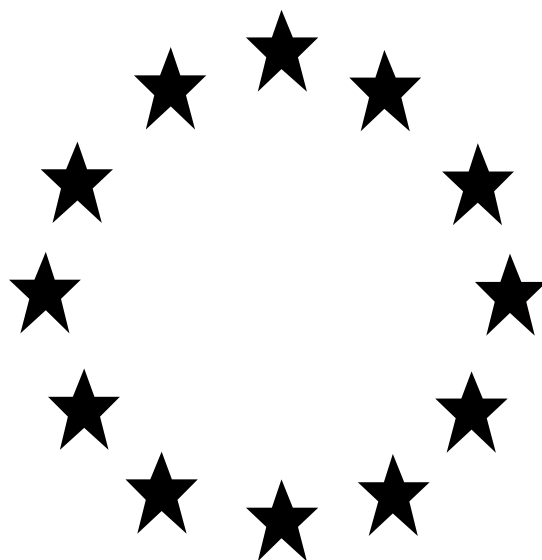




Draft Assessment Report (DAR)

- public version -

**Initial risk assessment provided by the rapporteur Member State
The Netherlands for the existing active substance**

DICHLOBENIL

**of the third stage (part B) of the review programme
referred to in Article 8(2) of Council Directive 91/414/EEC**

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B.8 ENVIRONMENTAL FATE AND BEHAVIOUR

B.8.1 ROUTE AND RATE OF DEGRADATION IN SOIL

B.8.1.1 Aerobic and Anaerobic studies

B.8.1.1.1 Aerobic studies

B.8.1.1.1/01 Aerobic studies with dichlobenil (IIA, 7.1.1.1.1/01)

Characteristics of the study

Reference	: Walstra <i>et al.</i> (1989)	GLP statement	: yes
Type of study	: aerobic soil degradation study	Guideline	: EPA 162-1
Year of execution	: 1988-1989	DT ₅₀	: not applicable
Test substance	: [¹⁴ C]dichlobenil (2,6-dichlorobenzonitrile, uniformly labelled with ¹⁴ C in the phenyl group) batch: AOI87H05A appearance: unknown	DT ₉₀	: not applicable
Purity	: radiochemical: 100.1% chemical: 98.3 %	Metabolites	: 2,6-dichlorobenzamide (BAM)
Specific radioactivity	: 17.1 mCi/g (633 MBq/g)	Acceptable	: No

One agricultural soil was used for testing, specified as “sandy loam”; it was collected from a field at Udenhout (The Netherlands). The soil history is not specified and it could thus not be verified whether there was any treatment with pesticides in the previous five years. The characterisation of the soil is given in Table B.8.1.1.1/01a.

Table B.8.1.1.1/01a Characterisation of the soil studied

Organic matter content (%)	1.5
Organic carbon content (%) ¹	0.9
Maximum water holding capacity	unspecified
Water content (%) at 0.33 bar	12.3
pH (KCl)	5.3
Soil classification ²	Sandy loam
Clay (%); < 0.002 mm	4.8
Silt (%); 0.002-0.05 mm	20.2
Sand (%); > 0.05 mm	75.0
Cation Exchange Capacity	5.3 meq/ 100 g dry soil

¹ Calculated by RMS by dividing the organic matter content by a factor 1.7

² USDA classification

The soil was sieved (2 mm) in a semi-dry state. After restoring the moisture content to 7%, approximately 40 g dry weight soil was transferred to each test container (biometer flasks), followed by an acclimatisation period of 15 days at 24°C under dark conditions.

A treatment solution was prepared by dissolving approximately 3 mg of [^{14}C]dichlobenil in 35 ml ethanol/water 2:5 (v/v). The concentration of the treatment solution was determined by HPLC and LSC analysis of five 1:50 dilutions in methanol. After acclimatisation of the soil, one ml aliquots of the treatment solution were applied to the soil surface in every biometer flask. The application rate was 2.1 mg/kg dw soil. Subsequently, the soil moisture content was adjusted to 75% of the water content at 0.33 bar. After the addition of 25 ml of a 0.3 M KOH solution to the absorption tubes, 21 flasks were placed in an incubation room, in the dark at 24°C. The six remaining flasks were used for sampling at $t = 0$.

At 0 h (three flasks were sampled before test substance application and three flasks were sampled after test substance application) and 2, 5, 10, 20, 30, 40, and 50 weeks after dosing, soil from each of three replicate flasks, was extracted four times with methanol. The first two times by milling at room temperature for 10 minutes and the second two times by refluxing for 30 minutes. The resulting methanol extract was centrifuged, after which the supernatant was decanted. Subsequently, pooled extracts (of each replicate flask) were analysed by LSC and HPLC. The radioactivity of the soil residue was determined by combustion LSC.

At each sampling time, the KOH solution was diluted and the radioactivity was determined by LSC. With a vapour pressure of 0.135 Pa at 25°C, a considerable part of [^{14}C]dichlobenil evaporates. In the trapping solution, [^{14}C]dichlobenil reacts with KOH to [^{14}C]-2,6-dichlorobenzamide ([^{14}C]-BAM). Therefore, the radioactivity in the KOH solution was not only represented by $^{14}\text{CO}_2$, but also by [^{14}C]-BAM. To distinguish, 25 ml of the KOH solution was extracted three times with 25 ml dichloromethane. The radioactivity of the extracted water layer as well as the pooled dichloromethane extracts was counted by LSC and some pooled dichloromethane extracts were analysed by HPLC.

[^{14}C]Dichlobenil and [^{14}C]-BAM were identified by spiking the aliquots that were taken from the extracts for analysis with unlabeled dichlobenil and BAM, which was detected by UV. Each BAM peak that was detected by UV-absorption at 214 nm, was trapped in a scintillation vial. The amount of radioactivity in these vials was measured by LSC.

Results

In Table B.8.1.1.1/01b the recovery of radioactivity is given, together with the results of the analysis of the extracts of the soil and the KOH solution.

Table B.8.1.1.1/01b Recovery of radioactivity and proportion of radioactive components in the extracts (expressed as % applied radioactivity (a.r.))

Time (week s)	Trapped volatiles			Extractable				Soil Residue	Total recovery
	total ¹⁴ C	¹⁴ CO ₂	[¹⁴ C]dichlobenil ¹	total ¹⁴ C	[¹⁴ C]dichlobenil	[¹⁴ C]-BAM	Other metabolites		
0	n.d.	n.d.	n.d.	101	101	<0.1	<0.1	<0.2	101
2	14.8	0.1	13.3	80.7	80.3	0.4	<0.1	22	97.8
5	19.0	0.7	18.0	74.2	71.7	0.8	0.5	5.1	98.2
10	39.2	0.7	37.2	52.9	49.8	1.3	<0.1	5.8	97.8
20	46.0	1.9	41.9	44.4	35.6	7.3	1.2	8.2	98.5
30	63.9	1.5	61.0	26.8	20.6	5.2	<0.6	8.2	98.9
40	62.3	2.7	58.5	26.1	16.2	8.4	0.5	8.0	96.4
50	61.0	2.3	56.8	26.7	11.6	13.1	0.7	10.2	97.9

n.d. = not determined

¹ converted to [¹⁴C]-BAM by the reaction with KOH.

At the last sampling day, the mean portion of ¹⁴CO₂ recovered from the replicate KOH solutions was 2.3% applied radioactivity a.r. and the portion of not-extracted radioactivity from the replicate samples was 10.2% a.r. By spiking extracts with unlabeled reference standards and detection with UV, the identity of the parent was confirmed and the metabolite BAM was identified. The highest percentage of BAM formed was 13.1% a.r. (at the end of the study).

Based on the concentrations in the soil extracts, a simple first order DT₅₀ of 91 days (13.0 weeks) was calculated for dichlobenil by the authors ($r^2 = 0.98$). Because this includes evaporation, it was decided to calculate the percentage of dichlobenil that was metabolised at each sampling time (% metabolism_t) with the below equation and determine a transformation DT₅₀ based on that data.

$$\% \text{ metabolism}_t = \frac{(CO_2)_t + (MET)_t}{(DBN_{av})_{0-t}} * 100\%$$

in which:

(CO₂)_t = amount of ¹⁴CO₂ (produced per flask) until sampling time t.(MET)_t = amount of metabolites including BAM present in a soil extract (of one flask) at sampling time t.(DBN_{av})_{0-t} = average amount (weighed mean) of dichlobenil present in a flask over the time period 0 – t weeks

In Table B.8.1.1.1/01c an overview is given of these parameters.

Table B.8.1.1.1/01c Percentage of metabolism and quantities of CO₂, metabolites and dichlobenil found in various fractions from sandy loam treated with [¹⁴C]dichlobenil (84.6 µg), expressed as µg [¹⁴C]dichlobenil equivalents (DBN)¹

time (weeks)	(CO ₂) _t	(MET) _t	DBN	(DBN _{av}) _{t1-t2} ²	(DBN _{av}) _{0-t}	% metabolism _t
0	0	0	85.7	85.7	85.7	0
2	0.1	0.4	67.9	76.8	76.8	0.7
5	0.6	1.1	60.7	64.3	69.3	2.5
10	0.6	1.1	42.2	51.5	60.4	2.8
20	1.6	6.5	30.1	36.2	48.3	16.8
30	1.2	4.7	17.5	23.8	40.1	14.7
40	2.3	7.5	13.7	15.6	34.0	28.8
50	2.0	11.7	9.8	11.8	29.6	46.3

¹ DBN = average amount of dichlobenil in soil extracts (of one flask)

² (DBN_{av})_{t1-t2} = average amount of dichlobenil in soil during the period between two sampling times

A simple first order transformation DT₅₀ of 324 days (= 46.3 weeks) ($r^2 = 0.87$) was calculated by the authors based on % metabolism_t. Using the Arrhenius equation, RMS converted this to 446 days at 20°C.

In another study (B.8.1.1.1/02, Lynn *et al.*, 2003), the dichlobenil concentrations are normalised according to the following equation:

$$\% \text{ DBN normalised} = \frac{\% \text{ DBN}}{T - P} \times 100\%$$

in which:

% DBN normalised = % dichlobenil, normalised for evaporation

%DBN = % dichlobenil in soil extracts

T = Percentage of total radioactivity recovered

P = Percentage of dichlobenil in polyurethane trap; in the present study this is the percentage of dichlobenil that was trapped in the KOH solution (it is assumed that this was converted to BAM by the reaction with KOH, see above.)

RMS prefers to calculate the DT₅₀ based on decay of the parent, rather than formation of metabolites.

Normalised percentages of dichlobenil, calculated by RMS, are given in Table B.8.1.1.1/01d.

Table B.8.1.1.1/01d Normalised percentages of dichlobenil, calculated by RMS.

time (weeks)	% normalised dichlobenil
0	101.0
2	95.0
5	89.4
10	82.2
20	62.9
30	54.4
40	42.7
50	28.2

Using the normalised percentages of dichlobenil and the Arrhenius equation (to convert to 20°C), RMS calculated a simple first order DT₅₀ of 296 days and an extrapolated DT₉₀ of 983 days ($r^2 = 0.99$)

Remarks

- It is not clear to RMS why evaporated dichlobenil was not trapped in a special volatile trap. The authors assume that BAM that is recovered from the KOH solution is originating from a reaction of trapped dichlobenil with KOH. There is however a theoretical possibility that (a small part of) the BAM in the KOH solution is not originating from dichlobenil, but evaporated from the soil, although BAM is not very volatile. The assumption of the authors is a worst-case assumption because it could lead to an underestimation of the degradation rate.
- To correct for evaporation, the transformation DT₅₀ was based on the formation of CO₂ and metabolites, rather than decay of the parent compound. RMS prefers to calculate a DT₅₀ based on decay of the parent compound, rather than the formation of metabolites and calculated normalised concentrations dichlobenil, in a similar manner as in study B.8.1.1.1/02 (Lynn *et al.*, 2003) for the present study.
- With concentrations exceeding 10% a.r., 2,6-dichlorobenzamide (BAM) is regarded as a major metabolite. No DT₅₀ could be calculated for BAM as the concentrations were still increasing at the end of this study. A separate study with BAM is part of the dossier.

Acceptability of the test

RMS calculated a DT₅₀ that is based on decay of the parent, rather than on formation of metabolites. The method used in the study deviates from the standard procedure for this type of studies. No separate traps were used for evaporated dichlobenil and metabolites. It is therefore not clear if the BAM found in the KOH solution was formed in soil before evaporation or originated from a reaction of dichlobenil and KOH in the trap. For this reason, the study is not considered acceptable. Also, the calculated DT₅₀ value was outside the range of DT₅₀ values obtained in the other experiments (see B.8.1.1.1/02), which supports the conclusion of RMS that the results of the study are unreliable.

Conclusion

The study is not considered acceptable.

