

**Section A7.1.2.2.2 Water/sediment degradation study (01)****Annex Point IIIA XII2.1**

		<b>1 REFERENCE</b>
<b>1.1 Reference</b>		Scholz, K. (1987): Degradation of Dichlofluanid in Water-Sediment Systems. Bayer AG, Crop Protection Development, Institute for Metabolism Research, PF Report No. 2800, date: 1987-06-02.  Hardy, IAJ and Patel, M (2005): Dichlofluanid: Kinetic Modelling Analysis of Data from Two Water Sediment Studies. Battelle UK Ltd., Report-No. CX/05/058, date: 2005-10-14.
<b>1.2 Data protection</b>		Yes
1.2.1	Data owner	Bayer Crop Science AG (Scholz 1987) / LANXESS Deutschland GmbH (Hardy 2005)
1.2.2	Companies with letter of access	LANXESS Deutschland GmbH
1.2.3	Criteria for data protection	Data submitted to the MS after 13 May 2000 on existing a.s. for the purpose of its entry into Annex I/IA
		<b>2 GUIDELINES AND QUALITY ASSURANCE</b>
<b>2.1 Guideline study</b>		No, no guidelines available, methods developed in co-operation with the Dutch authorities, comparable to (later) EPA guidelines
<b>2.2 GLP</b>		No, GLP was not compulsory at the time the study was performed
<b>2.3 Deviations</b>		No
		<b>3 MATERIALS AND METHODS</b>
<b>3.1 Test material</b>		a) [Phenyl-UL- <sup>14</sup> C] dichlofluanid b) non-active standard substance (dichlofluanid)
3.1.1	Lot/Batch number	No lot or batch no. mentioned
3.1.2	Specification	a) specific radioactivity was 1246.9 kBq/mg, sample provided from Bayer AG, Isotope Laboratory, Dr. Marsmann, Elberfeld, Germany. b) see purity, sample provided by Dr. Krohn (Elberfeld)
3.1.3	Purity	a) [redacted] radiochemical purity b) [redacted] purity
3.1.4	Further relevant properties	No problems related to abiotic stability or volatility are expected from the data available
3.1.5	Composition of Product	-
3.1.6	TS inhibitory to micro-organisms	Not to be expected because of the favourable results of the respiration inhibition tests in soil and sewage sludge
3.1.7	Specific chemical analysis	Radio thin layer and HPLC analysis (reversed phase)
<b>3.2 Reference substance</b>		No
3.2.1	Initial concentration	-

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	of reference substance	
<b>3.3</b>	<b>Testing procedure</b>	
3.3.1	Inoculum / test species	Two different aquatic micro ecosystems (500 ml volume) containing a sediment portion. The water/sediment samples were taken from a fish pond (Lienden, NL) and from a drainage ditch in a fruit orchard (Ijzendoorn, NL). The characterisation of the sediments is shown in table A7_1_2_2_2-1.
3.3.2	Test system	see table A7_1_2_2_2-2
3.3.3	Test conditions	see table A7_1_2_2_2-2
3.3.4	Method of preparation of test solution	Solution I: The radioactive compound (5.93 mg a.i.) was dissolved in 600 µl methanol and the radioactivity measured by liquid scintillation (= 7,394 kBq). Solution II: 19.07 mg of unlabelled a.i. were dissolved in 1400 µl methanol. Solution III = Solution I + solution II = 2000 µl  Experiment I: 100 µl of solution III was pipetted into each vessel, whereas in experiment II an aqueous suspension of the a.i. was introduced into the vessels. Experiments 2 and 3 served as controls (exp. 2: influence of solvent; exp. 3: blank control, influence of a.i.).
3.3.5	Initial TS concentration	The amount of dichlofluanid applied to the water sediment systems was 2.50 mg/l, which is related to the maximum application rate in agriculture (assumption: dosage is dissolved in a 10 cm deep water area). This quantity was in the region of the water solubility of the a.i.
3.3.6	Duration of test	up to 120 days
3.3.7	Analytical parameter (methods)	Radioactivity measurement of volatile compounds: a) sorption on oil coated quartz wool plugs, extraction with ethyl acetate, which was measured by liquid scintillation. b) sorption on sodium carbonate and release of CO <sub>2</sub> (after acidification) in a scintillation cocktail. Radioactivity measurement of solid samples (e.g. sediment): pre-treatment by e.g. drying and milling, than combustion and analysing radiolabelled CO <sub>2</sub>  The TLC separations were performed on silica gel F254 TLC plates with different solvent systems.  Methods for visualize the substance spots: 1. extinction of UV-induced fluorescence of the TLC plates; 2. Linear analyser with evaluation unit; 3. autoradiography with x-ray film
3.3.8	Sampling	a) Experiment I: processing dates for the incubation vessels were 7, 14, 30, 60 and 120 days after addition of a.i.  b) Experiment II and III: the two vessels were worked up at the end of the experiment (120 d)
3.3.9	Intermediates/ degradation products	Spectroscopic analysis of the test substance, DMSA and KUE 8630 B: GC-MS (HP 5970 GC 5880 A (DMSA) or HP 1084 B (KUE 8630 B))
3.3.10	Nitrate/nitrite	n.a.

