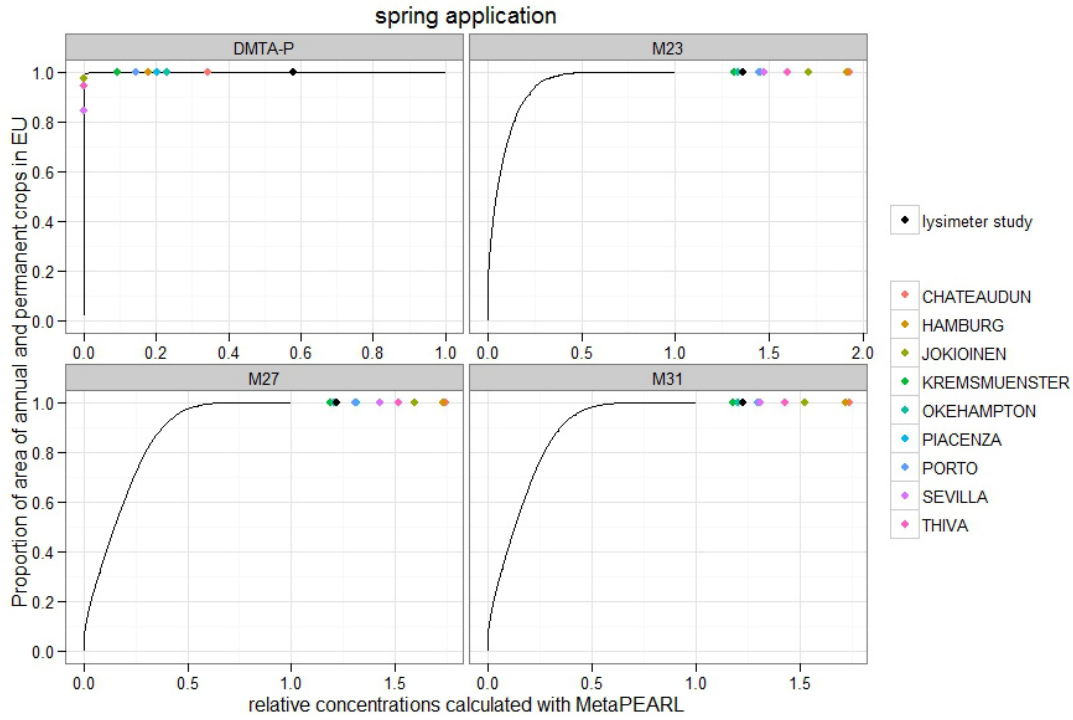


Figure B.8.1.4-5: Empirical cumulative distribution function of the relative MetaPEARL concentration for the agricultural area of Europe as well as the lysimeter study and the focus scenarios – spring application

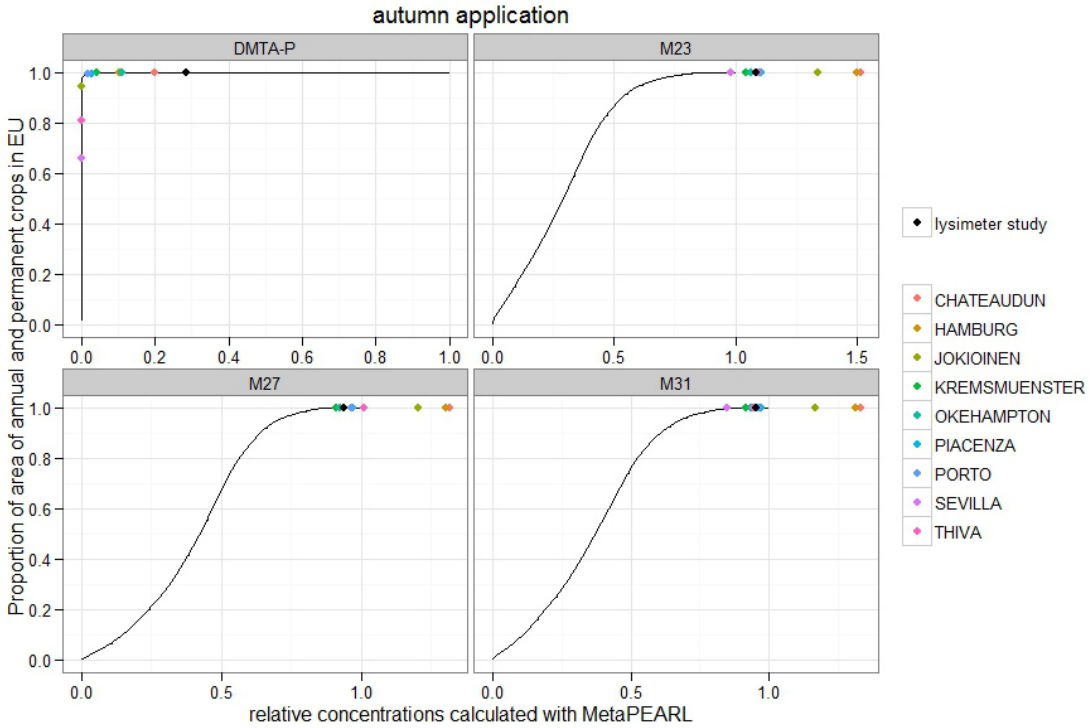


Figure B.8.1.4-6: Empirical cumulative distribution function of the relative MetaPEARL concentration for the agricultural area of Europe as well as the lysimeter study and the focus scenarios – autumn application

The lysimeter study shows mostly higher MetaPEARL concentrations than the entire agricultural area of Europe.
In most plots MetaPEARL concentrations of the lysimeter study is lower than FOCUS szenario Hamburg, even though the conditions at the lysimeter site are more vulnerable than FOCUS szenario Hamburg (same soil but higher rainfall amount). This could be explained by the disaggregation of Europe in four climatic zones for MetaPEARL calculations. With the higher annual rainfall amount (Itingen: 1046.5 mm/yr, FOCUS szenario Hamburg: 786 mm/yr) the lysimeter site has to be modelled with the temperate-wet model whereas FOCUS Hamburg lies within the temperate-dry class.
Bearing in mind that the cumulative distribution plots cover the entire agricultural area it may be confusing that the lysimeter site as well as several FOCUS scenarios have higher concentrations than the maximum concentration of the mapped values (relative MetaPEARL concentrations > 1.0), i.e. are more vulnerable than the entire area which is physically not possible. However, the differences in MetaPEARL concentrations between map and point calculations come from the different scales of measurements as well as the different sources of information, e.g. maps of climatic conditions (worldclim data) vs. local measurements, maps of topsoil organic matter vs. detailed description of soil profiles. In addition, some FOCUS scenarios as well as the lysimeter site are combinations of soil and weather data, which do not occur in reality, e.g. Borstel soil carried to Itingen or the West München weather station for Kremsmünster scenario, which may lead to higher concentrations as for the absolute location of Borstel or Kremsmünster (see FOCUS, 2000).

However, even taking these unavoidable inconsistencies due to the simplified character of MetaPEARL into account, the lysimeter study could be regarded as vulnerable regarding pesticide leaching to groundwater for entire agricultural area of Europe.

Conclusion

No guidance is available on how to compare site characteristics of one specific European location with climate and soil conditions throughout the whole agricultural area of Europe. Thus, the RMS believes that the study should be discussed by the experts before drawing a final conclusion on its acceptability, since the use of spatially distribution models as part of the higher tier leaching assessments is fairly new and experience from EU approval of other active substances is therefore lacking.
As a general issue, it should be noted, that the documentation of the study is very poor. Only the resulting empirical cumulative distribution functions shown in this study summary were provided in the original study report but no appendix with e.g. reports of the input parameter or modelling results were provided making an evaluation of the performed calculations difficult. Since to our knowledge, neither the analysis of the single site characteristics nor the MetaPEARL analysis were previously used in the current context for EU approval of a substance, we consider a very thorough documentation of the performed calculation, the modelling steps and of the results, including interim results, very important to allow Member States to understand and evaluate the performed analysis and the modelling.
For the MetaPEARL analysis, we believe, that it would have been important to have information on the derived regression variables X_1 and X_2 included. Besides, it should have been stated which climate years were used for derivation of the regression variables. For the FOCUS scenarios and the lysimeter the resulting regression variables could have been documented directly and for the MetaPEARL Scenarios at least some examples of the derived variables could have been given. Additionally, the regression coefficients used for the lysimeter and the FOCUS scenarios should have been stated and the derived MetaPEARL maps showing the modelled relative concentrations for dimethenamid-P and its metabolites should have been provided in the study report (again allowing an evaluation which part of the European area is covered by this evaluation). To our knowledge, EuroPEARL and MetaPEARL were both developed using soil and climate data only of the EU-15 area, which covers only 75 % of the entire EU. Thus, it appears that a new recalibration of MetaPEARL based on soil and climate maps of the entire EU would be required before using it for EU wide higher tier leaching assessment. It is also not clear to us, how this issue was solved in this study.

The results of the comparison of the site characteristics are considered acceptable as additional information by the RMS. Here only the data of the EFSA database covering the entire EU were used

and compared with the lysimeter site characteristics, but no spatial model was used.
The results show, that the annual average precipitation at the lysimeter study location over the three years of the lysimeter study (= 1046.5 mm/a) is higher than 98.1 % of the annual average precipitation of the whole agricultural area of Europe (although it was not stated which years of precipitation were used for comparison). The results further indicate that the organic matter content in the top 30 cm of the lysimeter soil (0.0181 kg/kg) is lower than 81.4 % of the agricultural area of Europe. Besides the Borstel soil exhibits a more coarse soil texture than the majority of the European soils. Thus the results indicate that the site characteristics of the lysimeter study over the three years study duration represent vulnerable conditions regarding groundwater leaching also for the whole area of Europe.

Regarding the modelling with MetaPEARL, there are some general issues with the model MetaPEARL that would need to be clarified before it should be used for higher tier groundwater leaching assessment. First, the model EuroPEARL, that was used to determine the regression coefficients for MetaPEARL is not available through EFSA and not under version control as was suggested as requirement before use as higher tier leaching model in the EFSA scientific opinion (EFSA Journal 2013; 11(6):3291).
Besides, the RMS wonders why the MetaPEARL modelling resulted in smaller groundwater concentrations for the whole area of Europe for the metabolites M656H023, M656H027 and M656H031 than in all available 10 FOCUS scenarios for spring application and in 3 FOCUS scenarios (Chateaudun, Hamburg and Jokoinen) for autumn application. While not actually existing scenarios like Borstel soil with Itingen climate (conditions of lysimeter study) or West Munich weather for the Kremsmünster scenario will not need to be covered by a spatially distributed leaching model for Europe, it needs to be made sure that all really existing vulnerable regions are covered. This does appear not to be the case for MetaPEARL. These differences between the FOCUS scenarios and MetaPEARL might have its cause already in the process-based EuroPEARL model (Tiktak, 2004) from which MetaPEARL is derived. The size of the basic units for predicted leaching concentrations within EuroPEARL constitutes of 30 x 30 km grids in the mean and up to maximum grids of 100 x 100 km maximum and is thus very coarse. This may cause bias if site specific data like the lysimeter study is set into context as was done here. This issue with the model MetaPEARL needs to be clarified before results of the model evaluation for specific substances can be accepted for higher tier leaching assessments. The applicant argued in its comments on the first draft of the RAR that these differences can be explained by the effect, that tier 1 scenarios (the FOCUS scenarios) are compared with tier 3 scenarios. However, the observed differences are still not clear to us, since neither EuroPearL nor MetaPEARL were originally developed as tier 3 models but as models that provide estimated spatially distributed groundwater concentrations for the European agricultural area. Besides, also the locations of the FOCUS scenarios were developed using spatially distributed models and therefore they should have been covered by the scenarios of the MetaPEARL model. Since according of the EFSA scientific opinion EFSA Journal 2013; 11(2):3114, Table 4 none of the FOCUS scenarios covers the whole European agricultural area, the modelled concentrations of the FOCUS scenarios should be not on the topmost part of the cumulative curve but somewhere in the middle of the curve.

Regardless of the uncertainties of the model or/and missing documentation of the input parameters, the results of the model indicate that the lysimeter is indeed a worst case for active substance dimethenamid-P. For the metabolites M656PH023, M656PH027 and M656PH031 however, the results for many of the FOCUS scenarios show higher concentrations than the model results for the lysimeter. Thus, we believe, that the model indicates, that the lysimeter cannot be considered a worst case compared to the accepted FOCUS scenarios.
Finally, after evaluation of the degradation and adsorption studies for dimethenamid-P, M656PH023, M656PH027 and M656PH031, different endpoints should have been derived to be used for the modelling of all four compounds. Thus the modelling would need to be repeated with the newly derived endpoints.

Thus, the MetaPEARL modelling results are currently not considered acceptable by the RMS.

KCA7.1.4.2/7 – Hein & Baudy, 2013 (new study)

Author:	Hein, W. Baudy, M.
Title:	Determination of the breakthrough behaviour of two metabolites (M23 and M27) of dimethenamid-P and of a conservative tracer using microlysimeters
Date:	19/09/2013
Doc ID:	BASF Doc ID 2013/1294765
Guidelines:	None
GLP:	Yes. (certified by Landesamt fuer Umwelt, Wasserwirtschaft und Gewerbeaufsicht, Mainz, Germany)
Validity:	Acceptable as additional information

Aim of the study

The purpose of the study was the determination of the breakthrough behaviour of the metabolites M656PH023 and M656PH027 (M23 and M27 in this study) of the herbicide dimethenamid-P using microlysimeters.

Material and Methods

The soil chosen for the study originates from "Birkenheide" (Rhineland-Palatinate / Germany). The physico-chemical characterisation of the soil is presented in Table B.8.1.4-40.

Table B.8.1.4-40: Characterisation of soil used in this study

Textural class (USDA scheme)	Loamy sand
Soil texture [%], (USDA scheme)	
Sand	84.7
Silt	9.1
Clay	6.2
Total organic carbon [%]	0.86
Microbial Biomass [mg C_{mikr}/kg Soil]	22.7
Soil depth (cm)	0-30
pH ($CaCl_2$)/(H_2O)	6.8/7.2

Stainless steel tubes (211 mm in diameter and 300 mm length) filled with undisturbed soil columns were used. The length of the soil core was approximately 280 mm. In total four soil columns were sampled. Three soil columns out of the four were used for the determination of the breakthrough curves. On top of the columns about 30 mm of the soil were replaced by 500 g of quartz sand ensuring a plain surface. A ceramic plate was mounted at the lower base of the soil column. The outlet tube had an internal diameter of 3 mm and was filled with a hanging water column of about 500 mm to apply a constant tension to the lower end of the soil column to prevent the formation of a capillary fringe.

Prior to application, the soil columns were equilibrated for 23 days using an irrigation rate of 105 - 210 mL/d. During this period the amount of leachate was measured (weight density = 1 g/mL) and recorded.
0.35 mg of M656H023 (100 % purity, M23 in this study) and M656H027 (97.1 % purity, M27 in this study) were applied onto each soil column (0.035 m^2 soil column surface) corresponding to an application rate of 200 g/ha.

Additionally, 500 mg bromide (as Br-) per column was applied as bromide tracer.

The irrigation was performed according to the scheme presented in Table B.8.1.4-41 for 150 days.

Table B.8.1.4-41: Irrigation programme

Day after application	Irrigation		Irrigation within 6 hours [mL]
Day of application (Friday) Day 0			None
Saturday – Sunday: Day 1 – Day 2 after application	24 hours	0.000 mL/min = 0.00 mm/h	None
Monday – Friday: Day 3 - Day 150 after application	6 hours 18 hours	0.194 mL/min = 0.33 mm/h 0.000 mL/min = 0.00 mm/h	70
Saturday and Sunday	24 hours	0.000 mL/min = 0.00 mm/h	None

At the end of each irrigation cycle the actual volume of water applied to each column was measured and recorded. Irrigation was with tap water until breakthrough of potassium bromide, afterwards 0.01 M $CaCl_2$ solution was used.
For each leachate specimen the actual volume/weight was determined. From each leachate specimen taken on Monday, Wednesday and Friday an aliquot was directly filtered through a 0.20 µm filter into a HPLC sample vial and injected into the HPLC for test item and bromide analysis. The bromide determinations were carried out in duplicate and the determination limit was 0.1128 mg/L. Based on the results of the analysis additional leachate specimens were analysed by HPLC.
Furthermore, the test item concentrations in the leachates were determined using LC-MS/MS.
The room temperature beside the soil columns was recorded every 20 minutes with a data logger.

Results and Discussion

Within the test period of 150 days the soil columns were irrigated with a total amount of water of 7.403 L (mean value) corresponding to 212 mm. The irrigation rate throughout the study was 2 mm/day within a five day period. Regardless of the irrigation volume applied, between 82.41 % and 83.32 % of the original irrigation amount was sampled as leachate. The difference between the total applied amount of water and the amount measured as leachate can be explained by evaporative losses and by increasing saturation of the soil.

Bromide concentrations were measured three times per week in order to characterise the tracer breakthrough behaviour. The final measurement was carried out on Day 120, at which time the tracer concentration had reached values lower than the method LOQ. The maximum concentration observed for the bromide tracer in column 1 was Day 50. The maximum concentrations for the bromide tracer in columns 2 and 3 were observed on Day 43.

For column 1 the maximum M656PH023 concentration was determined on Day 50. The maximum M23 concentration for column 2 and 3 was determined on Day 41.
The maximum M656PH027 concentration was determined for column 1 on Day 71, for column 2 on Day 41 and for column 3 on Day 50.
The maximum concentrations of both metabolites are given in Table B.8.1.4-42.

Table B.8.1.4-42: Day of maximum concentration and maximum concentrations of M656PH023 and M656PH027

Metabolite	Column	Day of maximum concentration	Maximum concentration (µg/L)	Maximum of % applied
M656H023	1	50	169.3	0.63
	2	41	321.0	2.33
	3	41	363.0	3.19
M656H027	1	71	161.10	0.2
	2	41	219.0	1.59
	3	50	180.3	0.74

Conclusion

The study was not performed according to a guideline, it is not a data requirement and the results were not used for environmental or risk assessment of dimethenamid-P in its representative uses. Thus the study was not evaluated by the RMS in detail.
The used soil is a typical lysimeter soil and the soil columns were filled in a correct way with undisturbed soil. Thus, the study seems acceptable as additional information.
Three undisturbed soil columns with soil taken from Birkenheide were used for the determination of the breakthrough behaviour of the dimethenamid-P metabolites M656H023und M656H027. Each column was treated with 0.35 mg of M656H023 and M656H027, respectively. Also 500 mg of Bromide tracer were applied in order to characterise the leachate breakthrough behaviour. The irrigation rate was 2 mm/day within a five day period. The maximum bromide concentration for column 2 and 3 was determined on day 43 for column 1 the maximum tracer concentration was determined on day 50.
Concentrations of M656H023 and M656H027 were determined three times per week using LC-MS/MS. The maximum M656H023 concentration for column 1 was determined on day 50, for column 2 and 3 the maximum concentrations were determined on day 41. For M656H027 the maximum concentration was determined for column 1 on day 71, for column 2 on day 41 and for column 3 on day 50.

KCA7.1.4.2/8 – Schroeder, 2014 (new study)

Author:	Schroeder, T.
Title:	Estimation of sorption and degradation parameters of metabolite M23 and M27 of BAS 656 H from mini-lysimeter studies by inverse modeling
Date:	02/10/2014
Doc ID:	BASF DocID 2013/1348579
Guidelines:	None
GLP:	Yes. (certified by Landesamt fuer Umwelt, Wasserwirtschaft und Gewerbeaufsicht, Mainz, Germany)
Validity:	Acceptable as additional information

Aim of the study

Inverse modelling using the results of the experimental study Hein & Baudy (2013) was performed with the goal to obtain sorption and degradation parameters of the two investigated metabolites M656PH023 (M23 in this study) and M656PH027 (M27 in this study) from the breakthrough curves (BTCs) of the soil columns.

Material and Methods

In a first step, from the breaktrough curves of the inert tracer soil and transport specific parameters for each lysimeter were determined. Therefore, the inverse modelling tool PEST was used to fit the following parameters for the tracer BTC: the saturated water content (θ_{sat}), the saturated soil hydraulic conductivity (K_{sat}), the dispersion length (D) and the application rate of bromide.
These parameters are then used for evaluation of the BTCs of the metabolites, with the goal to obtain sorption and degradation parameters of the metabolites. From the BTCs of the test items the degradation rate in soil ($DegT_{50}$), the sorption coefficient of equilibrium sorption on organic matter (K_{om}) and the Freundlich coefficient (1/n) were derived.
Parameter estimation was acquired by the inverse modeling tool PEST 11.3 in combination with the transport model PEARL 4.4.4.
PEST calls PEARL with predefined initial conditions for the parameters to be fitted and changes these variables within a pre-defined range until an optimised parameter set is acquired, in comparison to the measured BTC values. PEST stops when no better parameter set can be found statistically.
The quality of the fit as well as the quality of the parameters was evaluated in accordance to the recommendations of the FOCUS kinetics workgroup.

To determine transport specific parameters for each lysimeter using the BTCs of the tracer, the general procedure was to first estimate all parameters of interest at once, thus all parameters were released, and free to be optimised. If it was not possible to acquire statistically sound parameters, certain parameters were fixed based on initially estimated or conservative parameters.
When evaluation the BTCs of the metabolites, in a first run, it was tested whether the resulting parameters would fall within the boundary limits and are statistically sound. If yes, a second run with the first-run-results as initial parameter settings were performed to check whether a proper solution without correlation of coefficients was achieved.

Results and Discussion

A visual assessment of the raw data of bromide over time showed that for all three columns three data points (DAT 43, DAT 50 and DAT 53) had larger discrepancies from the mean (optimal) curve. Therefore, these observations were weighted, with a lesser weight than the other data points (0.5 instead of 1). In a first attempt, all parameters were released. However, neither was the fit of the bromide BTC statistically accurate (too high coefficients of variation), nor resembled the estimated water content a sandy soil physically. The next step was then to fix one of the four parameters. It was chosen to fix θ_{sat} to its initial value, since this parameter has physically the least influence. A K_{sat} belonging to this fixed value can be found to describe the soil hydraulic properties properly.
The BTCs of the metabolites were analysed for all parameters without any weighting of the experimental data.

The fitted parameters for modelling using the BTCs of the inert bromide tracer with their statistics are given in Table B.8.1.4-43. The chi^2 errors for the fitted parameters were 16.86 %, 13.58 %, 11.08 % for column 1, 2 and 3, respectively. The t-test of D, Θ_{sat}, and K_{sat} was passed at the 0.05 level for all three columns.

Table B.8.1.4-43: Fitted parameters from bromide BTCs in column 1, 2 and 3

Mini lysimeter	**D [m]**		
	mean	**st. dev**	**CV [%]**
Column 1	0.011	<0.001	6.4
Column 2	0.020	0.001	5.4
Column 3	0.009	<0.001	4.2
	Θ_{sat} [m^3 m^{-3}]		
	mean	**st. dev**	**CV [%]**
Column 1	0.380*	-	-
Column 2	0.380*	-	-
Column 3	0.380*	-	-
	K_{sat} [m d^{-1}]		
	mean	**st. Dev**	**CV [%]**
Column 1	0.734	0.052	7.1
Column 2	1.31	0.125	9.5
Column 3	2.46	0.154	6.3
	Application rate [kg ha^{-1}]		
	mean	**st. dev**	**CV [%]**
Column 1	113.6	2.29	2.0
Column 2	117.4	2.187	1.9
Column 3	108.1	1.49	1.4

st. dev = standard deviation
CV = coefficient of variation (= st. dev / mean *100 %)
* Parameter fixed

Statistically reliable adsorption and degradation parameters of M656PH023 could only be obtained for column 2 in the second run with a chi^2 error of 18.66 %. The t-test for $DegT_{50}$, K_{om} and 1/n value was passed at the 0.05 level. The results are presented in Table B.8.1.4-44.

Table B.8.1.4-44: Fitted adsorption and degradation parameters of M656PH023 in column 2 – run 2

Mini lysimeter	$DegT_{50}$ [d]		
	mean	**st. dev**	**CV [%]**
Column 2	26.51	0.695	2.6
	K_{om} [L kg^{-1}]		
	mean	**st. dev**	**CV [%]**
Column 2	1.12	0.286	25.5
	1/n [-]		
	mean	**st. Dev**	**CV [%]**
Column 2	0.991	0.220	22.2

st. dev = standard deviation
CV = coefficient of variation (= st. dev / mean *100 %)

Statistically reliable adsorption and degradation parameters of M656PH027 could be obtained for all three columns in the second run with a chi^2 errors of 23.58 %, 13.10 % and 15.13 %, respectively. The t-test for $DegT_{50}$, K_{om} and 1/n value was passed at the 0.05 level for all three columns. The results are presented in Table B.8.1.4-45.

Table B.8.1.4-45: Fitted adsorption and degradation parameters of M656H027 in column 1, 2 and 3 – run 2

Mini lysimeter	$DegT_{50}$ [d]		
	mean	**st. dev**	**CV [%]**
Column 1	39.64	0.782	2.0
Column 2	36.46	0.862	2.4
Column 3	33.05	0.658	2.0
	K_{om} [L kg^{-1}]		
	mean	**st. dev**	**CV [%]**
Column 1	5.51	0.346	6.3
Column 2	3.40	0.090	2.7
Column 3	2.19	0.054	2.5
	1/n [-]		
	mean	**st. Dev**	**CV [%]**
Column 1	1.12	0.056	5.0
Column 2	0.877	0.027	3.1
Column 3	0.662	0.024	3.6

st. dev = standard deviation
CV = coefficient of variation (= st. dev / mean *100 %)

The final $DegT_{50}$, K_{om} and 1/n values of M656PH023 and M656PH027 are summarised in Table B.8.1.4-46, Table B.8.1.4-47 and Table B.8.1.4-48.

Table B.8.1.4-46: Summary of $DegT_{50}$ values for M656PH023 and M656PH027

Mini-lysimeter study	$DegT_{50}$ [d]	
	M656PH023	**M656PH027**
Column 1	-	39.64
Column 2	26.51	36.46
Column 3	-	33.05
Geometric mean	**26.51**	**36.28**

Table B.8.1.4-47: Summary of K_{om} values for M656PH023 and M656PH027

Mini-lysimeter study	K_{om} [L kg^{-1}]	
	M656PH023	**M656PH027**
Column 1	-	5.51
Column 2	1.12	3.40
Column 3	-	2.19
Arithmetic mean	**1.12**	**3.70**

Table B.8.1.4-48: Summary of 1/n values for M656PH023 and M656PH027

Mini-lysimeter study	Freundlich exponent (1/n) [-]	
	M656PH023	**M656PH027**
Column 1	-	1.12
Column 2	0.991	0.877
Column 3	-	0.662
Arithmetic mean	**0.991**	**0.887**

Conclusion

The study was not performed according to a guideline, it is not a data requirement and the results were not used for environmental or risk assessment of dimethenamid-P in its representative uses. Thus the study was not evaluated by the RMS in detail.

It was noted by the RMS that the application rate obtained by inverse modelling of the inert tracer with 112.75 kg/ha (arithmetic mean) is lower than the applied 143 g/ha BR^- (500 mg Br^{--} on a surface area of 0.035 m^2). However, since the soil parameters mainly affect by the steepness of the bromide BTC, which was fitted properly with the model, the soil parametes are likely to be modelled correctly.

The obtained degradation parameters of M656PH023 and M656PH027, however, are in the range of the DT_{50} values obtained in the laboratory studies with dimethenamid-P according to OECD 306 (see B.8.1.1 of this document). In the aerobic soil degradation studies, M656PH023 degraded with normalised DT_{50} values in the range of 15.0 – 63.94 d with a geometric mean of 35.4 d. In the aerobic soil degradation studies, M656PH023 degraded with normalised DT_{50} values in the range of 20.6 – 149.5 d with a geometric mean of 60.2 d.

The adsorption values obtained for M656PH027 also agree very well with the adsorption values derived in the adsorption and desorption studies according to OECD 106 (see B.8.1.3 of this document). The arithmetic mean of the K_{foc} values of the OECD 106 studies is with 7.0 always the same as the K_{oc} value 6.38 obtained when multiplying the here derived K_{om} with 1.724. The arithmetic mean of the Freundlich exponents of the OECD 106 studies is with 0.979 slightly higher than the here obtained value.

The adsorption values obtained for M656PH023 do not agree well with the adsorption parameters obtained in the adsorption and desorption studies according to OECD 106. The arithmetic mean of the K_{foc} values of the OECD 106 studies is with 12.0 considerably higher than the K_{oc} value 1.93 obtained when multiplying the here derived K_{om} with 1.724. The arithmetic mean of the Freundlich exponents of the OECD 106 studies is with 0.722 smaller and thus also less conservative than the here obtained value.

The study is considered acceptable as additional information; however the degradation and adsorption studies performed according to OECD 306 and 106 are considered more acceptable and will be used for environmental fate assessment of dimethenamid-P instead.

B.8.1.4.3 Field leaching studies

KCA 7.1.4.3/1 – Gasser, 1998a (study evaluated in the monograph, 2000)

Author:	Gasser, A.
Title:	Mobility and dissipation of residues of dimethenamid under field conditions following application of frontier to corn in Switzerland, 1994 - 1997
Date:	25/03/1998
Doc ID:	BASF RegDoc.# 98/10384
Guidelines:	None
GLP:	Yes
Validity:	Acceptable as additional information

Material and Methods

A soil dissipation and mobility study of dimethenamid in the field was conducted over a period of three years (1994-1997) in north-west Switzerland (Lindenacker) on a site representative for corn production and under typical soil and climatic conditions. The soil charactersistcs of the test site are presented in Table B.8.1.4-49.

Table B.8.1.4-49: Soil characteristic of the sandy loam at test site (upper 90 cm)

Layer in cm	0 - 30	30 - 60	60 - 90
Sand (%)	60.9	61.7	67.4
Silt (%)	25.7	25.6	22.2
Clay (%)	13.4	12.7	10.4
Organic carbon (%)	1.1	0.8	0.4
$CaCO_3$ (%)	12.0	13.3	18.5
pH (H_2O)	7.75	7.80	8.05
pH ($CaCl_2$)	7.35	7.35	7.50
Cation exchange capacity (meq/100g)	10.6	9.9	7.0

The test plot was divided into two subplots (T1 and T2, 200 m² each) and cropped with corn throughout the entire study period. On May 21, 1994 and May 23, 1995 each subplot was treated once with 1.6 L/ha of FRONTIER, equivalent to 1440 g/ha dimethenamid per hectare per year.
Subplot T1 was used for pore water collection. Water samples were taken from suction cups installed at two different soil depths of 1.0-1.2 m and 2.6-3.0 m; samples were taken 5 days before and 17 days after the first application and then at monthly intervals up to 36 months following the first application in 1994. Soil samples were collected from subplot T2 at 0, 3, 6, 13, 30, 65, 147, 180, 243, 305 and 359 days after the first application. Samples were also taken 0, 3, 7, 16, 29, 62, 121, 184, 245, 308, and 365 days after the second application in 1995. Sampling was continued every 2 months up to 24 months after the second application. Each soil core consisted of three segments corresponding to a depth of 0-30 cm, 30-60 cm and 60-90 cm. Prior to analysis, the soil cores were separated into segments representing the 0-10 cm, 10-30 cm, 30-50 cm, 50-70 cm and 70-90 cm layers.

The residues of dimethenamid and its major metabolites M656H023 (M23 or Oxalamide in this study) and M656H027 (M27 or Sulfonate in this study) in soil were determined by HPLC/DAD after extraction with methanol/water (6:4 v/v) and SPE clean-up. The limit of quantification of the analytical method was 0.01 mg/kg. Average recoveries in fortified control soil samples (0.01 – 1.15 mg/kg) were 91.9 %, 99.5 % and 92.8 % for dimethenamid, M656H023 and M656H027, respectively.
The residues of dimethenamid (parent only) in pore water were determined by GC/MS after solid phase extraction. The limit of quantification of the analytical method was 0.1 µg/L. Average recovery of dimethenamid in fortified control water samples (0.1 – 1.0 was 77.5 %, The analytical methods used in this study allow the determination of dimethenamid, M656H023 and M656H027 in soil samples or dimethenamid in water samples with the accuracy, reproducibility and selectivity required.

Results and Discussion

The verification of the test substance just after its application to the soil represented 93.8 % (1994) and 92.7 % (1995) of the theoretical value expected and confirmed the correctness of the application, sampling and sample preparation methodology.
The average temperature and precipitation recordings from the weather station Basel/Binningen (approx 40 km from the test site) are presented in Table B.8.1.4-50.

Table B.8.1.4-50: Weather recordings of weather station Basel/Binningen (approx 40 km from the test site)

Period	Average Temperature (°C)	Total Precipitation (mm)
1st of May to 31st of Dec 1994 (Trial period 1994)	14.1	767
Year 1995	10.5	1381
Year 1996	9.4	1052.8
1st of Jan to 30th of April 1997 (Trial period 1997)	5.8	302

No dimethenamid residues above 0.1 µg/L were detectable in any of the pore water samples collected from the suction cups installed at a depth of 1.0-1.2 m or 2.6-3.0 m and taken at monthly intervals up to 36 months after the first application in 1994.
The soil residues of dimethenamid and its metabolites M656H023 and M656H027 are presented in Table B.8.1.4-51.

Table B.8.1.4-51: Residues of dimethenamid and its metabolites M656H023 and M656H027 in soil at testplot T2

Testplot T2			
Year 1994 - 1995			
DAT	dimethenamid	M656H023	M656H027
0	0.9	< 0.01	< 0.01
3	0.44	0.01	0.02
6	0.39	0.02	0.03
13	0.22	0.02	0.04
30	0.07	0.02	0.05
65	0.03	0.03	< 0.01
147	< 0.01	< 0.01	< 0.01
180	< 0.01	< 0.01	< 0.01
243	< 0.01	< 0.01	< 0.01
305	< 0.01	< 0.01	< 0.01
359	< 0.01	< 0.01	< 0.01
Year 1995 - 1996			
DAT	dimethenamid	M656H023	M656H027
0	0.89	0.01	< 0.01
3	0.64	0.01	0.01
7	0.66	< 0.01	0.02
16	0.18	0.02	0.05
29	0.04	0.02	0.03
62	< 0.01	< 0.01	< 0.01
121	< 0.01	< 0.01	< 0.01
184	< 0.01	< 0.01	< 0.01
245	< 0.01	< 0.01	< 0.01
308	< 0.01	< 0.01	< 0.01
365	< 0.01	< 0.01	< 0.01
428	< 0.01	< 0.01	< 0.01

The concentrations of dimethenamid found in the soil samples decreased from a maximum concentration of 0.90 mg/kg just after the application to < 0.01 mg/kg five months after the application in 1994. In 1995, the maximum concentration was 0.89 mg/kg and decreased to < 0.01 mg/kg two

months after the application.
Residues of metabolites M656H023 and M656H027 were very low and found mainly in the upper 10 cm of the soil horizons between 3 days and 65 days after the 1994 application (concentration range from 0.01 mg/kg to 0.05 mg/kg), and between 0 and 29 days after the 1995 application (concentration range from 0.01 mg/kg to 0.05 mg/kg).

Conclusion

The study was accepted as additional information for the first EU approval of dimethenamid-P. After re-evaluation the RMS considers the study still acceptable as additional information although the clay and silt content of the upper soil horizon does not represent worst case conditions for leaching (more than 10 % clay, more than 30 % clay + silt). Besides information regarding the representativeness of the site conditions for European agricultural conditions are not available.
However, the changes of the soil residues with time found in this study broadly agree with the finding of the field dissipation studies with dimethenamid summarised under B.8.1.2.6 of this document. Besides, the results of the pore water analysis agree with the results of the lysimeter Burgener (1996), where dimethenamid was also not detected in the leachate.

KCA 7.1.4.3/2 – Gasser, 1998b (study evaluated in monograph, 2000)

Author:	Gasser, A.
Title:	Determination of residues of dimethenamid in corn cropped field soil treated with frontiere, in groundwater withdrawn from piezometers and from a well, Arc et Senans, Cramans, Villers Farlay, experimental area of Bel Air, France, 1996
Date:	17/03/1998
Doc ID:	BASF RegDoc.# 98/10385
Guidelines:	None
GLP:	Yes
Validity:	Not acceptable

Material and Methods

Analyses of soil and groundwater samples for dimethenamid were conducted in France during season 1996 at the test site of Bel Air, Arc et Sénans, Villers Farlay. FRONTIER was applied once at the recommended use rate of 1.4 to 1.6 L/ha corresponding to 1260 to 1440 g/ha of dimethenamid on 6 different corn cropped plots from the test site. A pre-emergent application (April 1996) was performed as per label recommendation and according to local good agricultural practices.
Treated soil was sampled directly after application and at about 14, 30, 60 and 90 days after the application on two of the plots down to a depth of 50 cm. Treated soil was additionally sampled 19 days after the application on one of these 2 plots. Groundwater was collected at 5 sampling points (4 piezometers and one well) in the test site and at 8 sampling dates from April to October. All soil and water samples were analysed for dimethenamid by GC/MS. The limit of quantitation was 0.05 µg/L for water and 0.01 mg/kg for soil samples. Average recoveries in fortified control samples were 99.5 % and 84.3 % for soil (0.013 – 1.26 mg/kg) and water (0.05 – 0.5 µg/L), respectively.

Results and Discussion

No dimethenamid residues were detectable in any of the groundwater samples taken between April and October 1996.
The concentration of dimethenamid found in the soil samples are presented in Table B.8.1.4-52.

Table B.8.1.4-52: Dimethenamid- residues in soil at site 1 & 2

Site 1		Site 2	
DAT	**dimethenamid**	**DAT**	**dimethenamid**
1	0.67	2	0.68
14	0.35	15	0.30
19	0.35	30	0.11
34	0.16	56	<0.01
60	0.01	85	<0.01
89	<0.01		

Dimethenamid decreased from a maximum concentration of 0.67 mg/kg just after the application to < 0.01 mg/kg three months after the application on the first test plot (site 1). On site 2, the concentration of dimethenamid found in the soil decreased from a maximum concentration of 0.68 mg/kg just after the application to < 0.01 mg/kg three months after the application.

Conclusion

The study was accepted as additional information for the first EU approval of dimethenamid-P. However, after re-evaluation the RMS does not consider the study acceptable anymore.
Mainly, the documentation of the study conditions are very poor: no information is given on plot size or soil characteristic, it is not clear if the sampled groundwater wells and perimeters are upstream or downstream of treated sites and no weather data like precipitation are provided. Thus, the results of the study are of limited use.

B.8.1.4.4 Other studies on mobility in soil

No study on the plant uptake factor (PUF) of dimethenamid-P was performed, however a default PUF of 0.5 was assumed in the environmental fate modelling of dimethenamid-P in the representative uses. Thus, RMS requested a statement from the applicant, why a default PUF is justified. The submitted statement is summarised below.

KCA 7.1.4/1 – Schroeder & McCall, 2014 (new study)

Author: Schroeder, T.
McCall, W.
Title: Statement on the use of a default PUF of 0.5 for dimethenamid-P
Date: 14/11/2014
Doc ID: BASF DocID 2014/1293203
Guidelines: Non-Guideline
GLP: Yes
Validity: Not acceptable

Content of the statement

According to the EFSA Scientific Opinion (EFSA Journal 2013; 11(6): 3291) on the report of the FOCUS groundwater working group (FOCUS,2009), the argument of directly applying a default value of 0.5 to compounds such as dimethenamid-P (a systemic herbicide) is no longer valid. However, subsequently in the EFSA opinion it is stated that, "As a second step, the Briggs formula is recommended, i.e. estimating the uptake factor using the K_{ow}…" to determine the plant uptake factor (PUF).

Therefore, the appropriate procedure for a tiered approach for dimethenamid-P would be:

Tier 1: plant uptake factor of 0 (regardless of systemicity)
Tier 2a: plant uptake factor using K_{ow} (Briggs *et al.*1982)

The Briggs equation gives:

$$TSCF = 0.78 \exp^{-(\log (k_{ow})-1.78)2/2.44}$$

where TSCF (equivalent to the PUF) is the plant uptake factor and K_{ow} is the octanol-water partitioning coefficient.
Using the log (K_{ow}) of 1.89 of dimethenamid-P, a plant uptake factor of 0.78 is obtained, indicating that indeed dimethenamid-P is subject to uptake by plant roots. According to the EFSA opinion (2013), the relation found by Briggs also indicates that substances with intermediate log(K_{ow}) (*around 2*) have *highest* plant uptake and that substances with lower or higher K_{ow} are taken up less."

Thus, a default PUF of 0.5 deemed valid for dimethenamid-P.

Conclusion

The applicant argued with the Brigg's equation to justify a default PUF of 0.5 on dimethenamid-P. However, the RMS expressed doubt on the universal use of the Briggs equation for all crops in its comments from August 2014 on the updated FOCUS groundwater report (2009, updated by EFSA in May 2014, version 2, Sanco/13144/2010):
'The Briggs equation to derive uptake factors was not considered as state-of-the-art to predict PUF values: As discussed also at the EU PUF workshop (2nd September 2013 in York) the study of Briggs on TSCF values in barley is not up-to-date and is applicable to non-ionic substances applied in barley, only. The Briggs equation may not be applicable for all substances, crop combinations or experimental conditions as documented in several studies due to the high variability of uptake factors found for substances having a similar logKow in different crops. This indicates that the uptake factor is not only characteristic for a substance (logKow, pKa) but also depends on the experimental conditions (duration of exposure, temperature, pH of the pore water and nutrient solution in the experiment, respectively) and the crop (content of lipid, fiber, and carbohydrate of roots and shoots; root system).'

The RMS searched for additional evidence on the plant uptake of dimethenamid-P: In Volume 3, B.7 (residues) of this document, several studies on the magnitude of residues in plants are summarised. In the studies *Meyer, 2014a, BASF Doc ID 2013/1335420, Gabriel & Meyer, 2013a, BASF Doc ID 2012/1272621, Perny, 2013b, BASF Doc ID* 2012/1209625, *Erdmann, 2013d, BASF Doc ID* 2013/1003729 and *Perny, 2012a, BASF Doc ID* 2013/1003729, residues of dimethenamid-P were measured in the whole crop plants without roots of oilseed rape, maize and sugar beet. Residues were measured after one application of 500 – 1008 g/ha dimethenamid-P (equivalent to 0.67 – 1.34 mg/kg dimethenamid-P in soil when assuming a distribution over 5 cm depth and a soil density of 1.5 g/m^3) to the different crops starting with the day of application. On day 0 after application, dimethenamid-P was found in all crops in considerable amounts. These results of the studies are considered relevant to assess the plant uptake of dimethenamid-P are summarised in Table B.8.1.4-53.

Table B.8.1.4-53: Residues in oilseed rape, maize and sugar beet plants immediately after treatment with dimethenamid-P

Reference	crop	Application rate (g DMTA-P[1] /ha)	Matrix	Dimethenamid-P residues on day 0 after application (mg/kg)
Meyer, 2014a, BASF Doc ID 2013/1335420	Oilseed rape (EU North)	500	Whole plant without roots	4.84 - 15.25
	Oilseed rape (EU South)			0.36 – 37.16
Gabriel & Meyer, 2013a, BASF Doc ID 2012/1272621	Maize (EU North)	864	Whole plant without roots	21 - 77
	Maize (EU South)			8.8 - 48
Perny, 2013b, BASF Doc ID 2012/1209625	Maize (EU North)	1008	Whole plant without roots	34.4 – 64.4
	Maize (EU South)			8.72 – 21.90
	Maize (EU North)	864	Whole plant without roots	15.20 – 50.00
	Maize (EU South)			5.00 – 19.80
Erdmann, 2013d, BASF Doc ID 2013/1003729	Maize (EU North)	650	Whole plant without roots	22 - 41
	Maize (EU South)			22 - 33
Perny, 2012a, BASF Doc ID 2013/1182982	Maize (EU North)	650	Whole plant without roots	0.71 – 29.32
	Maize (EU South)			25.20 – 30.52

1 DMTA-P: dimethenamid-P

The results of these residue studies show that dimethenamid-P is taken up both by monocotyledonous and by dicotyledonous crops in considerable amounts. However, the dimethenamid-P formulation were applied to the plants itself in all studies and not the soil, thus it is not possible to distinguish between dimethenamid-P absorbed to the plant surfaces and dimethenamid-P taken up via the root systems.
In the light of all available information on the systemic herbicide dimethenamid-P, the RMS believes, that the use of a default PUF of 0.5 appears justified although the available evidence is very poor and does not allow a sufficient justification. The RMS suggests, that the issue will be discussed during the peer review of dimethenamid-P.

KCA 7.1.4/2 – Gourlay, 2013 (new study)

Author: Gourlay, V.
Title: Plant uptake of dimethenamid-P metabolite M656PH027 (Reg.No. 360714) in corn and oil seed rape under greenhouse conditions
Date: 15/10/2013
Doc ID: BASF DocID 2013/1251908
Guidelines: Non-Guideline
GLP: Yes
Validity: Not acceptable

Material and Methods

The purpose of this study was to determine the plant uptake factor (PUF) of soil metabolite M656PH027 of the herbicidal active substance dimethenamid-P for use in the parameterisation of leaching models.

As test substance, [thienyl-5-^{14}C] M650PH027 (99 % purity, 8.21 MBq/mg) was used.
For the test, corn "*Ronaldinio*" and oil seed rape "*Primavera*" plants were cultivated under greenhouse conditions for seven weeks. The daily cultivation conditions in the greenhouse were set up to achieve a mean daily temperature of 22 °C (recorded hourly in addition to the air humidity with a Tinytag temperature/humidity logger), with a light regime corresponding to 16 h light / 8 h dark (recorded with a Hobo® light logger [λ = 400–700 nm]). Additional artificial light was supplied when natural daylight was less than 5 klux (sodium light SON-T Agro 400W). Pots (ø = 13 cm) with removed bottoms, placed on trivets and filled with very silty sand were used to avoid root damage during the later withdrawal. For each plant, eight seeds per pot were sown between 0.5 and 1 cm depth into the soil.
The plant development stages of each test plant, on application, are given in Table B.8.1.4-54.

Prior to placing the plants into the test and control plants vessels, the loamy sand was completely removed by gently showering the roots with water. The plants were kept for about one hour in a non-buffered $CaCl_2$ solution without test item, before inserting them into the corresponding test and plant control solutions, in order to let them slowly adapt to the change of root medium. The number of plants per vessel was chosen in order to have similar fresh biomasses. The exact biomasses were determined gravimetrically by weighting the test systems before and after inserting the plants.

Table B.8.1.4-54: Deverloment stage and fresh biomass of test plants before application of M656PH027

Crop	BBCH	Fresh biomass [g]
Corn	32	179 – 204
Oilseed rape	32	55 – 85

To investigate the influence of the pH of the test solution on plant uptake, three different pH levels were tested (pH 5.5, 6.5 and 7.5). In order to keep the pH the solutions were buffered (0.01 M $CaCl_2$ solution with 0.01 M MES[2] buffer adjusted to target pH using 1 M NaOH for pH 5.5 and 6.5 and 0.01 M $CaCl_2$ solution with 0.01 M tris HCL[3] buffer adjusted to target pH using 1 M NaOH for pH 7.5).

The test system consisted of a 1 L brown glass test vessel filled with 1000 mL of 0.01 M $CaCl_2$ buffered solution. Brown glass was used in order to avoid algae growth and to exclude photolytic transformation processes. The diameter of the opening at the top of the glass vessel was sufficient to insert the plant roots without damage. Furthermore, the shape of the vessel ensured that during the experimental period the roots were freely suspended in the $CaCl_2$ solutions to enable continuous root exposure to the test solution.

The opening around the plant stems was covered with Parafilm® in order to prevent photolytic degradation, evaporation and algae growth. The whole setup was placed in a greenhouse at similar temperature and air humidity conditions used for the growth period in order to avoid stress for the test plants.

For application, the test vessels were filled with 500 mL of buffered solution and the test item was applied by pipetting 324.5 µL (80 µg) of the application solution into each test solution. The test vessels were then filled up to 1000 mL with buffered solution. The test solutions in the vessels were then magnetically stirred for two minutes after application. An additional 81.1 µL (20 µg) of the application solution was applied to each vessels and the test solution were magnetically stirred for another two minutes. The application was performed in two stages due to a protocol error. From each flask, duplicate 250 µL aliquots were taken and the concentration of the test substance was determined by LSC. The mean concentrations over all applied vessels were found to be 100.5 µg L^{-1}.

For each crop and pH level an *untreated plant control* (three replicates) was prepared in order to monitor the influence of the test item on the volume uptake of solution and on the variation in biomass

during the test period. The vessels were filled with 1000 mL of the corresponding buffered 0.01 M $CaCl_2$ solution and plants were inserted in such numbers that each vessel contained an almost equal amount of fresh plant biomass.

A *stability control* without plants was prepared for each pH level in order to monitor the stability of the test item under actual test conditions (one replicate). For this a vessel was filled with 1000 mL of buffered solution and treated with the test item. The vessel was sealed with Parafilm®, following the same application procedure as described above.
An *evaporation control* was prepared for each pH level in order to monitor the loss of water by direct evaporation in the absence of plants (one replicate). For this a vessel was filled with 1000 mL buffered solution and sealed with Parafilm® containing a hole about the same size as the one in the test vessels with plants.
An overview of the whole testing scheme is given in Table B.8.1.4-55.

Table B.8.1.4-55: Overview of the testing scheme for corn and oil seed rape

	pH 5.5			pH 6.5			pH 7.5			Sum of test vessels
	NP	C	OSR	NP	C	OSR	NP	C	OSR	
with test item										
Test solutions (^{14}C)	-	3	3	-	3	3	-	3	3	21
Stability controls (^{14}C)	1	-	-	1	-	-	1	-	-	
without test item										
Untreated plant controls	-	3	3	-	3	3	-	3	3	21
Evaporation controls	1	-	-	1	-	-	1	-	-	
Sum of test vessels	14			14			14			42

NP: no plants, C: Corn, OSR: Oilseed rape

The test was conducted under greenhouse conditions for eight days. The same greenhouse conditions as used for cultivation of the plants were applied.
Two intermediate samplings of the test solutions were performed after two and five days. The remaining volumes of the solutions were determined by weighting the test system and subtracting the masses of the test vessel, the initial fresh biomass of the plants and the Parafilm® cover. It was assumed that the mass density of the $CaCl_2$ solution was equivalent to water (ρ = 1000 g L^{-1}) and that the fresh biomass of the plant remained constant over time. From each test solution two 250 µL aliquots were measured by LSC to determine the concentration of the test item in solution.

After eight days, at the end of the incubation period, the plants were carefully removed from the test vessels. The test solution that retained on the root system was collected by placing the roots in a funnel and letting the excess solution drip into the corresponding test vessel for about ten minutes. Subsequently, the roots were carefully dried with tissue paper.

In order to quantify the amount of test item adsorbed on the root system the roots were shaken in 250 mL of water/acetonitrile (1:1, v/v) solution for three minutes. The washing solution was then filtrated and two 5 mL aliquots were analysed by LSC to determine the amount of radioactivity.

The remaining test solutions were transferred into tarred polyethylene flasks and weighted. Two 250 µL aliquots were measured for radioactivity by LSC to determine the concentration of the test item. For each pH level, a 2 mL aliquot was taken from one plant replicate and from the stability control to determine the radiochemical purity of the test item by means of radio-HPLC.