B.8.1.1.1/02 Aerobic studies with dichlobenil (IIA, 7.1.1.2.1/01)**Characteristics of the study**

reference	: Lynn <i>et al.</i> (2003)	GLP statement	: yes
type of study	: aerobic soil degradation study	guideline	: SETAC (1995)
year of execution	: 2002-2003	metabolite	: 2,6-dichlorobenzamide (BAM)
test substance	: [¹⁴ C]dichlobenil (uniformly labelled with ¹⁴ C in the phenyl group) batch: CFQ11075 appearance: unknown non-radiolabelled dichlobenil batch: ARS-9108-BA appearance: unknown	DT ₅₀	: clay loam: 38.9 d, $r^2 = 0.968$ silt loam: 39.0 d, $r^2 = 0.975$ loamy sand: 43.6 d, $r^2 = 0.821$
purity	: [¹⁴ C]dichlobenil: radiochemical: 100.0% chemical: 99.7 % non-radiolabelled dichlobenil: 100%	DT ₉₀	: clay loam: 129 d, $r^2 = 0.968$ silt loam: 130 d, $r^2 = 0.975$ loamy sand: 145 d, $r^2 = 0.821$
specific radioactivity	: 0.305 mCi/g	acceptable	: The study is considered acceptable in combination with study B.8.1.1.1/03

Three agricultural soils were used for testing, classified as “clay loam”, “silt loam” and “loamy sand”. The clay loam were freshly collected from Land Research Associates (Derby, UK) and the other soils were freshly collected from LandLook (Leamington, Spa, Midlands, UK). None of the soils had been treated with pesticides in the previous five years. The characterisation of the soils is given in Table B.8.1.1.1/02a.

Table B.8.1.1.1/02a Characterisation of the soils studied

Soil	Clay loam ¹	Silt Loam ¹	Loamy sand ¹
Organic carbon content (%)	3.9	3.6	1.1
Maximum water holding capacity	not specified	not specified	not specified
pH in 1M KCl	7.6	6.1	5.9
Dry matter content of air-dried soil (% m/m)	95.8	95.7	99.1
Water content of air dried soil (% m/m)	4.4	4.5	0.9
Clay (%); < 0.002 mm	31.84	22.52	9.13
Silt (%); 0.002-0.05 mm	31.61	64.62	6.88
Sand (%); > 0.05 mm	36.54	12.86	83.99
Cation Exchange Capacity (meq/100g)	35.5	29.5	10.5
Microbial biomass at the start (mg microbial C/kg dw)	894	460	246
Microbial biomass at the end (mg microbial C/kg dw)	625	238	172

¹ USDA classification

Samples of each soil type (50 g dw) were weighed into 250 mL Erlenmeyer flasks. The samples were adjusted to approximately 45% maximum water holding capacity (MWHC). However, this could not be verified by RMS, because the MWHC is not specified in the report. The soil samples were pre-incubated for 9 days under aerobic conditions in the dark at 20 ± 2°C.

A treatment solution was prepared by dissolving 3.48 mL of a stock solution with an unspecified concentration of [¹⁴C]dichlobenil to a 5 mL volumetric flask containing 18.81 mg of non-labelled

dichlobenil. The flask was made up to volume with acetonitrile. The homogeneity of the treatment solution was verified by LSC analysis of dilutions of three aliquots in acetonitrile. The dosing was verified by the LSC analysis of an acetonitrile solution to which a volume of test solution was dispensed, that was equivalent to the volume that was added to the soil samples. After pre-incubation of the soil and re-adjustment of the soil moisture content to approximately 45% MWHC, 100 μ L aliquots of the treatment solution were applied to the soil surface in every Erlenmeyer flask. The application rate was approximately 8.1 mg/kg dw soil. After application, each Erlenmeyer flask was connected to a flow through system which could be supplied with moist, CO₂ free air. Because of the volatility of dichlobenil, the system was aerated twice weekly at approximately 20-25 mL/min for a period of 15 minutes. The air leaving the system was led through two traps. The first trap was a safety trap to prevent back flow and the second trap contained NaOH solution. The system was further equipped with two polyurethane plugs for trapping volatile radioactive compounds. One was placed in the top of the Erlenmeyer flask and the other one was placed in the top of the safety trap. The incubation units were incubated for 273 days under aerobic conditions in the dark at $20 \pm 2^\circ\text{C}$.

At each sampling interval (0, 14, 28, 56, 84, 112, 182 and 273 days after dosing), an incubation flask of each soil type was removed and extracted three times with methanol. The first two times by shaking at room temperature for 1 hour (soil extracts 1 and 2) and the third time by refluxing (soxhlet method) for approximately 6 hours (soil extract 3). Extracts were analysed by LSC and HPLC. The radioactivity of the soil residue was determined by combustion LSC. The organic matter in selected extracted residues (day 112 clay loam and day 273 silt loam) was fractionated to a humin, humic acid and fulvic acid fraction according to procedures described by Kaufmann *et al* (1976)¹. This procedure was not applied to loamy sand, as non-extractable residues in this soil did not exceed 10% a.r.

The volatile traps and polyurethane plugs were sampled and replenished at weekly intervals during the first four weeks and then at 4 week intervals for the remaining test period. For each sample, the polyurethane plugs were combined and extracted with methanol. Aliquots of the polyurethane extracts and the NaOH trapping solutions were analysed by LSC.

Pooled and concentrated soil extracts were analysed by HPLC. Of each soil type, an aliquot of each individual sample from day 0 to day 112 and from day 140 to day 273 was combined, concentrated and analysed by HPLC. The identities of dichlobenil and metabolites from soil and polyurethane extracts were

¹ Kaufmann, Still, Paulson and Bandel (1976), Bound and conjugated residues, ACS Symposium 29, 379-

confirmed by TLC analysis of selected samples (day 0, 84 and 273). Reference standards of non-radiolabelled dichlobenil, 2,6-dichlorobenzoic acid and 2,6-dichlorobenzamide were chromatographed.

To correct for volatilisation, dichlobenil concentrations were normalised according to the following equation:

$$\% \text{ DBN normalised} = \frac{\% \text{ DBN}}{\text{T} - \text{P}} \times 100\%$$

in which:

% DBN normalised = % dichlobenil, normalised for evaporation

%DBN = % dichlobenil in soil extracts

T = Percentage of total radioactivity recovered

P = Percentage of dichlobenil in polyurethane trap

Results

In Tables B.8.1.1.1/02b - B.8.1.1.1/02d the recovery of radioactivity is given, together with the results of the analysis of the extracts of the soils and the polyurethane plugs.

Table B.8.1.1.1/02b Recovery of radioactivity and proportion of radioactive components in the extracts (expressed as % a.r.) of the clay loam soil

Time (d)	Soil Extract 1	Soil extract 2	Soil Extract 3	Total	DBN	BAM	DBN _{norm}	¹⁴ CO ₂	Volatiles	Non extractable	Apparatus wash	Total
0	68.19	23.48	8.13	99.80	99.80	n.d.	98.26	n.s.	n.s.	1.77	n.s.	101.57
14	54.32	21.60	15.30	91.22	67.17	24.05	68.81	0.34	6.33	6.02	0.04	103.95
28	46.20	20.53	14.93	81.66	45.86	35.80	49.68	0.53	10.82	10.12	0.00*	103.13
56	43.79	19.84	13.09	76.72	29.20	47.52	32.86	0.63	10.91	11.50	0.01*	99.77
84	44.93	17.89	14.43	77.25	19.91	57.34	22.18	0.68	12.55	11.84	0.00*	102.32
112	45.62	19.14	11.86	76.62	15.92	60.70	17.40	0.94	11.00	13.95	0.00*	102.51
182	40.42	17.87	15.38	73.67	10.20	63.47	11.62	1.20	13.51	12.90	0.01*	101.29
273	42.93	16.98	16.57	76.48	7.07	69.41	7.80	1.86	12.80	12.35	0.00	103.49

n.s. = no sample collected

n.d. = not detected

DBN = concentration dichlobenil

BAM = concentration 2,6-dichlorobenzoic acid

DBN_{norm} = concentration dichlobenil, normalised for volatilisation

*Result calculated from data less than 30 dpm above background radioactivity

Table B.8.1.1.1/02c Recovery of radioactivity and proportion of radioactive components in the extracts (expressed as % a.r.) of the silt loam soil

Time (d)	Soil Extract 1	Soil Extract 2	Soil Extract 3	Total	DBN	BAM	DBN _{norm}	¹⁴ CO ₂	Volatiles	Non extractable	Apparatus wash	Total
0	66.87	25.82	9.98	102.67	102.6	n.d.	97.99	n.s.	n.s.	2.11	n.s.	104.78
14	54.53	25.01	13.99	93.53	69.76	23.76	71.43	0.41	8.23	3.71	0.01	105.89
28	50.31	22.96	13.34	86.61	47.50	39.11	51.40	0.43	11.61	5.37	0.00	104.02
56	47.18	21.92	12.89	81.99	29.34	52.65	32.93	0.49	12.15	6.60	0.01	101.24
84	43.52	19.58	12.64	75.74	16.95	58.79	19.86	0.73	17.78	8.86	0.00	103.11
112	41.25	19.60	10.33	71.18	18.20	52.98	20.79	1.18	16.35	15.19	0.00*	103.90
182	37.56	18.69	14.09	70.34	7.80	62.54	8.98	1.81	16.47	14.70	0.02	103.34
273	36.65	8.33	11.88	56.86	5.13	51.73	6.68	2.55	17.87	17.35	0.00	94.63

n.s. = no sample collected

n.d. = not detected

DBN = concentration dichlobenil

BAM = concentration 2,6-dichlorobenzoic acid

DBN_{norm} = concentration dichlobenil, normalised for volatilisation

*Result calculated from data less than 30 dpm above background radioactivity

Table B.8.1.1.1/02d Recovery of radioactivity and proportion of radioactive components in the extracts (expressed as % a.r.) of the loamy sand soil

Time (d)	Soil extract 1	Soil Extract 2	Soil extract 3	Total	DBN	BAM	DBN _{norm}	¹⁴ CO ₂	Volatiles	Non extractable	Apparatus wash	Total
0	85.95	15.85	2.99	104.79	104.7	n.d.	99.54	n.s.	n.s.	0.48	n.s.	105.22
14	62.48	14.84	5.67	82.99	51.48	31.51	59.71	0.22	21.05	2.99	0.02*	107.22
28	54.70	12.55	5.35	72.60	26.86	45.74	35.00	0.29*	26.18	3.86	0.00*	102.93
56	44.98	11.02	4.79	60.79	20.63	40.16	31.41	0.40	35.94	4.48	0.00*	101.66
84	42.90	10.11	5.45	58.46	18.71	39.75	29.49	0.41	39.90	4.57	0.01*	103.33
112	36.81	9.42	4.12	50.35	13.50	36.85	24.35	0.43	46.46	4.66	0.02*	101.90
182	34.04	8.73	6.78	49.55	8.72	40.83	16.05	0.50	47.57	4.26	0.01*	101.88
273	32.13	16.65	5.08	53.86	6.40	47.46	10.58	0.91	50.20	5.69	0.01*	110.61

n.s. = no sample collected

n.d. = not detected

DBN = concentration dichlobenil

BAM = concentration 2,6-dichlorobenzoic acid

DBN_{norm} = concentration dichlobenil, normalised for volatilisation

*Result calculated from data less than 30 dpm above background radioactivity

At the last sampling day, the mean portion of ¹⁴CO₂ recovered from the replicate KOH solutions varied between 0.99 and 2.55% a.r. and the portion of non-extracted radioactivity from the replicate samples varied between 5.69 and 17.35% a.r. Radioactivity associated with the humin, fulvic acid and humic acid (following fractionating) accounted for up to 11.19, 1.32 and 0.20% a.r. respectively for the clay loam soil and 12.77, 1.55 and 1.68 respectively for the silt loam soil.

Using HPLC and TLC co-chromatography, the identity of the parent was confirmed and the metabolite BAM was identified. Dichlobenil was the only radioactive compound that was found in the polyurethane

plug. The highest percentage of BAM formed was 69.41% a.r. at the end of the study in the clay loam soil. Based on the normalised concentrations in the soil extracts, simple first order DT₅₀ and DT₉₀ values were calculated by RMS. These values are given in Table B.8.1.1.1/02e.

Table B.8.1.1.1/02e DT₅₀ values and DT₉₀ values for dichlobenil in three soils, calculated by RMS

Soil	clay loam	silt loam	loamy sand
DT ₅₀ (days)	38.9	39	43.6
DT ₉₀ (days)	129	130	145
r ²	0.968	0.975	0.821

Remarks

- With concentrations exceeding 10% a.r., 2,6-dichlorobenzamide (BAM) is regarded as a major metabolite. No DT₅₀ could be calculated for BAM as the concentrations were still increasing at the end of this study. A separate study with BAM is part of the dossier.
- The Maximum Water Holding Capacity of the soils was not specified in the report.

Acceptability of the test

The study is considered acceptable in combination with study B.8.1.1.1/03.

Conclusion

Dichlobenil degrades under aerobic conditions with calculated DT₅₀ values of 38.9 d, 39.0 d and 43.6 d in clay loam, silt loam and loamy sand soil, respectively. 2,6-dichlorobenzamide (BAM) was identified as a major metabolite.