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	measurement		
3.3.11	Controls	Experiments 2 and 3 served as controls (exp. 2: influence of solvent; exp. 3: influence of a.i.).	
3.3.12	Statistics	<p>In the original report of Scholz (1987) the DT<sub>50</sub> values were not derived.</p> <p>Therefore, the kinetic of the aerobic water/sediment systems with the metabolite of dichlofluanid, DMSA, was evaluated in 2005, based on the results obtained by Scholz in 1987. The water/sediment residue data were entered into the computer program ModelMaker 4.0 for optimisation of the degradation rate constant (Kp) and initial soil residue (M<sub>0</sub>).</p> <p>From the study report (Scholz, 1987), insufficient degradation data for the parent dichlofluanid meant it was not possible to model the partitioning between the water and sediment phases, therefore dissipation rates for each phase for the metabolite DMSA, were calculated as well as a conservative approach.</p> <p>A simple first order, non-linear regression model was used to describe the behaviour of DMSA in the aqueous, sediment phase and overall total system. Table A7_1_2_2_2-5 shows the calculated DT<sub>50</sub>'s for DMSA.</p>	X
		<b>4 RESULTS</b>	
<b>4.1</b>	<b>Degradation of test substance</b>		
4.1.1	Graph	Degradation curves are provided in both reports (initial report and evaluation report)	
4.1.2	Degradation	See tables A7_1_2_2_2-3, A7_1_2_2_2-4 and A7_1_2_2_2-5	X
4.1.3	Other observations	-	
4.1.4	Degradation of TS in abiotic control	Not relevant, because no hydrolytic degradation can be expected from the data, light induced degradation was excluded by running the experiment in the dark.	
4.1.5	Degradation of reference substance	n.a.	
4.1.6	Intermediates/degradation products	Main metabolite: DMSA (dimethylaminosulfanilide); no further metabolite exceeded the 10% mark, second metabolite: KUE 8630 B (methylaminosulfanilide) max. 6.9%	
		<b>5 APPLICANT'S SUMMARY AND CONCLUSION</b>	
<b>5.1</b>	<b>Materials and methods</b>	The degradation and metabolism behaviour of [phenyl-UL- <sup>14</sup> C]dichlofluanid in an aquatic micro ecosystem containing a sediment portion was investigated in two different water/sediment systems. The water/sediment samples were taken from a fish pond (Lienden, NL) and from a drainage ditch in a fruit orchard (Ijzendoorn, NL). A test system was used which was developed with the Dutch authorities. Material balances were performed using by radioactivity measurements of all test components.	
<b>5.2</b>	<b>Results and</b>	Dichlofluanid was so rapidly degraded to the metabolite	

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<b>discussion</b>	<p>dimethylaminosulfanilide (DMSA) by the water-sediment systems that already after 7 days the active ingredient was no longer detectable. Besides DMSA another metabolite, methylaminosulfanilide (KUE 8630 B), occurred at levels of up to 6.9%. After 120 days 3.3% (Ijzendoorn) and 5.1% (Lienden) of the applied radioactivity was detectable as [14C]CO<sub>2</sub>. 69.2% (Ijzendoorn) and 63.5% (Lienden), respectively, of the applied radioactivity was in the water while 25.8% (Ijzendoorn) and 23.9% (Lienden), respectively, had moved to the sediment during the incubation time of 120 days. 17.6% (Ijzendoorn) and 18.7% (Lienden), respectively, could not be extracted from the sediment using the described extraction procedure.</p> <p>In a report for kinetic modelling analysis of data, an excellent model fit to the data was obtained, with a high <math>r^2</math> value, low Min <math>x^2</math> errors, highly significant parameter estimations, and the residual plot showing random scatter of data.</p> <p>The calculated DT<sub>50</sub> values for DMSA with ModelMaker, expressed as the geometric mean, were: 189 days, 174.9 days and 187.9 days in the aqueous phase, sediment and total system, respectively.</p>	X
<b>5.3 Conclusion</b>	<p>The results in this test show that dichlofluanid was very rapidly degraded in aerobic aquatic systems to DMSA (dimethylaminosulfanilide). There was no further metabolite approaching or exceeding the 10% mark within the incubation time. Dichlofluanid does not constitute a lasting potential to contaminate surface water or sediment.</p> <p>The study is well documented and reported. A complete material balance was performed at all samplings by radioactive analysis.</p>	X
5.3.1 Reliability	Reliability indicator: 2	
5.3.2 Deficiencies	<p>Yes,</p> <p>No lot or batch no. of test compound mentioned</p>	