The plant material was fractionated into root and stem/leaves system. Fresh weights were determined for each fraction and the separated roots and stem/leaves were freeze dried. The plant materials were then homogenised using a ball mill and aliquots of the powders were combusted in a sample oxidiser

and analysed for radioactivity via LSC.

A radioactive mass balance was compiled taking into account the test solution, the root washing solution and the plant material. As all recoveries were found to be > 90 %, no further analysis of the tissue paper or the filter was pursued.

During the test phase the pH level, redox potential and oxygen saturation of the non-treated $CaCl_2$ solutions were determined every day during the week. Throughout the experimental period, the plant development stage, plant health and the condition of the root system were documented by photos, including the control plants.

PUF values were calculated for each test vessel according to Equation B.8.1.4-1. A statistical evaluation was performed on the PUF values and volume uptake values in order to investigate potential influences of the test item and pH levels. All statistical tests were obtained by using R statistical system and Excel® functions.

Equation B.8.1.4-1: Calculation of the plant uptake factor of M650PH027

$$PUF = \frac{\ln\left(\frac{m_{solution-8}}{m_{solution-0}}\right)}{\ln\left(\frac{V_{solution-8}}{V_{solution-0}}\right)} \text{ [-]}$$

With

PUF	plant uptake factor	[-]
$m_{solution-8}$	mass of test item remaining in test solution after eight days	[µg]
$V_{solution-8}$	remaining volume of test solution after eight days	[L]
$m_{solution-0}$	initial mass of test item	[µg]
$V_{solution-0}$	initial volume of test solution	[L]

Results and Discussion

Characterisation of the test system and test conditions

The daily cultivation conditions in the greenhouse during the eight days of incubation are given in Table B.8.1.4-56.

Table B.8.1.4-56: Test chamber conditions

Parameter	Mean	Min	Max
Temperature	20.8 °C	15.8 °C	32.3 °C
Air humidity	59 %	27 %	86 %
Luminance intensity (6:00 am – 9:00 pm)	16.0 klux h-1	13.7 klux h-1	20.6 klux h-1

The fresh biomass of the test plants was determined at the start and at the end of the test period. The fresh biomass was 56.8 % to 84.3 % of the initial biomass for all crop types and treatments. No substantial differences were observed between treated and control test systems.
Independent of crop type, plant tissue of older leaves partly turned yellow by the end of the test period, presumably due to senescence processes and allocation of plant nutrients towards younger plant tissues. The observed decrease in total fresh biomass may have been induced by plant stress due to the transfer of the plants from soil to pseudo-hydroponic nutrient-free medium and the resulting

differences in the physical and nutritional environment of the root system. Further, as test vessels were sealed with Parafilm® and the solutions were not continuously aerated, the root system may have been affected by a lack of oxygen towards the end of the test period. Nevertheless, all test plants showed sufficient water uptake during the eight days.

For the determination of a reliable PUF, a substantial uptake of water is required to ensure that differences in the test concentrations in the solution remaining in the vessel can be determined with accuracy (ideally volume uptake > 15 % of the initial volume). Data for the cumulative volume uptake for each crop and pH level show a volume uptake from 149–315 mL for all treated plants over the eight day period. Thus, the requirement of a minimum volume uptake to obtain a sufficient precision in the calculation of the PUF was met. For all experiments the plants continued to consume water until the last sampling day.

An analysis of variance was performed over crop type, pH levels and treatment (treated or control solution). No significant differences in the volume uptake were observed between pH levels. No significant differences were observed between the volume uptake of treated and control test systems, indicating that there is no effect of the test items on the volume uptake. A significantly higher uptake of water per initial fresh biomass was observed for oil seed rape compared to corn which presumably resulted from the natural variation in water needs of the different crops and growth stages.

In order to ensure that the volume loss in the different vessels was only a result of the plant transpiration, the volume of the evaporation control solutions without plants was recorded over time. For all control solutions, the water loss by direct evaporation was ≤ 1.1 %, indicating that the variation in volume observed with plants can be attributed primarily to water consumption by the respective plants.

The pH levels of the buffered solutions with plants were steady over time. For the incubations with corn, the pH 7.5 level decreased slightly. Nevertheless, the mean pH over eight days was close to pH 7. The pH level of the evaporation controls, without plants, showed low variation over the eight days.
The internal temperature of the solutions was determined and ranged between 22.6 °C and 24.0 °C.
The hydroponic-like test system used in this study may lead to oxygen deficiencies in the root system. However, aeration of the test solutions could not be carried out since this would have caused substantial evaporation losses that would conflict with the determination of the uptake volume. Air exchange of the test solutions was moreover limited due to the Parafilm® cover. Despite lower oxygen levels in the root zone sufficient water uptake was confirmed, indicating adequate plant health during the experimental period.

The redox potential of a given soil or sediment is a measure of its anaerobiosis. Aerated soils have redox potentials in the range of +400 to +700 mV and anaerobic conditions display redox potentials from +400 to as low as -300 mV (Pt electrode). Independent of crop type and pH level, measured redox potentials during the experiment were always < 250 mV indicating anaerobic conditions in the root zone of the test plants. Analogous to the low oxygen content of the solutions the anaerobic conditions did not limit sufficient water uptake indicating adequate plant health.

Characterisation of plant uptake behaviour

A radioactive mass balance was established at the end of the study. After eight days the sum of all processed fractions and solutions yielded in recoveries between 93.4 % and 98.7 % of applied radioactivity for both crops. A large proportion of the radioactivity was detected in the test solution and the plant parts. No substantial losses were observed during the experiment (volatilisation, glass adsorption) or during the analysis of the plant material (homogenisation, combustion).

With an initial purity of the application solution of 100 %, the purity of the test item in solution after eight days remained at 100 % in the stability control solutions without plants as well as in the test solutions with plants. This confirmed that the test item was stable in the test solutions over time and that the radioactivity measured in the solutions and taken up by the plants corresponded exclusively to

the test item.

The radioactivity in solution was measured in the stability controls without plants in order to ensure that there was no loss of test item by glass adsorption or volatilisation and that the variation was only due to plant uptake and/or root adsorption. The variations observed after eight days for all pH levels indicate that possible losses from glass adsorption or from volatilisation were negligible.

The concentrations of the metabolite M656PH027 in the test solutions are provided for both crops in Table B.8.1.4-57 and Table B.8.1.4-58. The changes in water volume in the test solutions are provided for both crops in Table B.8.1.4-59 and Table B.8.1.4-60. The mass of test item can be derived from the concentration in conjunction with the volume of water.

Table B.8.1.4-57: Concentration of M656PH027 in the test solution over eight days (corn)

pH	Replicate	Concentration in solution [µg L-1]			
		Day 0	Day 2	Day 5	Day 8
5.5	a	100.2	95.0	96.9	101.3
	b	101.2	97.6	97.9	100.8
	c	101.3	97.4	100.2	107.4
	Mean	100.9	96.7	98.3	103.2
	CV	*0.6 %*	*1.5 %*	*1.7 %*	*3.6 %*
6.5	a	100.9	97.3	99.5	106.6
	b	100.6	96.3	95.9	103.1
	c	101.5	97.1	96.0	106.0
	Mean	101.0	96.9	97.1	105.2
	CV	*0.5 %*	*0.5 %*	*2.1 %*	*1.8 %*
7.5	a	101.3	97.1	99.9	108.9
	b	100.7	96.8	98.2	107.2
	c	100.4	97.4	99.7	108.1
	Mean	100.8	97.1	99.3	108.1
	CV	*0.5 %*	*0.3 %*	*0.9 %*	*0.8 %*

Table B.8.1.4-58: Concentration of M656PH027 in the test solution over eight days (oil seed rape)

pH	Replicate	Concentration in solution [µg L-1]			
		Day 0	Day 2	Day 5	Day 8
5.5	a	100.6	98.1	100.5	98.8
	b	97.4	97.7	100.4	99.4
	c	100.7	98.3	99.5	97.8
	Mean	99.6	98.0	100.1	98.7
	CV	*1.9 %*	*0.3 %*	*0.6 %*	*0.8 %*
6.5	a	101.1	100.6	101.1	98.7
	b	100.7	100.1	101.8	100.5
	c	101.0	100.3	99.0	97.8
	Mean	100.9	100.3	100.6	99.0
	CV	*0.2 %*	*0.3 %*	*1.4 %*	*1.4 %*
7.5	a	100.2	99.5	100.2	100.3
	b	101.6	100.8	102.1	101.2
	c	101.0	99.8	101.2	99.8
	Mean	100.9	100.0	101.2	100.4
	CV	*0.7 %*	*0.7 %*	*0.9 %*	*0.7 %*

Table B.8.1.4-59: Change of volume of test solutions over eight days (corn)

pH	Replicate	Volume of test solution [mL]			
		Day 0	Day 2	Day 5	Day 8
5.5	a	999.4	866.1	776.3	737.4
	b	998.7	864.4	775.4	728.9
	c	999.0	884.8	813.8	738.1
	Mean	999.0	871.8	788.5	734.8
	CV	*0.0 %*	*1.3 %*	*2.8 %*	*0.7 %*
6.5	a	999.2	856.6	758.5	688.1
	b	998.4	868.2	790.3	734.7
	c	998.7	846.3	750.6	690.8
	Mean	998.8	857.0	766.5	704.5
	CV	*0.0 %*	*1.3 %*	*2.7 %*	*3.7 %*
7.5	a	998.8	863.2	782.9	700.5
	b	1002.0	836.8	745.7	671.4
	c	999.7	861.4	764.7	677.6
	Mean	1000.2	853.8	764.4	683.1
	CV	*0.2 %*	*1.7 %*	*2.4 %*	*2.2 %*

Table B.8.1.4-60: Change of volume of test solutions over eight days (oilseed rape)

pH	Replicate	Volume of test solution [mL]			
		Day 0	Day 2	Day 5	Day 8
5.5	a	1002.6	912.3	837.0	820.8
	b	999.8	866.3	797.2	790.6
	c	999.2	897.9	824.7	817.4
	Mean	1000.5	892.2	819.6	809.6
	CV	*0.2 %*	*2.6 %*	*2.5 %*	*2.0 %*
6.5	a	998.7	913.4	867.5	852.5
	b	998.8	902.9	847.0	811.0
	c	998.9	930.0	892.5	879.1
	Mean	998.8	915.4	869.0	847.6
	CV	*0.0 %*	*1.5 %*	*2.6 %*	*4.0 %*
7.5	a	999.7	887.0	814.1	774.8
	b	999.1	902.3	824.0	776.3
	c	998.9	876.5	804.3	774.3
	Mean	999.2	888.6	814.1	775.1
	CV	*0.0 %*	*1.5 %*	*1.2 %*	*0.1 %*

The derived PUF values are presented in Table B.8.1.4-61. Over all pH levels, the mean PUF values for oil seed rape ranged from 0.99 to 1.01, and from 0.72 to 0.81 for corn.

Table B.8.1.4-61: Average plant uptake factors after eight days

pH	Corn		Oilseed rape	
	PUF	CV	PUF	CV
5.5	0.81	13.7 %	1.00	12.1 %
6.5	0.77	0.7 %	1.09	9.0 %
7.5	0.72	5.3 %	0.99	3.0 %

The possible impact of test parameters such as crop type and pH level was statistically evaluated. There was no significant effect of the pH level on the plant uptake factor values, but there was a significant difference between crop types.

Conclusion

There is no guideline for plant uptake determination of plants available. However, after evaluation of the study the RMS found several shortcomings listed below and thus considers the study as not acceptable and the use of a default plant uptake factor of 0 is proposed by the RMS.
Growth of the plants and actual incubation were performed in different media. For incubation, the plants were removed from soil, washed and placed into the buffered solution, damage of the root hairs cannot be ruled out after such a procedure. While the roots were washed with 1:1 water/acetonitrile solution to remove the substance adsorbed to the root surfaces, this will not remove substances that entered the outer cell wall (‘apparent free space’) via diffusion and not by means of an active transport mechanism of the plant. Thus, this amount was added to the substance concentrations actively transported into the roots thus erroneouosly increasing the derived PUF.
Besides, small root hairs are very short living. Thus, substance that is only taken up into this root hairs can be released again when the root hairs wither and thus will continue to be subjected to leaching and run off processes. Thus, only plant uptake in the actual shoot of the plants is considered acceptable by the RMS to derive a plant uptake factor.

Finally, no nutritions were added to the buffered $CaCl_2$ solution and the solution was not aerated thus creating anaerobic conditions in the root system. Thus, the plants suffered a sufficient amount of stress

as can be confirmed by the attached photos in the original study report (all plants were partly withered after the 8 day incubation). The likely damaged root hairs and the incubation stress without nutritions and under anaerobic conditions will have strongly altered the metabolism of the plant and its uptake of water and test substance via the root system. No conclusion on the plant uptake of the metabolite M656PH027 can therefore be drawn from the study results.

For dimethenamid-P, the RMS discussed residue studies in oilseed rape, maize and sugar beet plants to support the use of a default plant uptake factor of 0.5 (see conclusion to Schroeder & McCall, 2014 under KCA 7.1.4/1). However, for the metabolite M656PH027 these studies do not provide any additional information that might support the use of a plant uptake factor of 0.5. M656PH027 was measured in the residue studies *Meyer, 2014a, BASF Doc ID 2013/1335420, Gabriel & Meyer, 2013a, BASF Doc ID 2012/1272621, Perny, 2013b, BASF Doc ID* 2012/1209625, *Erdmann, 2013d, BASF Doc ID* 2013/1003729 and *Perny, 2012a, BASF Doc ID* 2013/1003729, but M656PH027 residues remained < 0.01 mg/kg in all investigated crops throughout the residue studies.

B.8.2 Fate and behaviour in water and sediment

The hydrolytic degradation of dimethenamid and dimethenamid-P was investigated in one laboratory study each submitted already for first EU Annex I inclusion:

- Fostiak & Hsieh, 1988
- Guirguis, 1997a

The direct photochemical degradation of dimethenamid or dimethenamid-P was investigated in four laboratory studies submitted for first EU Annex I inclusion:

- Sabat & Yu, 1992
- Guirguis, 1997b
- Sen & Yu, 1994
- Scharf, 1999

No studies on the indirect photochemical degradation and on the ‘ready biodegradability’ of dimethenamid-P were available for EU Annex I inclusion.

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

- Voelkel, 2013.

Besides, a study on the fate of dimethenamid in water/sediment systems was submitted already for the first EU Annex I inclusion:

- Wyss-Benz & Voelkel, 1994.

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

- Bastiansen, 2011.

An additional water/sediment study with dimethenamid-P was submitted for the renewal of of the EU approval of dimethenamid-P:

- Voelkel, 2014.

A search for open literature which included papers in peer-reviewed journals and reports from the government and other agencies in the EU and several other countries was performed by the applicant. The literature search strategy of the applicant is decribed in more detail in the Appendix of this document.
No additional open-literature studies concerning the route and rate of dimethenamid-P in water and sediment were found.

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

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- Fostiak & Hsieh, 1988 (study evaluated in the monograph, 2000)

Author:	Fostiak, W. Hsieh, T.
Title:	Hydrolysis of SAN 582 H
Date:	10/06/1988
Doc ID:	BASF RegDoc.# 88/11332
Guidelines:	US-EPA, Subdivision N, 161-1
GLP:	Yes
Validity:	Acceptable

Material and Methods

To investigate the hydrolysis of dimethenamid, sterile buffer solutions at pH 5, 7 and 9 were fortified with 100 mg/kg ^{14}C-dimethenamid (3-^{14}C-thienyl dimethenamid, radiochemical purity > 98 %; dimethenamid, analytical reference standard) and incubated at 25±1 °C for 30 or 31 days. Samples were collected at day 0, 1, 7, 14, 21, and 30. Each sample was partitioned with ethyl ether and the organic layer was characterised by TLC. Identity of the parent compound was confirmed by GC-FID and GC-MS.

Results and Discussion

The results are summarised in Table B.8.2.1-1. Dimethenamid was stable under these conditions; no hydrolysis occurred through the study period. Total ^{14}C recoveries were in the range of 99 – 103 % AR, respectively. A minor degradation product accounting for < 1.3 % AR was present at day 0 in the pH 7 buffer solution. Other minor [^{14}C]-residues were detected by TLC throughout the study but individually never accounted for more than 1.0 % AR.

Table B.8.2.1-1: Recovery of radioactivity and distribution of degradation products during hydrolysis of [^{14}C]-dimethenamid (values in % AR)

d	Dimethenamid	Others*	Residual**	Total
pH 5				
0	99.28	1.04	0.92	101.24
1	99.47	0.99	1.01	101.47
7	97.92	0.75	1.07	99.74
14	97.25	1.24	0.93	99.42
21	97.69	2.1	0.95	100.73
30	97.37	1.55	1.10	100.03
pH 7				
0	100.74	1.73	0.97	103.45
1	100.15	0.80	1.18	102.14
7	100.06	1.62	1.24	102.92
14	98.34	1.57	1.20	101.11
21	99.50	0.81	1.30	101.61
30	100.37	0.86	1.42	102.64
pH 9				
0	99.08	1.11	1.24	101.43
1	98.60	0.69	1.62	100.85
7	96.80	0.80	1.73	99.32
14	96.66	0.76	1.85	99.27
21	97.38	1.50	1.77	100.65
30	98.29	1.12	1.97	101.39

* Sum of unidentified degradates in ether extract, each degradate ≤ 1.30 % AR

** Aqueous residual ^{14}C-activity

Conclusion

The study is considered acceptable by the RMS. Dimethenamid is stable to hydrolysis at 25 °C and pH 5, pH 7 and pH 9.

KCA 7.2.1.1/2- Guirguis, 1997a (study evaluated in the monograph, 2000)

Author: Guirguis, A.S.
Title: Hydrolysis of S-dimethenamid
Date: 24/03/1997
Doc ID: BASF RegDoc.# 97/5184
Guidelines: US-EPA, Subdivision N, 161-1
GLP: Yes
Validity: Acceptable

Material and Methods

To investigate the hydrolysis of dimethenamid-P, sterile buffer solutions at pH 5, 7 and 9 were fortified with 100 mg/kg ^{14}C-dimethenamid-P (3-^{14}C-thienyl dimethenamid-P, purity 99.2 %, enantiomeric purity ≥ 98 %; dimethenamid-P, purity 94.0 %) and incubated at 25±1 °C for 30 or 31 days. Samples were collected at day 0, 1, 7, 14, 21, and 31. Each sample was partitioned with ethyl acetate and the organic layer was characterised by TLC. Identity of the parent compound was confirmed by GC-MS.

Results and Discussion

The results are summarised in Table B.8.2.1-2. Dimethenamid-P was stable under these conditions; no hydrolysis occurred through the study period. Total ^{14}C recoveries were in the range of 98 – 101 % AR. No individual residues more than 1.0 % AR were detected throughout the study.

Table B.8.2.1-2: Recovery of radioactivity and distribution of degradation products during hydrolysis of [^{14}C]-dimethenamid-P (values in % AR)

d	Dimethenamid-P	Others*	Polar products **	Total
pH 5				
0	98.14	0.74	0.35	99.23
1	98.61	0.85	0.59	100.05
7	99.34	1.31	0.58	101.23
14	98.53	0.65	0.58	99.76
21	98.87	0.75	0.60	100.22
31	97.02	0.68	0.64	98.34
pH 7				
0	98.57	0.65	0.50	99.72
1	99.30	0.70	0.62	100.62
7	99.04	0.95	0.71	100.70
14	98.86	0.70	0.75	100.31
21	99.29	0.75	0.76	100.80
31	96.76	0.78	0.79	98.33
pH 9				
0	98.32	0.80	0.74	99.86
1	97.16	0.78	0.90	98.84
7	97.58	0.88	1.02	99.48
14	96.42	0.78	1.12	98.32
21	98.05	0.69	1.08	99.82
31	97.22	0.73	1.14	99.09

* Diffuse ^{14}C-activity recovered from TLC plates

** Aqueous residual ^{14}C-activity

Conclusion

The study is considered acceptable by the RMS. Dimethenamid-P is stable to hydrolysis at 25 °C and pH 5, pH 7 and pH 9. There is no difference in the hydrolysis of dimethenamid and dimethenamid-P.

B.8.2.1.2 Direct photochemical degradation

KCA 7.2.1.2/1 – Sabat & Yu, 1992 (study evaluated in the monograph, 2000)

Author: Sabat, M.
Yu, C.C.
Title: SAN 585 H: Photodegradation Study in Aqueous Solution
Date: 24/03/1992
Doc ID: BASF RegDoc.# 92/12388
Guidelines: US-EPA, Subdivision N, 161-2
GLP: Yes
Validity: Acceptable

Material and Methods

Photolysis of ^{14}C-dimethenamid (3-^{14}C-thienyl dimethenamid, radiochemical purity appr. 98 %; dimethenamid, analytical reference standard) in aqueous solutions (100 mg/L) at 25 °C was investigated in sterile pH 7 buffer under a xenon lamp (wavelengths less than 290 nm filtered out) approximating the spectrum of natural sunlight. Irradiation was continuous with an average intensity of $8.55 \cdot 10^2$ W/m^2 (or $3.1 \cdot 10^6$ W h/m^2, 1.47 times the spring noon sunlight intensity at 40 °N latitude). CO_2 and volatiles were trapped in NaOH and ethylene glycol traps. Samples were collected at 0, 1, 5, 11, 15, and 19 days after treatment. Dark control was analysed only at the end of the study. Each irradiated and dark control sample was partitioned with ethyl acetate, and the ethyl acetate layer was analysed by TLC. Identity of compounds was further investigated using HPLC and GC-MS.

Results and Discussion

The results are summarised in Table B.8.2.1-3. In the irradiated samples, the material balance ranged from 92.8 to 103 % AR. For the dark control samples, the material balance of radioactivity was 104 %. Dimethenamid was gradually photodegraded to 42.7 % after 19 days. Mineralisation amounted to 7.8 % after 19 days. The degradation of the irradiated samples was accompanied by formation of several minor degradation products. None of the degradates accounted for more than 3.9 % AR. No degradation was observed in the dark controls throughout the study periods. The metabolites M656H003 (M3 in this study), M656H009 (M9 in this study) and M656H011 (M11 in this study) were identified using TLC and HPLC co-chromatography with authentic reference standards and mass spectroscopy, however all remained below 1.5 % AR.

Table B.8.2.1-3: Recovery of radioactivity and distribution of degradation products during aqueous photodegradation of [^{14}C]-dimethenamid (% AR)

d	DMTA	M3	M9	M11	Others*	Residual**	Volatile	CO_2	Total
Irradiated									
0	94.4		0.6	0.3	3.5	0.8			99.6
1	96.1		0.7	0.5	2.5	2.9	0.0	0.3	103.0
5	82.3		0.7	0.5	6.4	9.2	0.1	1.0	100.2
11	66.9		1.2	1.2	9.7	18.0	0.3	3.0	100.3
15	52.7		0.7	0.5	10.0	24.2	0.4	5.0	93.5
19	42.7	0.6	1.2	0.5	13.2	26.4	0.4	7.8	92.8
Dark control									
19	99.8		0.4	0.2	2.1				103.6

DMTA= dimethenamid, M3 = M656H003, M9 = M656H009, M11= M656H011

∗ Sum of unidentified degradates in ethyl acetate extracts, each degradate < 3.1 % AR

∗∗ Sum of unidentified residual degradates in the aqueous fraction, each degradate < 3.9 % AR

Since degradation rates of dimethenamid in the study were determined before FOCUS kinetic guidance (2006, 2011) was established, a new kinetic evaluation was performed by the RMS applying SFO kinetics. The kinetic fit for dimethenamid using SFO is presented in Figure B.8.1.2-7. The statistical results are presented in Table B.8.1.2-12. SFO gave a statistical and visual acceptable fit, thus no further kinetic fits were tested.

SFO

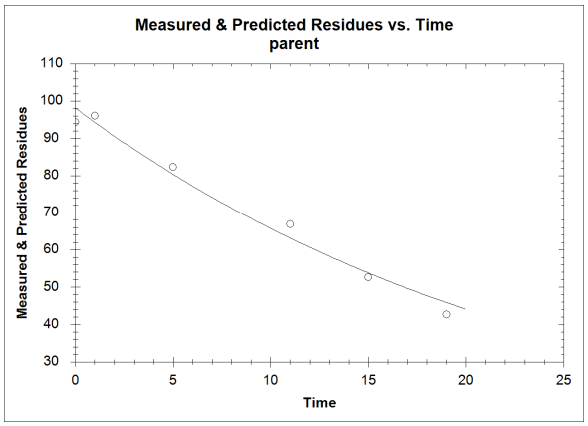


Figure B.8.2.1-1: SFO kinetic fit of dimethenamid after aqueous photolysis

Table B.8.2.1-4: Statistical parameters using SFO for dimethenamid after aqueous photolysis

Kinetic model	Parameter	Optimised value	Std. error	p-value (t-test)	% error χ^2 test	DT_{50} (d)	DT_{90} (d)	Visual assessment
SFO	M0_parent	98.142986	2.335367	9.58e-07	3.05 %	17.29	57.42	good
	k_ parent	0.040099	0.003031	9.43e-05				

Conclusion

The study is considered acceptable by the RMS. After irradiation with an average intensity of $8.55 \cdot 10^2$ W/m^2 for 19 days, dimethenamid degraded to 42.7 % AR in aqueous solution. Resulting DT_{50} and DT_{90} values were 17.29 and 57.42 d.

KCA 7.2.1.2/2 – Gurguis, 1997b (study evaluated in the monograph, 2000)

Author: Guirguis, A.S.
Title: S-dimethenamid: photodegradation study in an aqueous solution
Date: 22/01/1997
Doc ID: BASF RegDoc.#97/5195
Guidelines: US-EPA, Subdivision N, 161-2, study fulfills SETAC requirements
GLP: Yes
Validity: Acceptable

Material and Methods

Photolysis of ^{14}C-labelled dimethenamid-P (3-^{14}C-thienyl dimethenamid-P, purity > 99 %, enantiomeric purity ≥ 98 %; dimethenamid-P, purity 98.6 %) in aqueous solution (99.8 mg/L) at 25 °C was investigated in sterile pH 7 buffer under a xenon lamp (wavelengths less than 290 nm filtered out) approximating the spectrum of natural sunlight. Irradiation was continuous with an average intensity of $1.1 \cdot 10^3$ W/m^2 (or $3.95 \cdot 10^6$ W h/m^2; 1.88 times the spring noon sunlight intensity at 40 °N latitude). CO_2 and volatiles were trapped in NaOH, ethylene glycol and silica gel traps. Samples were collected at 0, 2, 5, 8, 12 and 16 days after treatment. Each irradiated and dark control sample was partitioned with ethyl acetate, and the organic layer was analysed using TLC. Identity of compounds was further investigated using HPLC and GC-MS.

Results and Discussion

The results are summarised in Table B.8.2.1-5. In the irradiated samples, the material balance ranged from 98 to 102 % AR. For the dark control samples, the material balance of radioactivity ranged from 102 to 104 % AR. Dimethenamid-P was gradually photodegraded to 43.51 % after 16 days.

Mineralisation amounted to 6.5 % after 16 days. The degradation of the irradiated samples was accompanied by formation of several minor degradation products. None of the degradates accounted for more than 4.3 % AR. No degradation was observed in the dark controls throughout the study periods. The metabolites M656PH003 (M3 in this study), M656PH009 (M9 in this study) and M656PH011 (M11 in this study) were identified using TLC and HPLC co-chromatography with authentic reference standards and mass spectroscopy, however all remained below 2 % AR.

Table B.8.2.1-5: Recovery of radioactivity and distribution of degradation products during aqueous photodegradation of [^{14}C]-dimethenamid-P (% AR)

d	DMTA-P	M3	M9	M11	Others*	Aqueous**	Volatile	CO_2	Total
Irradiated									
0	99.73			0.30	0.05	0.07			100.15
2	96.44			0.25	2.16	2.09	0.05	0.07	101.06
5	91.17			0.34	5.08	5.21	0.01	0.13	101.94
8	78.64			1.08	6.80	11.08	0.01	0.12	97.73
12	63.13			1.78	10.63	21.83	0.47	2.22	100.06
16	43.51	0.31	0.82	1.64	16.94	29.80	2.28	6.52	101.82
Dark control									
0	99.73				0.35	0.07			100.15
2	103.01				0.41	0.15			103.57
5	101.74				0.71	0.12			102.57
8	101.50				0.71	0.13			102.34
12	101.29				1.11	0.46			102.86
16	101.40				0.61	0.59			102.60

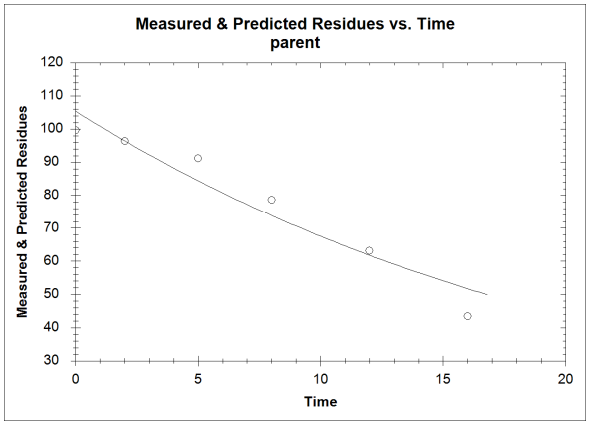
DMTA-P= dimethenamid-P, M3 = M656PH003, M9 = M656PH009, M11= M656PH011

* Sum of unidentified degradates in ethyl acetate extracts, each degradate < 2.5 % AR

** Sum of unidentified residual degradates in the aqueous fraction, each degradate < 4.3 % AR

Since degradation rates of dimethenamid in the study were determined before FOCUS kinetic guidance (2006, 2011), a new kinetic evaluation was performed by the RMS applying SFO kinetics. The kinetic fit for dimethenamid using SFO is presented in. The statistical results are presented in Table B.8.2.1-6. SFO gave a statistical and visual acceptable fit, thus no further kinetic fits were tested.

SFO



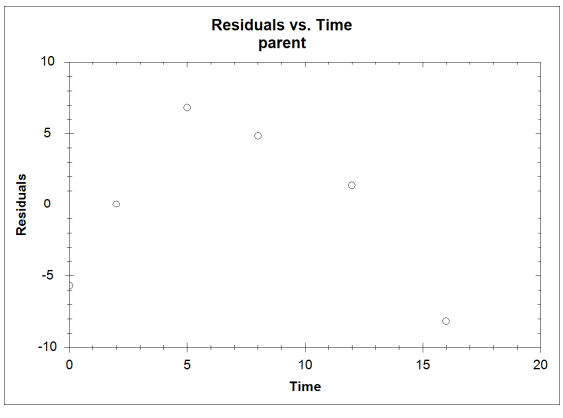


Figure B.8.2.1-2: SFO kinetic fit of dimethenamid-P after aqueous photolysis

Table B.8.2.1-6: Statistical parameters using SFO for dimethenamid-P after aqueous photolysis

Kinetic model	Parameter	Optimised value	Std. error	p-value (t-test)	% error χ^2 test	DT_{50} (d)	DT_{90} (d)	Visual assessment
SFO	M0_parent	105.39647	4.77773	1.25e-05	5.38 %	15.56	51.69	acceptable
	k_ parent	0.04454	0.00661	0.00126				

Conclusion

The study is considered acceptable by the RMS. After irradiation with an average intensity of $1.1 \cdot 10^3$ W/m^2 (or $3.95 \cdot 10^6$ W h/m^2; 1.88 times the spring noon sunlight intensity at 40 °N latitude) for 19 days, dimethenamid-P degraded to 42.7 % AR in aqueous solution. Resulting DT_{50} and DT_{90} values were 15.56 and 51.69 d.

KCA 7.2.1.2/3 – Sen & Yu, 1994 (study evaluated in the monograph, 2000)

Author: Sen, P. K.
Yu, C. C.
Title: SAN 582 H: Quantum Yield Determination
Date: 08/02/1994
Doc ID: BASF RegDoc.# 94/10636
Guidelines: US-EPA, Subdivision N, 161-2
GLP: Yes
Validity: Acceptable

Material and Methods

A 238.5 mg/L solution of non-radio-labelled dimethenamid (purity ≥ 98.5 %) in a 0.001 M sterile phosphate buffer at pH 7.0 was photolysed with monochromatic light at a wavelength of 313 nm generated from a medium pressure mercury arc lamp. The experiment was conducted in a photochemical reactor with "merry-go-round" feature at 25 ± 2 °C. Photolysis was allowed to proceed until about 20 % dimethenamid was photodegraded (13 min). The intensity of incident radiation on dimethenamid was determined by uranyl oxalate actinometry and the decrease in the concentration of dimethenamid was analysed by HPLC. The optical density of both the actinometer solution and dimethenamid was determined by using a double beam UV/VIS spectrophotometer.

Results and Discussion

The molar decadic absorption coefficient at of dimethenamid at 313 nm was determined to be $\varepsilon = 20.34$ L mol^{-1} cm^{-1}. The photolytic degradation rate of dimethenamid was found to be $k = 0.01976$ min^{-1}. The quantum yield was calculated to be $\Phi = 0.007402$. Based on the quantum yield a life-time of 5.97 days was estimated for photolysis in the top layer of aqueous systems under spring conditions at 40 °N.

Conclusion

The study is considered acceptable by the RMS.

KCA 7.2.1.2/4 – Scharf, 1999 (study evaluated in the monograph, 2000)

Author: Scharf, J.
Title: Photolytical Halflife of Dimethenamid in the top layer of aqueous systems
Date: 09/03/1999
Doc ID: BASF Reg-Doc.# 99/10073
Guidelines: None (Calculation)
GLP: No (not applicable)
Validity: Acceptable

Material and Methods

The photolytical half-life (DT_{50}) of dimethenamid in the top layer of aqueous systems was calculated using the quantum yield and a program (Quantum.301) which uses algorithms developed by Frank and Klöpfer, 1985[3] for the direct phototransformation of chemicals in water. The calculation was performed with the program Quantum.301 using the parameters listed in Table B.8.2.1-7 together with the quantum yield of $\Phi = 0.007402$ determined by KCA 7.2.1.2/3 – Sen & Yu, 1994 and the UV/VIS Spectrum of dimethenamid at pH 7.4 from 292.5 to 420 nm.

Table B.8.2.1-7: Parameters of the program Quantum.301 to calculate the photolytic half-life of dimethenamid

Application Month	April	May
Day length	13.67 hours	15.44 hours
Thickness of the aqueous layer	1 cm	1 cm
Substance concentration	1 µg/mL	1 µg/mL
Losses by reflection	10 %	10 %
Cut-off for photoreactions	420 nm	420 nm
Water	distilled	distilled

Results and Discussion

The results of the calculation are summarised in Table B.8.2.1-8.

Table B.8.2.1-8: Estimated photolytic half-life of dimethenamid in the top layer of aqueous systems under Central European conditions

Month of application	Half-life	Half-life (calendar days)
April	12852 s = 3.6 h irradiation	0.3
May	11346 s = 3.2 h irradiation	0.2

Conclusion

The study is considered acceptable by the RMS.

B.8.2.1.3 Indirect photochemical degradation

No study on the indirect photochemical degradation of dimethenamid-P in surface water is available.

[3] Frank, R. and Klöpffer, W. (1985): Ermittlung von Strahlungsdaten und Entwicklung eines Programms zur Abschätzung der abiotischen Transformation von Chemikalien in natürlichen Gewässern, Forschungsbericht Nr. 106 020 46

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

B.8.2.2.1 'Ready biodegradability'

No 'ready biodegradability' study with dimethenamid-P was submitted. Dimethenamid-P is not considered as ready biodegradable.

B.8.2.2.2 Aerobic mineralisation in surface water

KCA 7.2.2.2/1 – Voelkel, 2013 (new study)

Author: Voelkel, W.
Title: Aerobic mineralisation of 14C-dimethenamid-P in surface water
Date: 12/11/2013
Doc ID: BASF Doc ID 2013/1125944
Guidelines: OECD 309 (April 2004)
GLP: Yes
Validity: Acceptable

Material and Methods

In this study was performed to determine the aerobic mineralisation of ^{14}C-thienyl-5-dimethenamid-P (99.0 % purity) in surface water (pelagic test) under defined laboratory conditions. Additionally, it was investigated if a potential shift between the two enantiomers did occur under the applied test conditions. Water was freshly collected on May 7th, 2013 from Biederthal, a pond located at Biederthal (France). The water sample was transported to IES Ltd in clean containers, stored for about two weeks at about 4 °C in the dark. The water used for the main test was filtered through a 0.2 mm mesh and acclimated at room temperature for five days. The characterisation of the surface water is summarised in Table B.8.2.2-1.

Table B.8.2.2-1: Water characteristics of the surface water system

Name	Biederthal
Origin	68480 Biederthal, France 47.4701°N / 7.4342°E
Sampling date	May 07, 2013
Batch:	Biederthal 05/13
Water parameters measured at field sampling	
Temperature [°C]	16.1
pH (water)	7.86
Oxygen concentration [mg/L]	14.32
Redox potential (Eh)* [mV]	398
Sampling depth [cm]	0-20
Colour	Green
Turbidity/Visibility	About 50 cm
Water parameters measured post-handling	
TOC [mg/L]	3.35
DOC [mg/L]	2.43
Nitrate [mg/L]	0.54
Nitrite [mg/L]	<0.82
Ammonium [mg/L]	0.40
N total [mg/L]	2.70
P total [mg/L]	0.31

The test was performed with two different test item concentrations (high dose: 50 µg/L and low dose: 10 µg/L). Additionally, a test was run at the high concentration under sterile conditions in order to gain information about abiotic degradability of the test item. The test flasks were attached to a flow-through system for continuous aeration and incubated at a temperature of 20.0 ± 2.0 °C in the dark for 63 days. After treatment, the flasks (except for day 0 samples) were connected to a volatile trapping system, the first trap containing ethylene glycol and the second 2 N NaOH (in this sequence), for detection of organic volatiles and $^{14}CO_2$.
Duplicate samples (singles for sterile test) were taken for analysis at 0, 1, 3, 7, 14, 28 and 63 days after treatment (DAT). Microbial activity of the surface water was proven by the degradation of [^{14}C(U)]benzoic acid.

The amount of radioactivity in the water samples was determined by LSC. Volatiles trapped in appropriate trapping solutions were also analysed by LSC. Parent substance and metabolite identification and quantification was done by HPLC. Selected samples were analysed by Thin-Layer Chromatography (TLC) to confirm the results. For the high application rate, aliquots (17-19 mL) of the water samples at 0, 28 and 63 DAT were additionally concentrated to 2 mL under reduced pressure and at approximately 35 °C for chiral HPLC analysis to determine the enantiomer ratio.

Results and Discussion

The total mean recoveries were 99.7 ± 1.9 % of applied radioactivity (AR) for the high dose, 101.0 ± 2.3 % AR for the sterile high dose and 100.8 ± 3.0 % AR for the low dose experiments.

The control vessels treated with [^{14}C(U)]benzoic acid showed that the system was microbially active. After 7 days of incubation, [^{14}C(U)]benzoic acid was not detectable anymore in the aqueous phase.

During the incubation with dimethenamid-P, the O_2 concentration in the water of system had an averaged value of 8.38 ± 1.59, 8.37 ± 1.62, 8.43 ± 1.52 for the test vessel dosed at high, high sterile and low concentrations, respectively. The pH in the water of the viable vessels was slightly basic with most values around 8.0. The lowest pH was measured at 7.63 in the test vessels dosed at high concentration.

The distribution of radioactivity in the pelagic test for high and low concentrations are shown in Table B.8.2.2-2.

Table B.8.2.2-2: Pattern of degradation and formation of metabolites in system treated with ^{14}C-dimethenamid-P (high dose). Mean values in percent of the applied radioactivity [%AR]

days after treatment	^{14}C-dimethenamid-P in surface water (high dose)		
	Parent compound	$^{14}CO_2$	^{14}C total
0	100.6	n.p.	100.7
1	99.8	0.2	100.0
3	101.8	0.3	102.2
7	99.2	0.6	99.9
14	98.9	0.8	99.8
28	97.8	1.1	98.9
63	94.8	1.5	96.4
days after treatment	**^{14}C-dimethenamid-P in surface water (high dose, sterile)**		
0	99.3	n.p.	99.3
1	102.6	< 0.2	102.7
3	104.9	0.2	105.1
7	99.7	< 0.2	99.8
14	98.2	0.8	99.0
28	99.4	< 0.2	99.4
63	100.7	0.9	101.6
days after treatment	**^{14}C-dimethenamid-P in surface water (low dose)**		
0	101.7	n.p.	101.7
1	99.5	< 1.0	100.0
3	105.4	< 1.0	105.9
7	100.2	< 1.0	100.8
14	99.5	< 1.0	99.9
28	97.4	1.2	98.7
63	97.8	1.1	98.9

n.p. not performed

No significant degradation of dimethenamid-P in the pelagic test was observed. At 63 DAT, between 94.8 % and 100.7 % AR was still recovered as unchanged parent for the different concentrations. No metabolites were detected the aqueous phase.

The ratio between both types of isomers remained constant throughout the incubation time. The amount of R-Isomer ranged between 5.0 and 6.7 %, while the amount of S-Isomer ranged between 93.3 and 95.0 %.

No kinetic evaluation of dimethenamid-P degradation rates was performed since no significant degradation was observed under the applied test conditions.

Conclusion

The study is considered acceptable by the RMS.
Dimethenamid-P did not significantly degrade in the investigated pure surface water of a Pond close to Biederthal. After 63 days more than 94.8 % AR was recovered as the unchanged active substance. The enantiomer ratio of dimethenamid-P remained constant in all analysed samples.

B.8.2.2.3 Water/sediment studies

KCA 7.2.2.3/1 – Wyss-Benz & Voelkel, 1994 (study evaluated in the monograph, 2000)

Author:	Wyss-Benz, M. Völkel, W.
Title:	[3-^{14}C-thienyl] dimethenamid degradation and metabolism in aerobic aquatic systems
Date:	11/11/1994
Doc ID:	BASF RegDoc.# 94/10641
Guidelines:	BBA Guidelines, Part IV: 5-1
GLP:	Yes
Validity:	Acceptable

Material and Methods

The degradation of dimethenamid (3-^{14}C-thienyl dimethenamid, radiochemical purity > 98 %; dimethenamid, purity 99.8 %) was investigated in two water/sediment systems taken from Rhine River (sampling site near Mumpf, canton Aargau, Switzerland) and a pond (Anwil, canton Baselland, Switzerland). Temperature, pH, oxygen concentration, redox potential, hardness and phosphate concentration of the water and redox potential of the sediment were analysed before sampling. The chemical and physical properties of the water/sediment systems at the beginning and end of the study are shown in Table B.8.2.2-3.

Table B.8.2.2-3: Chemical and physical properties of sediment and water used in the aerobic water/sediment study of dimethenamid

Parameters	River Rhine, Mumpf, Switzerland		Pond, Anwil, Switzerland	
Sediment				
Textural Class (USDA)	Loamy sand		Sandy loam	
Sand [%]	78.0		62.0	
Silt [%]	18.3		22.5	
Clay [%]	3.7		15.5	
pH (KCl)	7.06		6.98	
N-total (Kjeldahl) (g/kg sediment)	1.02		1.7	
P-total (g/kg sediment)	0.185		0.277	
Total organic carbon [g C/100 g dry soil]	0.78		1.42	
Cation exchange capacity [mVal N/100g dry sediment]	8.9		12.3	
	Before	End of study	Before	End of study
Redox Potential (mV)	-95	-56	26	-75
Dry mass (kg dry soil/kg fresh sediment)	0.64	0.55	0.51	0.43
Biomass (mg microbial C/100 g dry soil)	62.5	60.3	112.0	137.7
Water				
Temperature (°C) – surface	10.0		6.7	
Temperature (°C) – 5 cm above sediment	10.0		6.7	
pH – surface	7.46	8.27	7.60	8.33
pH – 5 cm above sediment	7.46		7.54	
Redox potential – surface	167	187	186	202
Redox potential – 5 cm above sediment	167		171	
Oxygen concentration – surface	11.4	7.6	9.0	7.8
Oxygen concentration – 5 cm above sediment	11.4		9.0	
NO_3-N (mg/L)	1.3	0.035	3.6	0.03
NO_2-N (mg/L)	0.03	< 0.02	0.05	0.03
NH_4-N (mg/L)	0.04	0.015	0.1	0.03
N-total (mg/L)	1.37	< 0.07	3.75	0.09
P as ortho-phosphate (mg/L)	0.09	0.13	0.12	0.1
P total (mg/L)	0.1	0.17	0.13	0.10
TOC (total organic carbon) (mg C/L)	0.9	4.7	2.6	3.1
Hardness (°dH)	13	18.5	26	20.5

The study was done in glass metabolism flasks containing 200 g sediment and 530 mL water to which 256 µg dimethenamid were added (483 µg as/L water, corresponding to applying 1440 g active substance/ha to a 30 cm deep water body). The system was continuously ventilated, the effluent air was passed through a trapping system for CO_2 (NaOH) and organic compounds (ethylene glycol). The samples were incubated at 20 °C in the dark, the water was gently stirred from the top without disturbing the sediment. Sterile samples were autoclaved twice before the equilibration phase started and the incoming air was passed through a sterile filter.
Two flasks of each system were taken for analysis at day 0, 0.25, 1, 2, 7, 14, 28, 56, and 105. Sterile samples were collected and analysed only at day 105. At each sampling, the water layer was removed and partitioned with ethyl acetate. The sediment was extracted with acetonitrile and acetonitrile/water. The bound residues were characterised regarding the proportions pertaining to fulvic and humic acids, and humin. Extractable residues were characterised by TLC and HPLC.

Results and Discussion

The distribution and recovery of the radioactivity from the River Rhine and the Pond Anwil water/sediment systems is presented in Table B.8.2.2-4.

Table B.8.2.2-4: Distribution and recovery of radioactivity from River Rhine and Pond Anwil water/sediment systems after application of ^{14}C-dimethenamid (% AR)

DAT	Water	Sediment		Volatiles (CO_2)	Total
		total	NER		
River Rhine Mumpf					
0	100.0	0.8	0.1		100.7
0.25	92.8	6.9	0.8	<0.1	99.7
1	87.0	13.4	2.1	<0.1	100.4
2	80.6	19.6	3.1	<0.1	100.2
7	66.6	33.5	10.1	<0.1	100.2
14	50.9	46.0	21.4	0.2	97.1
28	43.4	54.9	32.8	0.4	98.7
56	34.5	61.1	43.9	1.3	96.8
105	30.0	67.3	53.5	2.7	100.0
105 (sterile)*	34.7	66.8	52.5	0.3	101.8
Pond, Anwil					
0	99.0	0.8	0.1		99.8
0.25	94.5	5.7	0.6	<0.1	100.1
1	89.5	11.7	1.4	<0.1	101.2
2	84.0	15.7	1.4	<0.1	99.7
7	71.8	28.0	5.4	<0.1	99.8
14	63.7	36.9	11.0	0.1	100.6
28	51.8	48.9	24.2	0.2	100.9
56	40.6	56.8	35.9	0.6	97.9
105	31.5	67.0	49.3	2.1	100.5
105 (sterile) *	30.2	68.6	52.7	0.3	99.0

* Sterile samples were analysed at day 105 only

Total recoveries of radioactivity in the River Rhine and Pond Anwil water/sediment systems varied between 96.8 and 101.8 % AR. In both systems, the proportion of radioactivity in water decreased below 32 % AR at 105 DAT, whereas, radioactivity in the sediment increased to above 67 % AR at 105 DAT. Similar results were observed in the non-sterile samples and in the sterile controls. In addition, the amount of non extractable residues (NER) increased to approximately 52 % AR in both systems. Fractionation of the non extractable residues showed that the major part of the residual radioactivity was contained in the fulvic acid fraction (23.0 % AR river; 21.7 % AR pond) and in the humin fraction (18.7 % AR river; 23.0 % AR pond). Minor portions were found in the humic acids fraction (8.7 % AR river; 2.9 % AR pond). Volatile radioactivity ($^{14}CO_2$) accounted for ≤ 2.7 % AR at 105 DAT; organic volatiles were not found.

The proportions of dimethenamid and metabolites in the whole River Rhine and Pond Anwil water/sediment system are presented in Table B.8.2.2-5 and Table B.8.2.2-6. The portions of individual components recovered in water and sediment of the river and pond systems are specified in Table B.8.2.2-7 and Table B.8.2.2-8, respectively.