B.8.1.1.1/03 Aerobic studies with the metabolite 2,6-dichlorobenzamide (IIA 7.1.1.2.1/02)

Characteristics of the study

Reference	: Griffen (2002)	GLP statement	: yes
Type of study	: aerobic soil degradation study	Guideline	: EPA 162-1
Year of execution	: 2000-2001		
Test substance	: [¹⁴ C]-BAM (2,6-dichlorobenzamide, labelled with ¹⁴ C in the phenyl group) batch: DUPH016 appearance: unknown	DT ₅₀ (extrapolated values)	: Bethany soil: SFO: 2666 d (r ² = 0.761) FOMC: 3.1·10 ¹⁰ d (r ² = 0.936) North Dakota soil: SFO: 795 d (r ² = 0.872) FOMC: 4.8·10 ⁴ d (r ² = 0.996)
Purity	: radiochemical: 96.74%	Metabolites	: none
Specific radioactivity	: 6.86 mCi/mmol	Acceptable	: yes

Study design

Two agricultural soils were used for testing, specified as Bethany soil and North Dakota soil. They were freshly collected from Bethany (Connecticut, USA) and Northwood Township, Grand Forks County (North Dakota, USA). The soil history is not specified and it could thus not be verified whether there was any treatment with pesticides in the previous five years. The soils were sieved through a 2 mm sieve prior to use. The characterisation of the soils is given in Table B.8.1.1.1/03a.

Table B.8.1.1.1/03a Characterisation of the soils studied

Soil	Bethany soil	North Dakota soil
Organic matter content (%)	1.6	9.6
Organic carbon content ¹ (%)	0.9	5.6
Maximum water holding capacity	unspecified	unspecified
Moisture capacity at 0.33 bar (%)	15.1	45.7
pH in 1:1 soil : water mixture	4.8	7.7
Soil classification ²	Sandy loam	Sandy loam
Clay (%); < 0.002 mm	6	10
Silt (%); 0.002-0.02 mm	20	28
Sand (%); > 0.02 mm	74	62
Cation Exchange Capacity (meq/ 100 g)	7.0	23.1
Microbial biomass at the start (mg microbial C/kg dw)	75	1480
Microbial biomass at the end (mg microbial C/kg dw)	46	n.d.

1 Calculated by RMS by dividing the organic matter content by a factor 1.7

2 USDA classification

n.d. = not determined

Samples of both soil types (10 g dw) were weighed into 50 mL Teflon® incubation tubes. Subsequently the soils were acclimated for several days (the exact number of days was not specified. RMS assumes that the acclimatisation period was less than one week) at $25 \pm 1^\circ\text{C}$ and the moisture content was adjusted to 75% of the 0.33 bar moisture content. The moisture content should be adjusted prior to acclimatisation. From the report it appears that adjustment of the moisture content occurred after acclimatisation.

A treatment solution of 0.24 mg/mL was prepared in methanol. After pre-incubation of the soil and adjustment of the soil moisture content to approximately 75% of the 0.33 bar moisture capacity, 50 μL aliquots of the treatment solution were applied to the soil surface in every incubation tube. The application rate was approximately 1.2 mg/kg dw soil. After was continuously supplied with moist, CO_2 free air at approximately 0.5 mL/min. The air leaving the system was led through four volatile traps, containing ethylene glycol, 1 M NaOH (x2) and 1 M H_2SO_4 , respectively. The incubation tubes were incubated for 365 and 180 days for Bethany and North Dakota soil, respectively, under aerobic conditions in the dark at $25 \pm 1^\circ\text{C}$ (except at two time points).

At each sampling interval (0, 1, 3, 7, 14, 30, 61, 91, 120, 180, 268 and 365 days for Bethany soil and 0, 7, 14, 31, 61, 119 and 180 days for North Dakota soil), a pair of incubation tubes and associated volatile traps were removed. The soil was extracted twice with methanol, once with Milli-Q water (1:1 methanol/water for day 0 through day 7 Bethany soils) and once with acetonitrile (ACN) by shaking and

centrifugation. Extracts were combined and analysed by LSC and HPLC. The dried solids were further extracted by exhaustive soxhlet extraction with methanol for 24 hours, followed by soxhlet extraction with Milli Q water for 24 hours. Each soxhlet extract was analysed by LSC and HPLC. The radioactivity of the remaining soil residue was determined by combustion LSC. Aliquots of the trapping solutions and the NaOH trapping solutions were analysed by LSC. A barium carbonate precipitation test was carried out with a composite NaOH trapping solution from each soil type to confirm that the radioactivity trapped in these solutions was $^{14}\text{CO}_2$. The identity of BAM in the treatment solution and in a composite mix of solvent extracts of Bethany soil was confirmed by LC-MS/MS analysis.

Results

In Tables B.8.1.1.1/03b and B.8.1.1.1/03c the recovery of radioactivity is given, together with the results of the analysis of the soil extracts.

Table B.8.1.1.1/03b Recovery of radioactivity and proportion of radioactive components in the extracts (expressed as % a.r.) of the Bethany soil (averages of duplicate samples)

Time (d)	Solvent extract	Soxhlet CH ₃ OH	Soxhlet H ₂ O	Ethylene Glycol trap	NaOH trap	Non-extracta	Total recovery	Total BAM in soil extracts
0	97.80	1.03	0.74	n.a.	n.a.	0.87	100.44	99.57
1	94.95	2.90	0.69	n.d.	0.59	1.11	99.74	98.03
3	91.75	4.39	0.77	0.03	0.93	1.15	99.01	96.91
7	89.10	5.39	1.51	0.02	1.14	1.58	99.21	95.99
14	87.97	5.86	1.39	0.04	1.80	1.89	99.39	92.73
30	83.74	6.69	2.31	0.03	2.08	2.64	97.91	95.22
61	78.51	8.60	2.12	0.02	3.28	3.26	96.36	89.22
91	80.38	7.28	2.85	0.02	4.22	4.34	99.70	90.50
120	78.80	9.87	2.12	n.d.	4.43	3.88	99.48	90.14
180	75.53	6.58	6.30	n.d.	5.33	5.15	99.60	88.40
268	75.14	8.06	2.79	n.d.	5.86	4.68	97.29	85.98
365	68.75	10.00	6.85	0.06	6.12	4.83	97.43	85.58

n.a. = not applicable

n.d. = not detected

Table B.8.1.1.1/03c Recovery of radioactivity and proportion of radioactive components in the extracts (expressed as % a.r.) of the North Dakota soil (averages of duplicate samples)

Time (d)	Solvent extract	Soxhlet CH ₃ OH	Soxhlet H ₂ O	Ethylene Glycol trap	NaOH trap	Non-extracta	Total recovery	Total BAM in soil extracts
0	98.36	4.05	1.19	n.a.	n.a.	0.55	104.15	103.60
7	89.95	9.77	1.27	n.d.	1.56	1.88	104.67	100.88
14	85.43	8.02	3.06	n.d.	1.98	2.16	100.98	96.51
31	79.30	11.43	2.20	n.d.	2.83	2.26	98.28	92.93
61	72.78	11.66*	4.27	n.d.	3.39	2.87	94.44	88.48
119	67.49	13.34	4.00	n.d.	5.70	3.57	93.70	84.10
180	62.18	15.14	4.49	n.d.	8.23	4.59	94.99	81.80

n.a. = not applicable

n.d. = not detected

* % a.r. in one replicate sample (the other replicate sample was lost due to volatilisation during Soxhlet extraction)

At the last sampling day, the mean portion of $^{14}\text{CO}_2$ recovered from the NaOH solutions was 6.12 and 8.23% a.r. for the Bethany and North Dakota soil, respectively. The portion of not-extracted radioactivity was 4.83 and 4.59% a.r. for the Bethany and North Dakota soil, respectively.

By HPLC co-chromatography and LC-MS/MS, the identity of 2,6 dichlorobenzamide (BAM) in soil extracts was confirmed. The only radioactive compound that was found in the solvent and the Soxhlet methanol extracts was [^{14}C]BAM. In the Soxhlet water extracts, one metabolite was detected at very low concentrations ($\leq 0.63\%$ a.r.). HPLC co-chromatography indicated that this could be 2,6-dichlorobenzoic acid, but due to the low concentrations no further identification work was done to confirm this. The barium carbonate precipitation reaction demonstrated that more than 90% of the radioactivity that was recovered from the NaOH solutions was represented by $^{14}\text{CO}_2$.

Based on the concentrations in the soil extracts, extrapolated simple first order DT_{50} values were calculated by the authors. As the degradation curve appeared to be bi-phasic, separate calculations were made for the period 0 - 61 days and for the whole test period. The calculated values are given in Table B.8.1.1.1.2d.

Table B.8.1.1.1/03d Extrapolated DT_{50} values for the metabolite 2,6-dichlorobenzamide in two soils at 25°C

Soil	Bethany soil		North Dakota soil	
Period	0 - 61 days	0 - 365 days	0 - 61 days	0 - 180 days
DT_{50} (days)	431	1831	227	557
r^2	0.941	0.775	0.934	0.874

Remarks

The amount of soil in each incubation tube should be at least 50 g according to OECD guideline 307. The soil samples in the present study are therefore considered to be too small. However, this does not change the conclusion for the test.

The authors calculated (extrapolated) DT_{50} values for the period 0 – 61 days and for the whole test period. RMS does not agree with this approach because there is no reason to reject the last part of the study. Therefore, extrapolated simple first-order (SFO) DT_{50} values were calculated by RMS, for the whole study period, using Modelmanager. As the degradation curve appeared to be bi-phasic, new calculations were made according to a first-order multi-compartment (FOMC) model. The calculated values are given in Table B.8.1.1.1/03e.

Table B.8.1.1.1/03e. Extrapolated DT₅₀ values for the metabolite 2,6-dichlorobenzamide in two soils, calculated by RMS with a SFO and FOMC model and converted to 20°C using the Arrhenius equation

Soil	Bethany soil (study period 0 – 365 d)		North Dakota soil (study period 0 – 180 d)	
Model	SFO	FOMC	SFO	FOMC
DT ₅₀ (days)	2666	$3.1 \cdot 10^{10}$	795	$4.8 \cdot 10^4$
r ²	0.761	0.936	0.872	0.996

Acceptability of the test

The study is considered acceptable.

Conclusion

The metabolite 2,6-dichlobenzamide does not degrade under aerobic conditions. DT₅₀ values (extrapolated) of 2666 and 795 days were calculated for Bethany and North Dakota soil using SFO kinetics and $3.1 \cdot 10^{10}$ and $4.8 \cdot 10^4$ days using FOMC kinetics, respectively. Metabolites were not identified.

B.8.1.1.2 Anaerobic studies

There are no data available.

B.8.1.1.3 Photolysis in soil (IIA, 7.1.1.1.2/02)

Characteristics of the study:

Reference	: Kabler and Carpenter (1990)	Chemical purity	: not reported
Guideline	: EPA, Subdiv. N, 161-3	Photo-DT ₅₀	: no value; no photodegradation
GLP	: yes	Metabolites	: none
Test substance	: dichlobenil	Acceptable	: yes
Radiochemical purity	: 95.6%		

Study design

The test substance was [*ring*-U-¹⁴C]dichlobenil (lot no. AOI87HO5A, radiochemical purity 95.6%, specific activity 0.629 MBq/mg). The study was conducted with one agricultural soil, a sandy loam. The characterisations of the soil are given in Table B.8.1.1.3a. The origin, sampling and the agricultural history of the soil were not reported. Pre-treatment of the soil (e.g. sieving) was not reported.

Table B.8.1.1.3a Characterisation of the studied soil

Soil texture class	Sandy loam
Organic matter content (%)	1.9
Water content at field capacity (%)	12.85
pH	7.6
Cation Exchange Capacity (mmol/kg)	111

Soil samples for irradiation were prepared by caking 1.0 g of wet soil with water in 22 mL Liquid Scintillation vials and allowing the soil to air-dry. These samples were then dosed with 27.9 μL of a hexane solution of [^{14}C]dichlobenil. The final concentration in the soil was 10.4 mg/kg, equivalent to a dosage rate of 2 $\mu\text{g}/\text{cm}^2$ (0.2 kg/ha). The vials were placed in a water cooled photolysis chamber covered with a borosilicate glass plate and kept at $25 \pm 1^\circ\text{C}$. The irradiation was carried out continuously with an Atlas Xenon Arc Light system provided with glass filters to eliminate wave lengths $< 290\text{ nm}$. The intensity of the irradiation was about half of average natural irradiation at 40°N at spring equinox during a solar day. As irradiation was continuous, the total irradiation received by the soil samples was comparable with natural irradiation. Vials with soil placed in a dark chamber were used as dark, non-irradiated degradation controls.