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<b>Evaluation by Competent Authorities</b>																																
Use separate "evaluation boxes" to provide transparency as to the comments and views submitted																																
<b>EVALUATION BY RAPPORTEUR MEMBER STATE</b>																																
<b>Date</b>	09/12/2013																															
<b>Materials and Methods</b>	<p>The water/ sediment study itself was evaluated as part of the submission for dichlofluanid PT8 (wood preservative). Here only the kinetic treatment of the data was evaluated by the UK CA.</p> <p>3.3.12: The evaluator accepted that dichlofluanid was reported as &lt; 0.1 %AR in all samples therefore it would be hard to disagree with the statement that there was insufficient data to model the partitioning between the water and sediment phases. The approach to calculation of dissipation rates for DMSA in the water, sediment, and whole system using SFO kinetics was accepted. The applicant has assumed the instantaneous formation of DMSA in the system which leads to conservative DT<sub>50</sub> values.</p>																															
<b>Results and discussion</b>	<p>4.1.2: No evaluation has been made of the data in Tables A7_1_2_2_2-1 to A7_1_2_2_2-4.</p> <p>DT<sub>50</sub> values presented in Table A7_1_2_2_2-5 were accepted by the evaluator.</p>																															
<b>Conclusion</b>	<p>5.2: The modelling was checked independently by the evaluator using Modelmaker version 4 and within an EXCEL spreadsheet. The <math>\chi^2</math> values were less than 15% and the visual fitting was good in all cases after fitting with SFO kinetics. DT<sub>50</sub> values were the same or very similar to the applicant (evaluator values summarised below) and so the values presented by the applicant in Table A7_1_2_2_2-5 were accepted.</p>																															
	<table border="1"> <thead> <tr> <th>Test system</th> <th>Parameter</th> <th>Aqueous phase</th> <th>Sediment phase</th> <th>System</th> </tr> </thead> <tbody> <tr> <td rowspan="3">Ijzendoorn</td> <td>DT<sub>50</sub></td> <td>229.5</td> <td>261.6</td> <td>233.1</td> </tr> <tr> <td><math>\chi^2</math> error level (%)</td> <td>1.4</td> <td>6.7</td> <td>1.1</td> </tr> <tr> <td>Visual fitting</td> <td>good</td> <td>good</td> <td>good</td> </tr> <tr> <td rowspan="3">Lienden</td> <td>DT<sub>50</sub></td> <td>155.6</td> <td>116.9</td> <td>151.4</td> </tr> <tr> <td><math>\chi^2</math> error level (%)</td> <td>2.2</td> <td>3.9</td> <td>2.0</td> </tr> <tr> <td>Visual fitting</td> <td>good</td> <td>good</td> <td>good</td> </tr> </tbody> </table>	Test system	Parameter	Aqueous phase	Sediment phase	System	Ijzendoorn	DT <sub>50</sub>	229.5	261.6	233.1	$\chi^2$ error level (%)	1.4	6.7	1.1	Visual fitting	good	good	good	Lienden	DT <sub>50</sub>	155.6	116.9	151.4	$\chi^2$ error level (%)	2.2	3.9	2.0	Visual fitting	good	good	good
Test system	Parameter	Aqueous phase	Sediment phase	System																												
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<b>Reliability</b>	1																															
<b>Acceptability</b>	Acceptable (only kinetic treatment of the data was evaluated)																															
<b>Remarks</b>	No other comments																															

	<b>COMMENTS FROM ...</b>
<b>Date</b>	<i>Give date of comments submitted</i>
<b>Materials and Methods</b>	<i>Discuss additional relevant discrepancies referring to the (sub)heading numbers and to applicant's summary and conclusion. Discuss if deviating from view of rapporteur member state</i>
<b>Results and discussion</b>	<i>Discuss if deviating from view of rapporteur member state</i>
<b>Conclusion</b>	<i>Discuss if deviating from view of rapporteur member state</i>
<b>Reliability</b>	<i>Discuss if deviating from view of rapporteur member state</i>
<b>Acceptability</b>	<i>Discuss if deviating from view of rapporteur member state</i>
<b>Remarks</b>	

**Table A7\_1\_2\_2\_2-1: Properties of the Natural Water Sediment Systems**

System	Particle Size Distribution			N(total) [g/100 g]	P(total) [g/100 g]	C org. [%]	pH	CaCO <sub>3</sub> [%]
	16-2000 µm [%]	16 µm [%]	2 µm [%]					
IJzendoorn	50	43	25	0.32	0.23	4.6	8.4	2.6
Lienden	88	9	5	0.02	0.05	0.5	8.5	2.5