Table B.8.2.2-5: Proportion of radioactive components in % AR in River Rhine water/ sediment system after application of ^{14}C-dimethenamid

DAT	Dimethenamid	M3	M13	M23	M31	PL 36-88	Unknowns[1]
River Rhine Mumpf,							
0	99.8	n.d.	n.d.	n.a.	n.a.	n.d.	n.d.
0.25	98.6	n.d.	n.d.	n.d.	n.a.	n.d.	n.d.
1	97.5	0.2	n.d.	n.d.	n.a.	n.d.	0.1
2	95.6	0.6	n.d.	n.d.	n.a.	n.d.	0.1
7	83.0	3.5	n.d.	0.4	0.5	n.d.	2.2
14	60.3	7.4	0.9	1.7	0.5	n.d.	3.7
28	34.9	12.5	1.6	3.2	0.9	2.0	9.3
56	16.6	13.2	2.1	4.5	1.2	2.0	10.3
105	4.7	14.3	2.5	5.7	2.0	0.5	11.4
105 (sterile)[2]	25.9	2.2	1.2	8.0	n.d.	n.d.	8.6

n.d. = not detected, n.a. = not analysed
[1] Four unknowns were detected in the river system, none of which exceeded 5.2% AR.
[2] sterile samples were analysed at day 105 only
M3 = M656H003, M13 = M656H013, M23 = M656H023, M31 = M656H031

Table B.8.2.2-6: Proportion of radioactive components in % AR in Pond Anwil water/ sediment system after application of ^{14}C-dimethenamid

DAT	Dimethenamid	M3	M13	M23	M31	PL 36-88	Unknowns[1]
Pond, Anwil							
0	98.8	n.a.	n.a.	n.a.	n.a.	n.d.	n.a.
0.25	99.4	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
1	99.5	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
2	97.9	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
7	92.0	1.0	n.d.	n.d.	n.d.	n.d.	0.2
14	82.8	3.7	n.d.	n.d.	0.3	n.d.	2.1
28	57.2	6.8	0.5	2.5	0.2	0.7	7.4
56	31.8	11.0	1.3	4.2	1.7	1.2	8.9
105	11.6	14.0	1.6	7.0	0.7	1.0	10.6
105 (sterile)[2]	27.5	1.9	0.7	5.3	n.d.	n.d.	8.6

n.d. = not detected, n.a. = not analysed
[1] Five unknowns were detected in the pond system, none of which exceeded 4.6 % AR.
[2] sterile samples were analysed at day 105 only
M3 = M656H003, M13 = M656H013, M23 = M656H023, M31 = M656H031

Table B.8.2.2-7: Proportion of radioactive components in % AR in River Rhine water and sediment after application of ^{14}C-dimethenamid

Water phase							
DAT	**Dimethenamid**	**M3**	**M13**	**M23**	**M 31**	**PL 36-88**	**Unknown**
0	99.8	n.d.	n.d.	n.a.	n.a.	n.d.	n.d./n.a.
0.25	92.5	n.d.	n.d.	n.a.	n.a.	n.d.	n.d./n.a.
1	86.5	n.d.	n.d.	n.a.	n.a.	n.d.	n.d./n.a.
2	79.8	n.d.	n.d.	n.a.	n.a.	n.d.	n.d./n.a.
7	62.8	1.5	n.d.	0.4	0.5	n.d.	0.9
14	41	4.5	0.9	1.4	0.5	n.d.	1.6
28	22.7	8.1	1.6	1.9	0.9	0.8	6.2
56	10.5	8.5	2.1	3	1.2	0.8	6.9
105	2.6	9.1	2.5	4.2	2	n.d.	6.9
Sediment extract							
DAT	**Dimethenamid**	**M3**	**M13**	**M23 (+ M 31)**		**PL 36-88**	**Unknown**
0	n.a.	n.a.	n.a.	n.a.		n.a.	n.a.
0.25	6.2	n.d.	n.d.	n.d.		n.d.	n.d.
1	11	0.2	n.d.	n.d.		n.d.	0.1
2	15.8	0.6	n.d.	n.d.		n.d.	0.1
7	20.1	2	n.d.	n.d.		n.d.	1.3
14	19.2	2.9	n.d.	0.3		n.d.	2.1
28	12.2	4.4	n.d.	1.3		1.2	3.1
56	6.1	4.7	n.d.	1.5		1.2	3.8
105	2	5.2		1.5		0.5	4.6

n.d. = not detected
n.a. = not analysed
M3 = M656H003, M13 = M656H013, M23 = M656H023, M31 = M656H031

Table B.8.2.2-8: Proportion of radioactive components in % AR in Anwil pond water and sediment after application of ^{14}C-dimethenamid

Water phase							
DAT	**Dimethenamid**	**M3**	**M13**	**M23**	**M 31**	**PL 36-88**	**Unknown**
0	98.8	n.a.	n.a.	n.a.	n.a.	n.d.	n.d./n.a.
0.25	94.3	n.d.	n.d.	n.d.	n.d.	n.d.	n.d./n.a.
1	89.2	n.d.	n.d.	n.d.	n.d.	n.d.	n.d./n.a.
2	83.6	n.d.	n.d.	n.d.	n.d.	n.d.	n.d./n.a.
7	70.6	n.d.	n.d.	n.d.	n.d.	n.d.	n.d./n.a.
14	60	1.7	n.d.	n.d.	0.3	n.d.	1
28	41	3.5	0.5	1.5	0.2	n.d.	3.9
56	21.2	6.3	1.3	2.8	1.7	n.d.	6.2
105	6.9	8	1.6	4.7	0.7	0.4	6.5
Sediment extract							
DAT	**Dimethenamid**	**M3**	**M13**	**M23 (+ M31)**		**PL 36-88**	**Unknown**
0	n.a.	n.a.	n.a.	n.a.		n.a.	n.a.
0.25	5.1	n.d.	n.d.	n.d.		n.d.	n.d.
1	10.3	n.d.	n.d.	n.d.		n.d.	n.d.
2	14.3	n.d.	n.d.	n.d.		n.d.	n.d.
7	21.4	1	n.d.	n.d.		n.d.	0.2
14	22.8	2	n.d.	n.d.		n.d.	1.1
28	16.3	3.3	n.d.	1.1		0.7	3.5
56	10.6	4.8	n.d.	1.4		1.2	2.9
105	4.6	6	n.a.	2.3		0.6	4.2

n.d. = not detected
n.a. = not analysed

In the River Rhine water/sediment system the active substance steadily decreased from 99.8 % AR at day 0 to 4.7 % AR at day 105. The major metabolite was M656H003 (M3 n this study) and accounted

for a maximum of 14.3 % AR at day 105 (9.1 % AR in the water phase and 5.2 % AR in the sediment). The metabolite M656H023 (M23 in this study) was formed with maximum concentrations of 5.7 % AR at day 105 (4.2 % AR in the water phase and 1.5 % AR in the sediment together with M656H031). The other metabolites, M656H013 (= M13 in this study), M656H031 (M31 in this study) and PL 36-88, accounted for less than 3 % AR.
Similarly, in the pond water/sediment system, the active substance steadily decreased from 98.8 % AR at day 0 to 11.6 % AR at day 105. The major metabolite was M656H003 and accounted for 14.0 % AR at day 105 (8.0 % AR in the water phase and 6.0 % AR in the sediment). The metabolite M656H023 (M23 in this study) was formed with maximum concentrations of 7.0 % AR at day 105 (4.7 % AR in the water phase and 2.3 % AR in the sediment). The other metabolites, M656H013, M656H031 and PL 36-88, accounted for an amount equal to or less than 2.0 % AR. Several unknown compounds were separated none of them exceeding 5.2 % AR and 4.6 % AR in the river and pond system, respectively.
The fulvic acid fraction of non extractable residues (day 105) were extracted with ethyl acetate and analysed by TLC. Up to 17 compounds were separated none of which exceeding 2.4 % AR; among these compounds the metabolites M656H003 (1.8 % AR), M656H011 (M11 in this study) (0.6 % AR), M656H013 (0.2 % AR) and M656H023 (1.0 % AR) were identified by co-chromatography.
Degradation also occurred in the sterile samples but to a lower extent either due to increasing microbial activity or through chemical degradation. In the sterile river and pond water/sediment systems the active substance accounted for 25.9 and 27.5 % AR at day 105, respectively.

Conclusion

The study is considered acceptable by the RMS.
The fate of dimethenamid was investigated for 105 d in two water/sediment studies River Rhine and Pond Anwil. Dimethenamid degraded quickly to 4.7 % and 11.6 % at the end of the study, while mineralisation amounted to 2.7 % and 2.1 % and 53.5 % and 49.3 % bound residues were formed. Maximum concentrations of dimethenamid in the sediment was 20.1 % at day 7 and 22.8 % at day 22 with subsequent decline in both systems. Five metabolites were identified in the study. The major metabolite M656H003 accounted for a maximum of 14.3 % AR at day 105 (9.1 % AR in the water phase and 5.2 % AR in the sediment), the metabolite M656H023 was formed with maximum concentrations of 5.7 % AR at day 105 (4.2 % AR in the water phase and 1.5 % AR in the sediment together with M656H031). The other metabolites, M656H013, M656H031 and PL 36-88 all accounted for less than 3 % AR.
Under sterile conditions, dimethenamid also degraded but with a slower rate: At day 105, 25.9 % and 27.5 % dimethenamid remained in water/sediment systems River Rhine and Pond Anwil, while mineralisation amounted to 0.3 % and 52.5 % and 52.7 % bound residues were formed. The metabolite M656H023 was formed with 8 % and 5.3 % at day 105 d, while the other metabolites remained below 3 %.
A new kinetic evaluation of the residues of dimethenamid in the water/sediment study was performed by Bastiansen, 2011. Thus, the DT_{50} and DT_{90} values determined in the study are not presented here anymore.

KCA 7.2.2.3/2 – Bastiansen, 2011 (new study)

Author:	Bastiansen F.
Title:	Kinetic evaluation of BAS 656 H in water/sediment systems under aerobic conditions
Date:	07/11/2011
Doc ID:	BASF DocID 2011/1102522
Guidelines:	FOCUS degradations kinetics (2006)
GLP:	No - not applicable
Validity:	Acceptable

Material and Methods

A new kinetic evaluation of dimethenamid and its metabolites M656H003 (M3 in this study) and M656H023 (M23 in this study) according to FOCUS kinetic guidance (2006) was performed for the two water/sediment systems River Rhine and Pond Anwil investigated by KCA 7.2.2.3/1 – Wyss-Benz & Voelkel, 1994.

The kinetic analysis was carried out following the recommendations of the FOCUS work group on degradation kinetics (*FOCUS, 2006)*. The analysis was done by non-linear regression methods (Marquardt algorithm, ordinary least squares optimisation) using the Model Maker software package, version 3.1.

Kinetic evaluation at P-I level (one compartement approach) was done for the degradation of dimethenamid in the whole system as well as dissipation from the water phase and dissipation in the sediment phase. AT P-II level (two-compartement approach), the kinetic analysis considered the degradation of dimethenamid in water and sediment and the partitioning between both phases.
Since no decline phase of the metabolites M656H003 and M656H023 occurred in the two systems, dissipation rates in the whole system, water or sediment could not be determined. However, kinetic evaluation was performed to determine degradation rates in the whole water-sediment systems of the metabolites M656H003 and M656H023.

The compartment model used for the estimation approach of the metabolites is shown in Figure B.8.2.2-1.

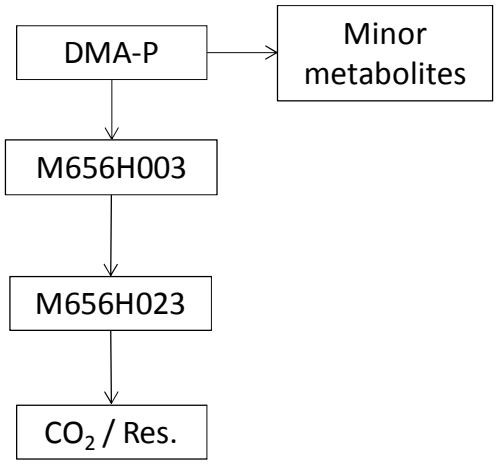


Figure B.8.2.2-1: Compartment model for modelling the degradation of the metabolites M656H003 and M656H023 in the water/sediment systems River Rhine and Pond Anwil (whole system)

Kinetic evaluation was performed in a stepwise approach. First, only for the parent was modelled according to recommendations of FOCUS (2006) using different kinetic models in order to identify the best model for the whole system as well as the individual compartments water and sediment. Afterwards a kinetic evaluation of dimethenamid-P using the best kinetic fit together with its metabolites M656H023 and M656H03 using SFO kinetics was performed. If no acceptable fit for the metabolites could be achieved using SFO kinetics, the default DT_{50} value of 1000 days was used. In addition to the parent substance and the metabolites M656H003 and M656H023, two sink compartments were defined: one sink compartment represents the minor metabolites PL36-88, M656H011 and M656H031, the second sink compartment represents CO_2 and bound residues, thus no concentration data is connected to this compartment. Two separate sink compartments are used since for one compartment data are available (minor metabolites) whereas no data are available for the second sink compartment (CO_2 and bound residues).

The residue data used for modelling of dimethenamid in the total system, water and sediment are presented in Table B.8.2.2-5, Table B.8.2.2-6, Table B.8.2.2-7 and Table B.8.2.2-8. Before modelling, the concentration of dimethenamid in the total system and the water phase on day 0 was set to the material balance (99.8 % AR for Anwill Pond and 100.7 % for River Rhine). The residue data used for the metabolites in the whole systems are presented in Table B.8.2.2-5 and Table B.8.2.2-6. Concentrations at day 0 and concentrations below detection limit were set to 0 before modelling.

Results and Discussion

Results of P-I modelling:

The statistical results for dimethenamid in the whole water/sediment systems Anwill Pond and River Rhine can be found in Table B.8.2.2-9 and Table B.8.1.2-18. SFO gave the best fit for both whole water/sediment systems. The visual fits and residual plots of dimethenamid in the whole water/sediment systems using SFO kinetics are presented in Figure B.8.2.2-2.

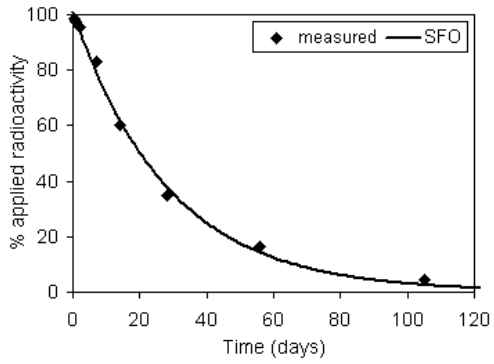
Table B.8.2.2-9: Statistical and visual assessment of kinetic models for dimethenamid in water/sediment system River Rhine, whole system (modelling and trigger endpoints)

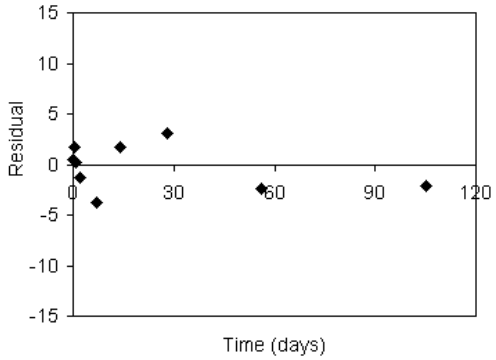
Step in FOCUS flowchart	Kinetic model	χ^2 error	p-value	Visual assessment	$DegT_{50}$ [d]	$DegT_{90}$ [d]
Run SFO & FOMC	SFO	2.6	k: <0.001	Good	19.8	65.8
	FOMC	2.6	β: 0.230	Good	19.4	69.7
→ SFO fit visually acceptable and statistically sufficient, FOMC visually acceptable but statistically not sufficient; moreover no improvement against SFO, therefore use of SFO						

Table B.8.2.2-10: Statistical and visual assessment of kinetic models for dimethenamid in water/sediment system Anwill Pond, whole system (modelling and trigger endpoints)

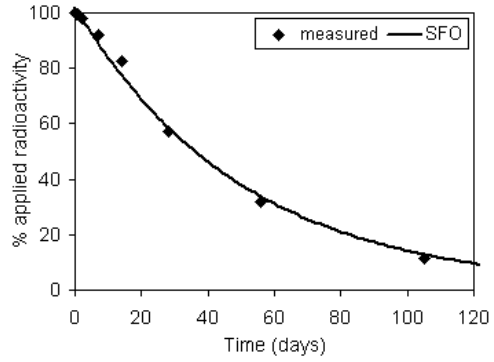
Step in FOCUS flowchart	Kinetic model	χ^2 error	p-value	Visual assessment	$DegT_{50}$ [d]	$DegT_{90}$ [d]
Run SFO & FOMC	SFO	2.7	k: <0.001	Good	35.1	116.5
	FOMC	2.8	β: 0.499	Good	35.1	116.5
→ SFO fit statistically sufficient and visually acceptable; FOMC visually acceptable but statistically not sufficient; moreover χ^2 error larger than SFO, therefore use of SFO						

River Rhine (whole system)





Anwill Pond (whole system)



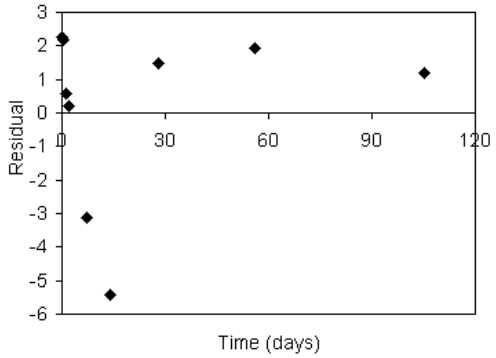


Figure B.8.2.2-2: Visual fit using SFO kinetics of dimethenamid in the two water sediment systems River Rhine, whole system and Anwill Pond, whole system

The statistical results and the visual assessment of dimethenamid dissipation in the water phase of the two water/sediment systems River Rhine and Anwill Pond can be found in Table B.8.2.2-12 and Table B.8.2.2-11. Only the results for trigger endpoints of dimethenamid are presented here, since dissipation rates in water and sediment are generally not used for modelling purposes. DFOP resulted in the best fit to describe the dissipation of dimethenamid in the water phase of Anwill Pond, FOMC gave the best fit to describe the dissipation of dimethenamid in the water phase of River Rhine. The visual fits and residual plots of dimethenamid in the water phase using DFOP kinetics for Anwill Pond and FOMC for River Rhine are presented in Figure B.8.2.2-3.

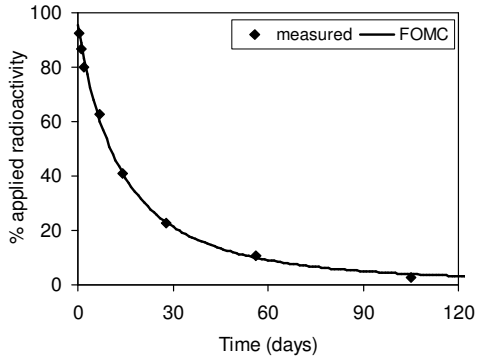
Table B.8.2.2-11: Statistical and visual assessment of kinetic models for dimethenamid in River Rhine, water phase (trigger endpoints)

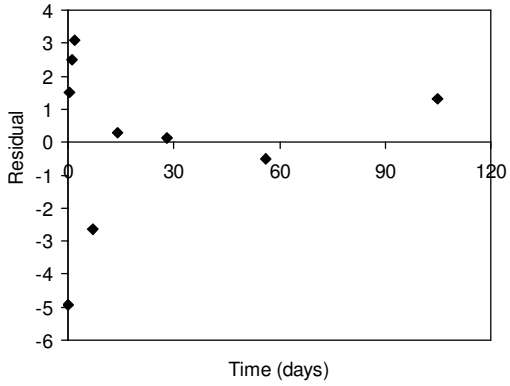
Step in FOCUS flowchart	Kinetic model	χ^2 error	p-value	Visual assessment	DT_{50} [d]	DT_{90} [d]
Run SFO & FOMC	SFO	5.4	k: <0.001	Moderate	12.7	42.1
	FOMC	3.6	β: 0.035	Good	11.1	57.7
→ SFO fit visually not acceptable but statistically sufficient, FOMC visually acceptable and statistically sufficient; therefore run of modified fitting: Constrain M0.						
Run modified fitting: Constrain M0.	SFO	7.7	k: <0.001	Not acceptable	11.0	36.6
	FOMC	5.1	β: 0.028	Moderate	9.5	60.9
→ SFO fit visually still not acceptable, but statistically sufficient. FOMC fit visually acceptable, but worse than without M0 constrained, and statistically sufficient. Therefore use FOMC. Modification does not yield significant improvements, therefore use of FOMC (unmodified).						
Run DFOP and HS	DFOP	6.1	k1: 0.452 k2: 0.454 g: 0.499	Moderate	12.8*	42.3*
	HS	3.9	M0: <0.001 hingepoint: 0.066 k1: 0.003 k2: <0.001	Good	11.8	47.5
→ DFOP fit visually moderate but statistically not sufficient. HS fit visually acceptable and statistically sufficient. FOMC fit visually better than HS fit, and statistically more appropriate (slightly lower χ^2 error). Therefore use of FOMC fit						

Table B.8.2.2-12: Statistical and visual assessment of kinetic models for dimethenamid in Anwill Pond, water phase (trigger endpoints)

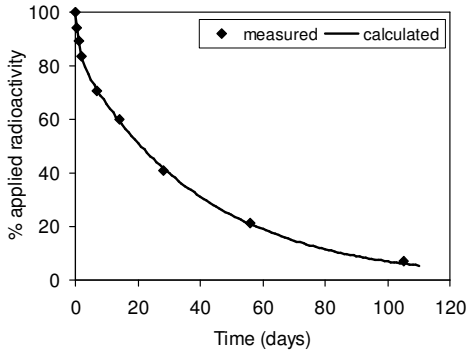
Step in FOCUS flowchart	Kinetic model	χ^2 error	p-value	Visual assessment	DT_{50} [d]	DT_{90} [d]
Run SFO & FOMC	SFO	4.5	k: <0.001	Moderate	23.6	78.3
	FOMC	3.7	β: 0.075	Good	21.1	102.2
→ SFO results in moderate visual fit and is statistically sufficient, FOMC visually and statistically acceptable and more appropriate than SFO; therefore run modified fitting: Constrain M0.						
Run modified fitting: Constrain M0.	SFO	7.0	k: <0.001	Not acceptable	21.1	102.2
	FOMC	5.1	β: 0.061	moderate	17.8	114.3
→ Modified SFO fit visually not acceptable. FOMC fit visually moderate, but worse than without M0 constrained, though statistically sufficient. Therefore use FOMC. Modification does not yield significant improvements, therefore use FOMC (unmodified).						
Run DFOP and HS	DFOP	1.1	k1: <0.001 k2: 0.003 g: <0.001	Good	21.4*	86.2*
	HS	2.3	M0: <0.001 hingepoint: 0.059 k1: 0.065 k2: <0.001	Good	21.3	81.2
→ Conclusion: DFOP fit and HS fit visually acceptable and statistically sufficient. DFOP fit statistically better than HS fit and FOMC fit. Therefore use half-life back-calculated from DFOP fit: $DT_{50} = DT_{90} / 3.32 = 26.0$ d.						

River Rhine (water phase)





Anwill Pond (water)



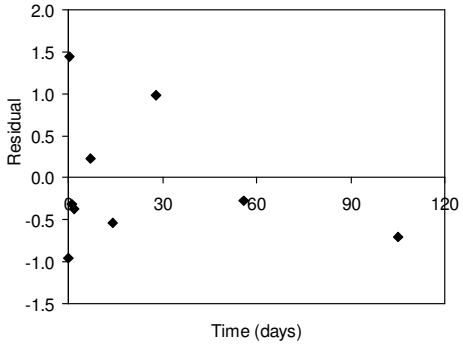


Figure B.8.2.2-3: Visual fit of dimethenamid in the water phase using FOMC for the water sediment system River Rhine and DFOP for the water sediment system Anwill Pond

The statistical results and the visual assessment of the dimethenamid dissipation in the sediment phase of the two water/sediment systems River Rhine and Anwill Pond can be found in Table B.8.2.2-13 and Table B.8.2.2-14. Only the results for trigger endpoints of dimethenamid are presented here, since dissipation rates in water and sediment are generally not used for modelling purposes. SFO gave the best fit for the sediment phase of both whole water/sediment systems. The visual fits and residual plots of dimethenamid in the whole water/sediment systems using SFO kinetics are presented in Figure B.8.2.2-4.

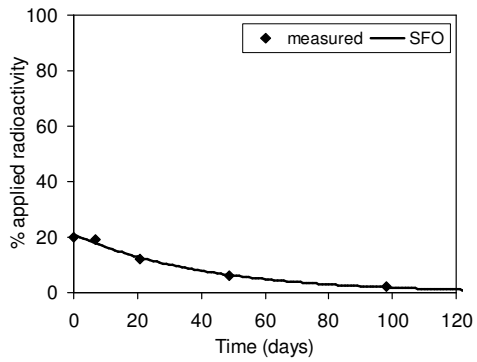
Table B.8.2.2-13: Statistical and visual assessment of kinetic models for dimethenamid in River Rhine, sediment phase (trigger endpoints)

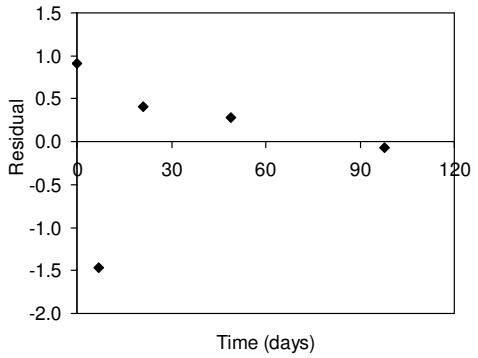
Step in FOCUS flowchart	Kinetic model	χ^2 error	p-value	Visual assessment	DT_{50} [d]	DT_{90} [d]
Run SFO & FOMC	SFO	5.4	k: 0.006	Good	28.5	94.7
	FOMC	6.2	β: 0.500	Good	28.5	94.7
→ SFO fit visually acceptable and statistically sufficient, FOMC visually acceptable but statistically not sufficient; therefore use SFO						

Table B.8.2.2-14: Statistical and visual assessment of kinetic models for dimethenamid in Anwill Pond, sediment phase (trigger endpoints)

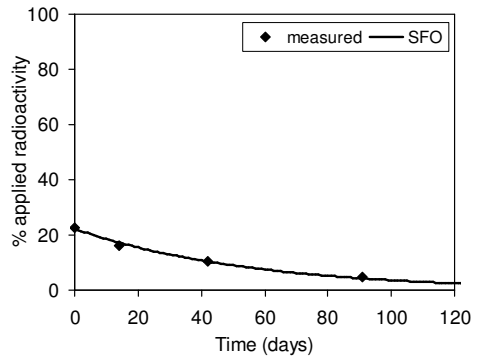
Step in FOCUS flowchart	Kinetic model	$\chi 2$ error	p-value	Visual assessment	DT50 [d]	DT90 [d]
Run SFO & FOMC	SFO	3.5	k: 0.004	Good	38.2	126.9
	FOMC	3.1	β: 0.500	Good	35.1	159.1
→ SFO fit is visually acceptable and statistically sufficient, FOMC is visually acceptable but statistically not sufficient; therefore use SFO						

River Rhine (sediment phase)





Anwill Pond (sediment phase)



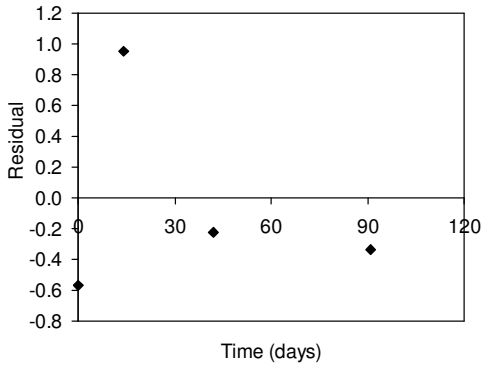


Figure B.8.2.2-4: Visual fit of dimethenamid in the sediment phase using SFo for the water sediment system River Rhine and Anwill Pond

The final results of P-I modelling for dimethenamid in the two water/sediment systems River Rhine and Anwill Pond are summarised in Table B.8.2.2-15.

Table B.8.2.2-15: P-I level endpoints for dimethenamid for the River Rhine and the Pond Anwill water/ sediment systems

Whole system	**Trigger and modelling endpoints**		
	Kinetic model	**$DegT_{50}$**	**$DegT_{90}$**
Pond	SFO	35.1	116.5
River	SFO	19.8	65.8
Geometric mean:		26.4	87.6
Water compartment	**Trigger endpoints**		
	Kinetic model	**$DisT_{50}$**	**$DisT_{90}$**
Pond	DFOP	21.4	86.2
River	FOMC	11.1	57.7
Sediment compartment	**Trigger endpoints**		
	Kinetic model	**$DisT_{50}$**	**$DisT_{90}$**
Pond	SFO	38.2	126.9
River	SFO	28.5	94.7

Results of P-II modelling:

The statistical results of P-II modelling to estimate the degradation of dimethenamid in water and sediment as well as the partitioning between these compartments for the water/sediment systems River Rhine and Anwill Pond are shown in Table B.8.2.2-16 and Table B.8.2.2-17. The degradation in the water phase could not be estimated reliably; therefore no degradation rates in the individual compartments could be determined.

Table B.8.2.2-16: Statistical results of level P-II water and sediment modelling for the water/ sediment system Rhiver Rhine

Test system	**Parameter**	**estimated value**	**std error**	**P-value**
River Rhine	M_0 [%TAR]	98.18	1.82	<0.001
	kwP [d^{-1}]	$7.2*10^{-14}$	0.022	0.500*
	ksP [d^{-1}]	0.134	0.061	0.023
	r_sw [d^{-1}]	0.216	0.067	0.002
	r_ws [d^{-1}]	0.129	0.022	<0.001

* not significantly different from zero (for a 10 % significance level)

Table B.8.2.2-17: Statistical results of level P-II water and sediment modelling for the water/ sediment system Anwill Pond

Test system	**Parameter**	**estimated value**	**std error**	**P-value**
Anwill Pond	M_0 [%TAR]	99.54	1.48	<0.001
	kwP [d^{-1}]	$5.34*10^{-14}$	0.014	0.500*
	ksP [d^{-1}]	0.073	0.029	0.036
	r_sw [d^{-1}]	0.252	0.056	<0.001
	r_ws [d^{-1}]	0.114	0.016	<0.001

* not significantly different from zero (for a 10 % significance level)

Results of M-I modelling:

The statistical results of M-I modelling to estimate the formation and degradation of the dimethenamid metabolites M656H003 and M656H023 in the water/sediment systems River Rhine and Anwill Pond (whole system) are presented in Table B.8.2.2-18 and Table B.8.2.2-19.

According to FOCUS recommendations (FOCUS, 2006) as a case by case decision a default DT_{50} of 1000 days is used for the metabolite M656H003. After adding the metabolite M656H023 to the model using SFO kinetics for the degradation to sink, no appropriate fit to the data could be obtained. Therefore, for M656H023 a default DT_{50} of 1000 days was assessed as well.

Table B.8.2.2-18: Statistical and visual assessment of kinetic models at level M-I for dimethenamid and metabolites M656H003 and M656H023 inRiver Rhine, whole system (modelling endpoints)

Step in FOCUS flowchart	Kinetic model	χ^2 error	p (t-test)	Visual assessment	DT_{50} [d]	DT_{90} [d]
Run Parent best-fit from P-I (SFO) and metabolite M3 SFO	M3: SFO	59.4	k: 0.489	Not acceptable	M3: 7.6	M3: 25.3
→ SFO fit visually not acceptable and statistically not sufficient. Therefore decide case-by-case: Use default DT_{50} = 1000 days. Set degradation of M3 to the metabolite M23 to the respective degradation rate k=ln(2)/1000 = 6.93E-04.						
Run parent best-fit (SFO), metabolite M3 SFO with fixed degradation rate, metabolite M23 SFO	M23: SFO	64.1	k: 0.500	Not acceptable	M23: - ($6.93*10^{18}$)**	M23: - ($2.3*10^{19}$)**
→ SFO fit visually not acceptable and statistically not sufficient. Therefore decide case-by-case: Set default DT_{50} = 1000 days for metabolite M23.						

* β parameter was not different from zero according to t-test, therefore no reliable DT_{50} and DT_{90} could be calculated.
** degradation rate ($k=10^{-19}$) was not different from zero according to t-test, therefore no reliable DT_{50} and DT_{90} could be calculated.

Table B.8.2.2-19: Statistical and visual assessment of kinetic models at level M-I for dimethenamid and metabolites M656H003 and M656H023 in Anwill Pond, whole system (modelling endpoints)

Step in FOCUS flowchart	Kinetic model	χ^2 error	p (t-test)	Visual assessment	DT_{50} [d]	DT_{90} [d]
Run Parent best-fit from P-I (SFO) and metabolite M3 (SFO)	M3: SFO	69.3	k: 0.006	Not acceptable	4.0	13.5
→ SFO kinetics visually not acceptable and statistically not sufficient. Therefore decide case-by-case: Use default DT_{50} = 1000 days. Set degradation of M3 to the metabolite M23 to the respective degradation rate k=ln(2)/1000 = 6.93E-04.						
Run parent best-fit (SFO), metabolite M3 SFO with fixed degradation rate, metabolite M23 SFO	M23: SFO	78.9	k: 0.500	Not acceptable	-** ($6.93*10^{18}$)	-** ($2.30*10^{19}$)
→ SFO fit visually not acceptable and statistically not sufficient. Therefore decide case-by-case: Use default DT_{50} of 1000 days for metabolite M23.						

* Half-lives could not be determined from the calculated values since no decline occurs within the study period
** degradation rate ($k=10^{-19}$) was not different from zero according to t-test, therefore no reliable DT_{50} and DT_{90} could be calculated.

Conclusion

The kinetic evaluation for dimethenamid is considered acceptable by the RMS. For the metabolites M656H003 and M656H023, the data points below the detection limit except after day 0 and the first residue value above the detection limit should have been excluded before the kinetic evaluation. However, this would probably not have changed the outcome of the modelling, which resulted in no reliable fits for both metabolites.

Dimethenamid degraded in the two water/sediment systems Anwill Pond and River Rhine with DT_{50} values of 35.1 d and 19.8 d and DT_{90} values of 116.5 d and 65.8 d following SFO kinetics. The dissipation from the water phase followed biphasic kinetics in both systems. In the water/sediment system Anwill Pond, dimethenamid dissipated with a DT_{50} and DT_{90} values of 21.4 d and 86.2 d, respectively, following DFOP kinetics. In the water/sediment system River Rhine, dimethenamid dissipated with a DT_{50} and DT_{90} values of 11.1 d and 57.7 d, respectively, following FOMC kinetics.

In the sediment, dimethenamid dissipated following SFO kinetics again with DT_{50} values of 38.2 d and 28.5 d and DT_{90} values of 126.9 d and 94.7 d in the two water/sediment systems Anwill Pond and River Rhine, respecively.

KCA 7.2.2.3/3 –Voelkel, 2014 (new study)

Author:	Voelkel W.
Title:	Route and rate of degradation of ^{14}C-dimethenamid-P in one aerobic aquatic sediment system
Date:	27/01/2014
Doc ID:	BASF Doc ID 2013/1125942
Guidelines:	OECD 308, EC 1107/2009 (14 June 2011), EEC 79/117, EEC 91/414
GLP:	Yes
Validity:	Acceptable

Material and Methods

The degradation of thienyl-5-^{14}C- dimethenamid-P (purity 99.0 %) was investigated in an aerobic water/sediment system under dark conditions. A natural water/sediment system was collected from the river Rhine near 4322 Mumpf, Switzerland (47.546° N / 7.931° E). The water and sediment were filled in test flasks within two days of sampling. The physico-chemical parameters of the systems measured at field sampling and prior to acclimatisation are summarised in Table B.8.2.2-20. The sediments were passed through a 2 mm sieve. The parameters of the water sediment system measured during incubation are summarised in Table B.8.2.2-21.

Table B.8.2.2-20: Chemical and physical properties of the aerobic water/sediment system

Batch:	Rhein near Mumpf 04/13
Sampling date:	24.04.2013
Parameters at field sampling day	
Water	
Temperature [°C]	9.3
pH (water)	8.17
Oxygen concentration [mg/L]	16.85
Redox potential (E_h)* [mV]	530
Sediment	
Depth [cm]	0-10
Colour	Grey
Smell	none
Parameters prior to acclimatisation	
Water	
TOC [mg/L]	1.09
Sediment	
pH ($CaCl_2$) [a]	7.27
pH (water) [a]	7.70
TOC [mg/kg]	13.9
Microbial biomass [mg/kg]	326
Dry weight [g/g]	0.52
Soil (sediment) type (USDA):	Sandy loam
Particle size analyses:	
< 0.002 mm (clay) [a] [%]	7.48
0.002-0.05 mm (silt) [a] [%]	23.38
> 0.05 mm (sand) [a] [%]	69.14

* The measured redox potential was corrected to E_h of a standard hydrogen electrode (SHE)

Table B.8.2.2-21: Parameters for river water/sediment system measured during incubation

Water			
pH (water)		Start of incubation Average during incubation End of incubation	8.14 8.07 7.97
TOC	[mg/L]	Start of incubation End of incubation	1.85 9.39
Oxygen conc.	[mg/L]	Start of incubation Average during incubation End of incubation	8.54 8.89 9.17
Redox potential (E_h) *	[mV]	Start of incubation Average during incubation End of incubation	459 417 387
Sediment			
pH ($CaCl_2$)		Start of incubation During incubation [c] End of incubation	7.42 7.43 7.43
TOC	[mg/g]	Start of incubation End of incubation	13.7 13.0
Redox potential (E_h) *	[mV]	Start of incubation Average during incubation End of incubation	91 23 81
Microbial biomass	[mg/kg]	Start of incubation End of incubation	249 200

* The measured redox potential was corrected to E_h of a standard hydrogen electrode (SHE)

The test systems consisted of 1 L all-glass metabolism flasks (inner diameter: approximately 10.6 cm) filled with wet sediment to a height of approximately 2.3 cm (corresponding to about 200 g river sediment). Thereafter, approximately 6.4 cm river water (corresponding to about 600 mL) was added to reach a sediment/water volume ratio of about 1:3. Following the start of acclimation the flasks were ventilated with moistened air. The samples were allowed to equilibrate in the dark for four weeks at a target temperature of 20 ± 2 °C, in order to achieve stable redox potential and oxygen conditions. Appropriate amounts (720 µL) of the respective application solution were pipetted to the water surface to achieve a nominal amount of about 200 µg test item per test vessel. The test item ^{14}C-dimethenamid-P (batch no. 824-6027) was purified before use. The application solution contained 3.07 mg ^{14}C-labelled test item and 3.97 mg of unlabelled test item resulting in a specific activity of 3.58 MBq/mg. After application of the test item to the flasks, the flasks were connected to a series of two volatile traps. The first trap contained ethylene glycol, the second trap 2 M NaOH. For sampling on day 0, no absorption traps were set up.

Two replicates of treated samples were taken for extraction and analyses immediately after treatment (day 0) and after 3, 8, 14, 28, 56, 77 and 100 days of incubation. The pH, oxygen concentration, and redox potential in water and/or sediment were measured in each sampled test vessel. Additionally, the parameters in control flasks were determined at all sampling intervals. The volume of the liquid in each sodium hydroxide and ethylene glycol trap was recorded at the corresponding sampling intervals. Thereafter, the radioactivity in the absorption solutions was determined by LSC. Untreated control samples were taken to determine the microbial biomass at the start and the end of incubation.

For sampling the water was withdrawn from the test vessel using a glass pipette. The volume was recorded and aliquots of 1 mL were analysed by LSC to determine the radioactivity.
The sediment samples were exhaustively extracted using acetonitrile/water (4:1, v/v) up to two times (until less than 5 % of the radioactivity applied was recovered in a single extraction step) and Soxhlet extraction with acetonitrile/water (4:1, v/v) for at least four hours (not performed for sampling intervals 0 and 3 days). The amount of solvent used for each room temperature extraction step was 100 mL, and about 200 mL for Soxhlet extractions. Each room temperature extraction was performed on a shaker at approximately 250 revolutions per minute (rpm) for 30 minutes. The individual extracts

were centrifuged at approximately 1300 G for 10 minutes. The volume of individual extracts was recorded and the radioactivity quantified by LSC. Room temperature and Soxhlet extracts containing more than 2 % of the radioactivity applied were combined. The pooled extracts were concentrated under a stream of nitrogen, if needed, and analysed by LSC for recovery before chromatographic analysis.
Chromatographic analysis of water and sediment extracts was performed by TLC. HPLC was used as additional method for chromatographic analysis of selected samples. Furthermore, chiral HPLC analysis was performed to investigate a possible shift of the enantiomer ratio over time. The residual radioactivity in sediment after extraction was determined by combustion of aliquots of the air-dried and homogenised sediments in a sample oxidiser with subsequent LSC analysis.

The rate of degradation of ^{14}C-dimethenamid-P in the aquatic sediment system incubated under aerobic conditions was calculated according to FOCUS degradation kinetics guidance (2006) using the CAKE kinetic program V2.0. Dissipation and degradation rates to derive modelling endpoints according to level P-I were calculated using SFO kinetics. Calculations were performed for the water compartment ($DisT_{50}$ water), the sediment compartment ($DisT_{50}$ sediment) and the whole system (sum of water and sediment) $DegT_{50}$. Additionally, the RMS testes DFOP, FOMC and HS kinetics for the dissipation of dimethenamid-P from the water phase using the kinetic program KinGui, version 2.0.

Results and Discussion

The recovery of the applied radioactivity in the different compartments of the water/sediment system treated with ^{14}C-dimethenamid-P is presented in Table B.8.2.2-22.
The material balance in the test vessels was between 90.6 % and 96.1 % applied radioactivity (AR).

Table B.8.2.2-22: Recovery of the applied radioactivity in water/sediment system River Rhine treated with ^{14}C-dimethenamid-P (Values in percent of applied radioactivity, mean of two replicates)

DAT	water	sediment					volatiles		material balance
		extractable			NER	total	ethylene -glycole	NaOH (CO_2)	
		Room temp. extracts	Soxhlet extracts	total extractability					
0	93.9	1.5	n.p.	1.5	0.7	2.2	n.p.	n.p.	96.1
3	76.2	14.7	n.p.	14.7	4.9	19.5	<0.1	0.3	96.0
8	64.4	18.1	3.6	21.6	7.6	29.2	<0.1	1.5	95.2
14	58.2	17.0	5.1	22.0	12.4	34.4	<0.1	2.1	94.7
28	47.5	15.3	4.7	20.0	21.7	41.8	0.1	3.5	92.9
56	36.7	12.5	6.0	18.5	34.8	53.3	<0.1	3.6	93.6
77	35.5	11.3	5.3	16.6	36.2	52.8	<0.1	3.8	92.1
100	34.3	9.6	4.5	14.1	35.6	49.6	0.1	6.6	90.6

DAT = days after treatment
NER = non extractable residues
n.p. = not performed

The amount of radioactivity in the water decreased from 93.9 % at the beginning to 34.3 % AR after 100 days of incubation. The amount of radioactivity extracted from river sediments at room temperature increased over time from 1.5 % AR to a maximum of 18.1 % AR after 8 days of incubation. Thereafter, the amount slowly decreased and accounted for 9.6 % AR at the end of the incubation. The amount of radioactivity recovered by Soxhlet extraction varied between 3.6 % and 6.0 % AR. Non-extractable radioactivity increased over time from 0.7 % AR to 35.6 % AR at the end of incubation.
Mineralisation of ^{14}C-dimethenamid-P in the aquatic sediment system was rather slow. The amount of radioactivity in sodium hydroxide increased from 0.3 % AR at sampling day 3 to 6.6 % AR at day 100, and was identified as $^{14}CO_2$. Organic volatile products other than CO_2 did not exceed 0.1 % AR at

any sampling interval.

The distribution of dimethenamid-P and the identified metabolites in the water and the sediment extracts are presented in Table B.8.2.2-23 and Table B.8.2.2-24, respectively.

Table B.8.2.2-23: Distribution of ^{14}C-dimethenamid-P and its metabolites in the water of the water/sediment system (values in percent of applied radioactivity, mean of two replicates)

DAT	Dimethenamid-P	M656PH027	M656PH031	M656PH023	M656PH003
0	92.8	n.d.	n.d.	n.d.	n.d.
3	73.6	n.d.	0.4	0.6	0.5
8	58.7	n.d.	0.7	0.9	n.d.
14	51.1	n.d.	0.6	1.4	2.0
28	32.9	n.d.	1.0	4.0	2.6
56	17.3	2.5	1.4	5.4	5.7
77	8.1	4.8	1.9	8.5	4.6
100	5.4	6.3	2.2	9.6	4.0

DAT = days after treatment

Table B.8.2.2-24: Distribution of ^{14}C-dimethenamid-P and its metabolites in the sediment of the water/sediment system (values in percent of applied radioactivity, mean of two replicates)

DAT	Dimethenamid-P	M656PH027	M656PH031	M656PH023	M656PH003
0	1.5	n.d.	n.d.	n.d.	n.d.
3	13.9	n.d.	n.d.	0.1	0.4
8	18.1	n.d.	0.1	0.2	1.0
14	17.9	n.d.	0.1	0.4	1.4
28	12.7	n.d.	0.2	0.8	2.0
56	8.2	n.d.	n.d.	1.9	3.8
77	5.4	n.d.	n.d.	2.2	3.8
100	3.0	n.d.	0.1	1.8	3.1

DAT = days after treatment

^{14}C-dimethenamid-P was mainly present in the water phase. The amount of ^{14}C-dimethenamid-P decreased from 92.8 % AR (sampling day 0) to 5.4 % AR at the end of the incubation period (day 100). The amount of ^{14}C-dimethenamid-P in the sediment extracts increased from 1.5 % AR (day 0) to a maximum of 18.1 % AR (day 8), followed by a decrease to 3.0 % AR at the end of the experiment.
^{14}C-dimethenamid-P degraded overall into 15 radioactive fractions. The dimethenamid-P-metabolite M656PH027 (M656H027 in this study) reached a maximum of 6.3 % AR at the end of the experiment. The metabolite M656PH023 (M656H023 in this study) accounted for a maximum of 9.6 % AR at the end of the experiment. The metabolite M656PH003 reached a maximum of 5.6 % AR at day 56 with subsequent decline. The metabolite M656PH031 (M656H031 in this study) only accounted for 2.2 % at the end of the incubation. 12 additional radioactive fractions were detected in the water phase. All other radioactive fractions in the water phase never exceeded 4.1 % of AR and none of the radioactive fractions detected in the sediment extracts exceeded 3.8 % AR at any sampling interval.

The ratio between both types of enantiomers remained constant throughout the incubation time (the amount of R-enantiomer ranged between 5.3 and 6.4 %, while the amount of S-enantiomer ranged from 93.6 to 94.7 %).

The processed residues of ^{14}C-dimethenamid-P used for kinetic evaluation (P-I level) are given in Table B.8.2.2-25.

Table B.8.2.2-25: Processed ^{14}C-dimethenamid-P residues in water, sediment and whole system used for kinetic evaluation (values in percent of applied radioactivity)

Incubation time (day)	Parent (% AR)		
	Water	Sediment	Whole System
0	95.28*	-**	95.28*
0	96.97*	-**	96.97*
3	75.44	-**	88.06
3	71.8	-**	86.99
8	58.34	19	77.34
8	58.98	17.29	76.27
14	51.02	17.82	68.84
14	51.22	17.95	69.14
28	32.97	12.5	45.47
28	32.81	12.95	45.77
56	20.14	8.506	28.64
56	14.5	7.825	22.33
77	6.836	5.169	12.01
77	9.298	5.698	15
100	5.656	3.146	8.802
100	5.103	2.928	8.031

* total material balance
** kinetics were fitted to the decline of parent concentrations from the maximum onwards

The statistical results of the dissipation rates of dimethenamid-P from the water and the sediment phase and of the degradation rate of dimethenamid-P from whole water/sediment systems is summarised in Table B.8.2.2-26. The resulting visual fits are presented in Figure B.8.2.2-5.

Table B.8.2.2-26: Statistical and visual assessment of kinetic fits for dimethenamid-P in the water/sediment system River Rhine (Level P-I)

Compartment	Kinetic model	χ^2 error	p-value	Visual assessment	DT_{50} [d]	DT_{90} [d]
Water phase	SFO	9.25	k: <0.001	acceptable	19.5	64.9
Sediment phase	SFO	4.14	k: <0.001	good	38	126
Whole system	SFO	1.95	k: <0.001	good	28	93.1

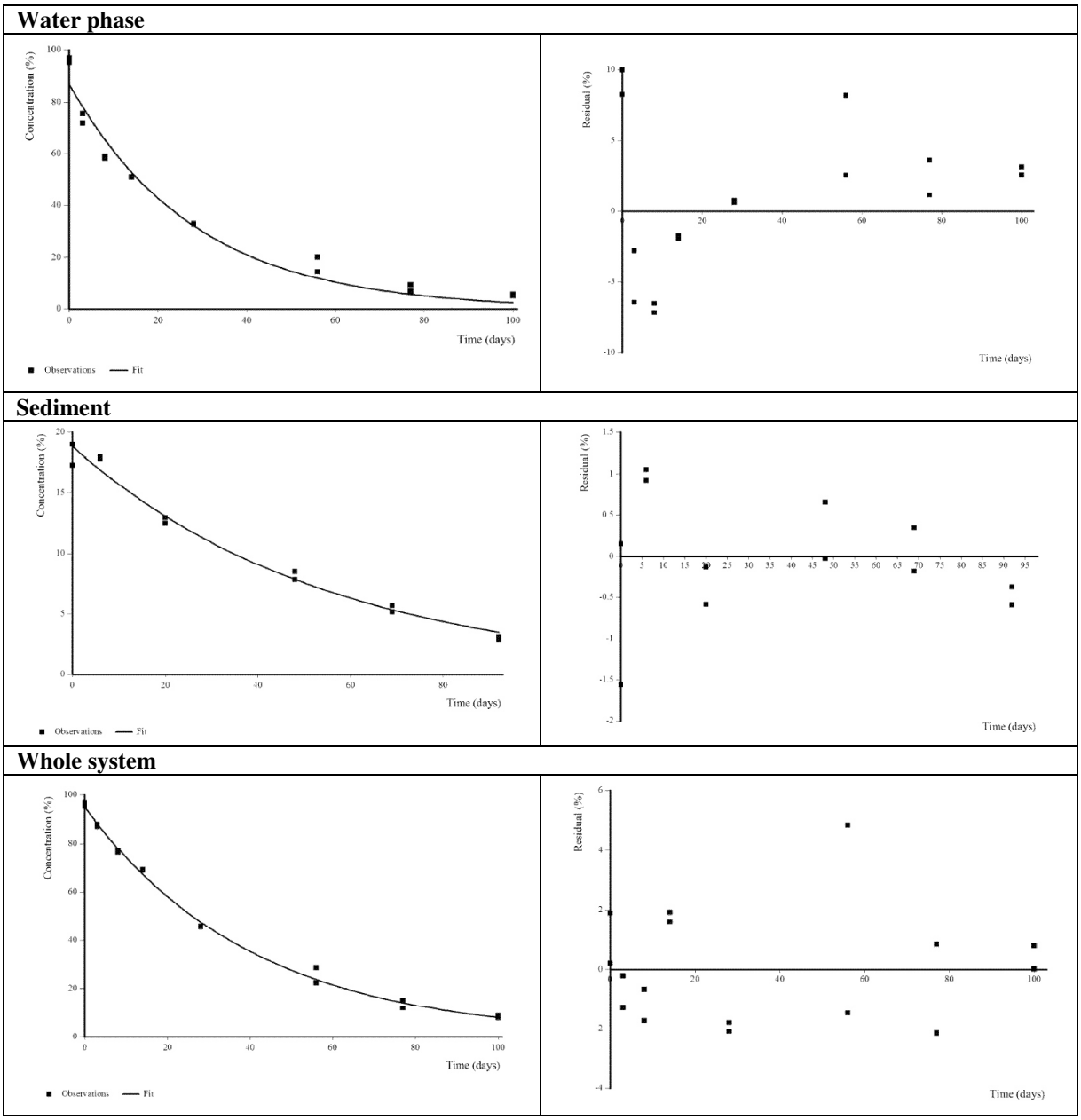


Figure B.8.2.2-5: Visual fit using SFO kinetics of dimethenamid-P in the water phase, the sediment phase and the whole system of the water sediment systems River Rhine

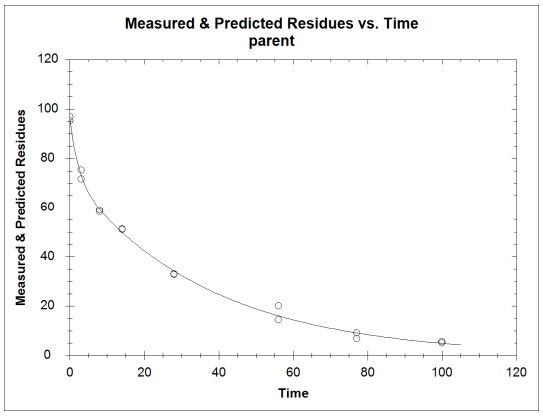
SFO described well the degradation of dimethenamid-P in the whole water/sediment system and the dissipation of dimethenamid-P from the sediment. However, the dissipation of dimethenamid-P from the water phase exhibited slightly biphasic behaviour. Thus, the RMS also tested FOMC, DFOP and HS kinetic fits for the dissipation of dimethenamid-P from the water. The statistical results are presented in Table B.8.2.2-27.

Table B.8.2.2-27: Statistical and visual assessment of biphasic kinetic fits to describe the dissipation of dimethenamid-P from the water phase (Level P-I, additional calculation by the RMS)

Compartment	Kinetic model	χ^2 error	p-value	Visual assessment	DT_{50} [d]	DT_{90} [d]
Water phase	DFOP	1.84	k: <0.001 k_{fast}: <0.001 k_{slow}:: <0.001 g: <0.001	Very good	15.36	74.99
	FOMC	6.22	k: <0.001 α: 0.001 β: 0.013	good	14.88	88.07
	HS	3.40	k: <0.001 k_{fast}: NA k_{slow}: <0.001 tb: NA	good	16.35	71.55

DFOP gave the statistically and visually fit to describe the dissipation of dimethenamid-P from the water phase. The visual fit for the DFOP fit is presented Figure B.8.2.2-6.