Air was drawn through the chambers (irradiated and non-irradiated) during the exposure period (30 days). The flow of CO_2 -free moist air was as follows:

Test system

Irradiation chamber

Post-test system

- a) Polyurethane foam (PUF) plug
- b) A trap containing toluene
- c) A trap containing KOH solution (1 mol/L) to trap $^{14}\text{CO}_2$
- d) A trap with ethylene glycol
- e) A trap with 2-ethoxyethanol/ethanol amine (1:1) ("mixed trap")

From both treatment groups (irradiated and non-irradiated) one duplicate set of vials was removed for analysis immediately after test substance application and after 1, 2, 3, 5, 7, 17 and 30 days. At the same sampling times, trapping solutions from the volatile traps were taken for analyses and changed.

The soil was extracted three times with methanol. The extracts were analysed by LSC and HPLC. Eluting fractions from the HPLC were analysed by LSC. The remaining soil residues were allowed to air-dry and triplicate samples of 0.2 g were analysed by combustion/LSC.

Results

At all sampling times the total average recovery of the radioactivity in the irradiated samples varied between 84.1% and 101%. In the non-exposed samples total average recovery of the radioactivity varied between 85% and 114%. In the irradiated samples at the end of the incubation (after 30 days) 53% a.r. was extracted from the soil. Small amounts remained unextracted (4.4%). On day 30 considerable amounts of radioactivity were found in the PUF, ethylene glycol trap and mixed trap, indicating high volatility of dichlobenil during the experiment. The amount of radioactivity which probably could be

ascribed to CO₂ was only 4.3% after 30 days. In Table B.8.1.1.3b the distribution and recovery of applied radioactivity in the irradiated samples are given.

Table B.8.1.1.3b Distribution and recovery of applied radioactivity in the irradiated samples (average values) (in % of applied radioactivity)

Sampling time (d)	Soil		Volatiles					Total
	Extracted	Non-extracted	PUF plug	Toluene trap	CO ₂	Ethylene glycol trap	Mixed trap	
0	98.8	1.7	-	-	-	-	-	100.6
1	89.7	2.6	0.5	0.0	0.1	0.0	0.0	92.9
2	95.6	2.7	0.8	0.0	0.0	0.0	0.0	99.2
3	91.7	3.2	2.1	0.0	0.0	0.1	0.0	97.2
5	73.5	4.0	7.9	0.1	0.0	0.1	0.4	86.0
7	74.0	3.6	10.2	0.3	0.0	0.1	0.1	88.4
17	72.1	4.1	11.5	0.3	1.7	1.6	0.4	91.7
30	52.9	4.4	16.7	0.3	4.3	4.1	1.4	84.1

In the non-irradiated samples at the end of the incubation (after 30 days) 0.8% a.r. was extracted from the soil. Small amounts remained non-extracted (0.7%). After 30 days considerable amounts of radioactivity were found in the toluene trap, indicating high volatility of dichlobenil during the experiment. The amount of radioactivity which probably could be ascribed to CO₂ was only 3.5% after 30 days. In Table B.8.1.1.3c the distribution and recovery of applied radioactivity in the non-irradiated samples are given.

Table B.8.1.1.3c Distribution and recovery of applied radioactivity in the non-irradiated samples (average values) (in % of applied radioactivity)

Sampling time (d)	Soil		Volatiles					Total
	Extracted	Non-extracted	PUF plug	Toluene trap	CO ₂	Ethylene glycol trap	Mixed trap	
0	98.8	1.7	-	-	-	-	-	100.6
1	60.5	7.1	¹⁾	17.0	0.0	0.0	0.0	84.6
2	43.8	7.1	¹⁾	40.1	0.1	0.0	0.0	91.1
3	31.9	5.0	¹⁾	49.7	0.1	0.0	0.0	86.6
5	21.3	4.9	¹⁾	65.1	0.1	0.0	0.0	91.3
7	16.4	3.7	¹⁾	71.3	0.1	0.0	0.0	91.4
17	5.6	2.3	¹⁾	94.9	0.5	0.1	0.1	103.4
30	0.8	0.7	¹⁾	108.5	3.5	0.3	0.1	114.0

¹⁾ Not reported

Virtually all extracts of irradiated soil and dark control soil (except for one sample which was discarded as an outlier) contained dichlobenil as the only radioactive component (94-100% in irradiated samples, 95-100% in the non-irradiated samples, but the 2-day sample 88%). The disappearance of dichlobenil from the soil samples could therefore be fully ascribed to volatilisation due to the relatively high vapour pressure of dichlobenil. The difference in volatility observed between the dark and the irradiated system was ascribed by the authors to volatilised dichlobenil coming into contact with the cooled inner surface of

the irradiation chamber. Volatilisation from the cooled glass surface would then be lower than from a dark soil surface.

Acceptability of the test

The origin, sampling and the agricultural history of the soil were not reported. Pre-treatment of the soil (e.g. sieving) was not reported. Nevertheless the results can be used for risk assessment.

The identity of the radioactivity in the traps was not established, but it is very probable that it is dichlobenil. The guideline followed is well in agreement with the SETAC procedures (Lynch 1995). The study is considered acceptable.

Conclusion

No photodegradation of dichlobenil (10.4 mg/kg) in a sandy loam soil was observed upon simulated sunlight irradiation for 30 days. No photo-DT₅₀ value could be derived. A large proportion of dichlobenil volatilised from the soil surface.

B.8.1.2 Field studies

B.8.1.2.1 Field dissipation study with the formulation Casoron G (IIA, 7.1.1.2.2/01)

Characteristics of the study

Reference	: Pouwelse and Van Loon (1991)	Content of a.s.	: 6.75% dichlobenil
Year of execution	: 1989-1991	Dissipation-DT ₅₀	: Goch-Nierswalde: 3.4 d Eschwege: 6.5 d Nottuln: 72 d
Guideline	: BBA IV, 4-1	Dissipation-DT ₉₀	: Goch-Nierswalde: 11.3 d Eschwege: 22 d Nottuln: 238 d
GLP	: yes (analytical part)	Metabolite	: BAM (max. 9.6% in Goch-Nierswalde)
Test substance	: CASORON G	Acceptable	: yes

Study design

Field dissipation studies were conducted in three fields in Germany according to BBA Guideline IV, 4-1 (1986). The analytical part of the study was carried out in compliance with GLP. The test substance was CASORON G (commercial granulate containing 6.75% dichlobenil; no batch no. mentioned).

The location and soil type of the fields were:

Field 1 and 2: 47574 Goch-Nierswalde: Sandiger Lehm - lehmiger Sand (sandy loam - loamy sand),

Field 3: 37269 Eschwege (Meissner-Vockerrode): Lehm (loam),

Field 4: 48301 Nottuln: Lehmiger Sand (loamy sand).

Two trials were performed at the location Goch-Nierswalde. The characteristics of the soils are given in Table 8.1.2.1a.

Table B.8.1.2.1a. Relevant characteristics of the soils (0-30 cm)

Location of collection	Goch-Nierswalde (field 1)	Goch-Nierswalde (field 2)	Eschwege (field 3)	Nottuln (field 4)
Texture class of soil ¹⁾	Sandiger Lehm- lehmiger Sand	Sandiger Lehm- lehmiger Sand	Lehm	Lehmiger Sand
Organic carbon content (%)	3.7	3.4	2.3	2.6
Organic matter content (%)	6.4 ²⁾	5.8 ²⁾	4.0 ²⁾	4.5 ²⁾
pH (KCl)	6.3	5.9	6.2	6.2
Soil microbial biomass (mg C/kg soil)	390	340	370	560
Maximum water holding capacity (%)	60	57.5	60	47

¹⁾ German classification. Data not sufficient for USDA classification

²⁾ Organic matter content (%) = Organic carbon content (%) x 1.72

Details of the agricultural use and maintenance of the fields were reported. Pesticides applied were: field 1: 1988: Corbel, Arelon Kombi, Sportak and Betanal T.; 1990: none; field. 2: no pesticides in 1988 and 1990; field 3: no pesticides in 1988 and 1990; field 4: 1988: Betanal (8 L/ha), Trammat (1.5 L/ha); 1990: Stomp (5 L/ha), Sportak Alpha (1.5 L/ha), Sumicidin (0.5 L/ha).

Plots of 50 m² were treated with 120 kg CASORON G/ha (8.1 kg a.s./ha) on bare soil. A duplicate plot, located close to the treated plot, remained untreated as control. Before the start of the experiment weeds were removed and the soil was ploughed and harrowed. The dates of treatment were as follows:

Field 1: June 8, 1989,

Field 2: February 9, 1990,

Field 3: June 15, 1989,

Field 4: February 10, 1990.

No crops were grown on the fields. Climatic data reported for each field were obtained from a nearby meteorological station in terms of average monthly temperature, total rainfall, total sun hours, frost days with average temperature < 0°C and days with heavy rainfall (≥ 10 mm). The spraying technique was not reported. The wind speed during application was not reported.

From each treated plot soil samples were taken prior to application, immediately following application and 1, 3, 7, 14, 28, 61, 183 and 365 days after treatment (DAT). The untreated plots were sampled prior to application and 28, 186 and 365 DAT. In field 1 instead of after 1 day samples were taken 2 DAT. Twenty cores were taken with a ground borer from each plot on the sampling dates. Samples were taken from 0-30 cm depth at 10 cm increments. They were stored frozen at -20°C until analysis.

The samples were analysed for dichlobenil and its metabolite 2,6-dichlorobenzamide (BAM). Homogenised soil samples were extracted with a mixture of 0.2% NH₄Cl solution, acetone and petroleum ether (17:75:75). After dilution with water, the mixture was either extracted with petroleum ether for dichlobenil analysis or with ethyl acetate for BAM analysis. The extracts were purified on Al₂O₃ cartridges. Final determination was performed by GC using EC detection. Mixed soil from control plots from field 1 was used for spiked samples to determine the recovery and LOQ. Recoveries at the 0.01 – 2.1 mg/kg level ranged from 73-91% (average 80%) for dichlobenil and from 91-105% (average 100%) for BAM. The LOQ was 0.01 mg/kg with a recovery of 91% for both compounds. At this level the coefficient of variation was 7% and 10% (n = 4) for dichlobenil and BAM, respectively. Storage tests did not indicate any major storage effect.

Results

Prior to the application, no dichlobenil was found in the soils. In the untreated soil plots no dichlobenil or BAM was detected. In the treated plots, except for four exceptions, no dichlobenil was found in the 20-30 cm soil layer. In the exceptions dichlobenil concentrations did not exceed 0.04 mg/kg. In field 2 0.134 mg/kg dichlobenil was found in the 20-30 cm layer on the day of application, which was obviously due to contamination. The results of the dichlobenil measurements in the 0-10 cm and 10-20 cm layer are given in Table 8.1.2.1b. The results of the BAM measurements in all layers are given in Table 8.1.2.1c.

Concentrations were based on soil dry weight.

Table 8.1.2.1b Concentrations (mg/kg dry soil) of dichlobenil in the 0-10 cm and the 10-20 cm soil layers of field trials

Sampling time (d)	Goch-Nierswalde (field 1)		Goch-Nierswalde (field 2)		Eschwege (field 3)		Nottuln (field 4)	
	0-10 cm	10-20 cm	0-10 cm	10-20 cm	0-10 cm	10-20 cm	0-10 cm	10-20 cm
0	5.53	<0.01	1.36	0.012 ²⁾	5.57	0.062	2.09	<0.01
1 ¹⁾	5.17	0.027	1.60	<0.01	6.56	0.191	1.77	<0.01
3	1.98	0.029	0.556	<0.01	6.79	0.908	2.37	0.023
7	1.22	<0.01	2.06	<0.01	1.39	<0.01	0.846	<0.01
14	0.658	<0.01	0.635	<0.01	1.58	0.029	1.82	<0.01
28	0.293	<0.01	2.68	0.251	0.404	<0.01	2.09	<0.01
61	0.273	<0.01	1.02	<0.01	0.371	<0.01	0.877	<0.01
183	0.099	<0.01	0.186	<0.01	0.525	0.013	0.187	<0.01
365	0.112	0.032	0.122	<0.01	0.277	0.012	0.219	<0.01

¹⁾ Field 1: day 2; ²⁾ 20-30 cm: 0.134 mg/kg

Table 8.1.2.1c Concentrations (mg/kg dry soil) of BAM in the 0-10 cm, 10-20 cm and 20-30 cm soil layers of field trials

Sampling time (d)	Goch-Nierswalde (field 1)			Goch-Nierswalde (field 2)			Eschwege (field 3)			Nottuln (field 4)		
	0-10 cm	10-20 cm	20-30 cm	0-10 cm	10-20 cm	20-30 cm	0-10 cm	10-20 cm	20-30 cm	0-10 cm	10-20 cm	20-30 cm
0	0.026	<0.01	<0.01	<0.01	<0.01	<0.01	0.010	<0.01	<0.01	<0.01	<0.01	<0.01
1 ¹⁾	0.029	<0.01	<0.01	<0.01	<0.01	<0.01	0.011	<0.01	<0.01	<0.01	<0.01	<0.01
3	0.030	<0.01	<0.01	<0.01	<0.01	<0.01	0.014	<0.01	<0.01	<0.01	<0.01	<0.01
7	0.043	<0.01	<0.01	<0.01	<0.01	<0.01	0.012	<0.01	<0.01	<0.01	<0.01	<0.01
14	0.041	<0.01	<0.01	0.011	<0.01	<0.01	0.070	<0.01	<0.01	0.028	<0.01	<0.01
28	0.044	<0.01	<0.01	0.056	0.013	<0.01	0.120	<0.01	<0.01	0.055	<0.01	<0.01
61	0.079	<0.01	<0.01	0.056	<0.01	<0.01	0.118	0.086	<0.01	0.068	<0.01	<0.01
183	0.069	<0.01	<0.01	0.120	<0.01	<0.01	0.107	0.122	0.010	0.117	<0.01	<0.01
365	0.050	0.034	0.013	0.052	0.066	0.026	0.114	0.063	0.043	0.035	0.057	0.052

¹⁾ Field 1: day 2

The initial concentrations of dichlobenil in fields 1 and 3 which were treated in the summer agreed well with the applied dosage rate, assuming a soil density of 1500 kg/m³. The initial concentrations of dichlobenil in fields 2 and 4 which were treated in the winter were much lower than expected from the applied dosage rate. No explanation could be given for this difference.