**Table A7\_1\_2\_2\_2-2: Test system and Test conditions**

Criteria	Details
Culturing apparatus	Glass vessels containing 500 ml water and 10% (w/w) sediment (portions corresponding to 50 g dry weight), a system to adsorb CO <sub>2</sub> and other volatile substances.
Number of culture flasks/concentration	8 flasks for each of the two water sediment system, 1 flask served as control for the influence of solvent, 1 flask was blank system (control for influence of a.i.)
Aeration device	Not applied
Measuring equipment	Measurements of pH, oxygen content, redox potential and temperature of the water were performed from each sampling vessel and in addition from the two control vessels.
Composition of medium	see table A7_1_2_2_2-1
Additional substrate	No
Pre-incubation of the test systems	yes, 14 days
Test temperature	22 ± 1 °C
pH	Ijzendoorn: 7.8-8.2 (blank (8.0-8.5)), Lienden: 8.1-8.4 (blank 7.9-8.8)
Oxygen content (in % of maximum oxygen content: at 22°C: 8.73 mg O <sub>2</sub> /l)	Ijzendoorn: 87-93 (blank (91-98)), Lienden: 86-93 (blank 93-99)
TOC content at the beginning of the study	Ijzendoorn: 3 mg/l, Lienden: 13 mg/l
Aeration of dilution water	No
Suspended solids concentration	not determined
Other relevant criteria	a) the test was conducted in the dark, b) the water phase was slowly stirred by a magnetic stirrer to maintain oxygen uptake

**Table A7\_1\_2\_2\_2-3: Distribution of radioactivity [% of applied] in two water/sediment systems after application of 2.50 mg/l [phenyl-UL-<sup>14</sup>C]dichlofluanid**

	Ijzendoorn					Lienden				
	days incubation					days incubation				
	7	14	30	60	120	7	14	30	60	120
<b>supernatant water</b>	<b>87.1</b>	<b>87.4</b>	<b>81.8</b>	<b>75.8</b>	<b>69.2</b>	<b>87.6</b>	<b>84.5</b>	<b>82.3</b>	<b>73.3</b>	<b>63.5</b>
sediment extractable	10.9	11.3	12.0	10.9	8.2	9.0	8.1	7.9	6.6	4.9
sediment non extractable	1.7	2.0	5.8	8.3	17.6	2.1	3.2	5.8	9.7	19.0
<b>sediment</b>	<b>12.6</b>	<b>13.3</b>	<b>17.8</b>	<b>19.2</b>	<b>25.8</b>	<b>11.1</b>	<b>11.3</b>	<b>13.7</b>	<b>16.3</b>	<b>23.9</b>

**Table A7\_1\_2\_2\_2-4: Distribution of dichlofluanid and metabolites [% of applied radioactivity] in two water/sediment systems after application of 2.50 mg/l [phenyl-UL-<sup>14</sup>C]dichlofluanid**

		Ijzendoorn					Lienden				
		days incubation					days incubation				
		7	14	30	60	120	7	14	30	60	120
<b>water</b>	<b>total</b>	<b>87.1</b>	<b>87.4</b>	<b>81.8</b>	<b>75.8</b>	<b>69.2</b>	<b>87.6</b>	<b>84.5</b>	<b>82.3</b>	<b>73.3</b>	<b>63.5</b>
	Dichlofluanid	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1
	DMSA	87.1	87.4	81.8	73.2	63.2	87.6	84.5	82.3	66.5	53.6
	KUE 8630 B	< 0.1	< 0.1	< 0.1	2.6	4.1	< 0.1	< 0.1	< 0.1	3.7	6.5
	unidentified	< 0.1	< 0.1	< 0.1	< 0.1	1.9	< 0.1	< 0.1	< 0.1	3.1	3.4
<b>sediment</b>	<b>total</b>	<b>10.9</b>	<b>11.3</b>	<b>12.0</b>	<b>10.9</b>	<b>8.2</b>	<b>9.0</b>	<b>8.1</b>	<b>7.9</b>	<b>6.6</b>	<b>4.9</b>
	Dichlofluanid	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1
	DMSA	10.9	10.9	11.6	10.5	7.7	9.0	7.8	7.6	6.3	4.4
	KUE 8630 B	< 0.1	0.1	0.2	0.3	0.4	< 0.1	0.1	0.2	0.2	0.4
	unidentified	< 0.1	0.3	0.3	0.1	0.1	< 0.1	0.2	0.1	0.1	0.1



**Table A7\_1\_2\_2\_2-5: DT<sub>50</sub> values for DMSA, a metabolite of dichlofluanid, calculated with ModelMaker in 2005**

Compound	System	DT <sub>50</sub> (days)		
		Aqueous phase	Sediment phase	Total system
Dimethylamino sulfanilide	IJzendoorn	229.5	261.7	233.1
	Lienden	155.6	116.9	151.4
	<b>Geometric mean</b>	189.0	174.9	187.9