Water phase



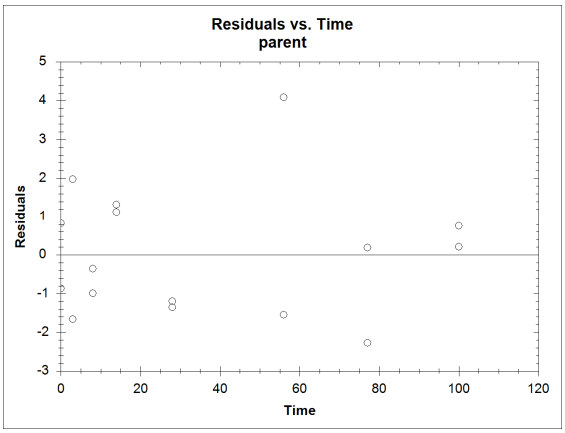


Figure B.8.2.2-6: Visual fit using DFOP kinetics of dimethenamid-P in the water phase of the water sediment systems River Rhine (additional calculation by the RMS)

The final results of P-I modelling for dimethenamid-P in the water/sediment systems River Rhine is summarised in Table B.8.2.2-28.

Table B.8.2.2-28: P-I level endpoints for dimethenamid for the River Rhine and the Pond Anwill water/ sediment systems

Whole system	**Trigger and modelling endpoints**		
	Kinetic model	**$DegT_{50}$**	**$DegT_{90}$**
River Rhine	SFO	28	93.1
Water compartment	**Trigger endpoints**		
	Kinetic model	**$DisT_{50}$**	**$DisT_{90}$**
River Rhine	DFOP	15.4	75
Sediment compartment	**Trigger endpoints**		
	Kinetic model	**$DisT_{50}$**	**$DisT_{90}$**
River Rhine	SFO	38	126

Conclusion

The study is considered acceptable by the RMS.
The fate and behaviour of dimethenamid-P was investigated in one water/sediment system River Rhine.
Dimethenamid-P degraded quickly to 8.4 % AR in the whole system after 100 d. Mineralisation accounted to 6.6 % while 35.6 % bound residues were formed. The maximum concentration of dimethenamid in the sediment was 18.1 % at day 8 with subsequent decline 3.03 % at the end of the study. The ratio between the R- and the S-entantiomer of dimethenamid-P remained constant throughout the study. Dimethenamid-P degraded in the whole water-sediment system following SFO kinetics with DT_{50} and DT_{90} values of 28 and 93.1 d, respectively. Dissipation from the water phase followed DFOP kinetics with DT_{50} and DT_{90} values of 15.4 and 75 d, respectively. Dissipation from the sediment phase followed SFO kinetics again with DT_{50} and DT_{90} values of 38 and 126 d, respectively.

Dimethenamid-P degraded overall into 15 radioactive fractions, however only three metabolites exceed concentrations of 5 % AR in the water phase: M656PH023 was formed with maximum concentrations of 8.5 and 9.6 % at day 77 and 100, M656PH027 amounted to 6.3 % at day 100 and M656PH003 reached a maximum of 5.7 % at day 56 with subsequent decline.

B.8.2.3 Degradation in the saturated zone

No study on the degradation of dimethenamid-P in the saturated zone was submitted.

B.8.3 Fate and behaviour in air

The photochemical oxidation of dimethenamid in air was estimated in one study submitted already for first EU Annex I inclusion:

- Scharf, 1999.

The volatilisation of dimethenamid in the formulated product ‘Frontier’ (EC formulation) from plants and soil was investigated in two laboratory studies submitted for first EU Annex I inclusion:

- Chen & Hsieh, 1993
- Jonas, 1994.

Since for the renewal of the EU-approval of dimethenamid-P two new formulations were used, a new study of the volatilisation of dimethenamid-P in the formulation BAS 656 12 H was submitted:

- Hassink, 2013.

Besides, two additional studies with the formulations BAS 656 12 H and BAS 830 01 H investigating the dissipation half life of dimethenamid-P in corn and oilseed rape were submitted for the renewal of the EU-approval of dimethenamid-P:

- Friedemann & Teresiak, 2014a & b.

A search for open literature which included papers in peer-reviewed journals and reports from government and other agencies in the EU and several other countries was performed by the applicant. The literature search strategy of the applicant is decribed in more detail in the Appendix of this document.
No additional open-literature studies concerning the fate of dimethenamid-P in air were found.

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

B.8.3.1 Route and rate of degradation in air

KCA 7.3.1/1 – Scharf, 1999 (study evaluated in the monograph, 2000)

Author:	Scharf, J.
Title:	Photochemical Oxidative Degradation of Dimethenamid (QSAR Estimates)
Date:	10/03/1999
Doc ID:	BASF Reg-Doc.# 99/10075
Guidelines:	none
GLP:	No (not applicable)
Validity:	Acceptable

Material and Methods

The rate constant for reactions of dimethenamid with OH radicals (photochemical oxidative degradation) in the atmosphere was calculated using the AOP program, Version 1.88 according to Atkinson's increment method (Atkinson, 1987).
The rate constant k_{OH} for the reaction of the active substance with OH radicals was estimated based on the chemical structure to be 52.336 10^{-12} cm^3 $molecule^{-1}$ s^{-1}. Assuming a stationary steady-state (and thus constant) concentration of OH-radicals in the troposphere, the degradation of the active substance follows a pseudo-first order kinetic with the rate constant $k` = k_{OH}$ [OH radicals].

Results and Discussion

Assuming an average concentration of tropospheric hydroxyl radicals of 1.5 10^6 cm^{-3}, the half-life for the degradation of dimethenamid by hydroxyl radicals is calculated to be 2.45 h (= 0.2 d) for a 12 h day.

Conclusion

Repeating the calculations with a more actual AOP model version led to the same results for dimethenamid-P. The study is thus considered acceptable by the RMS.
The estimated atmospheric lifetime of dimethenamid-P in the athmosphere is 0.2 d for a 12 h day and a OH radicals concentration of 1.5 10^6 cm^{-3}.

B.8.3.2 Transport via air

KCA 7.3.2/1– Chen & Hsieh, 1993 (study evaluated in the monograph, 2000)

Author:	Chen, H. Hsieh, T.
Title:	Laboratory volatility study of SAN 582 H 900 EC 408 DP
Date:	18/03/1994
Doc ID:	ASF Reg-Doc.# 93/11472
Guidelines:	Canadian Trade Memorandum T-1-255
GLP:	Yes
Validity:	Not acceptable anymore

Material and Methods

The volatilisation from sterile soil was investigated with dimethenamid in the formulated product 'Frontier' prepared as a mixture of ^{14}C-dimethenamid (purity ≥ 98 %) and EC formulation of the unlabelled active substance. Volatility of dimethenamid from Canadian (Ontario) soil at 25 ± 1 °C was measured in the laboratory following simulated preplant soil incorporation ("PPI") as well as spray ("topical") application on the soil surface. ^{14}C-Dimethenamid was applied to sterile loam soil with organic matter content of 2.7 %. The concentration of dimethenamid was equivalent to a

dimethenamid application of 1.1 to 1.2 kg/ha. Effluent air from the volatilisation chambers was washed in solutions of ethylene glycol and then NaOH. Samples were collected at 2, 6, 24, and 48 hours and at 7, 14, 21, and 30 days. Both ethylene glycol trap solutions and soil extracts were analysed by GC-MS.

Results and Discussion

Total recoveries ranged from 92.7 to 104.1 % AR and from 95.7 to 101 % AR for PPI and topical application, respectively. Only 0.84 % AR, PPI mode of application, volatilised over a period of 30 days. Nearly 1.18 % AR did so in the topical mode of application over the same period of time.
According to the GC-MS analysis the recovered radioactivity from the ethylene glycol traps can be attributed to the parent compound dimethenamid. Dimethenamid volatilisation rates after 24 h were calculated to reach a maximum value of 0.82 10^{-4} and 5.26 10^{-4} µg cm^{-2} h in the PPI and topical experiments, respectively. On or about the 30th day after application rates of 0.45 · 10^{-4} and 1.57 · 10^{-4} µg/cm^2/h were estimated. Calculated vapour concentrations of dimethenamid varied from highs of 1.63 and 10.29 µg m^{-3} reached after 24 hours to concentrations of 0.92 and 3.07 µg m^{-3} reached on or about the 30th day in the PPI and topical modes of application, respectively (see Table B.8.3.2-1 and Table B.8.3.2-2).

Table B.8.3.2-1: Calculated rates of volatilisation and vapour concentrations following a pre-plant incorporated (PPI) application of [^{14}C]-dimethenamid in the formulation 'Frontier'

Time	Rate of volatilisation		Vapor Concentration	
	Dimethenamid	CO_2	Dimethenamid	CO_2
	10^{-4} µg cm^{-2} h^{-1}		µg m^{-3}	
2 hours	0.36	6.55	0.71	12.96
6 hours	0.58	4.32	1.11	8.53
24 hours	0.82	3.74	1.63	7.43
48 hours	0.68	3.12	1.35	6.19
7 day	0.45	1.32	0.94	2.74
14 day	0.43	0.63	0.87	1.28
21 day	0.45	0.52	0.99	1.15
30 day	0.45	0.33	0.92	0.71

Table B.8.3.2-2: Calculated rates of volatilisation and vapour concentrations following a topical application of [^{14}C]-dimethenamid in the formulation 'Frontier'

Time	Rate of volatilisation		Vapor Concentration	
	Dimethenamid	CO_2	Dimethenamid	CO_2
	10^{-4} µg cm^{-2} h^{-1}		µg m^{-3}	
2 hours	0.36	6.55	0.71	12.96
6 hours	0.58	4.32	1.11	8.53
24 hours	0.82	3.74	1.63	7.43
48 hours	0.68	3.12	1.35	6.19
7 day	0.45	1.32	0.94	2.74
14 day	0.43	0.63	0.87	1.28
21 day	0.45	0.52	0.99	1.15
30 day	0.45	0.33	0.92	0.71

Conclusion

The study was considered acceptable as additional information for the first Annex I inclusion of dimethenamid-P. However, since it was performed with a different formulation than the current representative formulations BAS 656 12H and BAS 830 01H and the influence of the different formulations on the volatilisation of dimethenamid-P is not known, it is not considered acceptable

anymore. Besides, it was performed with racemic dimethenamid and not with dimethenamid-P.

KCA 7.3.2/2– Jonas, 1994 (study evaluated in the monograph, 2000)

Author:	Jonas, W.
Title:	Evaporation behaviour from soil and plants (large-scale model chamber) test product: frontier (SAN 582 H 900 EC 408 DP) test substance: [3-^{14}C-thienyl] dimethenamid
Date:	21/09/1994
Doc ID:	BASF Reg-Doc.# 94/10642
Guidelines:	BBA Guideline, Part IV 6-1
GLP:	Yes
Validity:	Not acceptable anymore

Material and Methods

The volatilisation from soil and plants was investigated with dimethenamid in the formulated product 'Frontier' (EC formulation) prepared as a mixture of 3-^{14}C-thienyl dimethenamid (purity 99.8 %), dimethenamid (purity 99.8 %) and blank formulation. To evaluate evaporation from soil, dimethenamid was applied at a dose of 51.0 mg as/0.42 m^2 (corresponding to an application rate of 1.21 kg as/ha) on German BBA standard soil 2.1 (soil humidity: 57 % of maximum capacity). Evaporation from plants was determined by applying 32.6 mg active substance on 14 bean plants distributed on an area of 0.28 m^2 (corresponding to an application rate of 1.16 kg as/ha, entirely deposited on the plant surfaces).
The volatilisation experiment was performed in a model chamber in the dark with a wind velocity of 1-2 m/s (flow rate of air 32 L/min corresponding to approx. 6 volume exchanges/h), 40 % relative air humidity. The temperature was kept at 21 °C (soil volatilisation) and 24 °C (plant volatilisation), respectively.
The air was sucked through a sampling unit consisting of a condenser for collection of humidity, an active charcoal filter for the collection of organic substances and a CO_2 trap (KOH). The air sampling was made after periods of 1, 3, 6 and 24 h. After 24 h the test substance was extracted from the soil or plants, respectively, and the amount of test substance on the inner surfaces of the test system was determined in order to obtain a mass balance. In order to assess the stability of the active substance the following samples were analysed using TLC and HPLC: soil extract, plant extract, combined condensate samples.

Results and Discussion

Total recoveries were 94.1 % AR and 96.1 % AR for volatilisation from soil and plants, respectively. 87.46 % AR and 81.95 % AR could be extracted from the soil and plants, respectively. No significant degradation of the test substance was observed during the study. The total recovered volatilised radioactivity amounted to 6.6 % AR (soil) and 14.1 % AR (plants). Results are summarised in Table B.8.3.2-3and Table B.8.3.2-4.

Table B.8.3.2-3: Recovery of ^{14}C radioactivity in different samples collected after volatilisation of dimethenamid from soil

Sample	Collected amounts % AR				
	0-1 hour	1-3 hours	3-6 hours	6-24 hours	Total
Condensate water	0.39	0.70	0.89	2.97	4.95
Activated charcoal	0.01	0.02	0.03	0.57	0.62
KOH	0.00	0.00	0.00	0.01	0.02
Chamber-wash					1.04
Total volatiles					6.63
Soil (mean of 4 samples)					87.46
Total					94.09

Table B.8.3.2-4: Recovery of ^{14}C radioactivity in different samples collected after volatilisation of dimethenamid from plants

Sample	Collected amounts % AR				
	0-1 hour	1-3 hours	3-6 hours	6-24 hours	Total
Condensate water	1.00	2.71	3.55	5.75	13.01
Activated charcoal	0.02	0.08	0.09	0.29	0.48
KOH	0.00	0.00	0.00	0.00	0.00
Chamber-wash					0.63
Total volatiles					14.12
Plants					81.95
Total					96.07

Conclusion

The study was considered acceptable for the first Annex I inclusion of dimethenamid-P. However, since it was performed with a different formulation than the actual representative formulations BAS 656 12H and BAS 830 01H and the influence of the different formulations on the volatilisation of dimethenamid-P is not known, it is not considered acceptable anymore. Besides, it was performed with racemic dimethenamid and not with dimethenamid-P.

KCA 7.3.2/3– Hassink, 2013 (new study)

Author: Hassink, J..
Title: Volatilisation of dimethenamid-P after application of BAS 656 12 H on soil and plant surfaces
Date: 25/03/2013
Doc ID: BASF DocID 2012/1282998
Guidelines: BBA Guideline, Part IV 6-1
GLP: Yes
Validity: Acceptable

Material and Methods

The volatilisation behaviour of [thienyl-5-^{14}C]-dimethenamid-P (purity 99 %) was investigated after application of the EC formulation BAS 656 12 H to soil and bush beans.

Based on a field application rate of 864 g BAS 656 12 H /ha and a treated area of 113 cm^2, the plant was treated with about 1212 µg and the soil was treated with about 1261 µg dimethenamid-P. The formulation BAS 656 12 H was spiked with about 0.8 % labelled dimethenamid-P, thus resulting in a total application rate of about 1072 g (plant trial) and 1115 g (soil trial) dimethenamid-P/ ha.

The soil and the plant were treated in a closed application chamber made of glass. The formulation was applied via a spray nozzle (1.2 bar) to the plant and to the soil.
For determination of volatilisation from the plant surface, a bush bean, planted in a soil-containing glass tray was used for the experiment. The soil was covered during application and application losses were determined by rinsing the glass container and all equipment with acetonitrile and subsequent analysis of the rinsate.
For determination of volatilisation from the soil surface, the soil (LUFA 5M) was adjusted to 60 % of the maximum water holding capacity (MWC). The soil characteristics (USDA: sandy loam) were: 58.8 % sand, 28.9 % silt, 12.2 % clay, organic carbon 1.99 %, pH 7.2, maximum water holding capacity 28.9 g/100 g dry soil. Moisture losses were compensated for, and evaporation of water from the soil surface led to an average air humidity of 60 %.
After application, the plant and/or the soil were removed from the application chamber and transferred directly to the circulation chamber which allowed the air exchange rate (200 L/h) and the temperature (20 - 21 °C) of the air to be controlled. The wind speed was adjusted to 1 m/s. In the plant experiment

the timer of the lamp was set to 12 h light, 9 h dark, and 3 h light during the testing period of 72 h. Volatiles were captured in charcoal traps, which were replaced and sampled 1, 3, 6, and 24 h after application. At the same intervals the cryo-traps and the CO_2 traps were exchanged and sampled. At the end of the experiment, the remaining radioactivity in soil and plant (parts of the plant above the soil surface) was determined. Furthermore, the equipment (chamber, tubes, fans) was rinsed and the solutions analysed.
The plant parts above the soil surface were macerated and extracted sequentially with acetonitrile, acetonitrile/water (1/1) and water. The extracts were combined and the radioactivity in the extracts was measured by liquid scintillation counting (LSC). The soil was treated in the same way. The remaining plant or soil material was combusted and also measured by LSC.
All traps were collected and analysed by direct LSC measurement and/or combustion.

The volatilisation rate was calculated in three ways:

1) the sum of the amount of active substance detected in the charcoal traps and the equipment wash (and for the plant experiment: the amount of a.s. in the soil) were defined as the volatile part. This value was related to the total amount of a.s. applied to the test system (= TAS, 'direct measurement)
2) the item in the test system (i.e. either sum of plant extract and plant residues or sum of soil extract and soil residue) plus the a.s. equivalents in the CO_2 traps were defined as the non-volatile part. The difference of this value to the amount applied to the test system was related to the total amount of a.s. applied to the test system. (= RAS, 'indirect' measurement)
3) the non-volatile part was calculated as RAS, but corrected with the recovery of the volatilisation experiment. (= RRV, 'indirect' measurement)

Recovery rates were calculated both for the complete experiment (all solutions, extracts, combusted samples vs. amount of dimethenamid-P in application system) and for the respective volatilisation experiment (traps at every sampling time, circulation chamber wash and test system after 24 h vs substance on the test system after deduction of application losses).

Results and Discussion

The volatilisation rate of BAS 656 H after application of EC formulation BAS 656 12 H to plants is significant with values from 17.5 % to 26.1 % after 24 h depending on the applied calculation. From soil, the volatilisation rate of BAS 656 H is significantly reduced to 2.8-5.3 % since adsorption to soil particles can be expected. The obtained recoveries and volatilisation rates are shown in Table B.8.3.2-5.

Table B.8.3.2-5: Recovery of radioactivity in % of dimethenamid-P during plant and soil experiment

Matrix	Recovery Rates [%]		Volatilisation Rate [%]		
	Complete experiment	Volatilisation experiment	TAS	RAS*	RRV*
Plant	97.4	91.4	17.5	26.1	19.1
Soil	100.6	102.5	5.3	2.8	5.2

* Indirect measurement, i.e. including eventual degradation and/or adsorption processes

Conclusion

According to BBA IV 6-1, the soil used in the study should contain at least 70 % sand and a maximum of 1.5 % oc, which is not the case for the soil used in the study. Thus, only the results for the plants are considered acceptable by the RMS.
The volatilisation potential of EC formulation BAS 656 12 H spiked with ^{14}C-dimethenamid-P from plants is significant with values from 17.5 % to 26.1 %.

KCA 7.3.2/4 – Friedemann & Teresiak, 2014a (new study)

Author:	Friedemann, A. Teresiak, H.
Title:	Amended report - Determination of dislodgeable foliar residues of dimethenamid-P (BAS 656 H) and determination of foliar DT_{50} after application of BAS 656 12 H to corn, 2013
Date:	21/01/2014
Doc ID:	BASF DocID 2014/1036905
Guidelines:	OPPTS 875.2100 (US EPA, February 1996) Guidance for the determination of dislodgeable foliar residue (Feb 2002)
GLP:	Yes
Validity:	Not acceptable for the use as modelling endpoint in environmental fate modelling

Material and Methods

The objective of this study was to determine the magnitude of dislodgeable foliar residues of dimethenamid-P resulting from a single application of BAS 656 12 H to corn.
As test item, the formulation BAS 656 12 H (batch no 0004701751, 720 g/L (nominal concentration) and 707.8 g/L (analysed concentration) dimethenamid-P) was used.
The test system consisted of corn plants (*Zea mays L.*) grown and maintained in plastic pots (12 cm in diameter) with commercial potting mixture (Floradur) in the greenhouse. The seeds were sown on 21st August 2013. At application the corn plants were at BBCH 17-18 and approximately 86 cm high on average. The plant density was one plant per pot. The total number of pots used in the test is given in Table B.8.3.2-6.

Table B.8.3.2-6: Treatment regime

Treatment description	Plot	Purpose	Number of pots	Plant pot IDs
Untreated	1	Control specimens	5	Plot 1
Treated	2	Treated specimens	61	Plot 2
Untreated	3	Field fortifications	20	Plot 3

After application the plants were cultivated in a in a greenhouse at defined environmental conditions (daily mean air temperature ranged between 17.9 and 20.5 °C, extremes 13 °C and 25 °C , daily mean relative humidity ranged from 68.9 to 79.3 %, extremes 45 % and 91 %) where they remained until the last sampling day.

Two fortification solutions at different concentrations containing dimethenamid-P as outlined in Table B.8.3.2-7 were prepared at the analytical test site and subsequently sent to agro - check on dry ice. The fortification experiments with dimethenamid-P were performed at day 0 before application of test item. To prepare the fortification samples the same routine in washing corn plant discs was used as described below.

Table B.8.3.2-7: Fortification samples

Matrix	DFR Dislodging Solution [mL]	No. of Repl.	LOQ (proposed) [µg/L]	Fortification Level	Fortification solution [mL]	Conc. of solution [µg/mL]
Fortification Control	20	1	5	control	-	-
Fortification Low	20	3	5	10 x LOQ	0.5	2
Fortification High	20	3	5	1000 x LOQ	0.5	200

A total of 61 plant pots were treated with an application rate of 1.060 L/ha BAS 656 12 H (88 % of the intended 1.2 L/ha), equivalent to 763 g/ha dimethenamid-P on the 07th of October 2013 via spray application.
For each sampling event 20 leaf discs (200 cm^2; both leaf sides) were collected randomly from the 5th

and 6th leaf which were not covered by other leaves at application time using a leaf puncher (1 inch in diameter). The leaf discs were collected directly into a pre-labelled wide mouth jar (Nalgene®, PC, 125 mL) and subsequently transferred at ambient temperature to the agro-check laboratory for weighing and dislodging procedure.
The leaf discs of untreated plants (S1, control and field fortification specimens) were sampled before application.
Within two hours after application once the spray deposit had fully dried, the sampling S2 was performed for plot 2. The sampling S3, S4, S5, S6 and S7 were performed 6 h, 24 h, 48 h, 4 d and 7 days after application. At sampling events S2 to S7 the leaf discs were randomly sampled from 10 treated plants each as described above. Five x 20 leaf discs were sampled per sampling point S2 to S7 plus 1 x 20 leaf discs for the control and 7 x 20 leave discs for the field fortifications.

For the leaf dislodging procedure, 20 leaf discs of one specimen were used. 100 mL of the dislodging solution (Water / Aerosol OT-B (0.01 %)) was added and the pre-labelled wide mouth jar containing the leaf discs was subsequently transferred to a reciprocating shaker. The jars were shaken at shaking level 2 for a period of 10 minutes. The dislodging solution was then decanted into a beaker and the jar with the leaf discs was subjected to a second dislodging process with another 100 mL of fresh dislodging solution (level 2, 10 minutes). The two dislodging solutions were pooled in the beaker and thoroughly mixed.

For determination of the Foliar DT_{50} and DT_{90} values for dimethenamid-P on corn leaves, the software program KinGUI, version 2.2 was used applying the SFO model.

Results and Discussion

The analytical results of the fortifications presented in Table B.8.3.2-8 show that frozen storage and transport did not influence the analytical results of this study.

Table B.8.3.2-8: Summarised results of the field fortification experiments with dimethenamid-P

Fortification levels	Recovery range (%)	Mean recovery ± RSD (%)
10 x LOQ 1000 x LOQ	70.1 – 95.5	86.6 ± 13 (n=6)

An overview on the dislodgeable dimethenamid concentrations from the plant leaves is given in Table B.8.3.2-9.

Table B.8.3.2-9: Dimethenamid in dislodging solution (summarised results)

Matrix	Time after application	Mean concentration of dimethenamid-P		
		[mg/specimen]*	[µg/cm²]	[mg/g leaf]
Mean	Control[1]	0.000	0.000	0.00
Mean	0 - 2 h	0.465	2.323	0.212
RSD		11.8 % (n=5)	11.8 % (n=5)	14.1 % (n=5)
Mean	6 h	0.285	1.427	0.136
RSD		11.1 % (n=5)	11.1 % (n=5)	11.3 % (n=5)
Mean	24 h	0.059	0.296	0.028
RSD		12.5 % (n=5)	12.5 % (n=5)	14.5 % (n=5)
Mean	48 h	0.009	0.046	0.004
RSD		24.7 % (n=5)	24.7 % (n=5)	23.4 % (n=5)
Mean	4 d	< LOQ	--	--
RSD		--	--	--
Mean	7 d	< LOQ	--	--
RSD		--	--	--

* specimen = 200mL dislodging solution of 20 leaf discs
1 before application
< LOQ: below limit of quantitation of 0.001 mg/specimen

Foliar DT_{50} and DT_{90} values were estimated from residue measurements of dimethenamid-P on the leaf surfaces of corn applying a SFO kinetic model. The results of the statistical and visual assessment are presented in Table B.8.3.2-10.

Table B.8.3.2-10: Statistical and visual assessment using a SFO kinetic model and the resulting foliar DT_{50} and DT_{90} values for dimethenamid-P on corn leaves

Kinetic model	χ^2 error (%)	type I error rate (Prob. > t)	Visual fit	$DisT_{50}$ [d]	$DisT_{90}$ [d]
SFO	2.86	k: < 0.001	excellent	0.36	1.21

Dimethenamid-P dissipates rapidly from the leaves with a DT_{50} of 0.36 days and a DT_{90} value of 1.21 days.

Conclusion

The study Friedemann & Teresiak, 2014a was performed according to the cited guidance documents. However, as stated in both guidance documents, their purpose is the exposure assessment of field worker to dislodgeable residues from plant surface, not the derivation of suitable endpoints for environmental fate modelling. A study that represents worst case conditions for field workers by aiming for maximum evaporation of active substance from the plant surfaces into the atmosphere will most likely represent a best case for the dissipation half life of the respective active substance on the plant surface. In the opinion of the RMS, the study has several shortcomings listed in the following that make the derived endpoints unsuitable for environmental fate modelling of dimethenamid-P:
First, detailed records on temperature and humidity are missing from the study report. The influence of the temperature on the half-life on plant surfaces is not implemented in FOCUS surface water. The influence of the air humidity on volatility from plant surfaces is not known and thus also not implemented in FOCUS surface water. Open literature studies that investigated the influence of air humidity on the volatilisation of different pesticides from soil surfaces showed an increase of volatilisation for an increase in air humidity (Igue et al, 1972, Grass et al, 1994, Schneider et al, 2013). This might also be the case for the volatilisation from plant surfaces and would need to be implemented in the FOCUS surface water. Under the greenhouse conditions of this study, a high temperature and air humidity in comparison to open field conditions is expected. Since the influence

of temperature, light and humidity on the half-life on plant surfaces are not implemented into the FOCUS SW model, we believe that the half-life should be obtained under worst case conditions. These will need to be defined before conducting an acceptable study.
Finally, dimethenamid-P is also subject to photodegradation from soil surfaces and thus most likely also from plant surfaces. The light regime in the greenhouse was not recorded and the effect of photodegradation on the derived foliar $DisT_{50}$ value cannot be quantified. Since the influence of light on the half life on plant surfaces is also not implemented in FOCUS SW, we believe that the study should have been conducted in the dark to represent worst case conditions.

KCA 7.3.2/5 – Friedemann & Teresiak, 2014b (new study)

Author:	Friedemann, A. Teresiak, H.
Title:	Amended report - Determination of dislogdeable foliar residues of dimethenamid-P (BAS 656 H) and determination of foliar DT_{50} after application of BAS 830 01 H to oilseed rape, 2013
Date:	21/01/2014
Doc ID:	BASF DocID 2014/1036906
Guidelines:	OPPTS 875.2100 (US EPA, February 1996) Guidance for the determination of dislodgeable foliar residue (Feb 2002)
GLP:	Yes
Validity:	Not acceptable for the use as modelling endpoint in environmental fate modelling

Material and Methods

The objective of this study was to determine the magnitude of dislodgeable foliar residues of dimethenamid-P resulting from a single application of BAS 830 01 H to oilseed rape.
As test item, the formulation BAS 830 01 H (batch no 451008, 333.0 g/L dimethenamid-P + 167 g/L quinmerac (nominal concentration) and 347.7 g/L dimethenamid-P + 173. g/L quinmerac (analysed concentration)) was used.
The test system consisted of oilseed rape plants (*Brassica napus L.*) grown and maintained in plastic pots (10.5 cm in diameter) with commercial potting mixture (Floradur) in the greenhouse. The seeds were sown on 21st August 2013. At application the oilseed rape plants were at BBCH 16 and approximately 23-32 cm high on average. The plant density was two plants per pot. The total number of pots used in the test is given in Table B.8.3.2-11.

Table B.8.3.2-11: Treatment regime

Treatment description	Plot	Purpose	Number of pots	Plant pot IDs
Untreated	1	Control specimens	20	Plot 1
Treated	2	Treated specimens	101	Plot 2
Untreated	3	Field fortifications	20	Plot 3

Irrigation was added to the bottom of the pots when necessary using tap water. Plants were fertilised with Hakaphos blau in accordance to good agricultural praxis for the time of cultivation. Two days before application Folicur (1 L/ha) was applied. After application the plants were cultivated in a greenhouse at defined environmental conditions (daily mean air temperature ranged between 16.0 and 19.1 °C, extremes 12 °C and 25 °C , daily mean relative humidity ranged from 63.9 to 76.8 %, extremes 46 % and 92 %, where they remained until the last sampling day.

Two fortification solutions at different concentrations containing dimethenamid-P as outlined in Table B.8.3.2-12 were prepared at the analytical test site and subsequently sent to agro - check on dry ice. The fortification experiments with dimethenamid-P were performed at day 0 before application of test item. To prepare the fortification samples the same routine in washing oilseed rape plant discs was used as described below.

Table B.8.3.2-12: Fortification samples

Matrix	DFR Dislodging Solution [mL]	No. of Repl.	LOQ (proposed) [µg/L]	Fortification Level	Fortification solution [mL]	Conc. of solution [µg/mL]
Fortification Control	20	1	5	control	-	-
Fortification Low	20	3	5	10 x LOQ	0.5	2
Fortification High	20	3	5	1000 x LOQ	0.5	200

A total of 101 plant pots were treated with an application rate of 1.5 L/ha BAS 830 01 H, equivalent to 500 g/ha dimethenamid-P and 250 g/ha quinmerac on the 14th of October 2013 via spray application.
For each sampling event 20 leaf discs (200 cm^2; both leaf sides) were collected randomly from the 5th and 6th leaf which were not covered by other leaves at application time using a leaf puncher (1 inch in diameter). Covered leaves were avoided. Vertical standing leaves at application were marked and not used for sampling due to the possibility of extensive runoff. The leaf discs were collected directly into a pre-labelled wide mouth jar (Nalgene®, PC, 125 mL) and subsequently transferred at ambient temperature to the agro-check laboratory for weighing and dislodging procedure.
The leaf discs of untreated plants (S1, control and field fortification specimens) were sampled before application.
Within two hours after application once the spray deposit had fully dried, the sampling S2 was performed for plot 2. The sampling S3, S4, S5, S6 and S7 were performed 6 h, 24 h, 48 h, 4 d and 7 days after application. Five x 20 leaf discs were sampled per sampling point S2 to S7 plus 1 x 20 leaf discs for the control and 7 x 20 leave discs for the field fortifications.

For the leaf dislodging procedure, 20 leaf discs of one specimen were used. 100 mL of the dislodging solution (Water / Aerosol OT-B (0.01 %)) was added and the pre-labelled wide mouth jar containing the leaf discs was subsequently transferred to a reciprocating shaker. The jars were shaken at shaking level 2 for a period of 10 minutes. The dislodging solution was then decanted into a beaker and the jar with the leaf discs was subjected to a second dislodging process with another 100 mL of fresh dislodging solution (level 2, 10 minutes). The two dislodging solutions were pooled in the beaker and thoroughly mixed.

For determination of the foliar DT_{50} and DT_{90} values for dimethenamid-P on oilseed rape leaves, the software program KinGUI, version 2.2 was used applying the SFO model.

Results and Discussion

The analytical results of the fortifications presented in Table B.8.3.2-13 show that frozen storage and transport did not influence the analytical results of this study.

Table B.8.3.2-13 Summarised results of the field fortification experiments with dimethenamid-P

Fortification levels	Recovery range (%)	Mean recovery ± RSD (%)
10 x LOQ 1000 x LOQ	94.6 – 116.4	105.8 ± 7 (n=6)

An overview on the dislodgeable dimethenamid concentrations from the plant leaves is given in Table B.8.3.2-14.

Table B.8.3.2-14: Dimethenamid in dislodging solution (summarised results)

Matrix	Time after application	Mean concentration of dimethenamid-P		
		[mg/specimen]*	[µg/cm²]	[mg/g leaf]
Mean	Control[1]	0.000	0.000	0.00
Mean	0 - 2 h	0.289	1.446	0.137
RSD		4.7 % (n=5)	4.7 % (n=5)	7.6 % (n=5)
Mean	6 h	0.086	0.432	0.040
RSD		15.7 % (n=5)	15.7 % (n=5)	14.6 % (n=5)
Mean	24 h	0.002	0.012	0.001
RSD		38.4 % (n=5)	38.4 % (n=5)	34.3 % (n=5)
Mean	48 h	0.001	0.005	0.000
RSD		11.8 % (n=5)	11.8 % (n=5)	12.0 % (n=5)
Mean	4 d	< LOQ	--	--
RSD		--	--	--
Mean	7 d	< LOQ	--	--
RSD		--	--	--

* specimen = 200 mL dislodging solution of 20 leaf discs
1 before application
< LOQ: below limit of quantitation of 0.001 mg/specimen

Foliar DT_{50} and DT_{90} values were estimated from residue measurements of dimethenamid-P on the leaf surfaces of oilseed rape applying a SFO kinetic model. The results of the statistical and visual assessment are presented in Table B.8.3.2-15.

Table B.8.3.2-15: Statistical and visual assessment using a SFO kinetic model and the resulting foliar DT_{50} and DT_{90} values for dimethenamid-P on leaves of oilseed rape

Kinetic model	χ^2 error (%)	type I error rate (Prob. > t)	Visual fit	$DisT_{50}$ [d]	$DisT_{90}$ [d]
SFO	0.30	k: < 0.001	excellent	0.14	0.47

Dimethenamid-P dissipates rapidly from the leaves with a DT_{50} of 0.14 days and a DT_{90} value of 0.47 days.

Conclusion

The study Friedemann & Teresiak, 2014b was performed according to the cited guidance documents. However, as stated in both guidance documents, their purpose is the exposure assessment of field worker to dislodgeable residues from plant surface, not the derivation of suitable endpoints for environmental fate modelling. The RMS considers the study unsuitable for environmental fate modelling of dimethenamid-P for reasons listed under the conclusion to Friedemann & Teresiak, 2014a.

B.8.3.3 Local and global effects

No study on the local and global effects of dimethenamid-P or its metabolites was submitted.

B.8.4 Monitoring data concerning fate and behaviour of the active substance,

metabolites, degradation and reaction products

Several monitoring studies including papers from peer-reviewed journals and reports found in the open literature search were submitted for EU approval.

Eight studies on groundwater monitoring of the metabolites M656PH003, M656PH010, M656PH023, M656PH027, M656PH031, M656PH032, M656PH043, M656PH045, M656PH047 and M656PH054 were submitted for EU approval.

In three studies the procedure and sampling of a groundwater monitoring program in Germany was described:

- Schmidt et al (2010)
- Schmidt & Schulz, 2012
- Schmidt & Schneider, 2013.

The analytical results of the groundwater samples for the metabolites of dimethenamid-P are presented in two additional studies:

- Class (2013)
- Mewis (2014a).

In one additional study the validity of the German groundwater monitoring study was assessed and the validity of the monitoring for the agricultural areas in Europe were assessed using spatially distributed modelling

- Haering & Miles, 2014.

Besides, one study describing the results of a groundwater monitoring campaign of the metabolites M656PH003, M656PH010, M656PH023, M656PH027, M656PH031, M656PH032, M656PH043, M656PH045, M656PH047 and M656PH054 in the Netherlands was submitted:

- Mewis, 2014b.

One published study found in the open literature search on groundwater measurements of the metabolites M656PH027 and M656PH023 is also summarised here:

- Hames & Freudenberger, 2011.

Three studies on surface water monitoring of dimethenamid-P and its metabolites M656PH003, M656PH027, M656PH023, and M656PH031 were submitted for EU approval.

In one study surface water concentrations of dimethenamid-P and its metabolites M656PH003, M656PH027, M656PH023, and M656PH031 in five European rivers were presented:

- Laabs, 2010.

In two published studies found in the open literature search surface water concentrations of dimethenamid in a small surface water regime, the brooks, near the Lake Greifensee and in the lake Geneva were presented:

- Leu et al, 2004
- Chevre et al, 2008.

Additionally, in one published study found in the open literature search concentrations of dimethenamid in air in the central region of France were presented:

- Coscolla et al, 2010.

The final results of all acceptable monitoring studies for dimethenamid-P and its metabolites in groundwater, surface water and air are summarised in Volume 1 under 2.8.4.

B.8.4.1 Monitoring data of groundwater

KCA 7.5/1– Schmidt et al (2010), Schmidt & Schulz, 2012 and Schmidt & Schneider, 2013 (new studies)

Author:	Schmidt, B. Richter, Th. Schulz, H.
Title:	Groundwater monitoring for Topramezone (BAS 670 H) in four representative regions in Germany- Final Report, study period May 2007 to March 2010
Date:	04/08/2010
Doc ID:	BASF DocID 2010/1069470
Guidelines:	None
GLP:	Yes
Validity:	Acceptable regarding the description of the monitoring sites and the sampling procedure

Author:	Schmidt, B. Schulz, H.
Title:	Groundwater monitoring for Topramezone (BAS 670 H) in four representative regions in Germany (study period 2010 to 2012)
Date:	10/06/2012
Doc ID:	BASF DocID 2012/1159571
Guidelines:	None
GLP:	Yes
Validity:	Acceptable regarding the description of the monitoring sites and the sampling procedure

Author:	Schmidt, B. Schneider, M.
Title:	Groundwater sampling in four representative regions in Germany (study period 2012 - 2013)
Date:	21/11/2013
Doc ID:	BASF DocID 2013/1338065
Guidelines:	OECD-DOC ENV/MC/CHEM(98)17 Paris 1998
GLP:	Yes
Validity:	Acceptable regarding the description of the monitoring sites and the sampling procedure

Aim of the studies

The purpose of this study was the monitoring of shallow groundwater in four maize growing regions in Germany. The three reports are summarised together since they are part of a single monitoring study. Schmidt et al (2010) summarises the samplings from 2007 to 2010, Schmidt and Schulz (2012) summarises from 2010 to 2012, and Schmidt and Schneider, 2013 summarises the samplings from June 2012 to March 2013. Only the selected groundwater wells and the field work of the study including sampling is summarised here since the sampling was originally performed for the active substance topramazone. The analytical results of the groundwater samples for the metabolites of dimethenamid-P are presented in Class (2013) and Mewis (2014a).

Material and Methods

Monitoring regions:

On the basis of statistical agricultural use data, regions were selected which represent centers of maize cultivation in Germany with regard to their total acreage and the relative percentage of the total agricultural use area. Four regions, the Nordwestdeutsches Tiefland / Geest (Northwest German Lowlands), the Altmark-Prignitz region, the Unterbayerisches Huegelland (Lower Bavarian Hilly Country) and the Suedliches Oberrheintal (Southern Upper Rhine Valley) were chosen.

Figure B.8.4.1-1 gives an overview of the monitoring regions.

Figure B.8.4.1-1: Locations of the groundwater monitoring regions

Selection of monitoring points:

The monitoring points are located in regions in Germany, typical for cultivation of maize, with a shallow, vulnerable groundwater table and where maize is cultivated in an upstream area relative to the wells. The selection of the monitoring points was in accordance with recommendations from the water authorities in the Federal States. Selection criteria found in the guidance paper from the German

regulatory authorities for explanation of findings in groundwater (Aden et al. 2002[4]) were used.
The topmost aquifers (most sensitive and near-surface primary aquifers) which are also used for water management purposes were monitored at groundwater measurement points which are representative of the regional hydrogeological conditions. The conditions in the selected monitoring regions represent sensitive groundwater situations. These areas are identified as having the potential for infiltration of crop protection products from the proper and intended use. The regions also represent areas of intense maize cultivation.
Table B.8.4.1-1 gives an overview of the selected measuring sites and the hydrogeological conditions in the respective regions.

Table B.8.4.1-1: Groundwater monitoring sites / hydrogeological situation

No.	Location	Distance of groundwater* [m]	Hydrogeological situation
Suedliches Oberrheintal (Baden-Wuerttemberg)			
1	Rheinau	~ 2.5 - 3	sands and gravels (Quaternary / fluviatile sediments)
2	Ichenheim	~ 2 - 3	sands and gravels (Quaternary / fluviatile sediments)
3	Oberhausen	~ 3 - 4	sands and gravels (Quaternary / fluviatile sediments)
4	Hartheim	~ 6 - 7	sands and gravels (Quaternary / fluviatile sediments)
Unterbayerisches Huegelland (Bavaria)			
5	Glaslern	~ 1.5 - 3	gravel / sand (Quaternary / fluviatile terrace sediments)
6	Osterholzen	~ 9 - 10	gravel / sand (Quaternary / fluviatile terrace sediments)
7	Pfarrkirchen	~ 1 - 2	sand (Quaternary / fluviatile terrace sediments)
8	Rossbach	~ 2.5 – 3.5	gravel / sand / silt (Quaternary - Holocene / fluviatile sediments and slope debris)
9	Asing	~ 8	gravel / sand (Quaternary / fluviatile terrace sediments)
Altmark/Prignitz region (Saxony-Anhalt / Brandenburg)			
10	Gardelegen	~ 8	sand (Pleistocene / glaciofluviatile sediments)
11	Quadendambeck	~ 6 - 7	sand (Pleistocene / glaciofluviatile sediments)
12	Drewen	~ 3 – 4	sand and silt / marl lenses (Pleistocene / glacial moraine sediments)
Nordwestdeutsches Tiefland (Schleswig-Holstein / Lower Saxony / North Rhine-Westphalia)			
13	Albersloh	~ 1 - 2	sand (Pleistocene / glacial moraine sediments)
14	Ostbevern	~ 1.5- 2.5	sand (Pleistocene / glacial moraine sediments)
15	Veltrup	~ 1 - 2	sand (Pleistocene / glaciofluviatile sediments)
16	Flechum	~ 2.5 - 3.5	sand / silt (Pleistocene / glaciofluviatile and moraine sediments)
17	Vinnen-Ahmsen	~ 3.5 - 4	sand / silt (Pleistocene / glaciofluviatile and moraine sediments)
18	Wedel	~ 3 - 4	sand (Pleistocene / moraine sediments)
19	Krogaspe	~ 1 - 2	sand / silt (Pleistocene / glacial sediments)
20	Brekendorf	~ 5 - 6	sand / silt / gravel (Pleistocene / ground moraine sediments)

* distance of groundwater table to soil surface measured at the monitoring well

The filter depth of the sampled groundwater wells are listed in the following table:

[4] Aden, K. et al (2002). 'Protection of groundwater from entry of plant protection products: guidance on explanation of findings and on implementation of post registration monitoring studies.' Fachgruppe Chemische Mittelprüfung, Braunschweig / Kleinmachnow und Umweltbundesamt Berlin. Nachrichtenbl. Deut. Pflanzenschutzd. 54, 125 129

Table B.8.4.1-2: Filter depth of groundwater wells

No.	Location	filter depth (m)	
		top	bottom
1	Rheinau	8	9
2	Ichenheim	7.5	9.5
3	Oberhausen	n.a.	9.3
4	Hartheim	1.2	9.6
5	Glaslern	2.52	4.45
6	Osterholzen	no information	
7	Pfarrkirchen	1.6	6.6
8	Rossbach	3	6
9	Asing	11	13
10	Gardelegen	19*	23*
11	Quadendambeck	10.5	12.5
12	Drewen	6.8	7.8
13	Albersloh	5	7
14	Ostbevern	8	10
15	Veltrup	7	18
16	Flechum	~5**	~6**
17	Vinnen-Ahmsen	5	8
18	Wedel	7.4**	9.3**
19	Krogaspe	3	6
20	Brekendorf	5	7

n.a. not available
* Since the GWM is located on a higher level referred to the upgradient, the filter screen is installed in more than 100 m depth below the surface but taps the uppermost groundwater level
** contradictory information in data base and drilling profile

Retrospective and prospective groundwater monitoring:

The study design of the groundwater monitoring covers a retrospective monitoring aspect as well as a prospective monitoring purpose.

Products containing dimethenamid/P and formerly dimethenamid were used since a long time in maize cultivation in Germany and it can thus be assumed that they were also used in the selected monitoring regions in the past. Thus, the main purpose of the retrospective groundwater monitoring is to determine whether dimethenamid-P may have affected the shallow groundwater.

For this purpose groundwater monitoring points, which penetrate into the upper groundwater layers, were sampled regularly. The groundwater wells were chosen with regard to recommendations of the environmental or water authorities of the Federal States of Germany. The groundwater units sampled are located in sedimentary rocks of the Quaternary which consists mostly of sands. The monitoring regions are typical for maize cultivation and represent the prominent maize growing areas in Germany. Groundwater from major agricultural areas with intensive maize cultivation flows in the direction of the wells. The groundwater wells tap into shallow groundwater; the groundwater table is generally at about 2 – 10 m depth. The typical soils in the area of the monitoring points are sands and loams above sandy sediments. The environmental scenario around each well represents a vulnerable situation with regard to pesticide leaching due to the soil conditions or the shallow groundwater table.

In order to address the aspect of a prospective ground water monitoring, that means to observe possible inputs into the groundwater in the direct up-gradient of the monitoring points, products containing dimethenamid-P were applied on fields in the upstream of the wells.

For this, an area from which groundwater may flow to the monitoring points within three years was defined. The groundwater flow direction may vary and flow velocities of the ground water were conservatively calculated to be at about 0.1 – 2 m per day (40 – 700 m per year). Hence a segment of a circle, which has an apex angle of approx. 45° and a length of approx. 1000 m was defined. Within this segment products containing dimethenamid-P (besides topramezone) were applied on areas under maize cultivation.

For this purpose farmers, which cultivate maize fields within a distance of approx. 1 km up-gradient from the monitoring wells were asked for using products containing dimethenamid-P (besides topramezone) on their fields. BASF SE provided the farmers with the commercial products as Clio® Super or Clio® Top Pack. The exact sizes and locations of the fields treated with products containing dimethenamid-P in the area directly upgradient from the wells are shown in the report.

The applications were done under normal agricultural practice. Applications and gathering of related information were not conducted according to GLP regulations. Applications upgradient from the wells were attempted every year as far as possible. The documentation of the actually treated areas upstream to the monitoring wells was collected and compiled in the report.

Substantial amounts of dimethenamid-P were applied in the course of the documented sponsored applications:
In the years 2007 and 2008, 1.8 L/ha Clio® Super, which is equivalent to 968.4 g/ha dimethenamid-P.
In the year 2009, 1.5 L/ha Clio® Super, which is equivalent to 807 g/ha dimethenamid-P, was applied.
In many cases, Clio® Super was provided as the "Clio® Top Pack" which is a package of Clio® Super and terbuthylazine for use as a tank mix. Thus, the application rates for DMTA-P documented in the monitoring study are comparable with the current maximum application rate of 864 g/ha DMTA-P.
On average the products Clio® Top or Clio® Super were applied on more than 10 hectares in the direct upstream areas and with more than 20 hectares in the broader upstream areas, each year and each monitoring well.

After 2009 product applications were no longer sponsored by BASF. However further use of dimethenamid-P and especially of Clio® products containing dimethenamid-P can be assumed after the successful market introduction and the favorable performance of the Clio® product family.

Selection of monitoring wells:

To assess the state of the groundwater, monitoring wells (GWM) were selected that meet the following requirements:
1. The monitoring wells allow the investigation of the topmost vulnerable groundwater;
2. Sampling from the monitoring wells permits evaluation of both local influences (directly upstream areas with documented application of the test item) and regional influences (farther upgrade area) to the groundwater;
3. The monitoring wells are in technically good conditions in accordance with existing guidelines (e.g. LAWA 1999) and suitable for taking residue specimens.
Possible influences of natural conditions (such as the direct inflow of surface water into the monitoring well and contributions from farms unconnected to the wastewater system) must be excluded.

Groundwater sampling:

Groundwater samples were taken on a bimonthly interval between May 2007 and March 2010 and on a quarterly interval between June 2010 and March 2013 from all 20 monitoring wells. Steps were taken to ensure contamination-free sampling of the shallow groundwater. The well head was cleaned with water/isopropanol before opening the seals. The groundwater-level was measured with an electric level probe. The electric level probe was rinsed with tap water after each measurement.

A submersible pump (Grundfos MP 1) was installed in the well. The pump was lowered to a depth, which represents the middle of the well casing filled with groundwater or at least 3 meters below the

groundwater table if the well was deeper than 20 m. The pump was rinsed with tap water after each sampling procedure and all components used were made from inert materials. This ensured that the specimen taken was neither influenced nor altered by the sampling procedure. After obtaining the specimen, the tube material was discarded. For each monitoring well and each sampling new tube material was used.
Before taking the specimen the stagnant water was removed from the well (about three well volumes; at wells deeper than 20 m one well volume was pumped). If during the sampling procedure no sufficient amount of groundwater entered the well tube, it was sufficient to pump until the stability of conductivity was achieved. During pumping the groundwater parameters were monitored on site. pH, conductivity, redox potential and water temperature were determined and recorded.
Specimens were added to four HDPE bottles with a volume of 0.5 L each and put on dry ice immediately after sampling (< -18 °C).

Measurement of dimethenamid-P and its metabolites:

The analytical procedure of the measurements of metabolites of dimethenamid-P in the groundwater samples is described in the study reports Class & Class (2013) and Mewis (2014a).

Results and Discussion

The analytical results on concentrations of metabolites of dimethenamid-P determined in selected samples of the German monitoring sites are presented in the study reports Class & Class (2013) and Mewis (2014a).

Conclusion

Detailed description including the geological and hydrogeological situation of the investigated regions is provided in the study reports. Groundwater flow direction were provided in maps showing the treated fields in vicinity of the wells and their distance to the monitored wells, however no catchment sector was shown on this maps. The catchment sector was only estimated and provided on separate maps by drawing a quadrant with a 1 km radius in groundwater flow direction. This makes it difficult to evaluate whether all of the treated areas were indeed within the catchment of the monitoring wells. However, more detailed modelling of the travel time from the treated fields to the wells were performed by Haering & Mewis, 2014. No description of soil profiles of the treated fields was provided, these were provided by Haering & Mewis, 2014. The description of monitoring wells and sampling is considered acceptable by the RMS.