Residues of dichlobenil declined over time in the 0-10 cm layer. Small amounts of dichlobenil were occasionally found in deeper layers, but it cannot be excluded that these are caused by contamination. BAM residues found in the soil showed an increase up to 1 year. Maximum percentages (corrected for molecular mass) were: fields 1 and 2, Goch-Nierswalde: 9.6%; field 3, Eschwege (Meissner-Vockerröde): 3.6%; field 4, Nottuln: 7.7%. The metabolite 2,6-dichlorobenzamide (BAM) was found in the 20 – 30 cm soil layer after 1 year.

Dissipation DT₅₀ and DT₉₀ values were calculated using the models of Frehse and Timme. No value could be obtained from field 2 (winter application in Goch-Nierswalde). Since at present the models of Frehse and Timme (1986) are considered to be not very useful, DT₅₀ and DT₉₀ values were recalculated by RMS (see Remarks).

Remarks

Since at present the models of Frehse and Timme (1986) are not considered to be very useful, dissipation DT₅₀ and DT₉₀ values were recalculated by RMS. The sum of the concentrations in the 0-10 cm and 10-20 cm soil layers (assuming equal soil densities) were fitted by non-linear regression to single first-order (SFO) kinetics. The data were not corrected for temperature.

Field 1: DT₅₀ = 3.4 d; DT₉₀ = 11.3 d (r² = 0.91).

Field 2: no DT₅₀ value could be calculated, data presented were too variable.

Field 3: DT₅₀ = 6.5 d; DT₉₀ = 22 d (r² = 0.82).

Field 4: $DT_{50} = 72$ d; $DT_{90} = 238$ d ($r^2 = 0.70$).

Since temperatures were below 20°C these values may be regarded as worst-case values.

Because volatilisation of dichlobenil cannot be excluded as one of the processes responsible for dissipation, these data cannot be used as input for leaching model calculations.

RMS could not calculate DT_{50} values for BAM, because the sum of the BAM concentrations in the different soil layers was still increasing at the end of the experiment.

Acceptability of the test

The study is considered acceptable.

Conclusion

The following dissipation DT_{50} and DT_{90} values were obtained from field degradation experiments with dichlobenil in Germany: Goch-Nierswalde (summer application): $DT_{50} = 3.4$ d, $DT_{90} = 11.3$ d

Eschwege (Meissner-Vockerode) (summer application): $DT_{50} = 6.5$ d; $DT_{90} = 22$ d

Nottuln (winter application): $DT_{50} = 72$ d, $DT_{90} = 238$ d.

Because volatilisation of dichlobenil cannot be excluded as one of the processes for dissipation, these data cannot be used as input for leaching model calculations. The metabolite 2,6-dichlorobenzamide (BAM) was found in the 20 – 30 cm soil layer after 1 year. Maximum percentages were: Goch-Nierswalde: 9.6%; Eschwege (Meissner-Vockerode): 3.6%; Nottuln: 7.7%. RMS could not calculate DT_{50} values for BAM, because the sum of the BAM concentrations in the different soil layers was still increasing at the end of the experiment.

B.8.1.2.2 Kinetic evaluation of field dissipation studies (IIA, 7.1.1.2.2/02)

Characteristics of the study

Reference	: Kley (2003)	Purity	: not applicable
Year of execution	: not applicable	Dissipation- DT_{50}	: 131.1 days (arithmetic mean) 125.0 days (geometric mean)
Guideline	: not applicable	Acceptable	: yes
GLP	: not applicable		
Test substance	: AE C638206; batch no. and appearance not applicable		

In this report, data obtained in six field dissipation studies with the fungicide AE C638206 and its metabolites (among which 2,6-dichlorobenzamide (BAM)) were analysed with ModelMaker, PEARL, and PEST.

This kinetic evaluation was based on the data from field studies (two at the same location, Senas in Southern France) with the a.s. fluopicolide (DAR prepared by UK). BAM is a major metabolite of this a.s. The endpoint derived in the DAR of fluopicolide is a DT_{50} value for BAM of 137.7 days (geometric mean). It is considered by RMS that the data derived from these field studies and used in the kinetic evaluation can serve for the assessment of the degradation rate of BAM under field conditions in the dichlobenil dossier as well.

In deviation from the fluopicolide dossier, RMS considers that three of the seven studies in the fluopicolide dossier are not useful for the derivation of a DT_{50} for modelling purposes for BAM, due to either a demonstrated leaching of BAM to deeper soil layers, or to the lack of sufficient data points to achieve at a reliable DT_{50} calculation.

Therefore, the $DT_{50\text{field}}$ value for BAM is based on the four remaining studies (all single first order degradation kinetics). Both non-normalised and standardised (ModelMaker, temperature and moisture content) values are presented briefly in Table 8.1.2.2. For details, please refer to the DAR of fluopicolide.

Table 8.1.2.2 Overview of reliable field studies with fluopicolide and resulting field degradation half-lives for BAM.

Location	Layer over which the DT_{50} was derived (cm)	$DT_{50\text{field}}$ (days) (1 st order)	standardised DT_{50} (20 °C, field capacity)
Southern Germany (Rödelsee)	0-20	315.2	73.0
Northern Germany (Huntlosen)	0-30	257	141.5
Southern France (Senas 1999)	0-20	267	136.6
Northern France (Appily, Picardie)	0-20	185.7	173.3
Arithmetic mean		256.3	131.1
Geometric mean			125.0

The worst-case non-normalised field degradation half-life, 315.2 days, will be used in the calculation of PECsoil (B.8.3.1). The geometric mean of the normalised values, 125 days, will be used in the PEC calculations for surface water, sediment and groundwater (B.8.6).

Acceptability of the test

Only a summary of the methods and the data was given in the report of Kley. When the DAR of fluopicolide is also considered, sufficient data is available to make an adequate evaluation. The study results in Kley together with the studies in the DAR of fluopicolide and the evaluation by RMS are therefore considered acceptable. Furthermore, the notifier has access to the dossier of fluopicolide and submitted the original field study reports.

B.8.1.3 Other studies

There are no other studies with respect to route and rate of degradation in soil.

B.8.1.4 Summary

The aerobic degradation of dichlobenil and its metabolite 2,6-dichlorobenzamide was studied in two laboratory tests and in a field dissipation study. Photodegradation of dichlobenil was also studied. An anaerobic degradation study is not available, because it is expected that dichlobenil will not be exposed to anaerobic conditions in general.

Aerobic degradation of the parent compound and the metabolite 2,6-dichlorobenzamide in laboratory studies

Aerobic degradation of dichlobenil was studied in a test with one soil over a period of 50 weeks. The study was not considered acceptable because the method that was followed deviated from the standard procedure. No separate traps were used for evaporated dichlobenil and metabolites. This may have resulted in an underestimation of the DT_{50} value because no difference could be made between metabolite formed in the soil or formed in the trap. Also, the calculated DT_{50} was outside the range of DT_{50} values obtained in the other experiments, which supports the conclusion that the results of the study are unreliable.

Another aerobic degradation study with three soils is available; it was carried out over a period of 273 days. Dichlobenil degraded under aerobic conditions with calculated DT_{50} values of 38.9 d, 39.0 d and 43.6 d in clay loam, silt loam and loamy sand soil respectively (see Table B.8.14a). 2,6-dichlorobenzamide (BAM) was identified as the major metabolite; the highest percentage formed was 69.41% a.r. (at the end of the study in the clay loam soil). Simple first order DT_{50} and DT_{90} values were calculated by RMS. These values are given in Table B.8.1.4a.

Table B.8.1.4a DT_{50} values and DT_{90} values for dichlobenil in three soils, calculated by RMS

Soil	clay loam	silt loam	loamy sand
DT_{50} (days)	38.9	39	43.6
DT_{90} (days)	129	130	145
r^2	0.968	0.975	0.821

A separate aerobic degradation study for 2,6-dichlorobenzamide with two soils showed that this metabolite did not degrade under aerobic conditions. DT_{50} values were calculated in two ways (assuming simple first-order (SFO) or first-order multi-compartment (FOMC) kinetics). This resulted

in DT₅₀ values (extrapolated) of 2666 and 795 days (SFO kinetics) and $3.1 \cdot 10^{10}$ and $4.8 \cdot 10^4$ days (FOMC kinetics); see Table B.8.1.4b. Metabolites were not identified.

Table B.8.1.4b Extrapolated DT₅₀ values for the metabolite 2,6-dichlorobenzamide in two soils, calculated by RMS with a SFO and FOMC model and converted to 20°C using the Arrhenius equation

Soil	Bethany soil		North Dakota soil	
Model	SFO	FOMC	SFO	FOMC
DT ₅₀ (days)	2666	$3.1 \cdot 10^{10}$	795	$4.8 \cdot 10^4$
r ²	0.761	0.936	0.872	0.996

Photolysis in soil

A photodegradation study with one agricultural soil, sandy loam, was conducted. No photodegradation of dichlobenil (10.4 mg/kg) was observed upon simulated sunlight irradiation for 30 days and a DT₅₀ value could not be derived. A large proportion of dichlobenil volatilised from the soil surface.

Field dissipation tests

Field dissipation studies were conducted in three fields in Germany with CASORON G (commercial granulate). The following dissipation DT₅₀ and DT₉₀ values were obtained from the experiments:

- Germany: Goch-Nierswalde (sandy loam - loamy sand, summer application): DT₅₀ = 3.4 d, DT₉₀ = 11.3 d
- Eschwege (Meissner-Vockerode) (loam, summer application): DT₅₀ = 6.5 d; DT₉₀ = 22 d
- Nottuln (loamy sand, winter application): DT₅₀ = 72 d, DT₉₀ = 238 d.

The DT₅₀ value to be used for PEC soil calculations is 72 days.

Because volatilisation of dichlobenil as one of the dissipation processes cannot be excluded, these data cannot be used as input for leaching model calculations. 2,6-dichlorobenzamide (BAM) was found as a metabolite. Maximum percentages were: Goch-Nierswalde: 9.6%; Eschwege (Meissner-Vockerode): 3.6%; Nottuln: 7.7%. The metabolite 2,6-dichlorobenzamide (BAM) was found in the 20 – 30 cm soil layer after 1 year.

For the dissipation under field conditions of BAM, studies from the DAR of fluopicolide were evaluated. The highest non-normalised DT_{50field} value, to be used for PEC soil calculations, is 315.2 days. The geometric mean of the normalised values, 125 days, will be used in the PEC calculations for surface water, sediment and groundwater (B.8.6).

B.8.1.5 Assessment

- Under aerobic conditions, the DT₅₀ values for the parent dichlobenil in laboratory studies with three soils were 38.9, 39 and 43.6 days. In these studies, 2,6-dichlorobenzamide was identified as major metabolite.
- The metabolite 2,6-dichlorobenzamide is poorly biodegradable under aerobic conditions in the laboratory studies. DT₅₀ values were calculated in two ways (assuming SFO or FOMC kinetics). This resulted in DT₅₀ values (extrapolated) of 2666 and 795 (SFO kinetics) and $3.1 \cdot 10^{10}$ and $4.8 \cdot 10^4$ days (FOMC kinetics).
- Dichlobenil is not photodegradable, as no photodegradation was observed upon simulated sunlight irradiation for 30 days. Metabolites were not identified.
- The following field DT₅₀ values were calculated for dichlobenil:
 - In a field test with sandy loam, summer application, the DT₅₀ = 3.4 d.
 - In a field test with loam, summer application, the DT₅₀ = 6.5 d.
 - In a field test with loamy sand, winter application, the DT₅₀ = 72 d.
 - The results did not allow the calculation of a DT₅₀ value for 2,6-dichlorobenzamide
- The following field DT₅₀ values were calculated for BAM, on the basis of field studies conducted in the fluopicolide dossier: 315.2, 257, 267, 185.7 days. The geometric mean of the normalised field DT₅₀ values is 125 days.