The description of the monitoring sites and the sampling of the groundwater were evaluated by the RMS against the quality criteria 1-6 for groundwater monitoring studies of the FOCUS groundwater report (2009, 2014).
The quality criteria 1 was fulfilled at least for the years 2007 to 2009, where products containing dimethenamid-P were freely provided to the farmers and the treated areas were documented in the study reports. According to Schmidt et al (2010), Schmidt & Schulz, 2012 and Schmidt & Schneider, 2013, the worst case application of 864 g/ha ha pre-emergence application of dimethenamid-P to maize is covered with the prospective monitoring study. However, according to the study Haering & Mewis, 2014, the Clio products provided to farmers for the prospective aspect of the monitoring study are applied as post-emergence herbicides onto maize in the BBCH growth stage range 12-16. Thus, considering an interception of 25 %, the amount of soil-relevant dimethenamid-P on the treated fields would only be 726 g/ha for the years 2007 & 2008 and 605 g/ha for 2009, thus the applied amounts of dimethenamid-P in the years 2007 to 2009 do not cover the worst case pre-emergence application rate of 864 g/ha to maize.
Regarding earlier use of dimethenamid and/or dimethenamid-P in the areas, no robust information is available. Products containing the racemic dimethenamid were available on the German market from 1997 to 2003. Products containing dimethenamid-P are available since 2000. Thus, some use of these products in the areas is likely however the amount is not known. Besides, no information is given on changes of cultivated crops in the area. It can be assumed that less maize was cropped before the start

of the prospective study since there is a constant increase in areas cropped with maize in Germany over last decades. Thus, for the years before 2007, sufficient use of dimethenamid or dimethenamid-P in the monitored areas cannot be proven.
The quality criteria 2 has been evaluated by Haering & Mewis, 2014 and is thus not discussed here.
The quality criteria 3, 4 and 6 are considered fulfilled by the RMS.
The amount of groundwater that was removed before sampling was kept at a minimum while trying to avoid potential contamination by stagnant water in the wells. Thus also the quality criteria 5 is considered fulfilled.

KCA 7.5/2– Class, 2013 & Mewis, 2014a (new studies)

Author:	Class, T.
Title:	Determination of the dimethenamid-P metabolites M23, M27 and M31 in ground water samples originating from BASF studies 262015 and 392191
Date:	04/11/2013
Doc ID:	BASF DocID 2013/1349144
Guidelines:	None
GLP:	yes
Validity:	Not acceptable

Author:	Mewis, A.
Title:	Determination of residues of metabolites of BAS 656 PH in groundwater (monitoring Germany)
Date:	21/02/2014
Doc ID:	BASF DocID 2013/1352172
Guidelines:	None
GLP:	no
Validity:	Not acceptable

Aim of the studies

The objective of these two studies was the determination of residues of metabolites of dimethenamid-P M656PH003 (M3 in the studies), M656PH010, M656PH023 (M23 in the studies), M656PH027 (M27 in the studies), M656PH031 (M31 in the studies), M656PH032, M656PH043, M656PH045, M656PH047 and M656PH054 in groundwater samples in Germany.

Material and Methods

The groundwater samples used for analysis in these studies originate from three separate successive groundwater monitoring studies with the active substance topramezone conducted in Germany Schmidt et al (2010), Schmidt & Schulz (2012) and Schmidt & Schneider (2013).
In these studies summarised under KCA 7.5/1, the groundwater wells and the field work of the study including sampling are described. Here only the analysis results of the groundwater samples for M656PH003, M656PH010, M656PH023, M656PH027, M656PH031, M656PH032, M656PH043, M656PH045, M656PH047 and M656PH054 are described.
In the study Class (2013) selected groundwater samples from all 20 groundwater wells were analysed for the metabolites M656PH023, M656PH027 and M656PH031. The analytical method for analysis of the dimethenamid-P metabolites M656PH023, M656PH027 and M656PH031 used by Class (2013) is described in Jooß (2012, BASF DocID 2012/1278546). It was concurrently validated with drinking water samples fortified at the limit of quantitation (LOQ) of 0.03 µg/L (5 replicates) and at 0.3 µg/L.

In the study Mewis (2014a), additional groundwater samples from all 20 groundwater wells were analysed for M656PH003, M656PH010, M656PH023, M656PH027, M656PH031, M656PH032, M656PH043, M656PH045, M656PH047, M656PH054. However, some of the additional samples were not analysed for M656PH023, M656PH027 and M656PH031. The analytical method for analysis of the dimethenamid-P metabolites M656PH003, M656PH010, M656PH023, M656PH027,

M656PH031, M656PH032, M656PH043, M656PH045, M656PH047, M656PH054 used by Mewis (2014a) is described in Mewis (2013, BASF DocID 2013/1349800). It was concurrently validated with drinking water samples fortified at the limit of quantification (LOQ) of 0.025 µg/L and at 0.1, 1 and 2 µg/L. The limit of detection was defined as 30 % of LOQ, i.e. 0.0075 µg/L.

Samples representing sampling events approximately every half year were selected by Class (2013) for analysis from the available samples. Part of the samples were first analysed for metabolites M656PH023, M656PH027 and M656PH031 by Class (2013). Later on they were analysed for the metabolites M656PH003, M656PH010, M656PH032, M656PH043, M656PH045, M656PH047 and M656PH054 by the method of Mewis (2014a).
If residues of the major metabolites M656PH023 or M656PH027 were detected in the first round of analyses, further samples in between the half year raster were selected and analysed for all 10 metabolites (M656PH003, M656PH010, M656PH023, M656PH027, M656PH031, M656PH032, M656PH043, M656PH045, M656PH047 and M656PH054) by Mewis (2013a). Furthermore, all samples originating from the last year of sampling (2012) were analysed for all 10 metabolites.

Results and Discussion

Resulting concentrations of M656PH003, M656PH010, M656PH023, M656PH027, M656PH031, M656PH032, M656PH043, M656PH045, M656PH047 and M656PH054 in all sampled groundwater wells are presented in Table B.8.4.1-3 to Table B.8.4.1-22.

Table B.8.4.1-3: Residues of the dimethenamid-p metabolites in the samples of the groundwater well Albersloh

Groundwater monitoring well Albersloh, measurement point 13					
Sampling Date (yy-mm)	**M656PH027 (µg/L)**	**M656PH023 (µg/L)**	**M656PH031 (µg/L)**	**M656PH032 (µg/L)**	**M656PH043 (µg/L)**
07-05	n.d.*	n.d.*	n.d.*	n.d.	n.d.
07-11	n.d.*	n.d.*	n.d.*	n.d.	n.d.
08-05	n.d.*	n.d.*	n.d.*	n.d.	n.d.
08-11	n.d.*	n.d.*	n.d.*	n.d.	n.d.
09-05	n.d.*	n.d.*	n.d.*	n.d.	n.d.
09-11	n.d.*	n.d.*	n.d.*	n.d.	n.d.
10-01	n.d.	n.d.	n.d.	n.d.	n.d.
10-03	n.d.	n.d.	n.d.	n.d.	n.d.
10-06	n.d.	n.d.	n.d.	n.d.	n.d.
10-09	n.d.	n.d.	n.d.	n.d.	n.d.
10-12	n.d.*	n.d.*	n.d.*	n.d.	n.d.
11-03	n.d.	n.d.	n.d.	n.d.	<LOQ
11-06	n.d.*	n.d.*	n.d.*	n.d.	n.d.
11-09	n.d.	n.d.	n.d.	n.d.	<LOQ
11-12	<LOQ*	n.d.*	n.d.*	n.d.	n.d.
12-03	0.042	<LOQ	n.d.	n.d.	n.d.
12-06	0.217	0.064	n.d.	n.d.	n.d.
12-09	0.483	0.090	n.d.	n.d.	<LOQ
12-12	1.071	0.192	n.d.	n.d.	n.d.
13-03	**1.277**	**0.246**	n.d.	n.d.	n.d.
Sampling Date (yy-mm)	**M656PH045 (µg/L)**	**M656PH047 (µg/L)**	**M656PH054 (µg/L)**	**M656PH003 (µg/L)**	**M656PH010 (µg/L)**
07-05	n.d.	<LOQ	n.d.	n.d.	n.d.
07-11	<LOQ	0.026	n.d.	n.d.	n.d.
08-05	n.d.	0.031	n.d.	n.d.	n.d.
08-11	n.d.	0.026	n.d.	n.d.	n.d.
09-05	n.d.	0.030	n.d.	n.d.	n.d.
09-11	n.d.	0.028	n.d.	n.d.	n.d.
10-01	n.d.	n.d.	n.d.	n.d.	n.d.
10-03	n.d.	n.d.	n.d.	n.d.	n.d.
10-06	<LOQ	0.129	n.d.	n.d.	n.d.
10-09	n.d.	n.d.	n.d.	n.d.	n.d.
10-12	<LOQ	0.118	n.d.	n.d.	n.d.
11-03	n.d.	n.d.	n.d.	n.d.	n.d.
11-06	n.d.	<LOQ	n.d.	n.d.	n.d.
11-09	n.d.	n.d.	n.d.	n.d.	n.d.
11-12	0.026	n.d.	n.d.	n.d.	n.d.
12-03	n.d.	n.d.	n.d.	n.d.	n.d.
12-06	n.d.	**0.149**	n.d.	n.d.	n.d.
12-09	n.d.	n.d.	n.d.	n.d.	n.d.
12-12	**0.027**	0.143	n.d.	n.d.	n.d.
13-03	n.d.	n.d.	n.d.	n.d.	n.d.

n.d. = not detectable (<0.0075 µg/L for each analyte); <LOQ: <0.025 µg/L
n.d.*= not detectable (<0.009 µg/L = 30 % LOQ, <LOQ*: <0.03 µg/L)

Table B.8.4.1-4: Residues of the dimethenamid-P metabolites in the samples of the groundwater well Asing

Groundwater monitoring well Asing, measurement point 9					
Sampling Date (yy-mm)	**M656PH027 (µg/L)**	**M656PH023 (µg/L)**	**M656PH031 (µg/L)**	**M656PH032 (µg/L)**	**M656PH043 (µg/L)**
07-05	n.d.*	n.d.*	n.d.*	n.d.*	n.d.
07-11	n.d.*	n.d.*	n.d.*	n.d.*	n.d.
08-05	n.d.*	n.d.*	n.d.*	n.d.*	n.d.
08-11	n.d.*	n.d.*	n.d.*	n.d.*	n.d.
09-05	n.d.*	n.d.*	n.d.*	n.d.*	n.d.
09-11	n.d.*	n.d.*	n.d.*	n.d.*	n.d.
10-06	n.d.	n.d.	n.d.	n.d.	n.d.
10-12	n.d.*	n.d.*	n.d.*	n.d.*	n.d.
11-06	n.d.*	n.d.*	n.d.*	n.d.*	n.d.
11-12	n.d.*	n.d.*	n.d.*	n.d.*	n.d.
12-06	n.d.	n.d.	n.d.	n.d.	n.d.
12-12	n.d.	n.d.	n.d.	n.d.	n.d.
Sampling Date (yy-mm)	**M656PH045 (µg/L)**	**M656PH047 (µg/L)**	**M656PH054 (µg/L)**	**M656PH003 (µg/L)**	**M656PH010 (µg/L)**
07-05	n.d.	n.d.	n.d.	n.d.	n.d.
07-11	n.d.	n.d.	n.d.	n.d.	n.d.
08-05	n.d.	n.d.	n.d.	n.d.	n.d.
08-11	n.d.	n.d.	n.d.	n.d.	n.d.
09-05	n.d.	n.d.	n.d.	n.d.	n.d.
09-11	n.d.	n.d.	n.d.	n.d.	n.d.
10-06	n.d.	n.d.	n.d.	n.d.	n.d.
10-12	n.d.	n.d.	n.d.	n.d.	n.d.
11-06	n.d.	n.d.	n.d.	n.d.	n.d.
11-12	n.d.	n.d.	n.d.	n.d.	n.d.
12-06	n.d.	n.d.	n.d.	n.d.	n.d.
12-12	n.d.	n.d.	n.d.	n.d.	n.d.

n.d. = not detectable (<0.0075 µg/L for each analyte); <LOQ: <0.025 µg/L
n.d.*= not detectable (<0.009 µg/L = 30 % LOQ, <LOQ*: <0.03 µg/L)

Table B.8.4.1-5: Residues of the dimethenamid-P metabolites in the samples of the groundwater well Brekendorf

Groundwater monitoring well Brekendorf, measurement point 20					
Sampling Date (yy-mm)	**M656PH027 (µg/L)**	**M656PH023 (µg/L)**	**M656PH031 (µg/L)**	**M656PH032 (µg/L)**	**M656PH043 (µg/L)**
07-05	n.d.*	n.d.*	n.d.*	n.d.	n.d.
07-11	n.d.*	n.d.*	n.d.*	n.d.	n.d.
08-05	n.d.*	n.d.*	n.d.*	n.d.	n.d.
08-11	n.d.*	n.d.*	n.d.*	n.d.	n.d.
09-05	n.d.*	n.d.*	n.d.*	n.d.	n.d.
09-11	n.d.*	n.d.*	n.d.*	n.d.	n.d.
10-06	0.121	n.d.	n.d.	n.d.	n.d.
10-09	**0.211**	n.d.	n.d.	n.d.	n.d.
10-12	<LOQ*	n.d.*	n.d.*	n.d.	n.d.
11-03	n.d.	n.d.	n.d.	n.d.	n.d.
11-06	0.034	n.d.*	n.d.*	n.d.	n.d.
11-09	<LOQ	n.d.	n.d.	n.d.	n.d.
11-12	<LOQ*	n.d.*	n.d.*	n.d.	<LOQ
12-03	<LOQ	n.d.	n.d.	n.d.	n.d.
12-06	<LOQ	n.d.	n.d.	n.d.	n.d.
12-12	<LOQ	n.d.	n.d.	n.d.	n.d.
Sampling Date (yy-mm)	**M656PH045 (µg/L)**	**M656PH047 (µg/L)**	**M656PH054 (µg/L)**	**M656PH003 (µg/L)**	**M656PH010 (µg/L)**
07-05	n.d.	n.d.	n.d.	n.d.	n.d.
07-11	n.d.	n.d.	n.d.	n.d.	n.d.
08-05	n.d.	n.d.	n.d.	n.d.	n.d.
08-11	n.d.	n.d.	n.d.	n.d.	n.d.
09-05	n.d.	n.d.	n.d.	n.d.	n.d.
09-11	n.d.	n.d.	n.d.	n.d.	n.d.
10-06	n.d.	n.d.	n.d.	n.d.	n.d.
10-09	n.d.	n.d.	n.d.	n.d.	n.d.
10-12	n.d.	n.d.	n.d.	n.d.	n.d.
11-03	n.d.	n.d.	n.d.	n.d.	n.d.
11-06	n.d.	n.d.	n.d.	n.d.	n.d.
11-09	n.d.	n.d.	n.d.	n.d.	n.d.
11-12	n.d.	n.d.	n.d.	n.d.	n.d.
12-03	<LOQ	n.d.	n.d.	n.d.	n.d.
12-06	n.d.	n.d.	n.d.	n.d.	n.d.
12-12	n.d.	n.d.	n.d.	n.d.	n.d.

n.d. = not detectable (<0.0075 µg/L for each analyte); <LOQ: <0.025 µg/L
n.d.*= not detectable (<0.009 µg/L = 30 % LOQ, <LOQ*: <0.03 µg/L)

Table B.8.4.1-6: Residues of the dimethenamid-P metabolites in the samples of the groundwater well Drewen

Groundwater monitoring well Drewen, measurement point 12					
Sampling Date (yy-mm)	**M656PH027 (µg/L)**	**M656PH023 (µg/L)**	**M656PH031 (µg/L)**	**M656PH032 (µg/L)**	**M656PH043 (µg/L)**
07-05	n.d.*	n.d.*	n.d.*	n.d.	n.d.
07-11	n.d.*	n.d.*	n.d.*	n.d.	n.d.
08-05	n.d.*	n.d.*	n.d.*	n.d.	n.d.
08-11	n.d.*	n.d.*	n.d.*	n.d.	n.d.
09-05	n.d.*	n.d.*	n.d.*	n.d.	n.d.
09-11	n.d.*	n.d.*	n.d.*	n.d.	n.d.
10-06	n.d.	n.d.	n.d.	n.d.	n.d.
10-12	n.d.*	n.d.*	n.d.*	n.d.	<LOQ
11-06	n.d.*	n.d.*	n.d.*	--	--
11-12	n.d.*	n.d.*	n.d.*	n.d.	n.d.
12-06	n.d.	n.d.	n.d.	n.d.	<LOQ
12-12	n.d.	n.d.	n.d.	n.d.	n.d.
Sampling Date (yy-mm)	**M656PH045 (µg/L)**	**M656PH047 (µg/L)**	**M656PH054 (µg/L)**	**M656PH003 (µg/L)**	**M656PH010 (µg/L)**
07-05	n.d.	n.d.	n.d.	n.d.	n.d.
07-11	n.d.	n.d.	n.d.	n.d.	n.d.
08-05	n.d.	n.d.	n.d.	n.d.	n.d.
08-11	n.d.	n.d.	n.d.	n.d.	n.d.
09-05	n.d.	n.d.	n.d.	n.d.	n.d.
09-11	n.d.	n.d.	n.d.	n.d.	n.d.
10-06	n.d.	n.d.	n.d.	n.d.	n.d.
10-12	n.d.	n.d.	n.d.	n.d.	n.d.
11-06	n.d.	n.d.	n.d.	n.d.	n.d.
11-12	n.d.	n.d.	n.d.	n.d.	n.d.
12-06	n.d.	n.d.	n.d.	n.d.	n.d.
12-12	n.d.	n.d.	n.d.	n.d.	n.d.

n.d. = not detectable (<0.0075 µg/L for each analyte); <LOQ: <0.025 µg/L
n.d.*= not detectable (<0.009 µg/L = 30 % LOQ, <LOQ*: <0.03 µg/L)

Table B.8.4.1-7: Residues of the dimethenamid-P metabolites in the samples of the groundwater well Flechum

Groundwater monitoring well Flechum, measurement point 16					
Sampling Date (yy-mm)	**M656PH027 (µg/L)**	**M656PH023 (µg/L)**	**M656PH031 (µg/L)**	**M656PH032 (µg/L)**	**M656PH043 (µg/L)**
07-05	0.240*	<LOQ*	n.d.*	n.d.	n.d.
07-07	0.595	0.073	n.d.	n.d.	n.d.
07-09	0.629	0.082	n.d.	n.d.	n.d.
07-11	0.570*	0.083*	n.d.*	n.d.	n.d.
08-01	0.532	0.084	n.d.	n.d.	n.d.
08-03	0.410	0.057	n.d.	n.d.	n.d.
08-05	0.280*	0.048*	n.d.*	n.d.	n.d.
08-07	0.526	0.062	n.d.	n.d.	n.d.
08-09	0.643	0.065	n.d.	n.d.	n.d.
08-11	0.510*	0.064*	n.d.*	n.d.	n.d.
09-01	0.616	0.063	n.d.	n.d.	n.d.
09-03	0.636	0.065	n.d.	n.d.	n.d.
09-05	0.710*	0.073*	n.d.*	n.d.	n.d.
09-07	0.808	0.084	n.d.	n.d.	n.d.
09-09	0.565	0.048	n.d.	n.d.	n.d.
09-11	0.650*	0.066*	n.d.*	n.d.	n.d.
10-01	0.771	0.066	n.d.	n.d.	n.d.
10-03	0.808	0.084	n.d.	n.d.	n.d.
10-06	0.530	0.068	n.d.	n.d.	n.d.
10-09	0.753	0.092	n.d.	n.d.	n.d.
10-12	0.810*	0.093*	n.d.*	n.d.	n.d.
11-03	0.987	0.106	n.d.	n.d.	n.d.
11-06	0.990*	0.160*	n.d.*	n.d.	n.d.
11-09	1.306	0.186	n.d.	n.d.	n.d.
11-12	0.850*	0.150*	n.d.*	n.d.	n.d.
12-03	1.532**	**0.359****	n.d.**	n.d.**	n.d.**
12-06	n.d.	n.d.	n.d.	n.d.	n.d.
12-09	0.892	0.169	n.d.	n.d.	n.d.
12-12	1.515	0.345	n.d.	n.d.	n.d.
13-03	**1.680**	0.355	n.d.	n.d.	n.d.
Sampling Date (yy-mm)	**M656PH045 (µg/L)**	**M656PH047 (µg/L)**	**M656PH054 (µg/L)**	**M656PH003 (µg/L)**	**M656PH010 (µg/L)**
07-05	n.d.	<LOQ	n.d.	n.d.	n.d.
07-07	n.d.	n.d.	n.d.	n.d.	n.d.
07-09	n.d.	n.d.	n.d.	n.d.	n.d.
07-11	n.d.	<LOQ	n.d.	n.d.	n.d.
08-01	n.d.	n.d.	n.d.	n.d.	n.d.
08-03	n.d.	n.d.	n.d.	n.d.	n.d.
08-05	n.d.	<LOQ	n.d.	n.d.	n.d.
08-07	n.d.	n.d.	n.d.	n.d.	n.d.
08-09	n.d.	n.d.	n.d.	n.d.	n.d.
08-11	n.d.	<LOQ	n.d.	n.d.	n.d.
09-01	n.d.	n.d.	n.d.	n.d.	n.d.
09-03	n.d.	n.d.	n.d.	n.d.	n.d.
09-05	n.d.	<LOQ	n.d.	n.d.	n.d.
09-07	n.d.	n.d.	n.d.	n.d.	n.d.
09-09	n.d.	n.d.	n.d.	n.d.	n.d.
09-11	n.d.	<LOQ	n.d.	n.d.	n.d.
10-01	n.d.	n.d.	n.d.	n.d.	n.d.
10-03	n.d.	n.d.	n.d.	n.d.	n.d.
10-06	n.d.	n.d.	<LOQ	n.d.	n.d.
10-09	n.d.	n.d.	n.d.	n.d.	n.d.

Groundwater monitoring well Flechum, measurement point 16					
10-12	n.d.	n.d.	n.d.	n.d.	n.d.
11-03	n.d.	n.d.	n.d.	n.d.	n.d.
11-06	n.d.	n.d.	n.d.	n.d.	n.d.
11-09	n.d.	n.d.	n.d.	n.d.	n.d.
11-12	n.d.	<LOQ	n.d.	n.d.	n.d.
12-03	n.d.**	n.d.**	<LOQ**	n.d.**	n.d.**
12-06	n.d.	0.038	n.d.	n.d.	n.d.
12-09	n.d.	n.d.	0.036	n.d.	n.d.
12-12	n.d.	**0.084**	**0.047**	n.d.	n.d.
13-03	n.d.	0.069	0.028	n.d.	n.d.

n.d. = not detectable (<0.0075 µg/L for each analyte); <LOQ: <0.025 µg/L
n.d.*= not detectable (<0.009 µg/L = 30 % LOQ, <LOQ*: <0.03 µg/L)
** mean of two values

Table B.8.4.1-8: Residues of the dimethenamid-P metabolites in the samples of the groundwater well Gardelegen

Groundwater monitoring well Gardelegen, measurement point 10					
Sampling Date (yy-mm)	**M656PH027 (µg/L)**	**M656PH023 (µg/L)**	**M656PH031 (µg/L)**	**M656PH032 (µg/L)**	**M656PH043 (µg/L)**
07-05	n.d.*	n.d.*	n.d.*	n.d.	n.d.
07-11	n.d.*	n.d.*	n.d.*	n.d.	n.d.
08-05	n.d.*	n.d.*	n.d.*	n.d.	n.d.
08-11	n.d.*	n.d.*	n.d.*	n.d.	n.d.
09-05	n.d.*	n.d.*	n.d.*	n.d.	n.d.
09-11	n.d.*	n.d.*	n.d.*	n.d.	n.d.
10-06	n.d.	n.d.	n.d.	n.d.	n.d.
10-12	n.d.*	n.d.*	n.d.*	n.d.	n.d.
11-06	n.d.*	n.d.*	n.d.*	n.d.	n.d.
11-12	n.d.*	n.d.*	n.d.*	n.d.	n.d.
12-06	n.d.	n.d.	n.d.	n.d.	n.d.
12-12	n.d.	n.d.	n.d.	n.d.	n.d.
Sampling Date (yy-mm)	**M656PH045 (µg/L)**	**M656PH047 (µg/L)**	**M656PH054 (µg/L)**	**M656PH003 (µg/L)**	**M656PH010 (µg/L)**
07-05	n.d.	n.d.	n.d.	n.d.	n.d.
07-11	n.d.	n.d.	n.d.	n.d.	n.d.
08-05	n.d.	n.d.	n.d.	n.d.	n.d.
08-11	n.d.	n.d.	n.d.	n.d.	n.d.
09-05	n.d.	n.d.	n.d.	n.d.	n.d.
09-11	n.d.	n.d.	n.d.	n.d.	n.d.
10-06	n.d.	n.d.	n.d.	n.d.	n.d.
10-12	n.d.	n.d.	n.d.	n.d.	n.d.
11-06	n.d.	n.d.	n.d.	n.d.	n.d.
11-12	n.d.	n.d.	n.d.	n.d.	n.d.
12-06	n.d.	n.d.	n.d.	n.d.	n.d.
12-12	n.d.	n.d.	n.d.	n.d.	n.d.

n.d. = not detectable (<0.0075 µg/L for each analyte); <LOQ: <0.025 µg/L
n.d.*= not detectable (<0.009 µg/L = 30 % LOQ, <LOQ*: <0.03 µg/L)

Table B.8.4.1-9: Residues of the dimethenamid-P metabolites in the samples of the groundwater well Gaslern

Groundwater monitoring well Gaslern, measurement point 5					
Sampling Date (yy-mm)	**M656PH027 (µg/L)**	**M656PH023 (µg/L)**	**M656PH031 (µg/L)**	**M656PH032 (µg/L)**	**M656PH043 (µg/L)**
07-05	n.d.*	n.d.*	n.d.*	n.d.	n.d.
07-11	n.d.*	n.d.*	n.d.*	n.d.	n.d.
08-05	n.d.*	n.d.*	n.d.*	n.d.	n.d.
08-11	n.d.*	n.d.*	n.d.*	n.d.	n.d.
09-05	n.d.*	n.d.*	n.d.*	n.d.	n.d.
09-11	n.d.*	n.d.*	n.d.*	n.d.	n.d.
10-06	n.d.	n.d.	n.d.	n.d.	n.d.
10-12	n.d.*	n.d.*	n.d.*	n.d.	n.d.
11-06	n.d.*	n.d.*	n.d.*	n.d.	n.d.
11-12	n.d.*	n.d.*	n.d.*	n.d.	n.d.
12-06	n.d.	n.d.	n.d.	n.d.	n.d.
12-12	n.d.	n.d.	n.d.	n.d.	n.d.
Sampling Date (yy-mm)	**M656PH045 (µg/L)**	**M656PH047 (µg/L)**	**M656PH054 (µg/L)**	**M656PH003 (µg/L)**	**M656PH010 (µg/L)**
07-05	n.d.	n.d.	n.d.	n.d.	n.d.
07-11	n.d.	n.d.	n.d.	n.d.	n.d.
08-05	n.d.	n.d.	n.d.	n.d.	n.d.
08-11	n.d.	n.d.	n.d.	n.d.	n.d.
09-05	n.d.	n.d.	n.d.	n.d.	n.d.
09-11	n.d.	n.d.	n.d.	n.d.	n.d.
10-06	n.d.	n.d.	n.d.	n.d.	n.d.
10-12	n.d.	n.d.	n.d.	n.d.	n.d.
11-06	n.d.	n.d.	n.d.	n.d.	n.d.
11-12	n.d.	n.d.	n.d.	n.d.	n.d.
12-06	n.d.	n.d.	n.d.	n.d.	n.d.
12-12	n.d.	n.d.	n.d.	n.d.	n.d.

n.d. = not detectable (<0.0075 µg/L for each analyte); <LOQ: <0.025 µg/L
n.d.*= not detectable (<0.009 µg/L = 30 % LOQ, <LOQ*: <0.03 µg/L)

Table B.8.4.1-10: Residues of the dimethenamid-P metabolites at the groundwater well Hartheim

Groundwater monitoring well Hartheim, measurement point 4					
Sampling Date (yy-mm)	**M656PH027 (µg/L)**	**M656PH023 (µg/L)**	**M656PH031 (µg/L)**	**M656PH032 (µg/L)**	**M656PH043 (µg/L)**
07-05	n.d.*	n.d.*	n.d.*	n.d.	n.d.
07-11	n.d.*	n.d.*	n.d.*	n.d.	n.d.
08-05	n.d.*	n.d.*	n.d.*	n.d.	n.d.
08-11	n.d.*	n.d.*	n.d.*	n.d.	n.d.
09-05	n.d.*	n.d.*	n.d.*	n.d.	n.d.
09-11	n.d.*	n.d.*	n.d.*	n.d.	n.d.
10-06	n.d.	n.d.	n.d.	n.d.	n.d.
10-12	n.d.*	n.d.*	n.d.*	n.d.	n.d.
11-06	n.d.*	n.d.*	n.d.*	n.d.	n.d.
11-12	n.d.*	n.d.*	n.d.*	n.d.	n.d.
12-06	n.d.	n.d.	n.d.	n.d.	n.d.
12-12	n.d.	n.d.	n.d.	n.d.	n.d.
Sampling Date (yy-mm)	**M656PH045 (µg/L)**	**M656PH047 (µg/L)**	**M656PH054 (µg/L)**	**M656PH003 (µg/L)**	**M656PH010 (µg/L)**
07-05	n.d.	n.d.	n.d.	n.d.	n.d.
07-11	n.d.	n.d.	n.d.	n.d.	n.d.
08-05	n.d.	n.d.	n.d.	n.d.	n.d.
08-11	n.d.	n.d.	n.d.	n.d.	n.d.
09-05	n.d.	n.d.	n.d.	n.d.	n.d.
09-11	n.d.	n.d.	n.d.	n.d.	n.d.
10-06	n.d.	n.d.	n.d.	n.d.	n.d.
10-12	n.d.	n.d.	n.d.	n.d.	n.d.
11-06	n.d.	n.d.	n.d.	n.d.	n.d.
11-12	n.d.	n.d.	n.d.	n.d.	n.d.
12-06	n.d.	n.d.	n.d.	n.d.	n.d.
12-12	n.d.	n.d.	n.d.	n.d.	n.d.

n.d. = not detectable (<0.0075 µg/L for each analyte); <LOQ: <0.025 µg/L
n.d.*= not detectable (<0.009 µg/L = 30 % LOQ, <LOQ*: <0.03 µg/L)

Table B.8.4.1-11: Residues of the dimethenamid-P metabolites in the samples of the groundwater well Ichenheim

Groundwater monitoring well Ichenheim, measurement point 2					
Sampling Date (yy-mm)	**M656PH027 (µg/L)**	**M656PH023 (µg/L)**	**M656PH031 (µg/L)**	**M656PH032 (µg/L)**	**M656PH043 (µg/L)**
07-05	n.d.*	n.d.*	n.d.*	n.d.	n.d.
07-11	n.d.*	n.d.*	n.d.*	n.d.	n.d.
08-05	n.d.*	n.d.*	n.d.*	n.d.	n.d.
08-11	n.d.*	n.d.*	n.d.*	n.d.	n.d.
09-05	n.d.*	n.d.*	n.d.*	n.d.	n.d.
09-11	n.d.*	n.d.*	n.d.*	n.d.	n.d.
10-06	n.d.	n.d.	n.d.	n.d.	n.d.
10-12	n.d.*	n.d.*	n.d.*	n.d.	n.d.
11-06	n.d.*	n.d.*	n.d.*	n.d.	n.d.
11-12	n.d.*	n.d.*	n.d.*	n.d.	n.d.
12-06	n.d.	n.d.	n.d.	n.d.	n.d.
12-12	n.d.	n.d.	n.d.	n.d.	n.d.
Sampling Date (yy-mm)	**M656PH045 (µg/L)**	**M656PH047 (µg/L)**	**M656PH054 (µg/L)**	**M656PH003 (µg/L)**	**M656PH010 (µg/L)**
07-05	n.d.	n.d.	n.d.	n.d.	n.d.
07-11	n.d.	n.d.	n.d.	n.d.	n.d.
08-05	n.d.	n.d.	n.d.	n.d.	n.d.
08-11	n.d.	n.d.	n.d.	n.d.	n.d.
09-05	n.d.	n.d.	n.d.	n.d.	n.d.
09-11	n.d.	n.d.	n.d.	n.d.	n.d.
10-06	n.d.	n.d.	n.d.	n.d.	n.d.
10-12	n.d.	n.d.	n.d.	n.d.	n.d.
11-06	n.d.	n.d.	n.d.	n.d.	n.d.
11-12	n.d.	n.d.	n.d.	n.d.	n.d.
12-06	n.d.	n.d.	n.d.	n.d.	n.d.
12-12	n.d.	n.d.	n.d.	n.d.	n.d.

n.d. = not detectable (<0.0075 µg/L for each analyte); <LOQ: <0.025 µg/L
n.d.*= not detectable (<0.009 µg/L = 30 % LOQ, <LOQ*: <0.03 µg/L)

Table B.8.4.1-12: Residues of the dimethenamid-P metabolites in the samples of the groundwater well Krograspe

Groundwater monitoring well Krograspe, measurement point 19					
Sampling Date (yy-mm)	**M656PH027 (µg/L)**	**M656PH023 (µg/L)**	**M656PH031 (µg/L)**	**M656PH032 (µg/L)**	**M656PH043 (µg/L)**
07-05	n.d.*	n.d.*	n.d.*	--	--
07-11	n.d.*	n.d.*	n.d.*	--	--
08-05	n.d.*	n.d.*	n.d.*	n.d.	n.d.
08-11	n.d.*	n.d.*	n.d.*	n.d.	n.d.
09-05	n.d.*	n.d.*	n.d.*	n.d.	n.d.
09-11	n.d.*	n.d.*	n.d.*	n.d.	n.d.
10-06	n.d.	n.d.	n.d.	n.d.	n.d.
10-12	n.d.*	n.d.*	n.d.*	--	--
11-06	n.d.*	n.d.*	n.d.*	n.d.	n.d.
11-12	n.d.*	n.d.*	n.d.*	n.d.	n.d.
12-06	n.d.	n.d.	n.d.	n.d.	n.d.
12-12	n.d.	n.d.	n.d.	n.d.	n.d.
Sampling Date (yy-mm)	**M656PH045 (µg/L)**	**M656PH047 (µg/L)**	**M656PH054 (µg/L)**	**M656PH003 (µg/L)**	**M656PH010 (µg/L)**
07-05	n.d.	n.d.	n.d.	n.d.	n.d.
07-11	n.d.	n.d.	n.d.	n.d.	n.d.
08-05	n.d.	n.d.	n.d.	n.d.	n.d.
08-11	n.d.	n.d.	n.d.	n.d.	n.d.
09-05	n.d.	n.d.	n.d.	n.d.	n.d.
09-11	n.d.	n.d.	n.d.	n.d.	n.d.
10-06	n.d.	n.d.	n.d.	n.d.	n.d.
10-12	n.d.	n.d.	n.d.	n.d.	n.d.
11-06	n.d.	n.d.	n.d.	n.d.	n.d.
11-12	n.d.	n.d.	n.d.	n.d.	n.d.
12-06	n.d.	n.d.	n.d.	n.d.	n.d.
12-12	n.d.	n.d.	n.d.	n.d.	n.d.

n.d. = not detectable (<0.0075 µg/L for each analyte); <LOQ: <0.025 µg/L
n.d.*= not detectable (<0.009 µg/L = 30 % LOQ, <LOQ*: <0.03 µg/L)

Table B.8.4.1-13: Residues of the dimethenamid-P metabolites in the samples of the groundwater well Oberhausen

Groundwater monitoring well Albersloh, measurement point 13					
Sampling Date (yy-mm)	**M656PH027 (µg/L)**	**M656PH023 (µg/L)**	**M656PH031 (µg/L)**	**M656PH032 (µg/L)**	**M656PH043 (µg/L)**
07-05	n.d.*	n.d.*	n.d.*	n.d.	n.d.
07-11	n.d.*	n.d.*	n.d.*	n.d.	n.d.
08-05	n.d.*	n.d.*	n.d.*	n.d.	n.d.
08-11	n.d.*	n.d.*	n.d.*	n.d.	n.d.
09-05	n.d.*	n.d.*	n.d.*	n.d.	n.d.
09-11	n.d.*	n.d.*	n.d.*	n.d.	n.d.
10-06	n.d.	n.d.	n.d.	n.d.	n.d.
10-12	n.d.*	n.d.*	n.d.*	n.d.	n.d.
11-06	n.d.*	n.d.*	n.d.*	n.d.	n.d.
11-12	n.d.*	n.d.*	n.d.*	n.d.	n.d.
12-06	n.d.	n.d.	n.d.	n.d.	n.d.
12-12	n.d.	n.d.	n.d.	n.d.	n.d.
Sampling Date (yy-mm)	**M656PH045 (µg/L)**	**M656PH047 (µg/L)**	**M656PH054 (µg/L)**	**M656PH003 (µg/L)**	**M656PH010 (µg/L)**
07-05	n.d.	n.d.	n.d.	n.d.	n.d.
07-11	n.d.	n.d.	n.d.	n.d.	n.d.
08-05	n.d.	n.d.	n.d.	n.d.	n.d.
08-11	n.d.	n.d.	n.d.	n.d.	n.d.
09-05	n.d.	n.d.	n.d.	n.d.	n.d.
09-11	n.d.	n.d.	n.d.	n.d.	n.d.
10-06	n.d.	n.d.	n.d.	n.d.	n.d.
10-12	n.d.	n.d.	n.d.	n.d.	n.d.
11-06	n.d.	n.d.	n.d.	n.d.	n.d.
11-12	n.d.	n.d.	n.d.	n.d.	n.d.
12-06	n.d.	n.d.	n.d.	n.d.	n.d.
12-12	n.d.	n.d.	n.d.	n.d.	n.d.

n.d. = not detectable (<0.0075 µg/L for each analyte); <LOQ: <0.025 µg/L
n.d.*= not detectable (<0.009 µg/L = 30 % LOQ, <LOQ*: <0.03 µg/L)

Table B.8.4.1-14: Residues of the dimethenamid-P metabolites in the samples of the groundwater well Ostbevern

Groundwater monitoring well Ostbevern, measurement point 14					
Sampling Date (yy-mm)	**M656PH027 (µg/L)**	**M656PH023 (µg/L)**	**M656PH031 (µg/L)**	**M656PH032 (µg/L)**	**M656PH043 (µg/L)**
07-05	n.d.*	n.d.*	n.d.*	n.d.	n.d.
07-11	n.d.*	n.d.*	n.d.*	n.d.	n.d.
08-05	n.d.*	n.d.*	n.d.*	n.d.	n.d.
08-11	n.d.*	n.d.*	n.d.*	n.d.	n.d.
09-05	n.d.*	n.d.*	n.d.*	n.d.	n.d.
09-11	n.d.*	n.d.*	n.d.*	n.d.	n.d.
10-12	n.d.*	n.d.*	n.d.*	n.d.	n.d.
11-06	n.d.*	n.d.*	n.d.*	n.d.	n.d.
11-12	n.d.*	n.d.*	n.d.*	n.d.	n.d.
12-06	n.d.	n.d.	n.d.	n.d.	n.d.
12-12	n.d.	n.d.	n.d.	n.d.	n.d.
Sampling Date (yy-mm)	**M656PH045 (µg/L)**	**M656PH047 (µg/L)**	**M656PH054 (µg/L)**	**M656PH003 (µg/L)**	**M656PH010 (µg/L)**
07-05	n.d.	n.d.	n.d.	n.d.	n.d.
07-11	n.d.	n.d.	n.d.	n.d.	n.d.
08-05	n.d.	n.d.	n.d.	n.d.	n.d.
08-11	n.d.	n.d.	n.d.	n.d.	n.d.
09-05	n.d.	n.d.	n.d.	n.d.	n.d.
09-11	n.d.	n.d.	n.d.	n.d.	n.d.
10-12	n.d.	<LOQ	n.d.	n.d.	n.d.
11-06	n.d.	n.d.	n.d.	n.d.	n.d.
11-12	n.d.	<LOQ	n.d.	n.d.	n.d.
12-06	n.d.	n.d.	n.d.	n.d.	n.d.
12-12	n.d.	n.d.	n.d.	n.d.	n.d.

n.d. = not detectable (<0.0075 µg/L for each analyte); <LOQ: <0.025 µg/L

n.d.*= not detectable (<0.009 µg/L = 30 % LOQ, <LOQ*: <0.03 µg/L)

Table B.8.4.1-15: Residues of the dimethenamid-P metabolites in the samples of the groundwater well Osterholzen

Groundwater monitoring well Osterholzen, measurement point 6					
Sampling Date (yy-mm)	**M656PH027 (µg/L)**	**M656PH023 (µg/L)**	**M656PH031 (µg/L)**	**M656PH032 (µg/L)**	**M656PH043 (µg/L)**
07-11	n.d.*	n.d.*	n.d.*	n.d.	n.d.
08-05	n.d.*	n.d.*	n.d.*	n.d.	n.d.
08-11	n.d.*	n.d.*	n.d.*	n.d.	n.d.
09-05	n.d.*	n.d.*	n.d.*	n.d.	n.d.
09-11	n.d.*	n.d.*	n.d.*	n.d.	n.d.
10-06	n.d.	n.d.	n.d.	n.d.	n.d.
10-12	n.d.*	n.d.*	n.d.*	n.d.	n.d.
11-06	n.d.*	n.d.*	n.d.*	n.d.	n.d.
11-12	n.d.*	n.d.*	n.d.*	n.d.	n.d.
12-06	n.d.	n.d.	n.d.	n.d.	n.d.
12-12	n.d.	n.d.	n.d.	n.d.	<LOQ
Sampling Date (yy-mm)	**M656PH045 (µg/L)**	**M656PH047 (µg/L)**	**M656PH054 (µg/L)**	**M656PH003 (µg/L)**	**M656PH010 (µg/L)**
07-11	n.d.	n.d.	n.d.	n.d.	n.d.
08-05	n.d.	n.d.	n.d.	n.d.	n.d.
08-11	n.d.	n.d.	n.d.	n.d.	n.d.
09-05	n.d.	n.d.	n.d.	n.d.	n.d.
09-11	n.d.	n.d.	n.d.	n.d.	n.d.
10-06	n.d.	n.d.	n.d.	n.d.	n.d.
10-12	n.d.	n.d.	n.d.	n.d.	n.d.
11-06	n.d.	n.d.	n.d.	n.d.	n.d.
11-12	n.d.	n.d.	n.d.	n.d.	n.d.
12-06	n.d.	n.d.	n.d.	n.d.	n.d.
12-12	n.d.	n.d.	n.d.	n.d.	n.d.

n.d. = not detectable (<0.0075 µg/L for each analyte); <LOQ: <0.025 µg/L

n.d.*= not detectable (<0.009 µg/L = 30 % LOQ, <LOQ*: <0.03 µg/L)

Table B.8.4.1-16: Residues of the dimethenamid-P metabolites in the samples of the groundwater well Pfarrkirchen

Groundwater monitoring well Pfarrkirchen, measurement point 7					
Sampling Date (yy-mm)	**M656PH027 (µg/L)**	**M656PH023 (µg/L)**	**M656PH031 (µg/L)**	**M656PH032 (µg/L)**	**M656PH043 (µg/L)**
07-11	n.d.*	n.d.*	n.d.*	n.d.	n.d.
08-03	<LOQ	n.d.	n.d.	n.d.	n.d.
08-05	<LOQ*	n.d.*	n.d.*	n.d.	n.d.
08-07	n.d.	n.d.	n.d.	n.d.	n.d.
08-09	n.d.	n.d.	n.d.	n.d.	n.d.
08-11	<LOQ*	n.d.*	n.d.*	n.d.	n.d.
09-01	<LOQ	n.d.	n.d.	n.d.	n.d.
09-03	0.025	n.d.	n.d.	n.d.	n.d.
09-05	<LOQ*	n.d.*	n.d.*	n.d.	n.d.
09-07	<LOQ	n.d.	n.d.	n.d.	n.d.
09-09	0.039	n.d.	n.d.	n.d.	n.d.
09-11	0.040*	n.d.*	n.d.*	n.d.	n.d.
10-01	0.035	n.d.	n.d.	n.d.	n.d.
10-03	0.039	<LOQ	n.d.	n.d.	n.d.
10-06	0.036	n.d.	n.d.	n.d.	n.d.
10-09	**0.056**	n.d.	n.d.	n.d.	n.d.
10-12	0.040*	n.d.*	n.d.*	n.d.	n.d.
11-03	0.049	n.d.	n.d.	n.d.	n.d.
11-06	0.039*	n.d.*	n.d.*	n.d.	n.d.
11-09	0.048**	n.d.**	n.d.**	n.d.**	n.d.**
11-12	<LOQ*	n.d.*	n.d.*	n.d.	n.d.
12-03	0.049	n.d.	n.d.	n.d.	n.d.
12-06	0.042	n.d.	n.d.	n.d.	n.d.
12-12	0.037	n.d.	n.d.	n.d.	n.d.
Sampling Date (yy-mm)	**M656PH045 (µg/L)**	**M656PH047 (µg/L)**	**M656PH054 (µg/L)**	**M656PH003 (µg/L)**	**M656PH010 (µg/L)**
07-11	n.d.	n.d.	n.d.	n.d.	n.d.
08-03	n.d.	n.d.	n.d.	n.d.	n.d.
08-05	n.d.	n.d.	n.d.	n.d.	n.d.
08-07	n.d.	n.d.	n.d.	n.d.	n.d.
08-09	n.d.	n.d.	n.d.	n.d.	n.d.
08-11	n.d.	n.d.	n.d.	n.d.	n.d.
09-01	n.d.	n.d.	n.d.	n.d.	n.d.
09-03	n.d.	n.d.	n.d.	n.d.	n.d.
09-05	n.d.	n.d.	n.d.	n.d.	n.d.
09-07	n.d.	n.d.	n.d.	n.d.	n.d.
09-09	n.d.	n.d.	n.d.	n.d.	n.d.
09-11	n.d.	n.d.	n.d.	n.d.	n.d.
10-01	n.d.	n.d.	n.d.	n.d.	n.d.
10-03	n.d.	n.d.	n.d.	n.d.	n.d.
10-06	n.d.	n.d.	n.d.	n.d.	n.d.
10-09	n.d.	n.d.	n.d.	n.d.	n.d.
10-12	n.d.	n.d.	n.d.	n.d.	n.d.
11-03	n.d.	n.d.	n.d.	n.d.	n.d.
11-06	n.d.	n.d.	n.d.	n.d.	n.d.
11-09	n.d.**	n.d.**	n.d.**	n.d.**	n.d.**

Groundwater monitoring well Pfarrkirchen, measurement point 7					
11-12	n.d.	n.d.	n.d.	n.d.	n.d.
12-03	n.d.	n.d.	n.d.	n.d.	n.d.
12-06	n.d.	n.d.	n.d.	n.d.	n.d.
12-12	n.d.	n.d.	n.d.	n.d.	n.d.

n.d. = not detectable (<0.0075 µg/L for each analyte); <LOQ: <0.025 µg/L
n.d.*= not detectable (<0.009 µg/L = 30 % LOQ, <LOQ*: <0.03 µg/L)
** mean of two values

Table B.8.4.1-17: Residues of the dimethenamid-P metabolites in the samples of the groundwater well Quadendambeck

Groundwater monitoring well Quadendambeck, measurement point 11					
Sampling Date (yy-mm)	**M656PH027 (µg/L)**	**M656PH023 (µg/L)**	**M656PH031 (µg/L)**	**M656PH032 (µg/L)**	**M656PH043 (µg/L)**
07-05	n.d.*	n.d.*	n.d.*	n.d.	n.d.
07-11	n.d.*	n.d.*	n.d.*	n.d.	n.d.
08-05	n.d.*	n.d.*	n.d.*	n.d.	n.d.
08-11	n.d.*	n.d.*	n.d.*	n.d.	n.d.
09-05	n.d.*	n.d.*	n.d.*	n.d.	n.d.
09-11	n.d.*	n.d.*	n.d.*	n.d.	n.d.
10-06	n.d.	n.d.	n.d.	n.d.	n.d.
10-12	n.d.*	n.d.*	n.d.*	n.d.	n.d.
11-06	n.d.*	n.d.*	n.d.*	n.d.	n.d.
11-12	n.d.*	n.d.*	n.d.*	n.d.	n.d.
12-06	n.d.	n.d.	n.d.	n.d.	n.d.
12-12	n.d.	n.d.	n.d.	n.d.	n.d.
Sampling Date (yy-mm)	**M656PH045 (µg/L)**	**M656PH047 (µg/L)**	**M656PH054 (µg/L)**	**M656PH003 (µg/L)**	**M656PH010 (µg/L)**
07-05	n.d.	n.d.	n.d.	n.d.	n.d.
07-11	n.d.	n.d.	n.d.	n.d.	n.d.
08-05	n.d.	n.d.	n.d.	n.d.	n.d.
08-11	n.d.	n.d.	n.d.	n.d.	n.d.
09-05	n.d.	n.d.	n.d.	n.d.	n.d.
09-11	n.d.	n.d.	n.d.	n.d.	n.d.
10-06	n.d.	n.d.	n.d.	n.d.	n.d.
10-12	n.d.	n.d.	n.d.	n.d.	n.d.
11-06	n.d.	n.d.	n.d.	n.d.	n.d.
11-12	n.d.	n.d.	n.d.	n.d.	n.d.
12-06	n.d.	n.d.	n.d.	n.d.	n.d.
12-12	n.d.	n.d.	n.d.	n.d.	n.d.

n.d. = not detectable (<0.0075 µg/L for each analyte); <LOQ: <0.025 µg/L
n.d.*= not detectable (<0.009 µg/L = 30 % LOQ, <LOQ*: <0.03 µg/L)

Table B.8.4.1-18: Residues of the dimethenamid-P metabolites in the samples of the groundwater well Rheinau