Aerobic degradation should be studied in four soils. As the degradation study with one soil was not considered acceptable, data for only three soils are available. However, the DT₅₀ values obtained for the three soils are within a narrow range and a DT₅₀ value obtained in a field study is available. Therefore, no additional laboratory study is required. The DT₅₀ value to be used for PEC soil calculations is the worst-case field DT₅₀ of 72 days; for the calculation of PEC surface water and PEC groundwater, the average lab DT₅₀ of 40.5 days is used.

For BAM, The DT₅₀ value to be used for PEC soil calculations is the worst-case field DT₅₀ of 315.2 days; for the calculation of PEC surface water and PEC groundwater, the geomean field DT₅₀ of 125.0 days is used.

The metabolic pathway of dichlobenil in soil is given in the figure below.

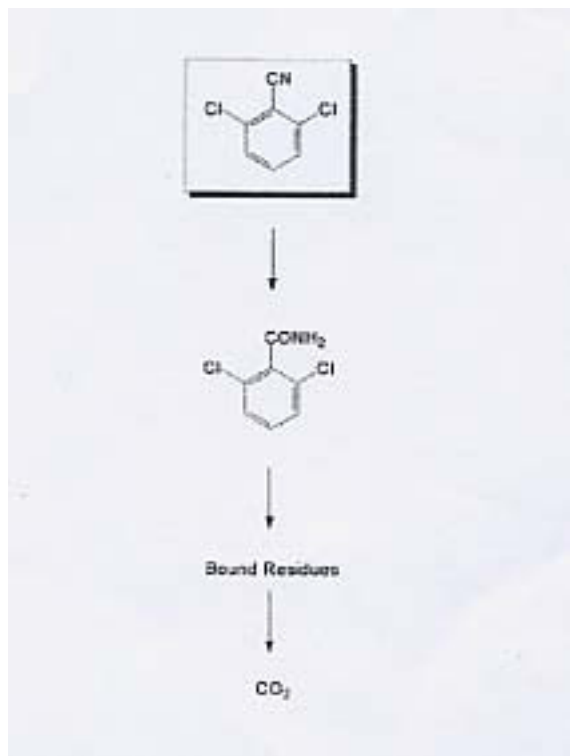


Figure B.8.1.5a Metabolic pathway of dichlobenil in soil.

B.8.2 ADSORPTION, DESORPTION AND MOBILITY IN SOIL

B.8.2.1 Adsorption and desorption

B.8.2.1.1 Adsorption and desorption of the active substance (IIA 7.1.2/01)

Characteristics of the study

Reference	: Thus and Van der Laan-Straathof (1995)	Chemical purity	: 99.2%
Year of execution	: 1994	Radiochemical purity	: 99.9%
Guideline	: US-EPA FIFRA 163-1	Specific activity	: 17.1 mCi/g
GLP	: Yes	Adsorption classification	: medium to high mobility
Test substance	: ¹⁴ C-dichlobenil; batch no. AOI87H05A; white powder	Acceptable	: yes

Study design

The adsorption/desorption test was performed with the radio-labelled active substance ¹⁴C-dichlobenil in order to obtain adsorption and desorption isotherms. Four agricultural soils and one hydrosol were used; the soil characterisation is given in Table B.8.2.1.1a.

Table B.8.2.1.1a. Characterisation of the studied soils¹

Soil type (USDA classification)	sandy loam	silty loam	clay	sand	hydrosol (silty clay loam)
% clay	8	23.2	41.2	3.2	37.2
% silt	28	64.0	24.0	4.0	48.0
% sand	64	12.8	34.8	92.8	14.8
% organic carbon	4.0	2.7	7.2	0.16	1.3
pH	6.6	7.3	7.4	7.4	6.3
CEC in meq/100 g	8.9	16.6	27.5	1.0	19.9

¹ The soils were sieved through a 2.0 mm sieve before use

In a preliminary test, the incubation time necessary to reach equilibrium was determined (1 – 2 d). After the adsorption phase, desorption of the test substance was studied by adding 10 mL of 0.01 M CaCl₂ to the test vessels (desorption step I). This step was repeated once (desorption step II). The following test design was applied:

duration of the test	: 2 d for the adsorption phase, and two times 2 d for desorption phase I and II
type of test vessel and content	: 20-mL glass vessels closed with Teflon underlined crimp caps; 2 g dw soil and 10 mL test substance solution
number of replicate test vessels	: 3
dosing of test substance	: from a stock solution in 0.01 M CaCl ₂
nominal test substance concentrations	: 0, 0.04, 0.20, 1.00, and 4.66 mg a.s./L
chemical analysis	: LSC
sampling times	: after 2 d of incubation for the adsorption phase and desorption phase I and II

Results

The mean total radioactivity recoveries ranged from 98.7 – 113%. The equilibrium pH of the adsorption phase was not determined. The results of the adsorption and the two desorption steps are given in Table B.8.2.1.1b.

The adsorption constants K_d and K_{OC} , as calculated from the Freundlich isotherms for the five soils, ranged from 0.3 – 10.5 L/kg and 133 – 323 L/kg, respectively. The desorption constants for phase I ranged from 1.2 – 12.9 L/kg and 164 – 750 L/kg, respectively. For desorption phase II, constants varied between 10.0 – 16.4 L/kg and between 210 – 769 L/kg, respectively. The authors state that the mobility of dichlobenil in soil is low. However, RMS classified the mobility potential according to McCall *et al.*² as follows:

- Sandy loam: medium
- Silty loam: medium
- Clay: high
- Sand: medium
- Hydrosol (silty clay loam): medium

Table B.8.2.1.1b Adsorption and desorption coefficients of ¹⁴C-dichlobenil in five soils

Soil type	% organic carbon	adsorption in L/kg		desorption in L/kg			
		K_d	K_{OC}	K_d phase I	K_d phase II	K_{OC}^1 phase I	K_{OC}^1 phase II
sandy loam	4	10.5	262	12.9	16.4	323	410
silty loam	2.7	7.4	272	10.0	13.1	371	485
Clay	7.2	9.6	133	11.8	15.1	164	210
Sand	0.16	0.3	195	1.2	n.d.	750	-
Hydrosol (silty clay loam)	1.3	4.2	322	6.2	10.0	477	769

¹ Calculated by RMS
n.d. Not determined

Acceptability of the test

Although the history of the soil with respect to the use of pesticides is not given, the test is considered acceptable.

² McCall, P.J., Laskowski, D.A., Swan, R.L. and H.J. Dishburger (1981). Measurement of sorption coefficients of organic chemicals and their use in environmental fate analysis. In: Test protocols for environmental fate and movement of Toxicants. Proceedings of AOAC Symposium, AOAC, Washington DC.

Conclusions

Dichlobenil can be classified as a compound with a medium to high mobility in soil.

B.8.2.1.2 Adsorption and desorption of the metabolite 2,6-dichlorobenzamide (BAM) (IIA 7.1.2/02A and 02B)

Characteristics of the study

Reference	: Dzialo (2001)	Radiochemical purity	: 97.38% (1 determination prior to test); 97.44% (average of 3 determinations)
Year of execution	: 2001	Specific activity	: 6.86 mCi/mmol
Guideline	: EPA 160-4, 160-5 and 163-1	Adsorption classification	: high to very high mobility
GLP	: yes	Acceptable	: yes
Test substance	: [¹⁴ C]2,6-dichlorobenzamide; lot no. DUPH016; appearance not indicated		

Study design

The adsorption/desorption test was performed with the radio-labelled metabolite [¹⁴C]2,6-dichlorobenzamide in order to obtain adsorption and desorption isotherms. Five soils were used; the soil characterisation is given in Table B.8.2.1.2a.

Table B.8.2.1.2a. Characterisation of the studied soils

	soil type ¹				
characteristic	sandy loam RL-51	sandy loam RL-81	sand RM-014	sand RM-019	sandy clay loam RM-022
pH	4.8	7.7	6.3	4.9	6.6
% sand	74	62	99	97	49
% silt	20	28	1	3	26
% clay	6	10	0	0	25
% organic matter	1.6	9.6	2.3	7.1	0.7
% organic carbon	0.9	5.7	1.4	4.2	0.4
CEC in meq/100 g	7.0	23.1	6.3	8.5	16.3
Field capacity (% at 1/3 bar)	15.1	45.7	3.8	13.3	21.3
Bulk density (gm/cc)	1.32	0.84	1.3	0.92	1.26

¹ The soils were air dried and sieved through a 2.0 mm sieve before use

In a preliminary study, the incubation time to reach equilibrium was determined (24 h). After the adsorption phase, desorption of the test substance was studied by adding 25 mL of 0.01 M CaCl₂ to the test vessels. The following test design was applied:

duration of the test	: 24 h for the adsorption phase and for the desorption phase
temperature	: 25 ± 1°C

light conditions	: darkness
test water	: Milli-Q reagent water
type of test vessel and content	: 50-mL Oak Ridge Teflon FEP centrifuge tubes with Teflon screw caps; ca. 5 g dw soil and ca. 25 mL test substance solution
number of replicate test vessels	: 2
dosing of test substance	: from a stock solution in 0.01 M CaCl ₂
nominal test substance concentrations	: 0, 0.20, 0.50, 1.0, 5.0, and 10.0 mg metabolite/L
chemical analysis	: LSC and HPLC
sampling times	: t = 24 h (adsorption phase) and t = 48 h (desorption phase)

Results

The mean total radioactivity recoveries ranged from 95.1 – 107%. The equilibrium pH of the adsorption phase was not determined. The results of the adsorption and desorption steps are given in Table B.8.2.1.2b. In sandy loam soil RL-51, the authors state that the adsorption data at 0.5 mg metabolite/L are outliers. In Hardy (2003, IIA 7.1.2/02B), the data was reanalysed without this test concentration. The exclusion of data resulted in an improved fit (R^2 increased from 0.86 to 0.99), a K_d of 0.3588 L/kg and a K_{OC} of 39.9 L/kg.

The adsorption constants K_d and K_{OC} , as calculated from the Freundlich isotherms for the five soils, ranged from 0.208 – 1.890 L/kg and 26 – 51 L/kg, respectively. The desorption constants ranged from 2.577 – 6.397 L/kg and 76 – 1560 L/kg, respectively. According to McCall *et al.*³, RMS classified the mobility potential of the metabolite 2,6-dichlorobenzamide as follows:

- Sandy loam RL-51: very high
- Sandy loam RL-81: very high
- Sand RM-014: very high
- Sand RM-019: very high
- Sandy clay loam: high

Table B.8.2.1.2b Adsorption and desorption coefficients of [¹⁴C]2,6-dichlorobenzamide in five soils

Soil type	% organic matter	adsorption in L/kg		desorption in L/kg	
		K_d	K_{OC}	K_d	K_{OC}
sandy loam RL-51 original data	0.9	0.241	26	4.652	494

³ McCall, P.J., Laskowski, D.A., Swan, R.L. and H.J. Dishburger (1981). Measurement of sorption coefficients of organic chemicals and their use in environmental fate analysis. In: Test protocols for environmental fate and movement of Toxicants. Proceedings of AOAC Symposium, AOAC, Washington DC.

without outliers		0.3588	39.9		
sandy loam RL-81	5.7	1.761	31	4.350	76
sand RM-014	1.4	0.529	38	2.577	184
sand RM-019	4.2	1.890	45	4.178	100
sandy clay loam	0.4	0.208	51	6.397	1560

Acceptability of the test

Although the history of the soil with respect to the use of pesticides is not given, the test is considered acceptable.

Conclusions

2,6-dichlorobenzamide can be classified as a compound with a high to very high mobility in soil.

B.8.2.2 Fresh residue-and aged residue column leaching

B.8.2.2.1 Lysimeter studies (IIA, 7.1.3.3/01A)

Characteristics of the study

Reference	: Traub-Eberhard (1992) ¹	Dichlobenil after 2 years	: 3-6%
Year of execution	: 1990-1992	BAM after 2 years	: 7-14%
Guideline	: BBA IV, 4-3	Average concentration in leachate	: dichlobenil: < 0.047 µg/L BAM: 2.4 kg/ha: 1 st year: 7.5 µg/L, 2 nd year 19.3 µg/L; 3.5 kg/ha: 1 st year: 54 µg/L, 2 nd year 50 µg/L; 7.1 kg/ha: 1 st year: 94 µg/L, 2 nd year 70 µg/L.
GLP	: yes	Acceptable	: yes
Test substance	: [¹⁴ C]dichlobenil		
Purity	: Radiochemical: 98.3% Chemical: 99.1%		

¹ Includes study Traub-Eberhard (1994) on the identification of unknown metabolites

Study design

A lysimeter study was conducted in three lysimeter systems, according to BBA Guideline IV, 4-3 in compliance with GLP. The test substance was [*ring*-U-¹⁴C]dichlobenil (batch no. AIS9010AC, radiochemical purity 98.3%, chemical purity 99.1%, specific activity 1.11 GBq/g). [¹⁴C]Dichlobenil was dispersed in a liquid formulation (batch no. FUS90D19P). The final preparation had a specific activity of 1.00 GBq/g.

Three undisturbed soil cores (surface area 1 m², depth 1.2 m) were taken from a light sandy soil in 31535 Neustadt am Rübenberge O.T. Borstel (Germany) and placed at the outdoor area of the laboratory in 57392 Smallenberg-Grafschaft (Germany). Characteristics of the soil and soil profile are given in Table

8.2.2.1a.

Table 8.2.2.1a Characteristics of the soil and soil profile of the lysimeters

Horizon	0-30 cm (Ap)	30-50 cm (Bhv)	50-90 cm (Bv)	> 90 cm (Cv)
Texture class of soil	Loamy sand	Loamy sand	Sand	Sand
% sand	78.0	81.2	89.8	98.2
% silt	18.0	14.2	7.1	1.0
% clay	4.0	4.6	3.1	1.0
Organic carbon content (%)	1.1	1.3	0.3	0.2
Organic matter content (%) ¹⁾	1.9	2.2	0.5	0.3
pH	6.9	6.3	5.9	5.5
Soil microbial biomass (mg C/kg soil)	17.4			
Maximum water holding capacity (%)	38.4	36.4	34.3	30.3

¹⁾ Organic matter content (%) = Organic carbon content (%) x 1.72

The lysimeters were embedded in the earth, with surface and surroundings level. No groundwater level was simulated. The date of application was May 16, 1990. Lysimeter 1 was treated with 239 mg dichlobenil (2.39 kg a.s./ha), lysimeter 2 with 346 mg (3.46 kg a.s./ha) and lysimeter 3 with 711 mg (7.11 kg a.s./ha). The amount of radioactivity applied was 240 MBq, 348 MBq and 1409 MBq for lysimeters 1, 2 and 3, respectively. The application suspension was applied by means of a special spraying nozzle. After application the soil surface was covered with 0.5 cm of soil, to prevent evaporation of dichlobenil. The lysimeters remained unplanted and any weed growth > 35 cm was cut and analysed. Weed contained negligible amounts of radioactivity ($\leq 0.5\%$).

The experiment lasted from May 1990 till May 1992. The average monthly air and soil temperature (at 10, 30 and 60 cm depth) and monthly precipitations were recorded and reported. The average year temperature of the soil at 10 cm depth and the yearly precipitation are given in Table 8.2.2.1b.

Table 8.2.2.1b Average year temperature of the soil at 10 cm depth, yearly precipitation and leachate per lysimeter

Period	Average soil temperature (10 cm) (°C)	Precipitation (mm)	Lysimeter 1 (L) (= mm)	Lysimeter 2 (L) (= mm)	Lysimeter 3 (L) (= mm)
Year 1 (05/90-04/91)	8.0	794.4	391.8	393.5	451.7
Year 2 (05/91/05/92)	7.4	917.2	510.9	514.8	588.8
Total year 1 + 2		1711.6	902.7	908.3	1040.5

The leachate from each lysimeter was collected 14-16 times per year at periodic intervals, with leachate volumes of about 20-50 L. The yearly amounts of leachate are given in Table 8.2.2.1b. Leachates were immediately analysed by LSC. Thereafter methanol was added to the samples (methanol/water = 65:35) and these were stored at -20°C. Before analysis the leachate was filtered. 2,6-Dichlorobenzamide (BAM) was determined directly in the filtered leachate by HPLC with UV detection and LSC of the eluting fractions. Dichlobenil and 2,6-dichlorobenzoic acid were determined in the ethyl acetate extract of selected leachates (after removal of methanol). Resulting extracts were analysed by 2-dimensional TLC.

Dichlobenil was also determined after enrichment on C-18 cartridges. The LOQ of the latter method was 0.047 µg/L and the limit of detection 0.017 µg/L.

Eleven months after the application samples from the 0-15 cm topsoil layer were taken from 9 sampling points per lysimeter. Total radioactivity was determined by combustion/LSC. Samples were analysed by a soil pre-column extraction/HPLC combination. At the end of the study the soil monoliths were cut into 10 cm horizontal segments, samples were taken from each segment and these were analysed by combustion/LSC and analysed by HPLC after extraction with methanol as described above.

Results

Dichlobenil was only detected in one leachate of lysimeter 3 in a concentration of 0.040 µg/L, which is below the LOQ (0.047 µg/L). The metabolite BAM occurred in all leachates of all three lysimeters. The identity of BAM was confirmed by 2-dimensional radio-TLC. The concentration of BAM in the leachates of the lysimeters is given in Table 8.2.2.1c.

Maximum concentrations of BAM were found about 8-17 months after application. The average concentration of BAM measured over 2 years was 14.2 µg/L, 51.7 µg/L and 80.4 µg/L for lysimeter 1, 2 and 3, respectively. Unidentified polar radioactive material was found in the leachates. This material was not identical with 2,6-dichlorobenzoic acid. The unidentified material was much more polar than dichlobenil, BAM and 2,6-dichlorobenzoic acid. The total average concentration of unknown material in the leachate over 2 years was (expressed as dichlobenil equivalents) 0.52 µg/L, 1.02 µg/L and 0.83 µg/L in lysimeter 1, 2 and 3, respectively. Elution occurred mainly about 6 to 7 month after application.

In an additional study (reported separately) the unidentified very polar material was further analysed by radio-TLC and HPLC on a more polar column. It was found that this material consisted of several compounds. Up to 5 different zones were detected on TLC plates. The pattern of the unknown zones varied with the lysimeter. The concentrations of the several zones found in the leachates of November 20, 1990 (one of the leachates that contained high amounts of unidentified material) are given in Table 8.2.2.1d.

Table 8.2.2.1c Concentrations of BAM ($\mu\text{g/L}$) in the leachates of the lysimeters

Date of sampling	Lysimeter 1	Lysimeter 2	Lysimeter 3
29/10/90	- ¹⁾	-	1.32
02/11/90	-	-	6.59
16/11/90	n.f. ²⁾	0.48	23.45
20/11/90	n.f.	6.13	57.57
29/11/90	n.f.	21.30	105.56
28/12/90	0.52	-	-
30/12/90	-	39.49	134.34
02/01/91	3.85	112.20	146.19
04/01/91	8.72	104.77	159.43
09/01/91	14.10	87.65	172.58
13/01/91	18.81	126.26	175.00
12/03/91	21.04	120.20	165.55
24/03/91	22.22	124.84	157.06
21/06/91	23.43	92.40	107.89
18/10/91	24.93	75.68	102.32
07/11/91	23.32	89.86	95.32
11/11/91	22.77	57.05	70.71
21/11/91	26.44	47.93	71.11
20/12/91	21.10	54.15	50.91
23/12/91	14.11	29.45	86.79
25/12/91	9.66	32.44	72.25
06/01/92	16.33	35.91	57.15
17/01/92	18.26	36.31	62.70
14/02/92	14.51	48.29	65.14
21/02/92	18.88	43.05	67.32
13/03/92	18.21	45.19	63.73
19/03/92	19.09	51.53	54.13
03/04/92	22.19	39.24	46.77
11/05/92	19.40	36.59	39.85
Average 1 st year	7.47	54.6	94.1
Average 2 nd year	19.3	49.5	69.9
Average both years	14.2	51.7	80.4

¹⁾ - : not sampled; ²⁾ n.f. = not found

Table 8.2.2.1d Concentrations of the several zones of unidentified material found in the leachates of November 20, 1990

	Concentration ($\mu\text{g/L}$, dichlobenil equivalents)		
	Lysimeter 1	Lysimeter 2	Lysimeter 3
Zone 1	0.76	not found	not found
Zone 2	0.03	1.93	1.21
Zone 3	0.20	1.64	0.82
Zone 4	0.50	0.33	not found
Zone 5	0.2	not found	not found

Analysis of soil taken after 11 months from the 0-15 cm topsoil revealed that a fraction of about 8-9% of the dichlobenil applied was recovered from the soil. The metabolite BAM was detected in amounts of ca. 1% of a.r. Table 8.2.2.1e gives a review of the recovered radioactive compounds.

Table 8.2.2.1e Review of the recovered radioactive compounds detected in 0-15 cm topsoil after 11 months

Lysimeter	dichlobenil (% a.r.)	BAM (% a.r.)	Non-extractable (% a.r.)	Total (% a.r.)
1	9.32	1.12	10.29	20.7
2	7.60	1.28	6.78	15.7
3	8.95	1.23	5.84	16.0

At the end of the experiment (after 2 years) the segmented lysimeters were analysed. Most of the total radioactivity situated in the lysimeters was in the top 10 cm. Dichlobenil was exclusively present in the top 30 cm. BAM was found till a depth of 50 cm. The distribution in the soil profile of the three lysimeters is given in Table 8.2.2.1f. The total recovery is also given in this Table.

Table 8.2.2.1f Distribution of radioactivity in the soil profile of the lysimeters and total recovery (in %)

Segment (cm)	Lysimeter 1				Lysimeter 2				Lysimeter 3			
	Dichlo-benil	BAM	Non-extract ¹	Total ²	Dichlo-benil	BAM	Non-extract ¹	Total ²	dichlo-benil	BAM	Non-extract ¹	Total ²
0-10	5.85	0.47	6.09	21.0	3.36	0.22	4.7	10.7	2.20	0.18	2.47	6.9
10-20	0.35	0.47	0.95	2.4	2.38	0.41	1.8	5.0	1.09	0.37	0.91	2.3
20-30	<0.20	0.57	0.42	1.4	0.52	0.36	0.78	2.2	<0.20	0.25	0.16	0.81
30-40	<0.20	0.41	0.26	0.95	<0.20	0.60	0.51	1.2	<0.20	<0.20	0.14	0.39
40-50	<0.20	0.30	0.17	0.59	<0.20	0.23	0.15	0.89	<0.20	<0.20	0.06	0.25
50-60	<0.20	<0.20	0.12	0.14	<0.20	<0.20	0.10	0.55	<0.20	<0.20	0.09	0.14
60-70	<0.20	<0.20	0.06	0.26	<0.20	<0.20	0.04	0.23	<0.20	<0.20	0.03	0.13
70-80	<0.20	<0.20	0.06	0.27	<0.20	<0.20	0.03	0.17	<0.20	<0.20	0.02	0.09
80-90	<0.20	<0.20	0.05	0.33	<0.20	<0.20	0.02	0.12	<0.20	<0.20	0.01	0.08
90-100	<0.20	<0.20	0.05	0.34	<0.20	<0.20	0.02	0.11	<0.20	<0.20	< 0.01	0.07
100-110	<0.20	0.21	0.03	0.40	<0.20	<0.20	0.01	0.18	<0.20	<0.20	< 0.01	0.10
110-120	-	-	-	-	<0.20	0.24	0.03	0.24	<0.20	<0.20	0.02	0.17
Total soil	6.20	2.43	8.26	28.1	6.26	2.06	8.19	21.7	3.29	0.80	3.91	11.5
Leachate				5.9				14.3				12.2
Weeds				0.44				0.51				0.15
Total				34.4				36.5				23.9

¹ Determined by combustion after extraction

² Determined by direct combustion of soil

From Table 8.2.2.1f it appears that after 2 years 24-36% of the applied radioactivity was recovered. When we take into account that almost (ca. 90%) of the radioactivity in the leachate is due to BAM, the formation of metabolite BAM (soil + leachate) was about 8-15% after 2 years. The missing amount in the balance is supposed to have escaped from the lysimeters by volatilisation and/or mineralisation.

Remarks

The occurrence of unidentified, very polar radioactive material is often found in lysimeter studies. It probably represents ¹⁴C-labelled residues associated with humic material or ¹⁴C completely mineralized and incorporated into new molecules. In view of the data presented it is not probable that the average concentration of any single compound will exceed an average of 0.4 µg/L (dichlobenil equivalents).

Acceptability of the study

The study is considered acceptable.

Conclusion

Dichlobenil was not mobile in lysimeters with application rates up to 7.1 kg/ha. Dichlobenil remained in the top 30 cm of the soil profile and was not found in the leachate ($< 0.047 \mu\text{g/L}$). Its metabolite 2,6-dichlorobenzamide (BAM) was mobile and was found in deeper soil layers as well as in all samples of leachate up to 2 years after application. The average concentration in the leachate of the 7.1 kg/ha lysimeter over the 2 years experimental period was $80 \mu\text{g/L}$. No other substances were identified in the leachate. Small amounts of very polar unidentified material consisting of several compounds were detected. The average concentrations were probably $< 0.4 \mu\text{g/L}$ (dichlobenil equivalents) per compound.

Dichlobenil was degraded in the lysimeter soil. After 2 years 3-6% of the applied radioactivity was present as dichlobenil in the soil profile. Four to 8% of the applied radioactivity was non-extractable residue. The formation of metabolite BAM (soil+ leachate) was about 8-15% after 2 years.

B.8.2.2.2 Characterisation of leachate (IIA 7.1.3.3/01B)

Characteristics of the study

Reference	: Traub-Eberhard (1994)	GLP	: yes
Year of execution	: 1994	Acceptable	: yes
Guideline	: not applicable		
Test substance	: dichlobenil lysimeter leachate		

Study design

The unknown radioactive material detected in lysimeter eluates (see Traub-Eberhard, 1992) of a lysimeter study with [^{14}C]dichlobenil was further investigated. It was checked whether the eluate after 1 – 2 years storage still contained the unknown material. This was the case. The leachates were subjected to HPLC on a polar phase and to 2-dimensional radio-TLC after removal of methanol under vacuum and pre-concentration by dry-freezing.