Groundwater monitoring well Rheinau, measurement point 1					
Sampling Date (yy-mm)	**M656PH027 (µg/L)**	**M656PH023 (µg/L)**	**M656PH031 (µg/L)**	**M656PH032 (µg/L)**	**M656PH043 (µg/L)**
07-05	n.d.*	n.d.*	n.d.*	n.d.	n.d.
07-11	n.d.*	n.d.*	n.d.*	n.d.	n.d.
08-05	n.d.*	n.d.*	n.d.*	n.d.	n.d.
08-11	n.d.*	n.d.*	n.d.*	n.d.	n.d.
09-05	n.d.*	n.d.*	n.d.*	n.d.	n.d.
09-11	n.d.*	n.d.*	n.d.*	n.d.	n.d.
10-06	n.d.	n.d.	n.d.	n.d.	n.d.
10-12	n.d.*	n.d.*	n.d.*	n.d.	n.d.
11-06	n.d.*	n.d.*	n.d.*	n.d.	n.d.
11-12	n.d.*	n.d.*	n.d.*	n.d.	n.d.
12-06	n.d.	n.d.	n.d.	n.d.	n.d.
12-12	n.d.	n.d.	n.d.	n.d.	n.d.
Sampling Date (yy-mm)	**M656PH045 (µg/L)**	**M656PH047 (µg/L)**	**M656PH054 (µg/L)**	**M656PH003 (µg/L)**	**M656PH010 (µg/L)**
07-05	n.d.	n.d.	n.d.	n.d.	n.d.
07-11	n.d.	n.d.	n.d.	n.d.	n.d.
08-05	n.d.	n.d.	n.d.	n.d.	n.d.
08-11	n.d.	n.d.	n.d.	n.d.	n.d.
09-05	n.d.	n.d.	n.d.	n.d.	n.d.
09-11	n.d.	n.d.	n.d.	n.d.	n.d.
10-06	n.d.	n.d.	n.d.	n.d.	n.d.
10-12	n.d.	n.d.	n.d.	n.d.	n.d.
11-06	n.d.	n.d.	n.d.	n.d.	n.d.
11-12	n.d.	n.d.	n.d.	n.d.	n.d.
12-06	n.d.	n.d.	n.d.	n.d.	n.d.
12-12	n.d.	n.d.	n.d.	n.d.	n.d.

n.d. = not detectable (<0.0075 µg/L for each analyte); <LOQ: <0.025 µg/L
n.d.*= not detectable (<0.009 µg/L = 30 % LOQ, <LOQ*: <0.03 µg/L)

Table B.8.4.1-19: Residues of the dimethenamid-P metabolites in the samples of the groundwater well Rossbach

Groundwater monitoring well Osterholzen, measurement point 8					
Sampling Date (yy-mm)	**M656PH027 (µg/L)**	**M656PH023 (µg/L)**	**M656PH031 (µg/L)**	**M656PH032 (µg/L)**	**M656PH043 (µg/L)**
07-05	n.d.*	n.d.*	n.d.*	n.d.	n.d.
07-11	n.d.*	n.d.*	n.d.*	n.d.	n.d.
08-03	n.d.	n.d.	n.d.	n.d.	n.d.
08-05	<LOQ*	n.d.*	n.d.*	n.d.	n.d.
08-07	n.d.	n.d.	n.d.	n.d.	n.d.
08-09	n.d.	n.d.	n.d.	n.d.	n.d.
08-11	n.d.*	n.d.*	n.d.*	n.d.	n.d.
09-01	n.d.	n.d.	n.d.	n.d.	n.d.
09-03	n.d.	n.d.	n.d.	n.d.	n.d.
09-05	n.d.*	n.d.*	n.d.*	n.d.	n.d.
09-07	n.d.	n.d.	n.d.	n.d.	n.d.
09-11	n.d.*	n.d.*	n.d.*	n.d.	n.d.
10-06	n.d.	n.d.	n.d.	n.d.	n.d.
10-12	n.d.*	n.d.*	n.d.*	n.d.	n.d.
11-06	n.d.*	n.d.*	n.d.*	n.d.	n.d.
11-12	n.d.*	n.d.*	n.d.*	n.d.	n.d.
12-06	n.d.	n.d.	n.d.	n.d.	n.d.
12-12	<LOQ	n.d.	n.d.	n.d.	n.d.
Sampling Date (yy-mm)	**M656PH045 (µg/L)**	**M656PH047 (µg/L)**	**M656PH054 (µg/L)**	**M656PH003 (µg/L)**	**M656PH010 (µg/L)**
07-05	n.d.	n.d.	n.d.	n.d.	n.d.
07-11	n.d.	n.d.	n.d.	n.d.	n.d.
08-03	n.d.	n.d.	n.d.	n.d.	n.d.
08-05	n.d.	n.d.	n.d.	n.d.	n.d.
08-07	n.d.	n.d.	n.d.	n.d.	n.d.
08-09	n.d.	n.d.	n.d.	n.d.	n.d.
08-11	n.d.	n.d.	n.d.	n.d.	n.d.
09-01	n.d.	n.d.	n.d.	n.d.	n.d.
09-03	n.d.	n.d.	n.d.	n.d.	n.d.
09-05	n.d.	n.d.	n.d.	n.d.	n.d.
09-07	n.d.	n.d.	n.d.	n.d.	n.d.
09-11	n.d.	n.d.	n.d.	n.d.	n.d.
10-06	n.d.	n.d.	n.d.	n.d.	n.d.
10-12	n.d.	n.d.	n.d.	n.d.	n.d.
11-06	n.d.	n.d.	n.d.	n.d.	n.d.
11-12	n.d.	n.d.	n.d.	n.d.	n.d.
12-06	n.d.	n.d.	n.d.	n.d.	n.d.
12-12	n.d.	n.d.	n.d.	n.d.	n.d.

n.d. = not detectable (<0.0075 µg/L for each analyte); <LOQ: <0.025 µg/L
n.d.*= not detectable (<0.009 µg/L = 30 % LOQ, <LOQ*: <0.03 µg/L)

Table B.8.4.1-20: Residues of the dimethenamid-P metabolites in the samples of the groundwater well Veltrup

Groundwater monitoring well Veltrup, measurement point 15					
Sampling Date (yy-mm)	**M656PH027 (µg/L)**	**M656PH023 (µg/L)**	**M656PH031 (µg/L)**	**M656PH032 (µg/L)**	**M656PH043 (µg/L)**
07-05	n.d.*	n.d.*	n.d.*	n.d.	n.d.
07-11	n.d.*	n.d.*	n.d.*	n.d.	n.d.
08-05	n.d.*	n.d.*	n.d.*	n.d.	n.d.
08-11	n.d.*	n.d.*	n.d.*	n.d.	n.d.
09-05	n.d.*	n.d.*	n.d.*	n.d.	n.d.
09-11	n.d.*	n.d.*	n.d.*	n.d.	n.d.
10-06	0.054	<LOQ	n.d.	n.d.	n.d.
10-09	0.068	0.027	n.d.	n.d.	n.d.
10-12	0.091*	<LOQ*	n.d.*	n.d.	n.d.
11-03	0.267	0.036	n.d.	n.d.	n.d.
11-06	0.230*	0.049*	n.d.*	n.d.	n.d.
11-09	**1.057**	**0.062**	n.d.	n.d.	n.d.
11-12	0.140*	0.033*	n.d.*	n.d.	n.d.
12-03	0.267	0.054	n.d.	n.d.	n.d.
12-06	0.218	0.055	n.d.	n.d.	<LOQ
12-09	0.243	0.059	n.d.	n.d.	n.d.
12-12	0.182	0.046	n.d.	n.d.	n.d.
13-03	0.198	0.048	n.d.	n.d.	n.d.
Sampling Date (yy-mm)	**M656PH045 (µg/L)**	**M656PH047 (µg/L)**	**M656PH054 (µg/L)**	**M656PH003 (µg/L)**	**M656PH010 (µg/L)**
07-05	n.d.	n.d.	n.d.	n.d.	n.d.
07-11	n.d.	n.d.	n.d.	n.d.	n.d.
08-05	n.d.	n.d.	n.d.	n.d.	n.d.
08-11	n.d.	n.d.	n.d.	n.d.	n.d.
09-05	n.d.	n.d.	n.d.	n.d.	n.d.
09-11	n.d.	n.d.	n.d.	n.d.	n.d.
10-06	<LOQ	n.d.	n.d.	n.d.	n.d.
10-09	n.d.	n.d.	n.d.	n.d.	n.d.
10-12	n.d.	n.d.	n.d.	n.d.	n.d.
11-03	<LOQ	n.d.	n.d.	n.d.	n.d.
11-06	n.d.	n.d.	n.d.	n.d.	n.d.
11-09	n.d.	n.d.	n.d.	n.d.	n.d.
11-12	<LOQ	n.d.	n.d.	n.d.	n.d.
12-03	n.d.	n.d.	n.d.	n.d.	n.d.
12-06	0.029	n.d.	<LOQ	n.d.	n.d.
12-09	<LOQ	n.d.	n.d.	n.d.	n.d.
12-12	0.038	**0.161**	<LOQ	n.d.	n.d.
13-03	**0.045**	n.d.	<LOQ	n.d.	n.d.

n.d. = not detectable (<0.0075 µg/L for each analyte); <LOQ: <0.025 µg/L

n.d.*= not detectable (<0.009 µg/L = 30 % LOQ, <LOQ*: <0.03 µg/L)

Table B.8.4.1-21: Residues of the dimethenamid-P metabolites in the samples of the groundwater well Vinnen-Ahmsen

Groundwater monitoring well Vinnen-Ahmsen, measurement point 17					
Sampling Date (yy-mm)	**M656PH027 (µg/L)**	**M656PH023 (µg/L)**	**M656PH031 (µg/L)**	**M656PH032 (µg/L)**	**M656PH043 (µg/L)**
07-05	n.d.*	n.d.*	n.d.*	n.d.	n.d.
07-11	n.d.*	n.d.*	n.d.*	n.d.	n.d.
08-05	n.d.*	n.d.*	n.d.*	n.d.	n.d.
08-11	n.d.*	n.d.*	n.d.*	n.d.	n.d.
09-05	n.d.*	n.d.*	n.d.*	n.d.	n.d.
09-11	n.d.*	n.d.*	n.d.*	n.d.	n.d.
10-06	<LOQ	n.d.	n.d.	n.d.	n.d.
10-12	n.d.*	n.d.*	n.d.*	n.d.	n.d.
11-03	n.d.	n.d.	n.d.	n.d.	n.d.
11-06	<LOQ*	n.d.*	n.d.*	n.d.	n.d.
11-09	<LOQ	n.d.	n.d.	n.d.	n.d.
11-12	n.d.*	n.d.*	n.d.*	n.d.	n.d.
12-03	<LOQ	n.d.	n.d.	n.d.	n.d.
12-06	<LOQ	n.d.	n.d.	n.d.	n.d.
12-12	<LOQ	n.d.	n.d.	n.d.	n.d.
Sampling Date (yy-mm)	**M656PH045 (µg/L)**	**M656PH047 (µg/L)**	**M656PH054 (µg/L)**	**M656PH003 (µg/L)**	**M656PH010 (µg/L)**
07-05	n.d.	n.d.	n.d.	n.d.	n.d.
07-11	n.d.	n.d.	n.d.	n.d.	n.d.
08-05	n.d.	n.d.	n.d.	n.d.	n.d.
08-11	n.d.	n.d.	n.d.	n.d.	n.d.
09-05	n.d.	n.d.	n.d.	n.d.	n.d.
09-11	n.d.	n.d.	n.d.	n.d.	n.d.
10-06	n.d.	<LOQ	n.d.	n.d.	n.d.
10-12	n.d.	**0.027**	n.d.	n.d.	n.d.
11-03	n.d.	n.d.	n.d.	n.d.	n.d.
11-06	n.d.	<LOQ	n.d.	n.d.	n.d.
11-09	n.d.	n.d.	n.d.	n.d.	n.d.
11-12	n.d.	<LOQ	n.d.	n.d.	n.d.
12-03	n.d.	n.d.	n.d.	n.d.	n.d.
12-06	n.d.	<LOQ	n.d.	n.d.	n.d.
12-12	n.d.	<LOQ	n.d.	n.d.	n.d.

n.d. = not detectable (<0.0075 µg/L for each analyte); <LOQ: <0.025 µg/L
n.d.*= not detectable (<0.009 µg/L = 30 % LOQ, <LOQ*: <0.03 µg/L)

Table B.8.4.1-22: Residues of the dimethenamid-P metabolites in the samples of the groundwater well Wedel

Groundwater monitoring well Wedel, measurement point 18					
Sampling Date (yy-mm)	**M656PH027 (µg/L)**	**M656PH023 (µg/L)**	**M656PH031 (µg/L)**	**M656PH032 (µg/L)**	**M656PH043 (µg/L)**
07-05	n.d.*	n.d.*	n.d.*	n.d.	n.d.
07-11	n.d.*	n.d.*	n.d.*	n.d.	n.d.
08-05	n.d.*	n.d.*	n.d.*	n.d.	n.d.
08-11	n.d.*	n.d.*	n.d.*	n.d.	n.d.
09-05	n.d.*	n.d.*	n.d.*	n.d.	n.d.
09-11	n.d.*	n.d.*	n.d.*	n.d.	n.d.
10-06	n.d.	n.d.	n.d.	n.d.	n.d.
10-12	n.d.*	n.d.*	n.d.*	--	--
11-06	n.d.*	n.d.*	n.d.*	n.d.	n.d.
11-12	n.d.*	n.d.*	n.d.*	n.d.	n.d.
12-06	n.d.	n.d.	n.d.	n.d.	n.d.
12-12	n.d.	n.d.	n.d.	n.d.	n.d.
Sampling Date (yy-mm)	**M656PH045 (µg/L)**	**M656PH047 (µg/L)**	**M656PH054 (µg/L)**	**M656PH003 (µg/L)**	**M656PH010 (µg/L)**
07-05	n.d.	n.d.	n.d.	n.d.	n.d.
07-11	n.d.	n.d.	n.d.	n.d.	n.d.
08-05	n.d.	n.d.	n.d.	n.d.	n.d.
08-11	n.d.	n.d.	n.d.	n.d.	n.d.
09-05	n.d.	n.d.	n.d.	n.d.	n.d.
09-11	n.d.	n.d.	n.d.	n.d.	n.d.
10-06	n.d.	n.d.	n.d.	n.d.	n.d.
10-12	--	--	--	--	--
11-06	n.d.	n.d.	n.d.	n.d.	n.d.
11-12	n.d.	n.d.	n.d.	n.d.	n.d.
12-06	n.d.	n.d.	n.d.	n.d.	n.d.
12-12	n.d.	n.d.	n.d.	n.d.	n.d.

n.d. = not detectable (<0.0075 µg/L for each analyte); <LOQ: <0.025 µg/L
n.d.*= not detectable (<0.009 µg/L = 30 % LOQ, <LOQ*: <0.03 µg/L)

Of the 20 sampling sites tested in Germany, 14 (70 %) showed no detectable levels (and/or < LOQ) of all 10 metabolites of dimethenamid-P. Six of the sites (Albersloh, Brekendorf, Flechum, Pfarrkirchen, Veltrup and Vinnen-Ahmsen) showed low levels of metabolites. The metabolite most often observed was M656PH027, the second most frequently observed was M656PH023. One site, Flechum, showed a higher degree of observances for the metabolites of dimethenamid-P. This site also gave the highest observed levels for M656H027 in the German groundwater monitoring study.

- Residues of M656PH027 were found in concentrations up to 1.680 µg/L mainly at the locations Pfarrkirchen, Flechum, Veltrup, Albersloh and Brekendorf.
- Residues of M656PH023 were found in concentrations up to 0.379 µg/L mainly at the locations Flechum, Veltrup and Albersloh.
- Residues of M656PH045 were found in concentrations up to 0.045 µg/L mainly at the locations Veltrup and Albersloh.
- Residues of M656PH047 were found in concentrations up to 0.161 µg/L mainly at the locations Flechum and Albersloh.
- Residues of M656PH054 were found once with a concentration of 0.049 µg/L at the location Flechum.
- Residues of M656PH031, M656PH010, M656PH032, M656PH043 and M656PH003 were not found in concentration above LOQ in any of the samples.

Conclusion

While no details on the analytical methods were provided in the study and could therefore not be evaluated by the RMS.
As a general issue, the RMS believes that it would have been good to analyse also the active substance dimethenamid-P itself. While according to groundwater modelling and the lysimeter study, the active substance shows no tendency to enter groundwater in concentrations ≥ 0.1 µg/L, actual measurements that confirm can these results are still useful.
Additionally, the RMS wonders, how the samples were stored that were first analysed by Class (2013) for the metabolites M656PH023, M656PH027 and M656PH031 and then later on by Mewis (2014a) for the remaining metabolites M656PH003, M656PH010, M656PH032, M656PH043, M656PH045, M656PH047 and M656PH054. These results are only considered acceptable, if all samples were defrosted only once and then immediately analysed afterwards, but were not stored defrosted for a long period of time or frozen and thawed more than once.
Besides, the RMS wonders if the storage stability of the groundwater samples might be an issue. The groundwater samples analysed were stored deep frozen (RMS assumes this means a storage temperature of -20 °C) for 2 up to 6 years. It is not clear if the metabolites are stable even under frozen conditions for such a long period of time. No storage stability tests were performed with the metabolites or according to the study report none were started (since it would take some time to be finalised). However, concentration and distribution pattern of the metabolites at the German and Dutch Monitoring sites described under Mewis, 2014 are quite similar supporting the assumption, that the metabolites remained stable during storage.

On the whole, the measurements of Class, 2013 and Mewis, 2014a are considered acceptable if details on the analytical methods will be provided.

Some mistakes were made in the summary regarding the maximum concentrations observed in the wells. Thus, the maximum concentrations and the number of groundwater sites, where the metabolites were detected are summarised again in Table B.8.4.1-23.

Table B.8.4.1-23: Maximum concentrations and number of groundwater wells where the metabolites were detected in the German Monitoring

Metabolite	No of wells with positive detections	Percent of wells with positive detections	Maximum concentrations [µg/L]
M656PH003	0	0 %	<LOQ
M656PH010	0	0 %	<LOQ
M656PH027	5	25 %	1.680
M656PH023	3	15 %	0.379
M656PH031	0	0 %	<LOQ
M656PH032	0	0 %	<LOQ
M656PH043	0	0 %	<LOQ
M656PH045	2	10 %	0.045
M656PH047	4	20 %	0.149
M656PH054	1	5 %	0.047

The wells where metabolites were detected show an increasing trend for the metabolites M656H023 and M656H027 over the years, which is most pronounced at Albersloh and Flechum as shown exemplary for Figure B.8.4.1-2 and Figure B.8.4.1-3.

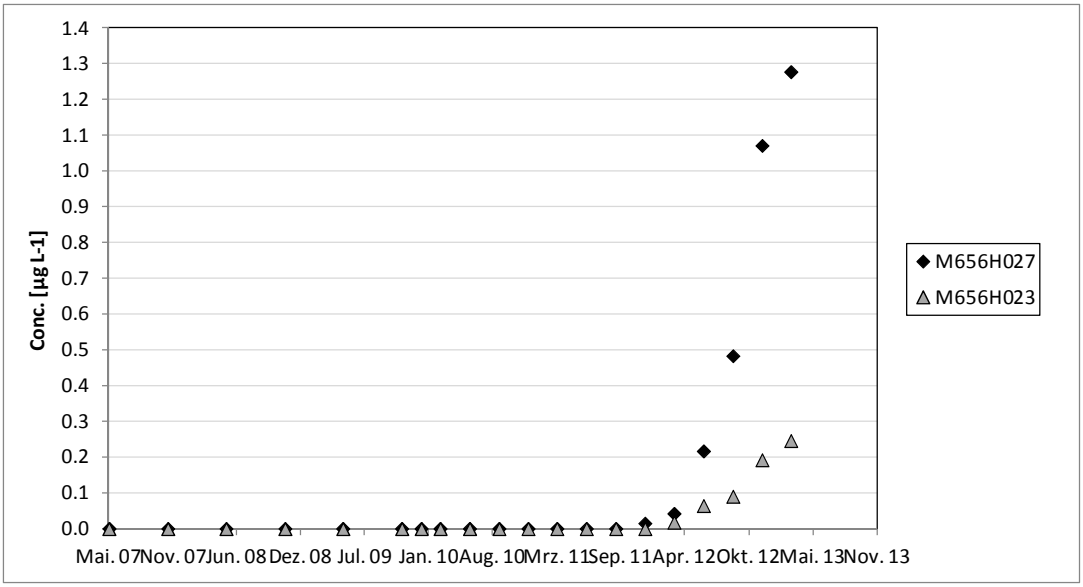


Figure B.8.4.1-2: Concentrations of M656PH023 and M656PH023 at the groundwater monitoring site Albersloh

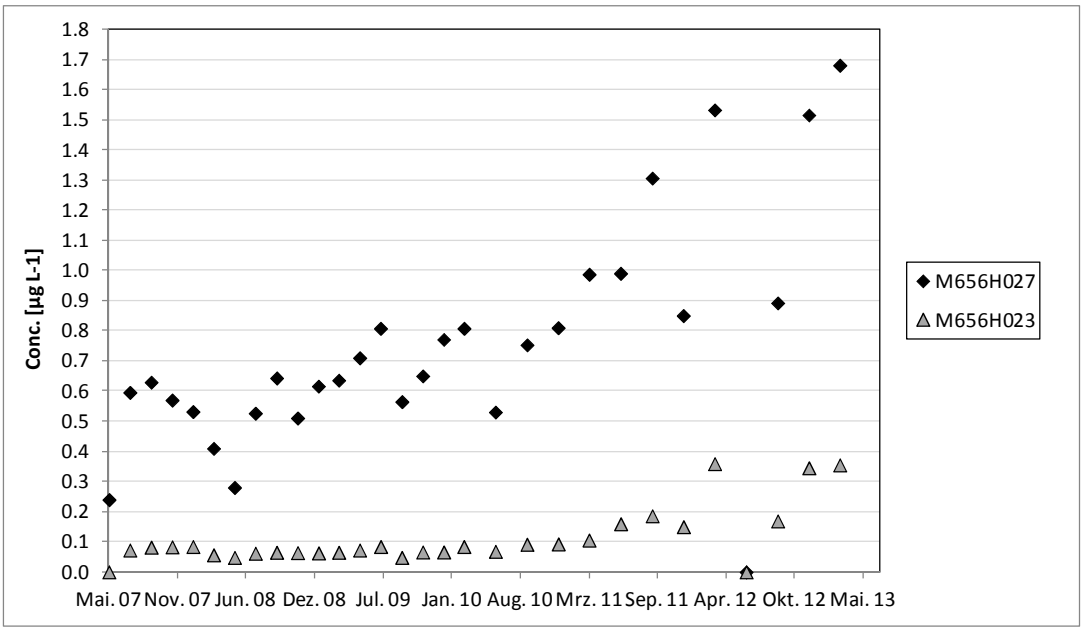


Figure B.8.4.1-3: Concentrations of M656PH023 and M656PH023 at the groundwater monitoring site Flechum

KCA 7.5/3– Haering & Miles, 2014 (new study)

Author:	Haering, T. Miles, B.
Title:	Evaluation of groundwater monitoring sites and context setting of groundwater monitoring data for metabolites of dimethenamid-P
Date:	09/01/2014
Doc ID:	BASF DocID 2013/1347948
Guidelines:	None
GLP:	No (not applicable)
Validity:	Partly acceptable

Aim of the study

The present report evaluates the validity of the monitoring study in Germany for the dimethenamid-P metabolites, assessing both the retrospective aspect of the study (whether the study can show how shallow groundwater in the monitoring regions may have been affected by historical applications of dimethenamid-P and previously the racemate dimethenamid) as well as the prospective aspect in which product applications were sponsored in the upstream vicinity of the monitoring wells. The monitoring sites and data from the study are then set into a European context. The representativeness of the German groundwater monitoring locations for agricultural areas in Europe is evaluated by applying a quantitative GIS-based spatial modelling approach to assess comparative leaching vulnerabilities.
The study also included a brief evaluation of the groundwater monitoring study Mewis, 2014b performed in the Netherlands. However, only the description already described under Mewis, 2014b were repeated and no new information was provided. Thus, this part of the study is not summarised by the RMS here but described and discussed in the study summary Mewis, 2014b.

Material and Methods

From 2007 to 2012 a groundwater monitoring study involving BASF commercial herbicide products containing dimethenamid-P was conducted at 20 monitoring sites in Germany.
The selection of the groundwater wells and the field work of the study including sampling is summarised under Schmidt et al (2010), Schmidt and Schulz (2012) and Schmidt and Schneider (2013). The determination of residues of metabolites of dimethenamid-P M656PH003, M656PH010, M656PH023, M656PH027, M656PH031, M656PH032, M656PH043, M656PH045, M656PH047 and M656PH054 in the groundwater samples are summarised under Class (2013) and Mewis (2014a).

In the study, groundwater monitoring points in four regions typical for maize cultivation and representing the prominent maize growing areas in Germany were selected. The wells, which penetrate the upper groundwater layers at the respective sites, were selected following recommendations of the environmental or water authorities of the Federal States. The monitoring sites themselves were all located downstream from major agricultural areas with intensive maize cultivation and represent situations vulnerable to leaching of agricultural chemicals, with shallow groundwater (generally at about 2 – 10 m depth) in unconsolidated sedimentary aquifers consisting mainly of sands and gravels below sand or loam soils.

The study design of the ground water monitoring thus clearly covers a retrospective approach for the metabolites of dimethenamid-P. It serves to show whether applications of the herbicide dimethenamid-P, which has been available for use in maize for many years (previously as dimethenamid), to maize fields in the monitoring regions may have affected the shallow groundwater.
In order to ensure that the timeframe of the monitoring study was appropriate for the metabolites of dimethenamid-P with regard to this prospective aspect of the monitoring study, leaching simulations were conducted for each monitoring site and used in conjunction with hydrogeological data to derive estimated potential arrival times at the monitoring wells for leachate from the known product applications.

Evaluation of validity of the prospective aspect of the monitoring study in Germany for the dimethenamid-P metabolites:

Leaching simulations were carried out using the model PEARL 4.4.4.

As the leaching behaviour of the metabolites strongly depends on the makeup of the soil profile of the treated field, soil profile data were assembled to create realistic profiles for the individual sites. State authorities were asked for detailed soil profile data, which were located near the monitoring sites and which were representative for the soil conditions at the well. In most cases, representative soil profiles which characterise a high-resolution soil map unit, so called *Leitprofile*, were available. The scale of the soil maps ranges from 1:5.000 to 1:25.000.
In areas, where no detailed soil map and no soil profiles were available, profile descriptions from coarser soil maps (s. Table 2.3-1) were used. In cases where more than one soil profile was available for a monitoring location modelling scenarios for each soil were set up.

Data on temperature, precipitation, and evapotranspiration were obtained from the MARS-project of the AGRI4CAST and FOODSEC units of the Directorate General Joint Research Center (JRC) of the European Commission in Ispra (Italy). These data are the only source available to obtain homogeneous weather data with all parameters necessary to run groundwater leaching simulations with a daily temporal resolution.
Data are provided by MARS for 25x25 km grid units. In total eighteen units were relevant for the groundwater monitoring sites. Data were obtained for the period January 1st 1984 – December 31st 2012, which was the latest available date at the time of writing.

The Clio products provided to farmers for the prospective aspect of the monitoring study are applied as post-emergence herbicides onto maize in the BBCH growth stage range 12-16. Taking 1.5 L/ha Clio® Super, which is equivalent to 807 g/ha dimethenamid-P, as a representative product use and assuming a conservative crop interception of 25 %, an application rate of 0.6 kg ha^{-1} dimethenamid-P was used in the simulations.

The application scenario that was therefore used for leaching simulations with PEARL 4.4.4 is presented in Table B.8.4.1-24.

Table B.8.4.1-24: Application scenario of dimethenamid-P considered for the PECgw calculations

Crop	Maize
Growth stage at application [BBCH]	Growth stage 1: Leaf development. 12-16
No. of applications	1
Application rate [g a.s. ha-1]	807
Crop interception [%]	25
Total yearly soil load [g a.s. ha-1]	600
Application dates	03-Jun-2007

The substance-specific and default parameter values of dimethenamid-P used in the leaching simulations are given in Table B.8.4.1-25. The substance specific and default parameter values of the metabolites M656H023, M656H023 and M656H031 used in the leaching simulations are given in Table B.8.4.1-26.
These parameters are endpoints used in the dossier of the applicant before Annex I renewal. No change in the outcome is expected due to the generation of new endpoints in the framework of Annex I renewal and the conclusions drawn in this study.

Table B.8.4.1-25: Substance related parameter for dimethenamid-P used for PECgw simulations

Input parameter	Unit	Dimethenamid-p	Default value
Physico-chemical parameters			
Molecular weight	[g mol^{-1}]	275.8	-
Water solubility	[mg L^{-1}]	1449 (25 °C)	-
Molar enthalpy of dissolution	[kJ mol^{-1}]	-	27
Saturated vapor pressure	[Pa]	2.51 x 10^{-3} (25 °C)	-
Molar enthalpy of vaporisation	[kJ mol^{-1}]	-	95
Diffusion coefficient in water	[m^2 d^{-1}]	-	4.3 x 10^{-5} (20 °C)
Diffusion coefficient in air	[m^2 d^{-1}]	-	0.43 (20 °C)
Degradation parameters			
Half-life at reference conditions	[d]	10.8 (20 °C, pF2)	-
Molar activation energy	[kJ mol^{-1}]	-	65.4
Exponent of moisture correction function	[-]	-	0.7
Sorption parameters			
$K_{f,oc}$ value	[mL g^{-1}]	170.2	-
$K_{f,om}$ value	[mL g^{-1}]	98.7	-
Freundlich exponent 1/n	[-]	0.985	-
Method of subroutine description	[-]	-	pH-independent
Crop related parameters			
PUF (plant uptake factor)	[-]	0.5	

Table B.8.4.1-26: Substance related parameter for dimethenamid-P used for PECgw simulations

Input parameter	Unit	M656H023	M656H027	M656H031
Physico-chemical parameters				
Molecular weight	[g mol^{-1}]	271	321.4	347
Water solubility	[mg L^{-1}]	1000 (20 °C)	1000 (20 °C)	1000 (20 °C)
Saturated vapor pressure	[Pa]	10^{-10} (20 °C)	10^{-10} (20 °C)	10^{-10} (20 °C)
Degradation parameters				
Half-life at reference conditions[1]	[d]	19.7 (20 °C, pF2)	30.4 (20 °C, pF2)	30.8 (20 °C, pF2)
Formation fraction	[-]	0.154 from parent	0.143 from parent 1 from M656PH031	0.067 from parent
Sorption parameters				
$K_{f,om}$ value	[mL g^{-1}]	6.9	5.9	2.5
Freundlich exponent $1/n^2$	[-]	0.72	1.01	0.93
Crop related parameters				
PUF (plant uptake factor)	[-]	0.5	0.5	0.5

The simulation timeframe in FOCUS PEARL 4.4.4 was defined as 01.01.2005 to 31.12.2012, allowing 2.5 years run-in time for the model before the herbicide application and continuing until the end of the available meteorological data time series. This was sufficient to obtain a clear peak solute breakthrough at the evaluation depth in all but two cases.

As the purpose of the simulations was to determine the potential leaching timeframes for solutes reaching groundwater, the evaluation depth for the PEARL simulations was for each site defined by the highest measured groundwater level. Where this was below the level of the defined soil profile, the lowest soil layer was assumed to extend to the lower boundary depth.

The FOCUS Hamburg Maize crop calendar with annual cropping was used for the simulations. The tillage depth was set to 20 cm.

Estimates of travel times in groundwater from the treated fields to the monitoring well were derived from the hydrogeological data provided in Schmidt el al (2010) and distances to the well from treated fields estimated from aerial photographs (Google Inc., 2013: Google Earth v. 7.1.1.188).
The estimated travel times were then combined with the breakthrough times determined for the metabolites from a single application in the leaching simulations to derive approximate timescales for the potential arrivals and peak concentrations of the metabolites from the closest treated field in each application year.

Spatial modelling approach to set monitoring locations in a European context:

To determine the representativeness of the German groundwater monitoring locations for the agricultural area of Europe, a quantitative modelling approach was applied. Representativeness with regard to pesticide leaching to groundwater has to consider several environmental as well as compound parameters which are relevant for groundwater leaching.
The presented assessment of representativeness of monitoring sites consists of two steps (Step 1 and Step 2). The workflow of the assessment is illustrated in Figure B.8.4.1-4.

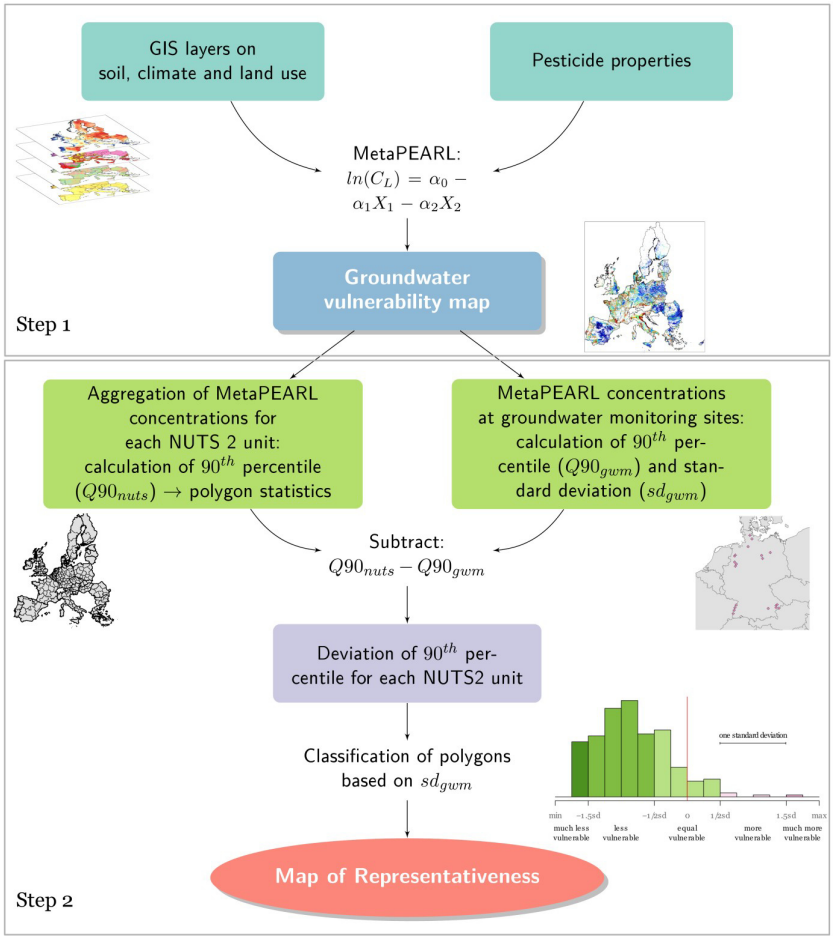


Figure B.8.4.1-4: Workflow for the GIS analysis to assess the representativeness of the German groundwater monitoring sites for the entire EU

In the first step of the assessment, a groundwater vulnerability map for each of the three relevant metabolites M656PH023, M656PH027 and M656PH031 was constructed. The groundwater vulnerability map was calculated with the spatially distributed groundwater leaching model MetaPEARL. The MetaPEARL model was applied to high resolution GIS raster data with a cell size of 1 km to get very detailed maps of groundwater vulnerability all over Europe.

To assess the representativeness of the monitoring locations, subsequently in Step 2, the vulnerability (i.e. the predicted MetaPEARL groundwater concentrations) at the monitoring locations was compared with the conditions in Europe. The comparison is done on the Nomenclature of Units for Territorial Statistics (=NUTS2) level, which is the official nomenclature in the EU. This was done to account for Europe`s diverse landscape with an appropriate spatial resolution on the one hand and to overcome possible uncertainties in the data and methods on the other hand. For each NUTS2 unit, the values of the vulnerability map were aggregated, i.e. aerial statistics of the raster values within each NUTS2 polygon were calculated. As reference values for the comparison, MetaPEARL values at the 20 monitoring locations in Germany were taken. As target value, the 90th percentile concentrations were chosen as a worst case approach compared to the protection goal of pesticide legislation in Europe (80th percentile vulnerability in space).
Thus, for each NUTS2 polygon, 90th percentile concentrations ($Q90_{nuts}$) as well as a 90th percentile concentrations at the monitoring locations ($Q90_{gwm}$) were obtained.

The actual comparison is then a simple subtraction of $Q90_{gwm}$ from $Q90_{nuts}$, i.e. the deviation of the vulnerability conditions in a NUTS2 unit from the conditions at the monitoring locations. If the difference is negative, it can be concluded that less vulnerable conditions of groundwater leaching exist compared to the monitoring study, i.e. $Q90_{nuts}$ is lower than $Q90_{gwm}$. The groundwater monitoring study could be regarded as representative for such NUTS2 units. If the deviation is positive, it can be concluded that there are some areas within this particular NUTS2 unit with higher potential of groundwater leaching of M656PH023, M656PH027, and/or M656PH031.

To add colors to the final map of representativeness, i.e. the classification of the map, the standard deviation of the values at the monitoring sites were used to define the divisions. Therefore, the NUTS2 units with a deviation less than 1.5 sd were classified as “much less vulnerable”, less than 0.5 sd as “less vulnerable”, more than 0.5 sd as “more vulnerable”, more than 1.5 sd as “much more vulnerable” and between -0.5 sd and 0.5 sd as “equally vulnerable. The classification of NUTS2 units based on standard deviation used for coloring the maps of representativeness is presented in Figure B.8.4.1-5.

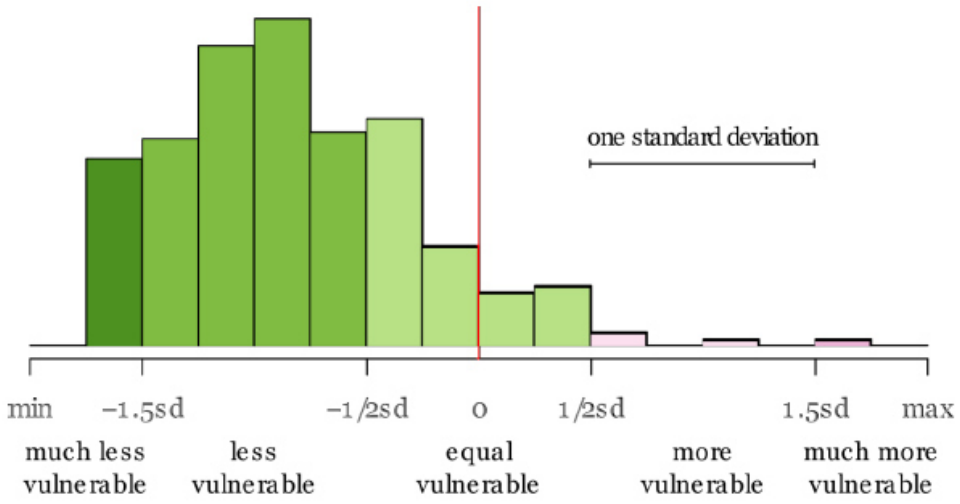


Figure B.8.4.1-5: Classification of NUTS2 units based on standard deviation used for coloring the maps of representativeness as an example for M656H023

Results and Discussion

Evaluation of validity of the prospective aspect of the monitoring study in Germany for the dimethenamid-P metabolites:

As the aim of the simulations is to provide just the potential leaching timeframes at each site resulting from a single application of the active substance, the simulated concentrations for the

metabolites are normalised to their respective maximum leachate concentrations during the simulation (C/C_{max}). Thus regardless of the actual magnitudes of their concentrations, the maximum normalised peak concentration is 1 for all metabolites. The times to the breakthrough and peak concentrations (defined respectively as C/C_{max} = 0.05 and C/C_{max} = 1 for the first arriving metabolite) at the evaluation depths in the simulations are given in Table B.8.4.1-27.

Table B.8.4.1-27: Calculated breakthrough and peak times for metabolites of dimethenamid-P at the monitored groundwater wells in leaching simulations

Simulation	Time after application [d]	
	Breakthrough (C/C_{max} = 0.05)	**Peak (C/C_{max} = 1)**
Albersloh	141	173
Asing1	1362	1812
Asing2	1329	1763
Brekendorf	347	621
Drewen	1305*	1925*
Flechum	251	674
Gardelegen	1661*	2037*
Glaslern1	752	1098
Glaslern2	460	1156
Glaslern3	447	787
Hartheim	735	1012
Ichenheim	382	710
Krogaspe	29	78
Oberhausen	715	1374
Ostbevern	192	264
Osterholzen	754	918
Pfarrkirchen	98	195
Quadendambeck	1186	1324
Rheinau	653	821
Rossbach1	446	667
Rossbach2	639	871
Veltrup	191	593
Vinnen Ahmsen	377	824
Wedel	248	385

* Peak not reached or not clearly reached before end of simulation

The concentration breakthrough occurs within 1 year or less at 10 of the monitoring sites, 2 years or less at 10 sites, and within 4 years at all but one of the sites (Quadendambeck). The peak concentrations occur within 1 year or less at 5 of the monitoring sites, 2 years or less at 16 sites, and within 5 years at all but two of the sites (Drewen, Quadendambeck). The sites with leaching times significantly longer than the others (Drewen, Gardelegen, Asing and Quadendambeck) have a combination of relatively deep groundwater and relatively high proportions of silt, and thus low vertical hydraulic conductivities, in their soil profiles, resulting in long breakthrough times.

The derived travel time from the closest treated field to the sampled groundwater well is presented in Table B.8.4.1-28.
The estimated arrival times of the breakthrough and peak concentrations of the dimethenamid-P metabolites are presented in Table B.8.4.1-29.

Table B.8.4.1-28: Groundwater flow velocity, distance of wells to treated fields and travel time of groundwater from closest treated field to monitored well

Location	groundwater flow velocity [m/d] **	Approximate distance to well from closest treated field in each year [m]			Approximate travel time to well for closest treated field in each year [days]		
		2007	2008	2009	2007	2008	2009
Southern Upper-Rhine Valley (Suedliches Oberrheintal)							
Rheinau	0.3	300	300	10	1000	1000	33
Ichenheim	1.4	500	10	10	357	7	7
Oberhausen	1.4	900	10	10	643	7	7
Hartheim	3.5	100	100	380	29	29	109
Northwest German Lowlands (Nordwestdeutsches Tiefland)							
Albersloh	0.4	100	300	100	250	750	250
Ostbevern	0.3	150	800	150	500	2667	500
Veltrup	0.5	10	10	10	20	20	20
Flechum	0.5	250	250	400	500	500	800
Vinnen-Ahmsen	0.8	500	250	1000	625	313	1250
Wedel	0.6	500	500	100	833	833	167
Krogaspe	0.9	200	400	600	222	444	667
Brekendorf	0.59	10	10	10	17	17	17
Lower Bavarian Hilly Country (Unterbayerisches Huegelland)							
Glaslern	1.5	900	300	1500	600	200	1000
Osterholzen	0.5	50	300	600	100	600	1200
Pfarrkirchen	0.6	200	300	200	333	500	333
Rossbach	1	300	10	100	300	10	100
Asing	1.3	300	600	300	231	462	231
Lower Bavarian Hilly Country (Niederbayerisches Huegelland)							
Gardelegen	0.6	10	400	10	17	667	17
Quadendambeck	0.26	300	500	200	1139	1899	760
Drewen	0.43	200	50	800	463	116	1852

** mean of values for each site calculated from hydrogeological parameters (kf value, porosity and filter velocity)

Table B.8.4.1-29: Aproximate arrival times for breakthrough and peak concentrations of dimethenamid-P metabolites at monitored well

Location	Approximate potential arrival times at well for breakthrough and peak concentrations from closest treated field in each year					
	Arrival 2007 Application	Arrival PEAK 2007 Application	Arrival 2008 Application	Arrival PEAK 2008 Application	Arrival 2009 Application	Arrival PEAK 2009 Application
Southern Upper-Rhine Valley (Suedliches Oberrheintal)						
Rheinau	Dec. 2011	May. 2012	Dec. 2012	May. 2013*	Apr. 2011	Oct. 2011
Ichenheim	Jun. 2009	May. 2010	Jun. 2009	May. 2010	Jun. 2010	May. 2011
Oberhausen	Feb. 2011	Dec. 2012	May. 2010	Mar. 2012	May. 2011	Mar. 2013*
Hartheim	Jul. 2009	Apr. 2010	Jul. 2010	Apr. 2011	Sep. 2011	Jun. 2012
Northwest German Lowlands (Nordwestdeutsches Tiefland)						
Albersloh	Jun. 2008	Jul. 2008	Nov. 2010	Dec. 2010	Jun. 2010	Jul. 2010
Ostbevern	Apr. 2009	Jul. 2009	Mar. 2016*	Jun. 2016*	Apr. 2011	Jul. 2011
Veltrup	Dec. 2007	Feb. 2009	Dec. 2008	Feb. 2010	Dec. 2009	Feb. 2011
Flechum	Jun. 2009	Aug. 2010	Jun. 2010	Aug. 2011	Apr. 2012	Jun. 2013*
Vinnen-Ahmsen	Mar. 2010	May. 2011	Apr. 2010	Jul. 2011	Nov. 2013*	Feb. 2015*
Wedel	May. 2010	Oct. 2010	May. 2011	Oct. 2011	Jul. 2010	Dec. 2010
Krogaspe	Feb. 2008	Mar. 2008	Sep. 2009	Nov. 2009	Apr. 2011	Jun. 2011
Brekendorf	May. 2008	Mar. 2009	Jun. 2009	Mar. 2010	Jun. 2010	Mar. 2011
Lower Bavarian Hilly Country (Unterbayerisches Huegelland)						
Glaslern	Jul. 2010	Nov. 2011	Jun. 2010	Sep. 2011	Sep. 2013*	Dec. 2014*
Osterholzen	Oct. 2009	Mar. 2010	Feb. 2012	Jul. 2012	Oct. 2014*	Mar. 2015*
Pfarrkirchen	Aug. 2008	Nov. 2008	Jan. 2010	Apr. 2010	Aug. 2010	Nov. 2010
Rossbach	Sep. 2009	May. 2010	Dec. 2009	Jul. 2010	Mar. 2011	Oct. 2011
Asing	Sep. 2011	Nov. 2017*	May. 2013*	Jun. 2019*	Sep. 2013*	Nov. 2019*
Lower Bavarian Hilly Country (Niederbayerisches Huegelland)						
Gardelegen	Jan. 2012	n/a	Oct. 2014*	n/a	Jan. 2014*	n/a
Quaden-dambeck	Oct. 2013	Mar. 2014*	Nov. 2016*	Mar. 2017*	Sep. 2014*	Feb. 2015*
Drewen	Apr. 2012	Dec. 2013*	Apr. 2012	Jan. 2014*	Jan. 2018*	Oct. 2019*

n/a not available
* estimated arrival or peak after end of sampling for closest field treated in year

The estimated arrival times at the monitoring well can be considered as indicative only, as there are a number of sources of uncertainty. The most significant uncertainties are in the actual soil profiles and depths to groundwater beneath the treated fields compared to those used in the simulations and the hydrogeological parameters such as the hydraulic gradient and effective porosity that are key parameters determining the apparent groundwater flow velocity (solute transport velocity). Taking this uncertainty into account, estimated arrival times of up to 6 months after the end of the groundwater sampling period in March 2013 (i.e. up to October 2013) are considered as still being within the timeframe of the monitoring fields and only some concentration breakthroughs from the closest fields in the three treatment years may be expected in the sampling period.

Overall the estimated arrival times for concentrations at the monitoring wells from the product applications show that the prospective aspect of the groundwater monitoring study is applicable to the metabolites of dimethenamid-P from the point of view of the sampling timeframe.

Spatial modelling approach to set monitoring locations in a European context:

Following the approach outlined in the methods section above, vulnerability maps for spring and

autumn application have been calculated for all three metabolites. Based on these maps the resulting maps of representativeness have been created. Only the maps of representativeness are presented here, since the vulnerability maps have been used only as input for these maps.
The resulting maps for the autumn application of M656PH023 and M656PH027 are illustrated in Figure B.8.4.1-6 and Figure B.8.4.1-7. Only the autumn application representativeness is depicted, since the highest NUTS2 concentrations were modelled for this scenario, and as such the largest deviations which respect to representativeness are obtained.

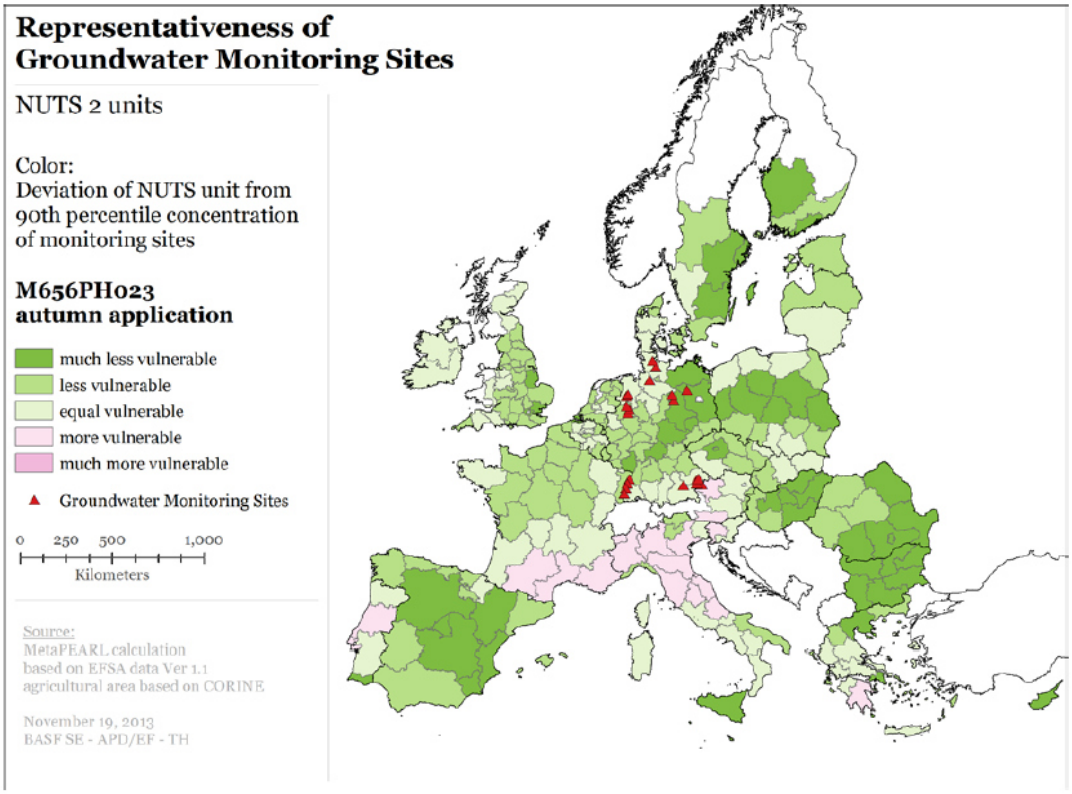


Figure B.8.4.1-6: Map of representativeness of the German groundwater monitoring locations for the agricultural area of Europe: M656PH023 – autumn application

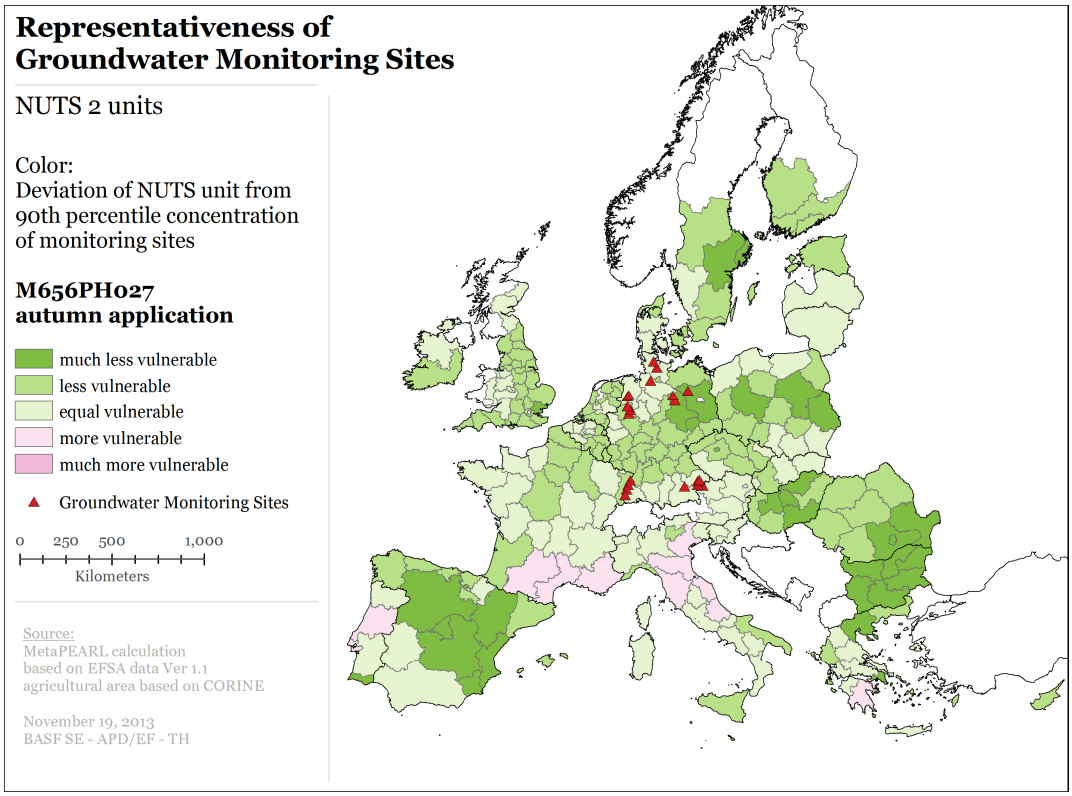


Figure B.8.4.1-7: Map of representativeness of the German groundwater monitoring locations for the agricultural area of Europe: M656PH027 – autumn application

The resulting maps of representativeness show that the groundwater monitoring wells could be regarded as representative for most of Europe's agricultural area, for both application times as well as for three metabolites. There are some areas (e.g. Northern Italy, Southern France) wich show a higher vulnerability compared to the German monitoring wells. However, since the proposed method follows a worst-case assumption by taking the 90th spatial percentile into account also for those NUTS2 areas only a small portion of the area could be considered as more vulnerable.

Conclusion

The retrospective aspects of the monitoring study is already discussed by the RMS under the study summaries of Schmidt et al (2010), Schmidt & Schulz, 2012 and Schmidt & Schneider, 2013 and is thus not further discussed here.

Acceptability of the evaluation of validity of the prospective aspect of the monitoring study in Germany for the dimethenamid-P metabolites:

As far as known by the RMS, there is no guidance how to estimate the response time of groundwater wells used in groundwater monitoring studies. The approach of the applicant used here is considered suitable by the RMS: The time for the metabolites to reach the groundwater level was simulated with an agreed model FOCUS PEARL 4.4.4. The selected soil profiles were acceptable except for the well Drewen where the soil information was taken from a generalised soil map 'BÜK1000' which is considered not precise enough for creating a FOCUS scenario for this well. The travel time with groundwater was estimated using hydrogeological data. For future studies it seems sensible to perform such modelling before actually performing the monitoring to make sure that wells with a response time outside of the sampling campaign would be excluded beforehand.
It is not clear to the RMS, however, why different input parameters for the metabolites M656PH023, M656PH027 and M656PH031 should not make a difference for the modelling as stated by the

applicant since different input parameter will influence the time the metabolites need to reach groundwater level. In the opinion of the RMS this modelling would need to be repeated with the correct input parameters to derive the correct travel times for the metabolites. However, the differences between the previously used endpoints and the new DT_{50} and K_{foc} endpoints for dimethenamid-P and metabolites are considerably small and go in both directions towards larger and smaller values. The overall effect on the transport/ travel times might therefore be small.
Besides, the documentation of the study is considered quite sparse by the RMS. Only breakthrough curves normalised to 1 were provided for the different groundwater wells, however, tables with modelled groundwater concentrations of the three metabolites for all wells would have been useful. This would have allowed a better comparison of the maximum modelled concentrations with the actual measurements of the wells and might have helped to explain some of the differences in the measurements found at the 20 wells. The travel times according to the breakthrough curves were sometimes different for the three metabolites M656PH023, M656PH027 and M656PH031. It is not clear how this is reflected in the derived travel times.
Finally, the RMS does not agree that a 6 month uncertainty of the arrival time of the application peaks should imply that modelled breakthrough curves six month outside of the sampling time should be considered as to be still within the timeframe of the monitoring study. In the opinion of the RMS, accounting for such an uncertainty should be done in a conservative worst-case approach. However mechanical dispersion was not accounted for in the modelling, which would lead to a broadening of the concentration peaks and thus an earlier arrival of the first molecules (although not of the concentrations peaks). Thus, we believe, that the RMS believes that it is sufficient that the arrival times should be used as they were modelled.

Thus, according to the modelled arrival times of the application peaks at the different wells, the sampling time of the monitoring studies was too short for the groundwater wells Asing, Gardelegen, Quadendambeck and Drewen. This is consistent with the fact, that none of the metabolites was detected at all at the four wells.
At some additional wells, Glaslern, Osterholzen, Ostbevern, Rheinau and Vinnen-Ahmsen, not all of the yearly peaks arrived in time, however at least two of the application peaks should have reached the wells in time.
Overall for 15 of the 20 wells, the travel times are considered sufficient to monitor the expected metabolite peaks of the period 2007 to 2009. Thus, for 16 wells, the quality criterion 1 of the FOCUS groundwater report (2009, 2014) is fulfilled.

Acceptability of the spatial modelling approach to set monitoring locations in a European context:

As far as known by the RMS, there is no guidance how to compare the vulnerability of certain monitoring sites with the vulnerability of the whole agricultural in Europe.
The RMS evaluated the approach used by the applicant and identified several shortcomings described in more detail below:
According to the FOCUS groundwater report (2011, p. 183) 20 monitoring sites specifically targeted to the pesticide of interest are sufficient for a higher tier groundwater assessment thus 16 acceptable wells are just slightly below the sufficient number. However, the RMS has doubts about the distribution of the wells, since all of the wells are located in Germany and not spread over Europe. Here, a study evaluating the represesentativeness of these wells for Europe, as was done by the applicant, is considered very important. However, a better distribution of the wells over the European area would still have been desirable.
Since the number of monitoring wells is so small compared to the entire area of Europe, the RMS also considers the use of the 90th percentile of the modelled groundwater concentrations at these 20 wells to determine $Q90_{gwm}$ very questionable. The wells might exhibit very different climatic, soil and hydrogeological conditions and an approach, where it is evaluated, which area of Europe would be covered by each well seems to be more appropriate than averaging the groundwater concentrations of the wells (to not loose a lot of information on the wells before even starting the modelling).
Also the use of the NUTS 2 areas is considered very questionable by the RMS. NUTS 2 areas represent large socio-economic regions for the application of regional policies. They present in no way

unities of comparable environmental conditions like similar soil or climate conditions. If larger areas are needed for comparison, the areas should be defined by conditions representing vulnerability for groundwater leaching instead. Only in these cases the use of the 90th percentile to derive values similar to $Q90_{nuts}$ is acceptable. When combining larger areas without defining similarities of conditions, simple large squares are more suitable but in these cases the maximum of all groundwater concentrations in each area should be applied for the whole area
Also the use of standard deviations to define vulnerability classes is very questionable in the eyes of the RMS. Currently areas that show higher concentrations than the 90th percentile of the 20 wells including 50 % of the standard deviation are considered as 'equal vulnerable'. This is not considered acceptable at all by the RMS. All regions that show higher concentrations than the 20 wells should be marked as such. A further classification in vulnerability classes is not considered necessary.
On this account it should be noted that Figure B.8.4.1-5 does not make much sense. A simple table including the colours of the vulnerability classes and the respective standard deviations would have served the purpose much better. In the Figure, it is not clear what the y-axis presents and while it is supposed to be an example for M656H023, it is not clear if pre- or post-emergence is shown here.
It should also be noted that the documentation of the study was very poor. Neither the derived $Q90_{gwm}$ or $Q90_{nuts}$ values were listed, nor the standard deviations used by the applicant for colouring of the maps were listed anywhere in the study thus not allowing a complete evaluation due to the poor documentation.
Besides, additionally to providing maps, some quantitative comparisons of the areas in form of tables containing information like the percentage of agricultural area in Europe more vulnerable than the three wells would have been helpful to allow the derivation of more precise conclusions from the study. So far it can only be concluded that despite the questionable combination of data by the applicant, still some European NUTS 2 areas are more vulnerable than the monitoring sites but no information is given on the number or the total area of this regions.

Three additional critical issues were identified that have been mentioned already when discussing part 1 of this study and the modelling study of the lysimeter Haering, 2013, respectively.

First, it is not clear to the RMS, why different input parameters for the metabolites M656PH023, M656PH027 and M656PH031 should not make a difference for the modelling as stated by the applicant since different input parameter will influence the concentration of the metabolites reaching the groundwater and thus their spatial distribution.
Besides, the EuroPEARL model on which the parameterisation of MetaPEARL is based on is not available through EFSA and not under version control as was suggested as requirement before use as higher tier leaching model in the EFSA scientific opinion (EFSA Journal 2013; 11(6):3291). Thus, the RMS is not able to check whether the model was used in a correct way e.g. by repeating some of the modelling.
And finally, MetaPEARL modelling resulted in smaller groundwater concentrations for the whole area of Europe for the metabolites M656PH023, M656PH027 and M656PH031 than all available 10 FOCUS scenarios for spring application and in smaller groundwater concentrations than three of the FOCUS szenarios (Chateaudun, Hamburg and Jokoinen) for autumn application in the modelling study Haering, 2013. This questions the general suitability of MetaPEARL to be used for higher tier groundwater modelling; since this requires that all really existing vulnerable regions are really covered by the model.
Thus, the spatial modelling to set monitoring locations in a European context is not considered acceptable by the RMS.

KCA 7.5/4 – Mewis, 2014b (new studies)

Author:	Mewis, A.
Title:	Determination of Residues of BAS 656 PH and Metabolites in groundwater (monitoring Netherlands)
Date:	24/02/2014
Doc ID:	BASF DocID 2013/1352173
Guidelines:	None
GLP:	Yes
Validity:	Acceptable as additional information, not suitable for groundwater water risk assessment

Aim of the studies

The objective of this study was the determination of residues of the dimethenamid-P metabolites M656PH003 (M3 in this study), M656PH010, M656PH023 (M23 in this study), M656PH027 (M27 in this study), M656PH031 (M31 in this study), M656PH032, M656PH043, M656PH045, M656PH047 and M656PH054 in groundwater samples in the Netherlands. North Brabant is a region in the South of the Netherlands. It is bordered by Belgium's Antwerp and Limburg provinces in the South, the Meuse River in the North, Limburg in the East and Zeeland in the West. 80 measuring sites in close vicinity to corn fields were chosen for sampling of shallow groundwater. The wells selected for analysis are all located in areas with predominantly agricultural land usage and where over 25 % of the agricultural area is used for maize production.
The distribution of the agricultural area and the 80 groundwater wells in the North Brabant province are shown in Figure B.8.4.1-8. The distribution of maize cultivation on the agricultural land in the Netherlands is shown in Figure B.8.4.1-9.

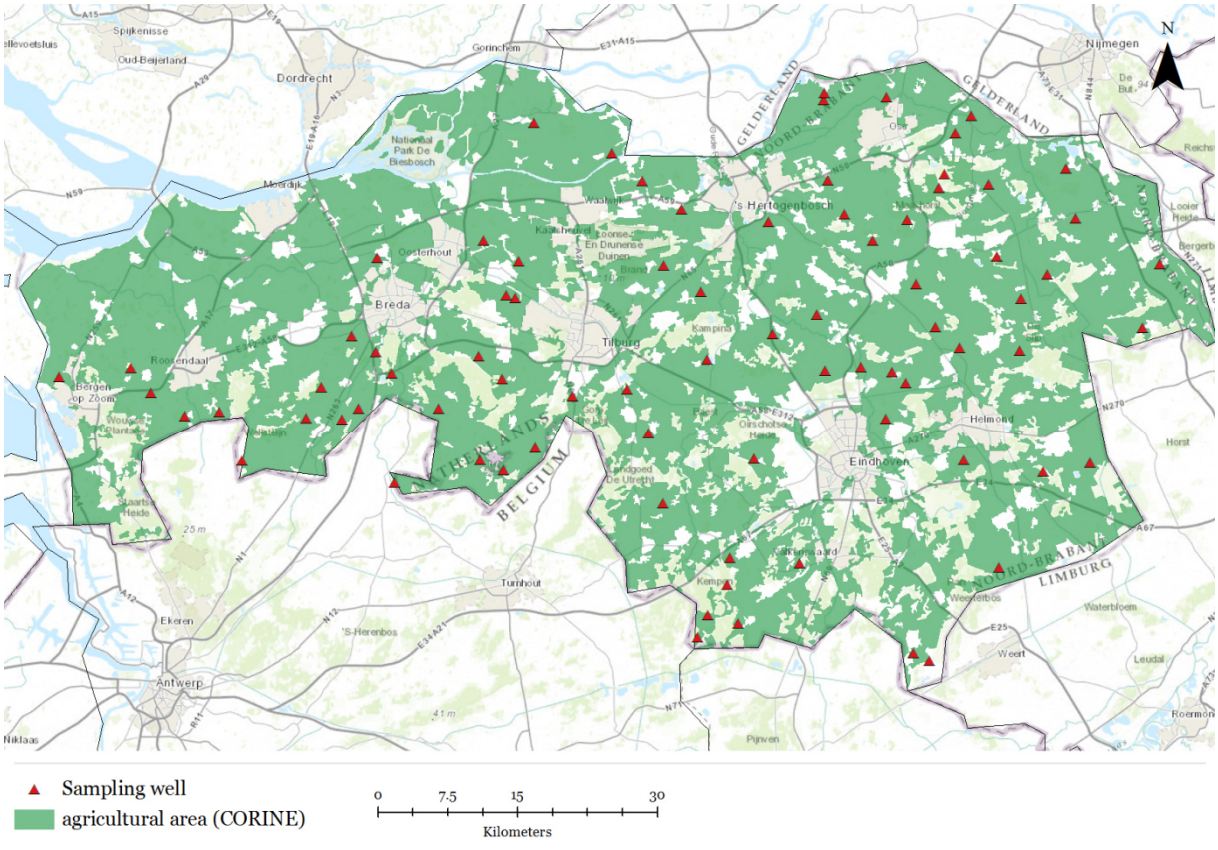


Figure B.8.4.1-8: Distribution of agricultural land and locations of sampled monitoring wells in North Brabant province

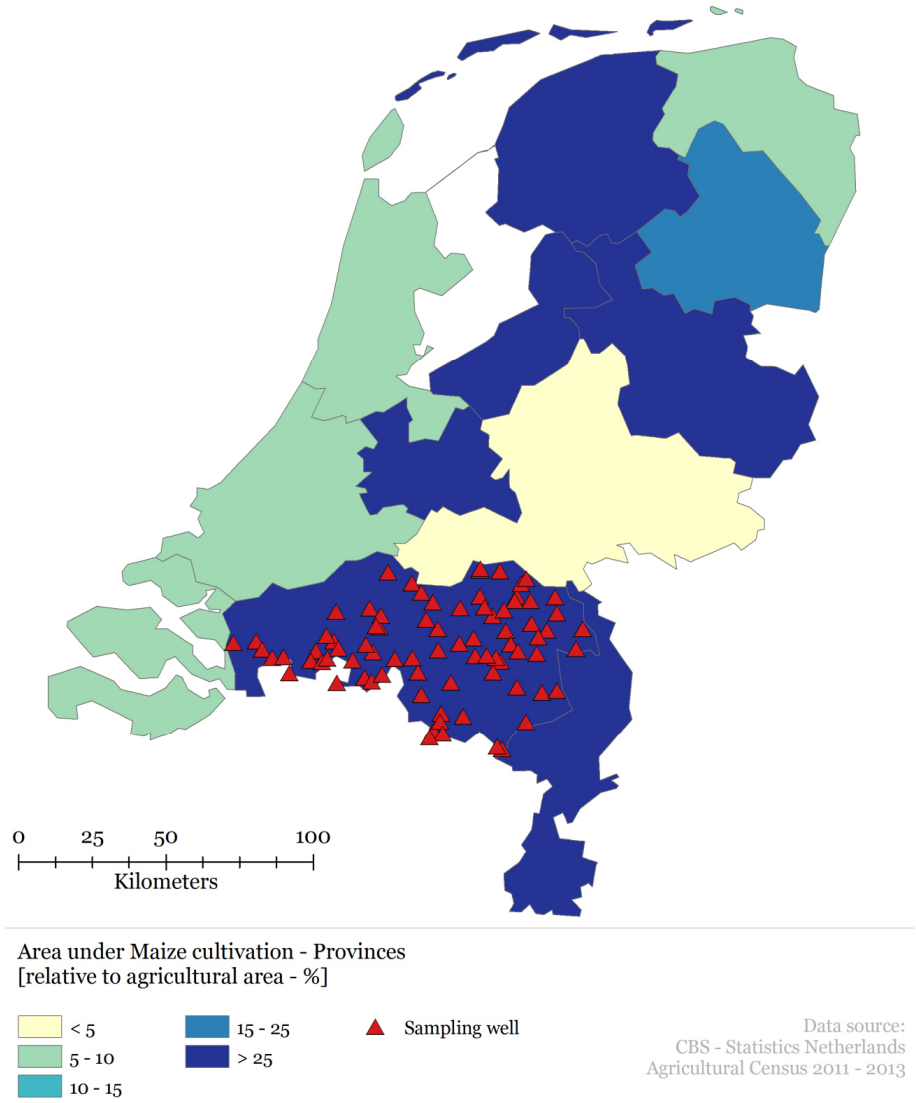


Figure B.8.4.1-9: Distribution of maize cultivation on agricultural land in the Netherlands and locations of sampled monitoring wells in North Brabant province

Material and Methods

Groundwater specimens were sampled from groundwater monitoring wells located in corn producing areas selected from the monitoring network of the province North Brabant, The Netherlands. Information on the sample points are provided in Table B.8.4.1-30.

Duplicate groundwater samples were collected in the period from 08 January to 16 April 2013. The sampling was carried out according to Nederlandse norm NTA 8017[5] and Stichting Infrastructuur Kwaliteitsborging Bodembeheer[6].
Therefore, first the lid of the measuring point was checked for damage and cleaned before being opened. After opening of the measuring point, the depth of the groundwater level was determined and a submersible pump with a flow rate of 500 mL/min was installed in the well. All components and instruments used were made of silicone or Teflon material to prevent influences on the sample. The stagnant water was pumped out and led away from the measuring point in order to prevent

[5] NTA 8017, 2008. Monsterneming van grondwater ten behoove van de monitoring van grondwaterkwaliteit (=Sampling of ground water for the monitoring of ground water quality)
[6] SIKB ver. 3.2, 2007.:Het nemen van grondwatermonsters VKB – PROTOCOL 2002

contamination. The sample containers (polyethylene [PE] bottles 500 mL) were rinsed three times with groundwater before the actual sample of groundwater was taken. While pumping out, the groundwater parameters pH, conductivity, redox potential and water temperature were measured and documented. When filling the containers, the tube of the pump was tilted to reduce turbulence. When containers were completely filled, they were sealed airtight, cooled to 4 °C and stored in the dark. The sampling dates for all sampling points are listed in Table B.8.4.1-31.
The samples were kept at 4 °C in an interim storage. Every Friday all samples collected within the week were transported to a refrigerated warehouse and stored at a temperature of -18 °C until April 29th. Then the samples were sent frozen to the laboratories of BASF at Limburgerhof and were stored frozen.

Table B.8.4.1-30: Information on sampled groundwater monitoring wells in the Netherlands

sample no	mpna	filter	depth class	location	coordinates		filter	
					xc	yc	top [m]	bottom [m]
95-1	95	1	shallow	NULAND	158975	413725	8.10	10.10
97-1	97	1	shallow	HAAREN	145337	401807	6.00	8.00
98-1	98	1	shallow	VENKANT	143200	410625	8.00	10.00
100-1	100	1	shallow	MACHAREN	165225	422650	8.00	10.00
101-1	101	1	shallow	SCHAIJK	171500	414450	9.50	11.50
103-1	103	1	shallow	VEGHEL	168463	402625	8.10	10.10
104-1	104	1	shallow	ODILIAPEEL	177075	405600	6.60	8.60
106-1	106	1	shallow	LANDHORST	182500	403638	8.00	10.00
107-1	107	1	shallow	SAMBEEK	194616	404809	6.60	8.60
108-1	108	1	shallow	BIEST	137406	391354	7.05	9.05
111-1	111	1	shallow	OLLAND	157730	399394	9.05	11.05
112-1	112	1	shallow	SON	158616	393372	6.00	8.00
115-1	115	1	shallow	LIESHOUT	167341	392068	11.10	13.10
116-1	116	1	shallow	GEMERT	179573	395518	10.00	12.00
122-1	122	1	shallow	OVERLOON	192759	397966	8.05	10.05
123-1	123	1	shallow	VLIERDEN	182065	382505	11.70	13.20
124-1	124	1	shallow	WEEBOSCH	146068	367045	7.90	9.90
125-1	125	1	shallow	WESTERHOVEN	155915	372595	11.10	13.10
128-1	128	1	shallow	SOMEREN-HEIDE	177325	372138	12.00	14.00
129-1	129	1	shallow	BUDEL	169813	362163	10.05	12.05
137-1	137	1	shallow	ALMKERK	127360	419875	9.05	11.05
138-1	138	1	shallow	GENDEREN	135725	416615	7.95	9.95
140-1	140	1	shallow	RIJEN	125383	401139	9.00	11.00
141-1	141	1	shallow	HALSTEREN	76360	392710	8.00	10.00
142-1	142	1	shallow	WOUW	84060	393685	13.00	15.00
146-1	146	1	shallow	ACHTMAAL	96009	383629	4.50	6.50
147-1	147	1	shallow	RIJSBERGEN	104553	391617	6.50	8.50
151-1	151	1	shallow	GILZE	123975	392450	5.15	7.15
420-1	420	1	shallow	SPOORDONK	145965	394540	8.05	10.05
423-1	423	1	shallow	Cuijk	184520	415050	7.50	9.50
425-1	425	1	shallow	Lith	158526	422379	8.15	10.15
426-1	426	1	shallow	DINTHER	163802	407312	8.05	10.05
1804-1	1804	1	shallow	WOUW	86214	391031	8.20	10.20
1806-1	1806	1	shallow	NISPEN	89852	388453	4.00	6.00
1807-2	1807	2	shallow	RUCPHEN	93603	388908	7.00	9.00
1808-2	1808	2	shallow	ZUNDERT	102945	388291	8.00	10.00
1809-1	1809	1	shallow	ZUNDERT	106754	388142	5.00	7.00
1810-3	1810	3	shallow	OEKEL	108556	389331	11.50	13.50
1811-1	1811	1	shallow	BREDA	110523	405446	4.00	6.00
1813-2	1813	2	shallow	BREDA	110387	395400	7.00	9.00
1814-2	1814	2	shallow	BREDA	107775	397071	8.00	10.00
1815-1	1815	1	shallow	GALDER	112088	393084	5.00	7.00
1816-2	1816	2	shallow	OOSTERHOUT	121925	407312	9.00	11.00
1817-2	1817	2	shallow	DONGEN	125770	405092	7.00	9.00

sample no	mpna	filter	depth class	location	coordinates		filter	
					xc	yc	top [m]	bottom [m]
1818-2	1818	2	shallow	RIJEN	124425	401425	9.00	11.00
1819-1	1819	1	shallow	GILZE	121413	394922	4.00	6.00
1821-2	1821	2	shallow	CHAAM	117174	389269	12.00	14.00
1822-1	1822	1	shallow	CASTELRE	112375	381325	5.00	7.00
1823-1	1823	1	shallow	BAARLE_ NASSAU	121559	383756	7.00	9.00
1824-1	1824	1	shallow	BAARLE_ HERTOG	124088	382593	8.00	10.00
1825-1	1825	1	shallow	KLEIN_ BEDAF	127489	385072	4.00	6.00
1827-2	1827	2	shallow	GOIRLE	131496	390651	5.50	7.50
1831-2	1831	2	shallow	BIEZENMORTEL	141314	404623	8.00	10.00
1833-1	1833	1	shallow	LIEMPDE	153045	397289	7.00	9.00
1835-2	1835	2	shallow	DIESSEN	139664	386590	6.00	8.00
1837-2	1837	2	shallow	H._EN_LAGE_ MIERDE	141244	379042	8.50	10.50
1840-2	1840	2	shallow	WINTELRE	150993	383906	9.00	11.00
1841-2	1841	2	shallow	EERSEL	148389	373234	8.00	10.00
1842-2	1842	2	shallow	EERSEL	148102	370333	8.00	10.00
1843-2	1843	2	shallow	LUYKSGESTEL	149331	366200	7.00	9.00
1844-2	1844	2	shallow	LUYKSGESTEL	144975	364702	7.00	9.00
1847-1	1847	1	shallow	BUDEL	168119	362997	7.00	9.00
1850-2	1850	2	shallow	DEURNE	187127	383420	7.00	9.00
1851-1	1851	1	shallow	WINKELSTRAAT	173563	383714	8.00	10.00
1852-1	1852	1	shallow	NUENEN	165140	388190	6.50	8.50
1853-2	1853	2	shallow	BREUGEL	165825	393241	9.00	11.00
1854-2	1854	2	shallow	WOLFWINKEL	162530	393755	8.00	10.00
1855-2	1855	2	shallow	ERP	170484	398068	8.00	10.00
1856-2	1856	2	shallow	DONK	173091	395851	6.00	8.00
1858-1	1858	1	shallow	VENHORST	179722	401094	5.00	7.00
1860-1	1860	1	shallow	WANROY	185536	409662	4.00	6.00
1861-2	1861	2	shallow	ZEELAND	176250	413300	8.00	10.00
1862-1	1862	1	shallow	SCHAYK	172695	418782	7.00	9.00
1863-2	1863	2	shallow	SCHAYK	170915	412915	9.00	11.00
1864-1	1864	1	shallow	LITH	158595	423097	9.00	10.00
1865-1	1865	1	shallow	NISTELRODE	167456	409564	4.50	6.50
1866-1	1866	1	shallow	HEESWIJK-DINTHER	160754	410089	8.00	10.00
1868-2	1868	2	shallow	ST.MICHIELS-GESTEL	152592	409272	8.00	10.00
1870-1	1870	1	shallow	RAVENSTEIN	174328	420661	7.50	8.50
1871-1	1871	1	shallow	HEUSDEN	139024	413661	7.00	8.00

mpna= Measurement point number

Table B.8.4.1-31: Sampling dates at for groundwater monitoring in the Netherlands in the year 2013

sample no	mpna	sampling date	sample no	mpna	sampling date	sample no	mpna	sampling date
95-1	95	17.01.	151-1	151	18.02.	1835-2	1835	09.01.
97-1	97	25.02.	420-1	420	18.03.	1837-2	1837	28.02.
98-1	98	25.02.	423-1	423	14.03.	1840-2	1840	07.02.
100-1	100	17.01.	425-1	425	11.02.	1841-2	1841	28.03.
101-1	101	16.04.	426-1	426	10.01.	1842-2	1842	28.03.
103-1	103	04.02.	1804-1	1804	12.03.	1843-2	1843	25.03.
104-1	104	12.02.	1806-1	1806	19.02.	1844-2	1844	13.02.
106-1	106	12.02.	1807-2	1807	19.02.	1847-1	1847	10.04.
107-1	107	30.01.	1808-2	1808	22.01.	1850-2	1850	06.03.
108-1	108	08.01.	1809-1	1809	22.01.	1851-1	1851	25.02.
111-1	111	15.04.	1810-3	1810	20.02.	1852-1	1852	05.03.
112-1	112	18.03.	1811-1	1811	26.02.	1853-2	1853	22.01.
115-1	115	25.02.	1813-2	1813	04.02.	1854-2	1854	12.02.
116-1	116	27.02.	1814-2	1814	06.02.	1855-2	1855	24.01.
122-1	122	30.01.	1815-1	1815	04.02.	1856-2	1856	24.01.
123-1	123	06.03.	1816-2	1816	21.02.	1858-1	1858	31.01.
124-1	124	13.02.	1817-2	1817	04.03.	1860-1	1860	19.02.
125-1	125	25.03.	1818-2	1818	23.01.	1861-2	1861	31.01.
128-1	128	11.03.	1819-1	1819	29.01.	1862-1	1862	14.03.
129-1	129	10.04.	1821-2	1821	18.02.	1863-2	1863	04.02.
137-1	137	21.01.	1822-1	1822	25.03.	1864-1	1864	11.02.
138-1	138	15.01.	1823-1	1823	25.03.	1865-1	1865	10.01.
140-1	140	23.01.	1824-1	1824	03.04.	1866-1	1866	31.01.
141-1	141	20.03.	1825-1	1825	03.04.	1868-2	1868	14.02.
142-1	142	12.03.	1827-2	1827	08.01.	1870-1	1870	07.03.
146-1	146	27.03.	1831-2	1831	14.02.	1871-1	1871	21.01.
147-1	147	20.02.	1833-1	1833	07.02.	1835-2	1835	09.01.

mpna= Measurement point number

The water specimens from sampling points were analysed for the dimethenamid-P metabolites M656PH003, M656PH010, M656PH023, M656PH027, M656PH031, M656PH032, M656PH043, M656PH045, M656PH047 and M656PH054 by using a validated method described in Mewis (2013, BASF DocID 2013/1349800).

Results and Discussion

Procedural recoveries were concurrently determined with drinking water samples fortified at the limit of quantitation (LOQ) of 0.025 µg/L and at 1 and 2 µg/L. The limit of detection was defined as 30 % of LOQ, i.e. 0.0075 µg/L.
Results of the recovery experiments indicated that the recovery efficiency and repeatability were within acceptable limits of 70 % - 110 % for mean recovery and < 20 % RSD. No peak interference occurred at the retention times of the analytes. A highly specific detection system was used (HPLC-MS/MS). The analytical method therefore meets the requirements of guideline SANCO/3029/99 rev 4.

The results of the analysis of the groundwater samples for M656PH003, M656PH010, M656PH023, M656PH027, M656PH031, M656PH032, M656PH043, M656PH045, M656PH047 and M656PH054

are presented in Table B.8.4.1-32 and Table B.8.4.1-33.

Table B.8.4.1-32: Residues of the dimethenamid-P metabolites M656PH023 (= M23), M656PH027 (= M27), M656PH031 (= M31), M656PH032 (= M32) and M656PH043 (= M43) in the samples of the groundwater wells in the Netherlands

Location	Sample no.	M27 (µg/L)	M23 (µg/L)	M31 (µg/L)	M32 (µg/L)	M43 (µg/L)
NULAND	95-1	0.439	0.130	n.d.	n.d.	n.d.
HAAREN	97-1	<LOQ	n.d.	n.d.	n.d.	n.d.
VENKANT	98-1	n.d.	n.d.	n.d.	n.d.	n.d.
MACHAREN	100-1	<LOQ	n.d.	n.d.	n.d.	n.d.
SCHAIJK	101-1	n.d.	n.d.	n.d.	n.d.	n.d.
VEGHEL	103-1	n.d.	n.d.	n.d.	n.d.	n.d.
ODILIAPEEL	104-1	n.d.	n.d.	n.d.	n.d.	n.d.
LANDHORST	106-1	0.179	0.100	n.d.	n.d.	n.d.
SAMBEEK	107-1	0.323	n.d.	n.d.	n.d.	n.d.
BIEST	108-1	n.d.	<LOQ	n.d.	n.d.	n.d.
OLLAND	111-1	n.d.	n.d.	n.d.	n.d.	n.d.
SON	112-1	n.d.	n.d.	n.d.	n.d.	n.d.
LIESHOUT	115-1	n.d.	n.d.	n.d.	n.d.	n.d.
GEMERT	116-1	1.509	0.810	0.042	n.d.	n.d.
OVERLOON	122-1	n.d.	n.d.	n.d.	n.d.	n.d.
VLIERDEN	123-1	n.d.	n.d.	n.d.	n.d.	n.d.
WEEBOSCH	124-1	0.656	0.250	n.d.	n.d.	n.d.
WESTER-HOVEN	125-1	1.299	n.d.	n.d.	n.d.	n.d.
SOMEREN-HEIDE	128-1	n.d.	n.d.	n.d.	n.d.	n.d.
BUDEL	129-1	n.d.	n.d.	n.d.	n.d.	n.d.
ALMKERK	137-1	n.d.	n.d.	n.d.	n.d.	n.d.
GENDEREN	138-1	n.d.	n.d.	n.d.	n.d.	n.d.
RIJEN	140-1	n.d.	n.d.	n.d.	n.d.	n.d.
HALSTEREN	141-1	n.d.	n.d.	n.d.	n.d.	n.d.
WOUW	142-1	n.d.	n.d.	n.d.	n.d.	n.d.
ACHTMAAL	146-1	n.d.	n.d.	n.d.	n.d.	n.d.
RIJSBERGEN	147-1	0.113	0.105	n.d.	n.d.	n.d.
GILZE	151-1	0.275	0.251	n.d.	n.d.	n.d.
SPOORDONK	420-1	0.081	0.046	n.d.	n.d.	n.d.
CUIJK	423-1	0.066	n.d.	n.d.	n.d.	n.d.
LITH	425-1	n.d.	n.d.	n.d.	n.d.	n.d.
DINTHER	426-1	n.d.	n.d.	n.d.	n.d.	n.d.
WOUW	1804-1	n.d.	n.d.	n.d.	n.d.	n.d.
NISPEN	1806-1	<LOQ	n.d.	n.d.	n.d.	n.d.
RUCPHEN	1807-2	n.d.	n.d.	n.d.	n.d.	n.d.
ZUNDERT	1808-2	n.d.	n.d.	n.d.	n.d.	n.d.
ZUNDERT	1809-1	0.030	n.d.	n.d.	n.d.	n.d.
OEKEL	1810-3	0.048	<LOQ	n.d.	n.d.	n.d.
BREDA	1811-1	n.d.	n.d.	n.d.	n.d.	n.d.
BREDA	1813-2	n.d.	n.d.	n.d.	n.d.	n.d.
BREDA	1814-2	n.d.	n.d.	n.d.	n.d.	n.d.
GALDER	1815-1	n.d.	n.d.	n.d.	n.d.	n.d.
OOSTERHOUT	1816-2	0.156	0.147	n.d.	n.d.	n.d.
DONGEN	1817-2	n.d.	n.d.	n.d.	n.d.	n.d.
RIJEN	1818-2	0.189	0.145	n.d.	n.d.	n.d.
GILZE	1819-1	n.d.	n.d.	n.d.	n.d.	n.d.
CHAAM	1821-2	n.d.	n.d.	n.d.	n.d.	n.d.
CASTELRE	1822-1	0.879	0.044	n.d.	n.d.	n.d.
BAARLE_NASSAU	1823-1	0.387	0.102	n.d.	n.d.	n.d.
BAARLE_HERTOG	1824-1	0.040	<LOQ	n.d.	n.d.	n.d.
KLEIN_BEDAF	1825-1	0.247	0.087	n.d.	n.d.	n.d.
GOIRLE	1827-2	n.d.	n.d.	n.d.	n.d.	n.d.

Location	Sample no.	M27 (µg/L)	M23 (µg/L)	M31 (µg/L)	M32 (µg/L)	M43 (µg/L)
BIEZEN-MORTEL	1831-2	n.d.	n.d.	n.d.	n.d.	n.d.
LIEMPDE	1833-1	0.040	0.036	n.d.	n.d.	n.d.
DIESSEN	1835-2	0.600	0.169	n.d.	n.d.	n.d.
H._EN_LAGE_MIERDE	1837-2	n.d.	n.d.	n.d.	n.d.	n.d.
WINTELRE	1840-2	0.855	0.269	n.d.	n.d.	n.d.
EERSEL	1841-2	0.170	0.121	n.d.	n.d.	n.d.
EERSEL	1842-2	n.d.	n.d.	n.d.	n.d.	n.d.
LUYKSGESTEL	1843-2	1.021	0.530	n.d.	n.d.	n.d.
LUYKSGESTEL	1844-2	0.400	0.100	n.d.	n.d.	n.d.
BUDEL	1847-1	0.144	0.159	n.d.	n.d.	n.d.
DEURNE	1850-2	n.d.	n.d.	n.d.	n.d.	n.d.
WINKELSTRAAT	1851-1	<LOQ	<LOQ	n.d.	n.d.	n.d.
NUENEN	1852-1	n.d.	n.d.	n.d.	n.d.	n.d.
BREUGEL	1853-2	n.d.	n.d.	n.d.	n.d.	n.d.
WOLFWINKEL	1854-2	n.d.	n.d.	n.d.	n.d.	n.d.
ERP	1855-2	n.d.	n.d.	n.d.	n.d.	n.d.
DONK	1856-2	n.d.	n.d.	n.d.	n.d.	n.d.
VENHORST	1858-1	0.285	0.238	n.d.	n.d.	n.d.
WANROY	1860-1	0.173	0.109	n.d.	n.d.	n.d.
ZEELAND	1861-2	<LOQ	<LOQ	n.d.	n.d.	n.d.
SCHAYK	1862-1	0.038	0.028	n.d.	n.d.	n.d.
SCHAYK	1863-2	<LOQ	<LOQ	n.d.	n.d.	n.d.
LITH	1864-1	0.025	<LOQ	n.d.	n.d.	n.d.
NISTELRODE	1865-1	n.d.	n.d.	n.d.	n.d.	n.d.
HEESWIJK-DINTHER	1866-1	<LOQ	n.d.	n.d.	n.d.	n.d.
ST.MICHIELS-GESTEL	1868-2	n.d.	n.d.	n.d.	n.d.	n.d.
RAVENSTEIN	1870-1	0.102	0.054	n.d.	n.d.	n.d.
HEUSDEN	1871-1	n.d.	n.d.	n.d.	n.d.	n.d.

Table B.8.4.1-33: Residues of the dimethenamid-P metabolites M656PH045 (= M45), M656PH047 (= M47), M656PH054 (= M54), M656PH003 (= M3) and M656PH010 (= M10) in the samples of the groundwater wells in the Netherlands

Location	Sample no.	M45 (µg/L)	M47 (µg/L)	M54 (µg/L)	M3 (µg/L)	M10 (µg/L)
NULAND	95-1	0.057	n.d.	0.027	n.d.	n.d.
HAAREN	97-1	n.d.	n.d.	n.d.	n.d.	n.d.
VENKANT	98-1	n.d.	n.d.	n.d.	n.d.	n.d.
MACHAREN	100-1	n.d.	n.d.	n.d.	n.d.	n.d.
SCHAIJK	101-1	n.d.	n.d.	n.d.	n.d.	n.d.
VEGHEL	103-1	n.d.	n.d.	n.d.	n.d.	n.d.
ODILIAPEEL	104-1	n.d.	n.d.	n.d.	n.d.	n.d.
LANDHORST	106-1	0.211	n.d.	<LOQ	n.d.	<LOQ
SAMBEEK	107-1	n.d.	n.d.	n.d.	n.d.	n.d.
BIEST	108-1	n.d.	n.d.	n.d.	n.d.	n.d.
OLLAND	111-1	n.d.	n.d.	n.d.	n.d.	n.d.
SON	112-1	n.d.	n.d.	n.d.	n.d.	n.d.
LIESHOUT	115-1	n.d.	n.d.	n.d.	n.d.	n.d.
GEMERT	116-1	0.048	n.d.	0.076	n.d.	<LOQ
OVERLOON	122-1	n.d	n.d.	n.d.	n.d.	n.d.
VLIERDEN	123-1	n.d	n.d.	n.d.	n.d.	n.d.
WEEBOSCH	124-1	<LOQ	0.328	n.d.	n.d.	n.d.
WESTER-HOVEN	125-1	<LOQ	0.459	<LOQ	n.d.	n.d.
SOMEREN-HEIDE	128-1	n.d.	n.d.	n.d.	n.d.	n.d.
BUDEL	129-1	n.d.	n.d.	n.d.	n.d.	n.d.
ALMKERK	137-1	n.d.	n.d.	n.d.	n.d.	n.d.
GENDEREN	138-1	n.d.	n.d.	n.d.	n.d.	n.d.
RIJEN	140-1	n.d.	n.d.	n.d.	n.d.	n.d.
HALSTEREN	141-1	n.d.	n.d.	n.d.	n.d.	n.d.
WOUW	142-1	n.d.	n.d.	n.d.	n.d.	n.d.
ACHTMAAL	146-1	n.d.	n.d.	n.d.	n.d.	n.d.
RIJSBERGEN	147-1	0.061	n.d.	n.d.	n.d.	n.d.
GILZE	151-1	n.d.	n.d.	0.044	n.d.	0.033
SPOORDONK	420-1	n.d.	n.d.	n.d.	n.d.	n.d.
CUIJK	423-1	0.033	n.d.	n.d.	n.d.	n.d.
LITH	425-1	n.d.	n.d.	n.d.	n.d.	n.d.
DINTHER	426-1	n.d.	n.d.	n.d.	n.d.	n.d.
WOUW	1804-1	n.d.	n.d.	n.d.	n.d.	n.d.
NISPEN	1806-1	n.d.	n.d.	n.d.	n.d.	n.d.
RUCPHEN	1807-2	n.d.	n.d.	n.d.	n.d.	n.d.
ZUNDERT	1808-2	n.d.	n.d.	n.d.	n.d.	n.d.
ZUNDERT	1809-1	n.d.	n.d.	n.d.	n.d.	n.d.
OEKEL	1810-3	n.d.	n.d.	n.d.	n.d.	n.d.
BREDA	1811-1	n.d.	n.d.	n.d.	n.d.	n.d.
BREDA	1813-2	n.d.	n.d.	n.d.	n.d.	n.d.
BREDA	1814-2	n.d.	n.d.	n.d.	n.d.	n.d.
GALDER	1815-1	n.d.	n.d.	n.d.	n.d.	n.d.
OOSTERHOUT	1816-2	0.070	n.d.	0.032	n.d.	n.d.
DONGEN	1817-2	n.d.	n.d.	n.d.	n.d.	n.d.
RIJEN	1818-2	0.097	n.d.	<LOQ	n.d.	n.d.
GILZE	1819-1	n.d.	n.d.	n.d.	n.d.	n.d.
CHAAM	1821-2	n.d.	n.d.	n.d.	n.d.	n.d.
CASTELRE	1822-1	0.159	n.d.	n.d.	n.d.	n.d.
BAARLE_NASSAU	1823-1	0.051	n.d.	n.d.	n.d.	n.d.
BAARLE_HERTOG	1824-1	n.d.	n.d.	n.d.	n.d.	n.d.
KLEIN_BEDAF	1825-1	n.d.	n.d.	<LOQ	n.d.	n.d.
GOIRLE	1827-2	n.d.	n.d.	n.d.	n.d.	n.d.

Location	Sample no.	M45 (µg/L)	M47 (µg/L)	M54 (µg/L)	M3 (µg/L)	M10 (µg/L)
BIEZEN-MORTEL	1831-2	n.d.	n.d.	n.d.	n.d.	n.d.
LIEMPDE	1833-1	0.213	n.d.	n.d.	n.d.	n.d.
DIESSEN	1835-2	0.161	n.d.	<LOQ	n.d.	n.d.
H._EN_LAGE_MIERDE	1837-2	n.d.	n.d.	n.d.	n.d.	n.d.
WINTELRE	1840-2	0.052	0.333	n.d.	n.d.	n.d.
EERSEL	1841-2	n.d.	n.d.	n.d.	n.d.	n.d.
EERSEL	1842-2	n.d.	n.d.	n.d.	n.d.	n.d.
LUYKSGESTEL	1843-2	n.d.	n.d.	0.032	n.d.	n.d.
LUYKSGESTEL	1844-2	n.d.	n.d.	n.d.	n.d.	n.d.
BUDEL	1847-1	0.038	n.d.	n.d.	n.d.	n.d.
DEURNE	1850-2	n.d.	n.d.	n.d.	n.d.	n.d.
WINKELSTRAAT	1851-1	n.d.	n.d.	n.d.	n.d.	n.d.
NUENEN	1852-1	n.d.	n.d.	n.d.	n.d.	n.d.
BREUGEL	1853-2	<LOQ	n.d.	n.d.	n.d.	n.d.
WOLFWINKEL	1854-2	n.d.	n.d.	n.d.	n.d.	n.d.
ERP	1855-2	n.d.	n.d.	n.d.	n.d.	n.d.
DONK	1856-2	n.d.	n.d.	n.d.	n.d.	n.d.
VENHORST	1858-1	n.d.	n.d.	<LOQ	n.d.	n.d.
WANROY	1860-1	<LOQ	n.d.	n.d.	n.d.	n.d.
ZEELAND	1861-2	<LOQ	n.d.	n.d.	n.d.	n.d.
SCHAYK	1862-1	<LOQ	n.d.	n.d.	n.d.	n.d.
SCHAYK	1863-2	n.d.	n.d.	n.d.	n.d.	n.d.
LITH	1864-1	n.d.	n.d.	n.d.	n.d.	n.d.
NISTELRODE	1865-1	n.d.	n.d.	n.d.	n.d.	n.d.
HEESWIJK-DINTHER	1866-1	<LOQ	n.d.	n.d.	n.d.	n.d.
ST.MICHIELS-GESTEL	1868-2	n.d.	n.d.	n.d.	n.d.	n.d.
RAVENSTEIN	1870-1	<LOQ	n.d.	n.d.	n.d.	n.d.
HEUSDEN	1871-1	n.d.	n.d.	n.d.	n.d.	n.d.

- Residues of M656PH027 were found in concentrations up to 1.509 µg/L.
- Residues of M656PH023 were found in concentrations up to 0.810 µg/L.
- Residues of M656PH045 were found in concentrations up to 0.213 µg/L.
- Residues of M656PH047 were found in concentrations up to 0.459 µg/L.
- Residues of M656PH031 were not detectable (<LOD; <0.0075 µg/L) except for one sample point with 0.042 µg/L.
- Residues of M656PH010 were not measurable (<LOQ; <0.025 µg/L) except for one sample point with 0.033 µg/L.
- Residues of M656PH054 were found in concentrations up to 0.076 µg/L.
- Residues of M656H032, M656PH043 and M656PH003 were not detectable (<LOD; <0.0075 µg/L) in all samples.

Conclusion

The study is accepted as additional information by the RMS. However, it is of limited use for groundwater risk assessment of dimethenamid-P for reasons described below:
No information on the amount of use and the duration of use of dimethenamid-P containing products in the catchment of the wells, the distance of the wells to areas treated with dimethenamid-P and the amount of areas treated with dimethenamid-P upstream of the wells is provided.
No information was provided on the hydrogeology, pedology or climate of the agricultural area. Besides, no information is provided on the catchment of the wells or their response time.
Thus, the quality criteria 1 and 2 of the FOCUS groundwater report (2009, 2014) cannot be evaluated by the RMS, since not enough information is available and no travel times were estimated.

As a general issue, the RMS believes that it would have been good to analyse also the active substance dimethenamid-P itself. While according to groundwater modelling and the lysimeter study, the active substance shows no tendency to enter groundwater in concentrations ≥ 0.1 µg/L, actual measurements that confirm can these results are still useful.

The maximum concentrations and the number of groundwater sites, where the metabolites were detected are summarised in Table B.8.4.1-34.

Table B.8.4.1-34: Maximum concentrations and number of groundwater wells where the metabolites were detected in the Dutch Monitoring

Metabolite	No of wells with positive detections	Percent of wells with positive detections	Maximum concentrations [µg/L]
M656PH003	0	0 %	<LOQ
M656PH010	1	1 %	0.033
M656PH027	30	38 %	1.509
M656PH023	23	29 %	0.810
M656PH031	1	1 %	0.042
M656PH032	0	0 %	<LOQ
M656PH043	0	0 %	<LOQ
M656PH045	13	16 %	0.213
M656PH047	3	4 %	0.459
M656PH054	5	6 %	0.076

Concentration and distribution pattern of the metabolites at the German presented under Class, 2013 & Mewis, 2014a and Dutch Monitoring sites are quite similar.

KCA 7.5/5– Hames & Freudenberger, 2011 (new study, open-literature)

Author: Hames, K.
Freudenberger, U.
Title: Pflanzenschutzrechtlich nicht relevante Metaboliten im Grundwasser
Date: 01/09/2011
Doc ID: BASF DOC ID 2013/1348575
Published in Fachzeitschrift ‚Wasser & Abfall' 2011, Vol. 9, p. 42-45
Guidelines: None
GLP: no
Validity: Acceptable as additional information,
not suitable for groundwater water risk assessment

Aim of the studies

The authorisation process of plant protection products differentiates between relevant and non-relevant metabolites. Also non-relevant metabolites are considered as undesired in drinking water. The aim of the paper was to discuss the current legal situation and to assess whether the legal regulation covers the risk assessment of non-relevant metabolites occurring in the environment. The legal situation was evaluated and summarised from the Bund-/Länder-Arbeitsgemeinschaft Wasser (LAWA) on authority of the Umweltministerkonferenz (Conference of Environmental Ministers).

Material and Methods

The paper presents a compilation of 24 substances investigated during groundwater monitoring of non-relevant metabolites in Germany from 2006 to 2008 (data obtained from secondary literature).

Among these are data on two metabolites of dimethenamid-P: M656PH027 (dimethenamid-sulfonic acid M27 in this study) and M656PH023 (dimethenamid oxalic acid M23 in this study). Both metabolites did not exceed the maximum level for groundwater of 1.0 µg/L (standard health orientation value for non-relevant metabolites recommended by the Federal German Environmental Agency - Umweltbundesamt [UBA]).

Results of regular groundwater measurements of M656PH027 and M656PH023 in Germany were available from 228 and 232 monitoring points, respectively, located in three Federal States of Germany. The measurements were undertaken from 2006 to 2008 to evaluate the occurrence of non-relevant metabolites in groundwater. No information about sampling technique or sampling frequency was provided in the paper.

Results and Discussion

M656PH027 and M656PH023 were not detected above the standard health orientation values (gesundheitliche Orientierungswerte GOW) in the water samples of all groundwater samples. For both metabolites a standard health orientation value of 1 µg/L was recommended by the UBA – the value recommended for substances without study of chronic toxicity.

Conclusion

The study is acceptable as additional information however it is of limited use for groundwater risk assessment of dimethenamid-P for reasons described below:

No information on the amount of use and the duration of use of dimethenamid-P containing products in the catchment of the wells, the distance of the wells to areas treated with dimethenamid-P and the amount of areas treated with dimethenamid-P upstream of the wells is provided. It is not even clear if the wells were situated in agricultural areas, where crops are cultivated that could have been treated with dimethenamid-P.
No information was provided on the hydrogeology, pedology or the climatic conditions of the areas upstream of the wells or the depth of the groundwater level tapped by the wells. Besides, no information is provided on the catchment of the wells or their response time.
Besides, no information on the sampling or measurement techniques of the groundwater are reported.

Thus, none of the quality criteria for groundwater monitoring listed in the FOCUS groundwater report (2009, 2014) can be evaluated by the RMS.

B.8.4.2 Monitoring data of surface water

KCA 7.5/6– Laabs, 2010 (new study)

Author:	Laabs, V.
Title:	Surface water screening for Dicamba, Dimethenamide-P, Bentazone, Tritosulfuron, Topramezone and selected metabolites in three corn growing regions of the EU
Date:	25/10/2010
Doc ID:	BASF DocID 2010/1148003
Guidelines:	None
GLP:	No
Validity:	Acceptable as additional information, not suitable for surface water risk assessment

Aim of the study

The purpose of the study was the monitoring of five corn herbicides, among them dimethenamid-P, and their metabolites in selected surface water bodies in three corn growing regions of Europe.
Here only the results for dimethenamid-P and its metabolites M656PH003 (= M3 in this study),

M656PH027 (= M27 in this study), M656PH023 (= M23 in this study), and M656PH031 (= M31 in this study) are summarised.

Material and Methods

Sampling locations were chosen within regions of Europe where corn cultivation is one of the major cropping systems. The Rott river (eastern Bavaria, Germany), the Adda and Oglio rivers (northern tributaries of the Po river, ltaly) and the Sió and Danube river (central-western part of Hungary) were chosen, which all drain areas with relatively intensive cultivation of corn. The surface water sampling spots were chosen to represent regionally independent catchments, providing information about the contamination situation in their basin areas.

An overview of the selected sites is given in Table B.8.4.2-1.

Table B.8.4.2-1: Sampling sites used for surface water sampling and sampling procedures

River	Rott (Germany)	Adda (Italy)	Oglio (Italy)	Sió (Hungary)	Danube (Hungary)
GPS coordinates	48.4282 N, 13.3341 E	45.1866° N, 9.7782° E	45.0415° N, 10.6499° E	46.3774° N, 18.7266° E	46.3522° N, 18.8945° E
Sample type	72-h time-integrated samples at several dates; grab samples (one sample) at all other sampling dates	Grab composite sample (three subsamples of river transect)			
Surrounding area	A mixture of cropland (corn, cereals) and scattered pastures dominates the land use in this region	Sampling spot located within the town centre of Pizzighettone (town surrounded by agricultural land)	Sampling spot located within agricultural land, dominated by cropped fields	Sampling spot surrounded by agricultural land cropped with corn and sunflowers	The larger area is dominated by agricultural land cropped with corn and sunflowers
Storm flow periods	Unknown	28 April, 01 May	28 April, 05 May	-	30 June, 07 July
Sampling device	Sampling tube of automated sampling device (72-h composite samples) or glass bottles	Horizontal water sampling bottle (PVC), inert silicone layer on inside		Horizontal water sampling bottle (PVC)	
Temperature	Unknown	12.4 to 23.5 °C	13.2 to 26.7 °C	16.4 to 27.6 °C	16.5 to 25.1 °C
pH	Unknown	7.9 to 8.9	8.0 to 8.9	8.2 to 9.1	7.5 to 9.4
Oxygen content	Unknown	7.0 to 8.1 mg/L	6.4 to 9.5 mg/L	62 to 250 % saturation	85 to 132 % saturation
Conductivity	Unknown	250 to 480 µS/cm	430 to 650 µS/cm	712 to 1145 µS/cm	292 to 416 µS/cm
Sample container	Glass bottles with Teflon-lined plastic screw caps	High-density polyethylene bottle (HDPE)			

Surface water samples were taken biweekly during the application season and weekly thereafter for five months (April to beginning of September in Italy, May to end of September in Hungary), or weekly from May to November (Germany) in 2009.
At the sampling site in Rott (Germany), sampling was done at a regular water monitoring site of the Bavarian Environmental Agency (LfU). The samples were either taken within the special pesticide monitoring program PSMRegio (72-h time-integrated samples, using an automated sampling device), or in between the regular intervals as grab samples using 1 L glass bottles. Samples were taken at approx. 30 cm depth, on the right-hand side of the river. Automated samples were pumped over a period of 72 h and cooled (<8 °C) within the automated sampling device. During transport to the laboratory and storage samples were kept cool (<8 °C).
At the sampling sites in Italy and Hungary, a horizontal water sampling bottle (cleaned, ethanol-

rinsed, and once rinsed with river water before use) was submerged in the surface water body to approx. 30 cm depth below the water surface level for sampling. To receive a composite grab sample, three subsamples of approx. 1 L were taken from the cross-section of the rivers; subsamples were evenly spaced out to achieve a representative composite sample for the river at this point. The subsamples were combined and mixed, and a portion of the sample was used to measure basic water parameters on site (temperature, pH, conductivity, and oxygen saturation). The sampling bottles were closed and stored on (dry)ice immediately after sampling and stored deep frozen (<-16 °C) until shipment on dry ice for analysis.
The analysis of samples for dimethenamid-P and its metabolites M656H003, M656H027, M656H023, and M656H031 was done centrally in the laboratory of BASF SE in Limburgerhof (Germany). Prior to routine sample analysis, an analytical multi-residue method was developed (BASF No. L149/01) and validated. For analysis, a 50 mL aliquot of the water sample was acidified with 6 M HCI to pH 2 and concentrated on a solid phase extraction column; the column was then washed with purified water (pH 2). After drying the column for 1 minute under vacuum the residues were eluted with methanol. The eluate was reduced to dryness by evaporation and the residue was dissolved in methanol/water to prepare the final volume for analysis. The sample was finally analysed using UPLC-MS/MS. The limit of quantification (LOQ) was determined at 0.010 µg/L, the limit of detection (LOD) at 0.002 µg/L.
For quality control, fortified samples (minimum of two samples) were routinely analysed with each batch of surface water samples. The average recovery rates ranged from 93 to 102 % of spiked amount for dimethenamide-P and its metabolites.

Results and Discussion

The maximum concentrations of dimethenamid-P and its metabolites M656PH003, M656PH027, M656PH023, and M656PH031 in the surface water samples at the five locations are presented in Table B.8.4.2-2.

Table B.8.4.2-2: Maximum concentration of dimethenamid-P and its M656PH003, M656PH027, M656PH023, and M656PH031 at sampling sites

Dimethenamid-P		
River System	**Maximum concentrations (µg/L)**	**Date of maximum concentration**
Rott (Germany)	0.46	03.06.09 (72 h sample)
Adda (Italy)	<LOQ	several sampling dates
Oglio (Italy)	0.02	10.06.2009
Sió (Ungary)	0.51	30.06.2009
Danube (Hungary)	0.01	07.08.2009
Metabolite M656PH003		
River System	**Maximum concentrations (µg/L)**	**Date of maximum concentration**
Rott (Germany)	0.02	10.06.09 (72 h sample)
Adda (Italy)	-	-
Oglio (Italy)	-	-
Sió (Ungary)	-	-
Danube (Hungary)	-	-
Metabolite M656PH023		
River System	**River System**	**Date of maximum concentration**
Rott (Germany)	0.11	30.06.09 (72 h sample)
Adda (Italy)	-	several sampling dates
Oglio (Italy)	< LOQ	10.06.2009
Sió (Ungary)	< LOQ	30.06.2009
Danube (Hungary)	0.01	30.06.2009
Metabolite M656PH027		
River System	**River System**	**Date of maximum concentration**
Rott (Germany)	0.13	30.06.09 (72 h sample)
Adda (Italy)	< LOQ	several sampling dates
Oglio (Italy)	< LOQ	10.06.2009
Sió (Ungary)	< LOQ	30.06.2009
Danube (Hungary)	0.02	30.06..2009
Metabolite M656H031		
River System	**River System**	**Date of maximum concentration**
Rott (Germany)	0.12	30.06.09 (72 h sample)
Adda (Italy)	< LOQ	several sampling dates
Oglio (Italy)	< LOQ	10.06.2009
Sió (Ungary)	0.01	30.06.2009
Danube (Hungary)	0.01	07.08.2009

Dimethenamid-P was frequently detected in surface water samples in this study. Its maximum concentration reached 0.46 µg/L (Germany, Rott) to 0.51 µg/L (Hungray, Sió) at two sampling locations, while much lower peak concentrations were measured at the other sampling locations (<LOQ to 0.02 µg/L). It was mostly present at low concentrations or in traces for medium long periods of time in surface water bodies (>2 months).
Dimethenamid-P metabolites were detected in traces at all sampling sites. At the German sampling site, peak concentrations were highest and ranged from 0.02 to 0.13 µg/L (M656PH027 ≈ M656PH031 ≈ M656PH023 > M656PH003). The metabolite maximum peak was recorded roughly one month after the highest observance of the active substance. While in the sampled Italian river bodies only sporadic traces of dimethenamid-P metabolites were measured, the metabolites M656PH023, M656PH027, and M656PH031 were frequently detected at the two Hungarian sites, however at low maximum concentrations ≤0.02 µg/L. M656PH003 was never detected in Italian or Hungarian surface water samples.

Conclusion

The study is considered acceptable as additional information but is considered of limited use for surface water risk assessment by the RMS due to the following issues:
The maps of the rivers indicate bigger water regimes and sampling close to the river mouths except for river Danube, which on the other hand is the biggest of the sampled rivers. The chosen water regimes

are therefore not representative for small ditches and small rivers relevant for environmental risk assessment. A strong dilution of the concentrations that would have been measured in small water regimes close to agricultural fields treated with dimethenamid-P is expected.
Besides more precise information on the catchments is missing and the area of the catchments that is used for cultivation with crops and the area that were treated with dimethenamid-P. Information on the amount of dimethenamid-P used in the catchments is also missing.
The mixed samples over 72 h of the river Rott show the highest concentrations of dimethenamid-P and its metabolites, although they are diluted by the length of the sampling time. This indicates, that it is very difficult to catch the actual peak concentration of an active substance like dimethenamid-P, that is applied only once in the growing season in a flowing river. It seems that the actual peaks in the other four rivers were probably not caught by the grab sampling.
To get surface water monitoring results that can really be compared with surface water modelling, it appears sensible to model the expected peak in the surface waters after application of the active substance first similar to the response time modelling performed for groundwater monitoring studies. The sampling period can then be chosen according to the expected peak times of the active substance and/or its metabolites in the surface water.

KCA 7.5/7– Leu et al, 2004 (new study, open literature)

Author:	Leu, C. Singer, H. Stamm, C. Müller, S.R. Schwarzenbach, R.P.
Title:	Simultaneous assessment of sources, processes, and factors influencing herbicide losses to surface waters in a small agricultural catchment
Date:	01/01/2004
Doc ID:	BASF DocID 2013/1348574 Published in Environmental Science Technology 2004, Vol 38, p. 3827 - 3834
Guidelines:	None
GLP:	No
Validity:	Acceptable as additional information, not suitable for surface water risk assessment

Aim of the study

The aim of the study was to gain a detailed knowledge about all factors that control the losses of 3 different pesticides, atrazine, dimethenamid and metolachlor from a point source (farmyard) and from diffuse sources (fields) at the scale of a small agricultural catchment into a surface water regime, the brooks.

Material and Methods

The investigated area comprises about 2.1 km^2 of the catchment of the Lake Greifensee, located 25 km southeast of Zurich, Switzerland, which drains into the river Aa Mönchaltorf. Agricultural land forms 91 % of the catchment area; 7 % of it are forest and the remaining area includes farmyard, buildings and roads. Topography is moderate with slopes between 5 and 10 % of the agricultural fields and with slopes between 5 and 10 % on another 63 % of the fields.
The annual precipitation is 1330 mm on average and higher rainfall may occur during the vegetation period. The average monthly temperatures range from -1 °C in January to 18 °C in July. In this area, 60 % of the 7.2 km brooks length flow in subsurface concrete tubes. 12 % of the catchment is systematically drained with tiles at 1.4 m depth and spaced at ~14 m.
The study investigated 13 cornfields including poorly drained (cambic) Gley soils (73 %) and well to relatively well drained (calcaric) Cambisol (27 %). Five fields were systematically drained and at least five additional fields were non-systematically drained. Top soils of these fields are loamy to clay

loamy with organic matter contents ranging from 2.8 to 8.5 %.
Dimethenamid was applied in the formulation Frontier 900 EC (in a mixture with two other herbicides) on 13 cornfields at 0.75 kg ha^{-1} using a boom sprayer on May 8, 2000. With each mixture a fourth pesticide (tracer pesticide) out of a selection of nine substances was applied to each field to identify losses from individual fields. Post- and pre-emergence field applications were performed. During the study year, dimethenamid was not used by other farmers in the catchment outside the test area.
Two rain gauges were used to record the amounts of rain every 10 min. Brook discharge at the outlet of the catchment was determined by two different methods. First, pressure at the bed of a flume was continuously recorded with a transducer connected to a data logger. The dilution method with NaCl was used to calibrate a pressure-discharge relation based on 16 calibration points over the whole discharge range, gauged during the sampling period. Second, the level and average flow velocity were continuously gauged by a sensor. Discharge data of both systems as well as conductivity were measured and stored in 5 min intervals. At the same station, water samples were taken from the brook using three portable automatic samplers. Two sampling approaches were followed. First, two samplers were used to collect time-proportional samples, triggered by elevated discharge levels. The sampling intervals were between 5 and 20 min and between 15 and 60 min, respectively. Second, a third sampler was set to take flow-proportional composite samples each composed of 9 subsamples.
A total of 596 water samples were analysed for dimethenamid using a SPME-GC/MS analytical method. Limits of quantification for the investigated substances were in the range from 0.02 to 0.12 µg L^{-1} for the different pesticides. Tracer pesticides were determined with the same analytical method. Another analytical method was used to quantify ethansulfonic acid and oxanillic acid degradates of dimethenamid. The limit of quantification for this method ranged from 0.003 to 0.01 µg L^{-1}.

Soil samples from all cornfields were taken once prior to herbicides application and eleven times after application during a time period of 50 days. Fifteen to 20 cores were taken randomly on every field and mixed to one composite sample per field. Samples were weighted, milled, homogenised and divided into aliquots of 8 g before analysis. An internal standard of d_3-dimethenamid was added to the soil aliquots before extraction and dimethenamid was quantified using GC-MS. The limit of quantification ranged from 0.03 to 0.05 µg g^{-1} dry matter.

Results and Discussion

The first nine days after application remained very dry with only 3 mm of rain (event 1 and 2). During the two following weeks, three rain events resulted in a total of 51 mm precipitation (event 3 – 5). However, only the 6^{th} rainfall event (46 mm, ~ 20-30 days after application) caused the first substantial hydrolical response from the catchment as well as major loss of herbicides. A total of 260 mm precipitation occurred during the 67 days from application until end of the sampling period. Thirteen rain events caused losses of herbicides from point sources (runoff from farmyards) or diffuse sources (runoff and preferential flow from fields) into the brook or subsurface drainage system.

Diffuse loss from the fields was the major source of herbicide removal into the brook. For dimethenamid, diffuse loss after rain events 6, 7, 9 and 13 accounted for 99 % of the total brook loads lost until day 67 after application.
Table B.8.4.2-3 gives maximum dimethenamid concentrations, loads, and maximum discharge measured in the brook at the outlet of catchment during the four most important diffuse loss events.

Table B.8.4.2-3: Maximum dimethenamid concentrations, loads, and maximum discharge measured in the brook at the outlet of catchment during the four most important diffuse loss events

Rain event	6	7	9	13
Days since application	23-29	29-33	37-41	61-67
Maximum concentrations ($\mu g\ L^{-1}$)	1.47	0.32	0.12	0.02
Load (g)	21.7 (93 %)	1.2 (5 %)	0.2 (1 %)	nd [a]
Maximum flow ($m^3\ s^{-1}$)	0.63	0.22	0.19	0.49

a The dimethenamid load during event 13 was not quantified since concentrations were below the quantification limit of the SPME-GC/MS method. Note that the difference of 2 g resulting from treating values below the quantification limit as 0 instead of treating them as 0.02 µg L^{-1} (i.e., the quantification limit itself) is small compared to the total load of 23.1 g dimethenamid.

() Parentheses list percentages of individual loads from the total load lost from the fields until day 67 after application.

Total mass losses of dimethenamid from the fields of the catchment accounted for 0.27 % of its total amount applied.
The dissipation of dimethenamid from soil was described by first-order kinetics with a field DT_{50} of 13 days as a median value from 11 fields.
The herbicides were mainly transported with limited soil-water contact via surface run-off of fresh rainwater and preferential flow into the drainage system and the main loss for all three herbicides occured during rain event 6. As a consequence, only small differences in the loss kinetics of the 3 herbicides atrazine, dimethenamid and metolachlor were found regardless of their different substance properties.
The load for dimethenamid metabolites M656H027 (ethansulfonic acid in this study) and M656H023 (oxanillic acid in this study) were 11.1 g and 15.5 g at the loss event 6. The ratio of molar amounts of metabolites to parent compound at this event was 0.54 and 0.73 for M656H027 and M656H023.

Conclusion

The study is acceptable as additional information but is considered of limited use for surface water risk assessment by the RMS due to the following issues:
Dimethenamid-P degrades in soil under aerobic conditions with a DT_{50} value of 11.5 d (combined laboratory and field data, normalised to 20 °C and pF). Thus, at the time of the major rain event 6, 23 – 29 d after application a major amount of dimethenamid would have been already degraded on the field surface. Thus, the dimethenamid concentrations in the river brooks cannot be considered as worst case compared to the concentrations modelled with FOCUS SW.
Besides, measurements after one application event from one small agricultural catchment area of course not enough to replace modelled concentrations from the agreed FOCUS SW scenarios and it is not clear how the climatic, hydrological and pedological conditions of the catchment compare to worst case conditions of small surface water regimes throughout Europe.

KCA 7.5/8– Chevre et al, 2008 (new study, open literature)

Author:	Chevre, N. Edder, P. Ortelli, D. Tatti, E. Erkmann, S. Rapin, F.
Title:	Risk assessment of herbicide mixtures in a large European lake
Date:	Accepted at the 06/09/2007, published at the 23/01/2008
Doc ID:	BASF Doc ID 2013/1348573 Published in Environmental Toxicology 2008, DOI 10.1002/tox.20337
Guidelines:	None
GLP:	No
Validity:	Acceptable as additional information, not suitable for surface water risk assessment

Aim of the study

The aim of the study was to determine the levels of various pesticides of the Geneva Lake.

Material and Methods

In this study, the levels of various pesticides, among them dimethenamid, in the Geneva Lake were monitored in 2004 and 2005. Samples were taken at different depths and different periods from a site situated in the middle of the lake. The sampling site has been used for long time as a reference point, therefore it was considered as representative of the average contamination of the lake.
Water samples (2 L) were collected two times in April 26, 2004 and April 26, 2005, and one time in September 6, 2004. The samples were taken at nine different depths; five at 0-10 m depths in the epilimnion-metalimnion (0, 1, 5, 7.5, and 10 m), and four at 10-309 m depth in the hypolimnion (30, 100, 305, and 309 m).
An aliquot of 500 mL samples were extracted on an Oasis HLB cartridge (Waters) concentrated to 100 µL and analysed using HPLC/MS-MS. The risk for RS-dimethenamid was assessed by comparing the measured concentration to the water quality criteria (WQC) set by the authors. High concentrated extracts of the water samples enabled reaching a limit of detection in the range from 1-100 ng $L^{-1}$for the different herbicides.

Results and Discussion

The method recovery ranged from 50-120 %. The method was validated with five concentration levels (1, 5, 20, 50, and 200 ng L^{-1}) using pure water, two repetitions for five days. The coefficient of variation for intra-day precision ranged from 8-18 %, and for inter-day from 18-38 %.

Dimethenamid was detected only at one sampling date at both depth ranges with an average concentration of 0.001 µg L^{-1}. The concentration of RS-dimethenamid was below the limit of detection at all other sampling dates and thus below the value for the WQC (0.16 µg/L) set by the authors, indicating no risk of RS-dimethenamid contamination.

Conclusion

The study is acceptable as additional information but is considered of limited use for surface water risk assessment by the RMS due to the following issues:
First the Lake Geneva is a large surface water body and is therefore not representative for small ponds relevant for environmental risk assessment. A strong dilution of the concentrations that would have been measured in small water regimes close to agricultural fields treated with dimethenamid-P is expected.
Besides information on the catchment of the Lake Geneva is missing and additionally, no information is available on the area of the catchment that is used for agriculture and that were treated with dimethenamid-P. Information on the amount of dimethenamid-P used in the catchment is also missing.

Besides, samples in the Lake Geneva were taken only at three sampling points. For a herbicide that is applied only once in the growing season and degrades fairly quickly in soil (DT_{50} = 11.5 d, geometric mean, combined laboratory and field data, normalised to 20 °C and pF) and in water/sediment systems (DT_{50} = 26.9 d, whole system at 20 °C, geometric mean) it is unlikely that peak concentrations after applications can be caught without continuous sampling or prior modelling to determine when the peak concentrations is likely to occur.

B.8.4.3 Monitoring data of air

KCA 7.5/9– Coscolla et al, 2010

Author:	Coscolla C., Colin, P., Yahyaoui, A., Petrique, O., Yusà, V., Mellouki, A., Pastor, A.
Title:	Occurrence of currently used pesticides in ambient air of Centre Region (France)
Date:	08/07/2010
Doc ID:	BASF DocID 2010/1229759 Published at Atmospheric Environment 4 (2010), 3915 - 3925
Guidelines:	No
GLP:	No
Validity:	Acceptable as additional information, not suitable for risk assessment

Aim of the study

The study aimed to improve the knowledge about the atmospheric behaviour of currently used pesticides in the central region of France.

Material and Methods

The study was carried out within the central region of France on three rural sites (Saint Martin d'Auxigny, Oysonville and Saint Aignan) and two urban sites (Tour and Orléans). The area of the region is about 40000 km^2 and about 57 % of the surface is used for agricultural activities. Pesticides are used intensively in the farming activities in this region. Details on the 5 sampling site are presented in Table B.8.4.3-1.

Table B.8.4.3-1: Description of the sampling site of the air sampling campaign

Sampling Site	Latitude	Longitude	Description
Tours (To)	47°25´62´´N	00°41´90´´E	Commercial and residential area. Samples collected at ground level.
Orléans (Or)	47°91´19´´N	01°89´54´´E	Parking in the city centre. Samples collected at 3.5 m above ground level.
Saint Martin d'Auxigny (SM)	47°20´34´´N	02°42´37´´E	Rural and agricultural area surrounded by apple tree fields. Samples collected at ground level.
Oysonville (Oy)	48°23´35´´N	01°56´57´´E	Rural and intensive agricultural area with mainly arable crops such as maize, wheat, soybean, barley and sunflowers. Samples collected at ground level.
Saint Aignan (SA)	47°26´63´´N	01°37´17´´E	Rural and agricultural area (vineyards). Samples collected at 6 metres above ground level.

Sampling was performed in three campaigns from 2006 to 2008 in the periods presented in Table B.8.4.3-2 using a low-volume sampler (Partisol 2000). Gas samples and particulate matter were collected together on quartz fibre filters (47 mm diameter) followed by polyurethane foam plugs (26 mm diameter x 76 mm length). Sampling was performed on a weekly basis by exposing filters and polyurethane plugs at a flow rate of 1 $m^3 h^{-1}$. A total volume of 168 m^3 was collected approximately.

Table B.8.4.3-2: Description of the sampling periods of the air sampling campaign

Year	Sampling period
2006	14 March - 12 September
2007	April -11 July, except for Saint Martin d'Auxigny (until 11 September)
2008	9 April - 2 July, except for Saint Martin d'Auxigny (until 5 November)

Samples were analysed for a group of 56 pesticides including dimethenamid after sampling or after a storage period of the filters at -18 °C. The studied pesticides were extracted from the samples and the concentrations were determined using LC-MS/MS and GC-MS techniques.

Meteorological data such as air temperature (T), wind direction (WD) and wind speed (WS) were collected from two weather stations located in Orléans and Tours.

Results and Discussion

The retention capacity for the polyurethane foam plugs ranged from 60-120 % and the obtained recoveries were in the range from 70 - 110 % for PUF plugs plus quartz filters.
In total, 262 air samples were tested for herbicides along the study period. Dimethenamid was detected at a low frequency of 2 % at concentrations ranging from 0.16 - 0.74 ng m^{-3}.

Conclusion

The study is acceptable as additional information but is considered of limited use for risk assessment by the RMS due to the following issues:
Sampling was performed at three rural sampling sites, but only at one of the three sites, Oysonville, crops where cultivated that could have potentially been treated with dimethenamid-P. However, no information was given, if dimethenamid-P was really applied in the area close to the sampling site, the size of treated fields or on the amount and distance of fields treated with dimethenamid to the sampling site. Besides, it is not stated if the fields with crops treated were within the wind direction of the sampling sites.
Thus, the study results are unsuitable to assess the amount of dimethenamid-P in the air after volatilisation and short-range transport close to treated fields.
Also the assessment of the potential of long-range transport is not possible, since it still requires information whether dimethenamid was used in considerable amounts in France in the sampling years and would require the choice of sampling sites not close but in the broad wind direction of areas treated with dimethenamid. To the potential of long-range transport using monitoring data, measurements from remote areas are more suitable, since in these areas input via short-range transport can be excluded.

B.8.5 References relied on

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 is decribed in more detail in the Appendix to this document.
No additional open-literature studies concerning the route and rate of dimethenamid-P in soil were found.

Data Point EU as of 2014	Author(s)	Year	Title Company Report No. Source (where different from company) GLP or GEP status Published or not	Vertebrate study Y/N	Data Protection Claimed Y/N	Justification if data protection is claimed	Owner	Previously submitted Y/N If yes, old data point
KCA 7.1.1.1	Wendt D.R.	1997	Comparative aerobic soil metabolism of SAN 1289H and SAN 582H SANDOZ Agro, Inc., Des Plaines, Illinois 60018 BASF RegDoc.# 97/5257 GLP, unpublished	N	N	Not applicable	BASF	Y relevant IIA. 7.1.1.1.1 [7.1/01]
KCA 7.1.1.1	Krueger J.P., Bade T.R.	1990	Aerobic soil metabolism of SAN 582H SANDOZ Agro, Inc., Des Plaines, Illinois 60018 BASF RegDoc.# 90/11105 GLP, unpublished	N	N	Not applicable	BASF	Y not relevant IIA. 7.1.1.1.1 [7.1/02]
KCA 7.1.1.1	Koenig, M.	1995	Aerobic degradation of [3-^{14}C-thienyl]-dimethenamid in BBA 2.2 and 2.3 soils under laboratory conditions SANDOZ Agro, Ltd., Basle, CH BASF RegDoc.# 95/10128 GLP, unpublished	N	N	Not applicable	BASF	Y relevant IIA. 7.1.1.1.1 [7.1/03]
KCA 7.1.1.1	Koenig, M.	1996	Aerobic degradation and metabolism of [3-^{14}C-thienyl] dimethenamid in flaach soil under laboratory conditions SANDOZ Agro, Ltd., Basle, CH BASF RegDoc.# 96/11006 GLP, unpublished	N	N	Not applicable	BASF	Y relevant IIA. 7.1.1.1.1 [7.1/04]
KCA 7.1.1.1/1	Stauden-maier H.	2013	Chiral analysis of dimethenamid-P after incubation in soil 2012/1073064 BASF SE, Limburgerhof, Germany Fed.Rep. GLP, unpublished	N	Y	New data for AIR3 renewal	BASF	N IIA. 7.1.1.1.1
KCA 7.1.1.1/2	Unsworth R.	2014	Dimethenamid-P: Chiral separation after degradation in soil 2013/1412031 Huntingdon Life Sciences Ltd., Huntingdon Cambridgeshire PE28 4HS, United Kingdom GLP, unpublished	N	Y	New data for AIR3 renewal	BASF	N IIA. 7.1.1.1.1
KCA 7.1.1.3	Nietsch-mann D., Yu C.	1997	Comparative photolysis of R,S-dimethenamid (SAN 582 H) and S-dimethenamid (SAN 1289 H) SANDOZ Agro, Inc., Des Plaines, Illinois 60018 BASF RegDoc.# 97/5181 GLP, unpublished	N	N	Not applicable	BASF	Y relevant IIA. 7.1.1.1.1 [7.1/05]
KCA 7.1.1.3	Sabat, M., Yu, C.	1992	SAN 582 H: photodegradation study on soil SANDOZ Agro, Inc., Des Plaines, Illinois 60018 BASF RegDoc.# 92/12387 GLP, unpublished	N	N	Not applicable	BASF	Y relevant IIA. 7.1.1.2.1 [7.1/06]

Data Point EU as of 2014	Author(s)	Year	Title Company Report No. Source (where different from company) GLP or GEP status Published or not	Vertebrate study Y/N	Data Protection Claimed Y/N	Justification if data protection is claimed	Owner	Previously submitted Y/N If yes, old data point
KCA 7.1.2.1.3	Nietsch-mann D., Yu C.	1997	Comparative photolysis of R,S-dimethenamid (SAN 582 H) and S-dimethenamid (SAN 1289 H) SANDOZ Agro, Inc., Des Plaines, Illinois 60018 BASF RegDoc.# 97/5181 GLP, unpublished	N	N	Not applicable	BASF	Y relevant IIA. 7.1.1.2.1 [7.1/05]
KCA 7.1.2.1.1/1	Platz K.	2008	Kinetic evaluation of different laboratory soil degradation experiments of Dimethenamid (BAS 656 H) for derivation of modeling endpoints of the parent compound and its metabolites M23, M27 and M31 2008/1048056 BASF SE, Limburgerhof, Germany Fed.Rep. Not GLP, unpublished	N	Y	New data for AIR3 renewal	BASF	N IIA. 7.1.1.2.1
KCA 7.1.2.1.1/2	Bronner G.	2010	Determination of kinetic parameters for the degradation in US-soil of BAS 656 H and its metabolites M23, M27 and M31 in laboratory incubation studies 2010/1135818 BASF SE, Limburgerhof, Germany Fed.Rep. Not GLP, unpublished	N	Y	New data for AIR3 renewal	BASF	N IIA. 7.1.1.2.1
KCA 7.1.2.1.2/3	Class T., Heinz N.	2014	Aerobic soil degradation of the three dimethenamid-P metabolites M656PH04 (Reg.No. 5920718), M656PH047 (Reg.No. 5917260), M656PH043 (Reg.No. 5917262) in three soils (OECD Guideline 307) 2013/1348091 PTRL Europe, Ulm, Germany Fed.Rep. GLP, unpublished	N	Y	New data for AIR3 renewal	BASF	N IIA. 7.1.1.2.1
KCA 7.1.2.2.1	Carrier, M.N., Blanz, J.	1992	Dissipation of residues of dimethenamid from field soil after application of SAN 582 H 900 EC under field conditions in France, 1992. (Field soil dissipation/leaching study) Novartis Agro c/o Clariant Huningue S.A., Huningue Cedex BASF RegDoc.# 97/11507 GLP, unpublished	N	N	Not applicable	BASF	Y relevant IIA. 7.1.1.2.2 [7.1/12]
KCA 7.1.2.2.1	Carrier, M.N.	1997	Dissipation of residues of dimethenamid from field soil after application of SAN 582 H 900 EC under field conditions in Italy, 1992. (Field soil dissipation/leaching study) Novartis Agro c/o Clariant Huningue S.A., Huningue Cedex BASF RegDoc.# 97/11508 GLP, unpublished	N	N	Not applicable	BASF	Y relevant IIA. 7.1.1.2.2 [7.1/13]
KCA 7.1.2.2.1	Fricker, P., Hertl, P.	1995	Mobility and dissipation of residues of dimethenamid from field soil after application of SAN 582 H 900 EC under field conditions in Germany, 1993. (Field soil dissipation/leaching study) SANDOZ Agro, Ltd., Basle, CH BASF RegDoc.# 95/10130 GLP, unpublished	N	N	Not applicable	BASF	Y relevant IIA. 7.1.1.2.2 [7.1/10]

Data Point EU as of 2014	Author(s)	Year	Title Company Report No. Source (where different from company) GLP or GEP status Published or not	Vertebrate study Y/N	Data Protection Claimed Y/N	Justification if data protection is claimed	Owner	Previously submitted Y/N If yes, old data point
KCA 7.1.2.2.1	Fricker, P., Hertl, P.	1995	Dissipation of residues of dimethenamid from field soil after application of SAN 582 H 900 EC under field conditions in France, 1992. (Field soil dissipation/leaching study) SANDOZ Agro, Ltd., Basle, CH BASF RegDoc.# 95/10133 GLP, unpublished	N	N	Not applicable	BASF	Y relevant IIA. 7.1.1.2.2 [7.1/11]
KCA 7.1.2.2.1	Bade, T.R.	1992	Stability of SAN 582 H and its metabolites in stored frozen soil samples QAU #89/11/27 SANDOZ Agro, Inc., Des Plaines, Illinois 60018 BASF RegDoc.# 92/12382 GLP, unpublished	N	N	Not applicable	BASF	Y relevant IIA. 7.1.1.2.3 [7.1/14]
KCA 7.1.2.2.1/1	Bayer H., Marwitz A.	2014	Field soil dissipation study of BAS 656 H (dimethenamid-P) in the formulation BAS 656 12 H on bare soil at four different sites in Europe, 2011-2013 2013/1343457 BASF SE, Limburgerhof, Germany Fed.Rep. GLP, unpublished	N	Y	New data for AIR3 renewal	BASF	N IIA. 7.1.1.2.3
KCA 7.1.2.2.1/2	Bayer H., Marwitz A.	2014	Field soil dissipation study of M27 (metabolite of BAS 656 H, Dimethenamid) in the formulation EXP 360714 H-AA on bare soil at four different sites in Europe, 2011-2013 2013/1343459 BASF SE, Limburgerhof, Germany Fed.Rep. GLP, unpublished	N	Y	New data for AIR3 renewal	BASF	N IIA. 7.1.1.2.3
KCA 7.1.2.2.1/3	Bayer H., Marwitz A.	2014	Field soil dissipation study of BAS 656 H (dimethenamid-P) in the formulation BAS 769 00 H on bare soil at two different sites in Europe, 2011-2013 2013/1343460 BASF SE, Limburgerhof, Germany Fed.Rep. GLP, unpublished	N	Y	New data for AIR3 renewal	BASF	N IIA. 7.1.1.2.3
KCA 7.1.2.2.1/4	Mewis A.	2014	Determination of the storage stability of dimethenamid-P and its metabolites M23, M27 and M31 in 4 soils under deep frozen conditions 2013/1348019 Eurofins Agroscience Services GmbH, Niefern-Oeschelbronn, Germany Fed.Rep. GLP, unpublished	N	Y	New data for AIR3 renewal	BASF	N IIA. 7.1.1.2.3
KCA 7.1.2.2.1/5	Mewis A.	2014	Determination of the storage stability of dimethenamid-P and its metabolites M23, M27 and M31 in 2 soils under deep frozen conditions 2013/1348029 Eurofins Agroscience Services EcoChem GmbH, Niefern-Oeschelbronn, Germany Fed.Rep. GLP, unpublished	N	Y	New data for AIR3 renewal	BASF	N IIA. 7.1.1.2.3

Data Point EU as of 2014	Author(s)	Year	Title Company Report No. Source (where different from company) GLP or GEP status Published or not	Vertebrate study Y/N	Data Protection Claimed Y/N	Justification if data protection is claimed	Owner	Previously submitted Y/N If yes, old data point
KCA 7.1.2.2.1/6	Wiedemann G.	2014	Calculation of normalised modelling half-lives from terrestrial field dissipation studies with dimethenamid-P and its metabolite M27 according to Focus kinetics 2014/1031648 BASF SE, Limburgerhof, Germany Fed.Rep. Not GLP, unpublished	N	Y	New data for AIR3 renewal	BASF	N IIA. 7.1.1.2.3
KCA 7.1.2.2.1/7	Wiedemann G.	2014	Calculation of persistence half-lives from terrestrial field dissipation studies with dimethenamid-P and its metabolite M27 according to Focus kinetics 2014/1031649 BASF SE, Limburgerhof, Germany Fed.Rep. Not GLP, unpublished	N	Y	New data for AIR3 renewal	BASF	N IIA. 7.1.1.2.3
KCA 7.1.3.1	Tong, T.M., Su, L.Y.	1997	Soil adsorption and desorption of SAN 1289H, unaged, by the batch equilibrium method SANDOZ Agro, Inc., Des Plaines, Illinois 60018 BASF RegDoc.# 97/5180 GLP, unpublished	N	N	Not applicable	BASF	Y relevant IIA. 7.1.2 [7.1/15]
KCA 7.1.3.1.1/1	Paulick R.	2007	Amendment 1: Soil adsorption and desorption of SAN-1289H, unaged, by the batch equilibrium method 2007/7003537 Sandoz Agro Inc., Des Plaines IL, United States of America GLP, unpublished	N	Y	New data for AIR3 renewal	BASF	N IIA. 7.1.2
KCA 7.1.3.1.2/1	Class T., Dorn U.	2004	Dimethenamid metabolite M27 (Sulfanate): Adsorption - desorption on different soils (OECD guidelines 106) 2004/1015224 PTRL Europe GmbH, Ulm, Germany Fed.Rep. GLP, unpublished	N	Y	New data for AIR3 renewal	BASF	N IIA. 7.1.2
KCA 7.1.3.1.2/2	Class T.	2011	Determination of adsorption/desorption behaviour of Reg.No. 360712 (metabolite M31 of BAS 656 H, dimethenamid-P) on soils (OECD guideline 106) 2011/1277426 PTRL Europe GmbH, Ulm, Germany Fed.Rep. GLP, unpublished	N	Y	New data for AIR3 renewal	BASF	N IIA. 7.1.2
KCA 7.1.3.1.2/3	Sacchi R.R.	2013	Adsorption behavior of M23, M27 and M31 (metabolites of dimethenamid-P) on different European soils 2013/3012762 BASF SA, Guaratingueta, Brazil GLP, unpublished	N	Y	New data for AIR3 renewal	BASF	N IIA. 7.1.2
KCA 7.1.3.1.2/4	Class T., Walter W.	2014	Determination of adsorption and desorption behavior of M656PH043 (Reg.No. 5917262, metabolite of dimethenamid-P) in 5 soils (OECD Guideline 106) 2013/1348092 PTRL Europe, Ulm, Germany Fed.Rep. GLP, unpublished	N	Y	New data for AIR3 renewal	BASF	N IIA. 7.1.2

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KCA 7.1.3.1.2/5	Class T., Walter W.	2014	Determination of adsorption and desorption behavior of M656PH047 (Reg.No. 5917260, metabolite of dimethenamid-P) in 5 soils 2013/1348093 PTRL Europe GmbH, Ulm, Germany Fed.Rep. GLP, unpublished	N	Y	New data for AIR3 renewal	BASF	N IIA. 7.1.2
KCA 7.1.3.1.2/6	Class T., Walter W.	2014	Determination of adsorption and desorption behavior of M656PH054 (Reg.No. 5920718, metabolite of dimethenamid-P) in 5 soils - (OECD guideline 106) 2013/1348094 PTRL Europe, Ulm, Germany Fed.Rep. GLP, unpublished	N	Y	New data for AIR3 renewal	BASF	N IIA. 7.1.2
KCA 7.1.3.2	Koenig, M.	1995	Leaching behaviour of [3-^{14}C-thienyl]-dimethenamid in aged BBA 2.1 soil under laboratory conditions SANDOZ Agro, Ltd., Basle, CH BASF RegDoc.# 95/10101 GLP, unpublished	N	N	Not applicable	BASF	Y relevant IIA. 7.1.3.2 [7.1/21]
KCA 7.1.3.2	Koenig, M.A.	1994	Leaching behaviour of [3-^{14}C-thienyl]-dimethenamid in aged BBA 2.2 soil under laboratory conditions SANDOZ Agro, Ltd., Basle, CH BASF RegDoc.# 94/10635 GLP, unpublished	N	N	Not applicable	BASF	Y relevant IIA. 7.1.3.2 [7.1/22]
KCA 7.1.4.1	Koenig, M.	1995	Leaching behaviour of [3-^{14}C-thienyul]-dimethenamid in five soils under laboratory conditions SANDOZ Agro, Ltd., Basle, CH BASF RegDoc.# 95/10122 GLP, unpublished	N	N	Not applicable	BASF	Y relevant IIA. 7.1.3.1 [7.1/20]
KCA 7.1.4.2	Burgener, A.	1996	[3-^{14}C-thienyl]dimethenamid: mobility and degradation in soil in outdoor lysimeters RCC, Research & Consulting Company AG, Switzerland BASF RegDoc.# 96/10707 GLP, unpublished	N	N	Not applicable	BASF	Y relevant IIA. 7.1.3.3 [7.1/23]
KCA 7.1.4.2/1	Fent G.	2008	Microlysimeterstudy (soil Borstel) with ^{14}C-dimethenamid-P for characterisation of the metabolite pattern in leachates 2008/1051489 Rheinland Pfalz AgroScience GmbH, Neustadt/Weinstrasse, Germany Fed.Rep. GLP, unpublished	N	Y	New data for AIR3 renewal	BASF	N IIA. 7.1.3.3
KCA 7.1.4.2/2	Stauden-maier H.	2009	Structure elucidation of metabolites of Dimethenamid in lysimeter leachate 2009/1011362 BASF SE, Limburgerhof, Germany Fed.Rep. GLP, unpublished	N	Y	New data for AIR3 renewal	BASF	N IIA. 7.1.3.3
KCA 7.1.4.2/3	Stauden-maier H.	2014	Structure elucidation of metabolites of Dimethenamid in lysimeter leachate 2014/1031599 BASF SE, Limburgerhof, Germany Fed.Rep. GLP, unpublished	N	Y	New data for AIR3 renewal	BASF	N IIA. 7.1.3.3

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KCA 7.1.4.2/4	Stauden-maier H., Kuhnke G.	2014	Further investigations on structural identity of metabolites of dimethenamid-P in lysimeter leachate 2013/1246087 BASF SE, Limburgerhof, Germany Fed.Rep. GLP, unpublished	N	Y	New data for AIR3 renewal	BASF	N IIA. 7.1.3.3
KCA 7.1.4.2/5	Stauden-maier H.	2014	Investigation of metabolites in the leachate of a lysimeter study with Dimethenamid - Updated version January 2014 2013/1334938 BASF SE, Limburgerhof, Germany Fed.Rep. Not GLP, unpublished	N	Y	New data for AIR3 renewal	BASF	N IIA. 7.1.3.3
KCA 7.1.4.2/6	Haering T.	2013	Relevance assessment of lysimeter study for BAS 656 H - dimethenamid-P and its metabolites for agricultural areas of Europe as well as Germany, France, and UK 2012/1262498 BASF SE, Limburgerhof, Germany Fed.Rep. Not GLP, unpublished	N	Y	New data for AIR3 renewal	BASF	N IIA. 7.1.3.3
KCA 7.1.4.2/7	Hein W., Baudy M.	2013	Determination of the breakthrough behaviour of two metabolites (M23 and M27) of dimethenamid-P and of a conservative tracer using microlysimeters 2013/1294765 RLP AgroScience GmbH, Neustadt/Weinstrasse, Germany Fed.Rep. GLP, unpublished	N	Y	New data for AIR3 renewal	BASF	N IIA. 7.1.3.3
KCA 7.1.4.2/8	Schroeder T.	2014	Estimation of sorption and degradation parameters of metabolite M23 and M27 of BAS 656 H from mini-lysimeter studies by inverse modeling 2013/1348579 BASF SE, Limburgerhof, Germany Fed.Rep. GLP, unpublished	N	Y	New data for AIR3 renewal	BASF	N IIA. 7.1.3.3
KCA 7.1.4.3/3	Friedmann A., Teresiak H.	2014	Amended report - Determination of dislogdeable foliar residues of dimethenamid-P (BAS 656 H) and determination of foliar DT 50 after application of BAS 830 01 H to oilseed rape, 2013 2014/1036906 Agro-Check, Lentzke, Germany Fed.Rep. GLP, unpublished	N	Y	New data for AIR3 renewal	BASF	N IIA. 7.1.3.3
KCA 7.2.1.1	Guirguis A. S.	1997	Hydrolysis of s-dimethenamid SANDOZ Agro, Inc., Des Plaines, Illinois 60018 BASF RegDoc.# 97/5184 GLP, unpublished	N	N	Not applicable	BASF	Y relevant IIA. 7.2.1.1 [7.2/01]
KCA 7.2.1.1	Fostiak W., Hsieh T.	1988	Hydrolysis of SAN 582 H SANDOZ Agro, Inc., Des Plaines, Illinois 60018 BASF RegDoc.# 88/11332 GLP, unpublished	N	N	Not applicable	BASF	Y relevant IIA. 7.2.1.1 [7.2/02]

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KCA 7.2.1.2	Guirguis A. S.	1997	S-dimethenamid: photodegradation study in an aqueous solution SANDOZ Agro, Inc., Des Plaines, Illinois 60018 BASF RegDoc.# 97/5195 GLP, unpublished	N	N	Not applicable	BASF	Y relevant IIA. 7.2.1.2 [7.2/03]
KCA 7.2.1.2	Sabat M., Yu C.C.	1992	SAN 582 H: photodegradation study in aqueous solution SANDOZ Agro, Inc., Des Plaines, Illinois 60018 BASF RegDoc.# 92/12388 GLP, unpublished	N	N	Not applicable	BASF	Y relevant IIA. 7.2.1.2 [7.2/04]
KCA 7.2.1.2	Sen P.K., Yu C.C.	1994	SAN 582 H: quantum yield determination SANDOZ Agro, Inc., Des Plaines, Illinois 60018 BASF RegDoc.# 94/10636 GLP, unpublished	N	N	Not applicable	BASF	Y relevant IIA. 7.2.1.2 [7.2/05]
KCA 7.2.1.2	Scharf J.	1999	Photolytic halflife of dimethenamid in the top layer of aqueous systems BASF Aktiengesellschaft, Limburgerhof, Germany BASF RegDoc.# 99/10073 Not GLP, unpublished	N	N	Not applicable	BASF	Y relevant IIA. 7.2.1.2 [7.2/06]
KCA 7.2.2.2/1	Voelkel W.	2013	Aerobic mineralisation of ^{14}C-dimethenamid-P in surface water 2013/1125944 IES - Innovative Environmental Services Ltd., Witterswil, Switzerland GLP, unpublished	N	Y	New data for AIR3 renewal	BASF	N
KCA 7.2.2.3	Wyss-Benz M., Volkel W.	1994	[3-^{14}C-thienyl] dimethenamid degradation and metabolism in aerobic aquatic systems RCC, Research & Consulting Company AG, Switzerland BASF RegDoc.# 94/10641 GLP, unpublished	N	N	Not applicable	BASF	Y relevant IIA. 7.2.1.3.2 [7.2/07]
KCA 7.2.2.3/1	Voelkel W.	2014	Route and rate of degradation of ^{14}C-dimethenamid-P in one aerobic aquatic sediment system 2013/1125942 IES - Innovative Environmental Services Ltd., Witterswil, Switzerland GLP, unpublished	N	Y	New data for AIR3 renewal	BASF	N IIA. 7.2.1.3.2
KCA 7.2.2.3/2	Bastiansen F.	2011	Kinetic evaluation of BAS 656 H in water/sediment systems under aerobic conditions 2011/1102522 BASF SE, Limburgerhof, Germany Fed.Rep. Not GLP, unpublished	N	Y	New data for AIR3 renewal	BASF	N IIA. 7.2.1.3.2
KCA 7.3	Scharf, J.	1999	Photochemical Oxidative Degradation of Dimethenamid (QSAR Estimates) BASF Aktiengesellschaft, Limburgerhof, Germany BASF RegDoc.# 99/10075 Not GLP, unpublished	N	N	Not applicable	BASF	Y relevant IIA. 7.2.2 [7.2/11]
KCA 7.3.1/1	Hassink J.	2013	Volatilisation of dimethenamid-P after application of BAS 656 12 H on soil and plant surfaces 2012/1282998 BASF SE, Limburgerhof, Germany Fed.Rep. GLP, unpublished	N	Y	New data for AIR3 renewal	BASF	N II A 7.2.2

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KCA 7.3.3/1	Coscolla C. et al.	2010	Occurrence of currently used pesticides in ambient air of Centre Region (France) 2010/1229759 Not GLP, published Source: Atmospheric Environment 44 (2010) 3915-3925	N	N	Not applicable	LIT	N
KCA 7.5	Gasser A.	1998	Mobility and dissipation of residues of dimethenamid under field conditions followoing application of frontier to corn in switzerland, 1994-1997 Novartis Agro c/o Clariant Huningue S.A., Huningue Cedex BASF RegDoc.# 98/10384 GLP, unpublished	N	N	Not applicable	BASF	Y relevant IIA. 7.4 [7.4/01]
KCA 7.5/1	Laabs V.	2010	Surface water screening for Dicamba, Dimethenamide-P, Bentazone, Tritosulfuron, Topramezone and selected metabolites in three corn growing regions of the EU 2010/1148003 BASF SE, Limburgerhof, Germany Fed.Rep. Not GLP, unpublished	N	Y	New data for AIR3 renewal	BASF	N IIA. 7.4
KCA 7.5/2	Schmidt B. et al.	2010	Groundwater monitoring for Topramezone (BAS 670 H) in four representative regions in Germany 2010/1069470 SGS Institut Fresenius GmbH, Taunusstein, Germany Fed. Rep. GLP, unpublished	N	Y	New data for AIR3 renewal	BASF	N IIA. 7.4
KCA 7.5/3	Schmidt B., Schulz H.	2012	Groundwater monitoring for Topramezone (BAS 670 H) in four representative regions in Germany (study period 2010 to 2012) 2012/1159571 SGS Institut Fresenius GmbH, Taunusstein, Germany Fed. Rep. GLP, unpublished	N	Y	New data for AIR3 renewal	BASF	N IIA. 7.4
KCA 7.5/4	Schmidt B., Schneider M.	2013	Groundwater sampling in four representative regions in Germany (study period 2012 – 2013) 2013/1338065 SGS Institut Fresenius GmbH, Taunusstein, Germany Fed. Rep. GLP, unpublished	N	Y	New data for AIR3 renewal	BASF	N IIA. 7.4
KCA 7.5/7	Mewis A.	2014	Determination of residues of metabolites of BAS 656 PH in groundwater (monitoring Netherlands) 2013/1352173 Eurofins Agroscience Services EcoChem GmbH, Niefern-Oeschelbronn, Germany Fed.Rep. GLP, unpublished	N	Y	New data for AIR3 renewal	BASF	N IIA. 7.4

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KCA 7.5/8	Haering T., Miles B.	2014	Evaluation of groundwater monitoring sites and context setting of groundwater monitoring data for metabolites of dimethenamid-P 2013/1347948 BASF SE, Limburgerhof, Germany Fed.Rep. Not GLP, unpublished	N	Y	New data for AIR3 renewal	BASF	N IIA. 7.4
KCA 7.5/9	Chevre N. et al.	2007	Risk assessment of herbicide mixtures in a large European lake 2013/1348573 Source: Environmental Toxicology DOI 10.1002/tox Not GLP, published	N	N	Not applicable	LIT	N IIA. 7.4
KCA 7.5/10	Leu C. et al.	2004	Simultaneous assessment of sources, processes, and factors influencing herbicide losses to surface waters in a small agricultural catchment 2013/1348574 Source: Environmental Science & Technology Vol. 38, No. 14, 2004 Not GLP, published	N	N	Not applicable	LIT	N IIA. 7.4
KCA 7.5/11	Hamer K., Freudenberger U.	2011	Pflanzenschutzrechtlich nicht relevante Metaboliten im Grundwasser 2013/1348575 Source: Wasser und Abfall, 13(9), 42-45, 2011 Not GLP, published	N	N	Not applicable	LIT	N IIA. 7.4