Results

It was found that this material consisted of several compounds. Up to five different zones were detected on TLC plates. The pattern of the unknown zones varied with the lysimeter. The concentrations of the several zones found in the leachates of November 20, 1990 (one of the leachates that contained high amounts of unidentified material) are given in Table 8.2.2.2a.

Table 8.2.2.2a Concentrations of the several zones of unidentified material found in the leachates of November 20, 1990.

	Concentration (µg/L, dichlobenil equivalents)		
	Lysimeter 1	Lysimeter 2	Lysimeter 3
Zone 1	0.76	not found	not found
Zone 2	0.03	1.93	1.21
Zone 3	0.20	1.64	0.82
Zone 4	0.50	0.33	not found
Zone 5	0.2	not found	not found

Remarks

The results of this experiment are already summarised in Traub-Eberard, 1992. The occurrence of unidentified, very polar radioactive material is often found in lysimeter studies. It probably represents ^{14}C -labeled residues associated with humic material or ^{14}C completely mineralised and incorporated into new molecules. In view of the data presented it is not probable that the average concentration of any single compound will exceed an average of 0.4 µg/L (dichlobenil equivalents).

Acceptability of the study

The study is considered acceptable.

Conclusion

The unknown unidentified, very polar material in lysimeter leachates (see Traub-Eberhard, 1992) of a lysimeter study with [^{14}C]dichlobenil consisted of up to five different compounds. In view of the data presented it is not probable that the average concentration of any single compound will exceed an average of 0.4 µg/L (dichlobenil equivalents).

B.8.2.3 Aged residue column leaching

B.8.2.3.1 Aged residue column leaching of the active substance in sandy loam soil (IIA 7.1.3.2/01)

Characteristics of the study

Reference	Walstra <i>et al.</i> (1989)	Chemical purity of dichlobenil	: 98.3%
Year of execution	: 1988 - 1989	Radiochemical purity	: 100.1%
Guideline	: FIFRA 163-1	Specific activity of dichlobenil	: 17.1 mCi/g
GLP	: yes	Mobility in soil	: majority remains in the upper 15 cm
Test substance	: ^{14}C -dichlobenil (batch no. AOI87H05A; white powder), aged in soil	Acceptable	: yes

Study design

The mobility of ^{14}C -dichlobenil, aged in sandy loam soil for 31 d under aerobic conditions, was investigated. The aged soil was added to columns, filled with coarse sand and sandy loam and leached with water. The soil characteristics are given in Table B.8.2.3.1a.

Table B.8.2.3.1a. Characterisation of the studied soil

Soil type ¹	sandy loam
Origin	Udenhout, The Netherlands
pH (KCl)	5.3
% organic matter	1.5
CEC in meq/100 g dw	5.3
% CaCO_3	0.1
% clay	4.8
% silt	20.2
% sand	75.0
% water content (0.33 bar)	12.3

¹ The soil was sieved through a 1.7 mm sieve before use.

The columns were leached with 2 L water during 12 d, corresponding to 52 cm of rain. The radioactivity in liquid samples was measured and the amount of dichlobenil and possible degradation products was determined by HPLC/LSC analysis. The following test design was applied:

Aging of [^{14}C]dichlobenil

duration of the test	: 31 d
temperature	: $24 \pm 2^\circ\text{C}$
soil water content	: ca. 9.2% (equal to 75% of water content at 0.33 bar)
type of test vessel and content	: closed biometer flasks; 40 g dw soil; 25 mL 0.3 M KOH solution was added to flasks used for aging of the a.s.
number of replicate test vessels	: 3 for determination of extraction efficiency and 5 for aging
dosing of test substance	: from a solution in methanol/water 1:4 (v/v)
nominal test substance concentration	: 2.4 mg a.s./L
chemical analysis	: HPLC/LSC
sampling times	: $t = 31$ d

Column leaching test

duration of the test	: 12 d
type of test vessel and content	: column made up of stainless steel segments (58 cm long x 7 cm internal diameter) with a spout with a polyethylene tap; small layer of untreated soil on top of layers of 40 g soil with aged [^{14}C]dichlobenil, moistened untreated soil and moistened coarse sand (0.8 – 1.3 mm)
number of replicate test vessels	: 2
dosing of test substance	: layer of soil incubated aerobically (see aging of [^{14}C]dichlobenil)
mean measured test substance	: 96.5 mg/column

concentration	
leaching water	: deionised water
leaching rate	: 10 mL/h (in total 2 L over 12 d, corresponding to 52 cm of rain)
chemical analysis	: HPLC/LSC
sampling times	: Leachate: on working days
	column segments: at test termination (t = 12 d)

Results

The mean total radioactivity recovery was 99.2% at initiation of the aging procedure and 95.9% after aging. 19.5% of the recovered radioactivity was found in the gas phase, 70.5% was extractable, and 5.9% was non-extractable. The aged soil used in the column leaching study contained 73.8 mg of [^{14}C]dichlobenil equivalents: 63.6 mg [^{14}C]dichlobenil, 2.2 mg [^{14}C]2,6-dichlorobenzamide, and 5.7 mg bound residue.

During the leaching period of 12 d, 2.18 and 2.27 mg of [^{14}C]dichlobenil equivalents leached through column 1 and 2 (3.0 and 3.1% of the initially applied radioactivity), respectively. The total radioactivity recovery was 93% for column 1 and 73% for column 2. The low recovery in column 2 was explained by the loss of two segments due to breakage. Radioactivity was mainly found in the upper 15 cm of the columns and consisted primarily of [^{14}C]dichlobenil (87 – 92%). A smaller amount was associated with the metabolite [^{14}C]2,6-dichlorobenzamide (< 1.8 – 3.7%). The results of the leaching study are given in Table B.8.2.3.1b. After a 12-d leaching period, [^{14}C]dichlobenil thus did not penetrate further than 15 cm in a sandy loam soil and only 3% of the radioactivity leached through the column.

Table B.8.2.3.1b. Distribution and recovery of radioactivity in two sandy loam columns loaded with sandy loam aerobically aged with [^{14}C]dichlobenil for 31 d. (The total amount of radioactivity brought onto each column was 73.8 mg [^{14}C]dichlobenil equivalents.)

		Radioactivity in soil (mg)	
Depth of soil column (cm)	dw soil (g)	extractable	non-extractable
<i>Column 1</i>			
1	99.6	6.83	1.1
3	92.8	10.71	1.4
5	94.4	10.82	0.8
7	100.8	13.97	1.1
9	93.2	11.82	0.8
11	98.8	6.50	< 0.7
13	76.8	0.58	< 0.5
15	94.7	< 0.24	< 0.6
17	99.6	< 0.24	< 0.7
19	85.9	< 0.08	< 0.6
21	104.9	< 0.08	< 0.7
23	105.8	< 0.08	< 0.7
25	n.d.	n.d.	n.d.
27	79.8	< 0.08	< 0.6
29	103.5	< 0.08	< 0.7
31	109.0	< 0.08	< 0.8
effluent	1974 ¹	2.18	-
<i>Column 2</i>			
1	110.9	6.63	1.4
3	n.d.	n.d.	n.d.
5	95.3	12.43	0.9
7	100.4	11.00	0.8
9	90.4	9.65	< 0.7
11	112.9	7.09	< 0.8
13	91.1	1.97	< 0.6
15	n.d.	n.d.	n.d.
17	94.1	< 0.24	< 0.7
19	89.1	< 0.08	< 0.6
21	99.0	< 0.08	< 0.6
23	98.9	< 0.08	< 0.7
25	83.2	< 0.08	< 0.7
27	85.7	< 0.08	< 0.6
29	78.7	< 0.08	< 0.6
31	110.2	< 0.08	< 0.7
effluent	1918 ¹	2.27	-

n.d. Not determined.

¹ weight of effluent in g

Acceptability of the test

The test is considered acceptable.

Conclusions

[^{14}C]Dichlobenil aged during 31 d did not penetrate further than 15 cm in sandy loam. A small amount of the applied radioactivity (3%) appeared in the leachate. 2,6-dichlorobenzamide was the only metabolite found in the columns.

B.8.3 PREDICTED ENVIRONMENTAL CONCENTRATIONS IN SOIL (PEC_s)

Authorisation is requested for the broadcast spreading of granules of dichlobenil involving a single application at a rate of 2.03 – 5.4 kg a.s./ha in spring.

Actual PEC_s and time weighted average (TWA) PEC values were calculated under the following assumptions: it is assumed that the complete dosage of dichlobenil is released into the soil during pre-emergence treatment of vines and non-crop situations. There is no interception by crops. The PEC values were calculated assuming an even distribution to a depth of 5 cm in soil with a bulk density of 1.5 g/cm³. PEC values were based on a worst-case DT₅₀ (field) value of 72 days.

One major metabolite (> 10%), 2,6-dichlorobenzamide (BAM), was detected in soil. The worst case field DT₅₀ value of 315.2 days (first order, derived from fluopicolide DAR) is used for the PEC calculations of 2,6-dichlorobenzamide (BAM). It is assumed that the metabolite is formed at a maximum of 69.41% of the applied dose, leading to an application rate of 4140 g/ha (corrected for relative molecular weight).

Under the above assumptions, application of dichlobenil will lead to the PEC_s values as given in Table B.8.3a (parent compound, single application) and B.8.3b (metabolite, single application).

Table B.8.3a Actual and TWA PEC_s (mg/kg) of dichlobenil following application on vines and non-crops during pre-emergence in the field, at a maximum rate of 5.4 kg a.s./ha

Day after application	Broadcast spreading of granules in the field (5.4 kg a.s./ha)	
	Actual PEC _s (mg a.s./kg)	TWA PEC _s (mg a.s./kg)
0	7.200	-
1	7.131	7.165
2	7.063	7.131
4	6.928	7.063
7	6.731	6.963
14	6.292	6.736
21	5.882	6.519
28	5.499	6.311
50	4.449	5.715
100	2.749	4.623

Table B.8.3b Actual and TWA PEC_s (mg/kg) of the soil metabolite 2,6-dichlorobenzamide following single application on vines and non-crops during pre-emergence in the field, at a maximum rate of 5.4 kg a.s./ha (this complies with 4.140 kg 2,6-dichlorobenzamide/ha¹)

Day after application	Broadcast spreading of granules in the field (5.4 kg a.s./ha)	
	Actual PEC _s (mg a.s./kg)	TWA PEC _s (mg a.s./kg)
0	5.520	
1	5.508	5.514
2	5.496	5.508
4	5.472	5.496
7	5.436	5.478
14	5.353	5.436
21	5.190	5.353
28	4.945	5.227
50	4.430	4.955
100	5.520	5.514

1 Calculated using: $\text{concentration}_{\text{metabolite}} = \text{application rate} \cdot \frac{\% \text{ formation}}{100\%} \cdot \frac{\text{molar mass}_{\text{metabolite}}}{\text{molar mass}_{\text{parent}}}$.

Since the maximum DT₅₀ of BAM is 315.2 days, the DT₉₀ is clearly larger than one year. Hence, a plateau concentration has to be calculated, according to:

PEC_{acc} = PEC_{soil, ini} / k * i, with i the interval between applications (365 days) and k equaling ln2/DT₅₀. This yields a plateau PEC of **6.88** mg/kg soil.

B.8.4 FATE AND BEHAVIOUR IN WATER

B.8.4.1 Hydrolysis studies

B.8.4.1.1 Hydrolysis of the active substance (IIA 2.9.1/01)

Characteristics of the study

Reference	: Buisman (1983 and 2005) ¹	purity	: > 99.5%
Year of execution	: 1982 en 1983	Result	: DT ₅₀ > 150 days
Guideline	: BBA merckblatt no. 55, 1982 (with deviations)		
GLP	: Yes	Metabolites	: no part of the study
Test substance	: dichlobenil; no further information available	Acceptable	: yes

1 in 2005 an addendum report has been prepared to provide additional information (Van Oevelen (2005))

Study design

The purpose of the study was to investigate the hydrolysis rate constants, DT₅₀ values of dichlobenil in buffer solutions and the formation and identity of possible metabolites. The hydrolysis experiment was carried out to identify hydrolysis products at three pH levels; in addition, the solubility of the test substance was determined using a column elution method. The following study design was applied for the hydrolysis test:

duration of the test	: 150 d at 22 ± 1°C
temperature	: 22 ± 1°C
light conditions	: darkness
type of buffers	: pH 5: 0.015 M phthalate buffer pH 7: 0.05 M phosphate buffer pH 9: 0.005 M boric acid buffer
pH measurements	: not reported, except on measurement on 4 February 1983 (reported as raw data in the addendum report)
type of test vessel and content	: closed non-sterile all glass vessels
number of replicate test vessels	: Not indicated
dosing of test substance	: Not indicated
nominal test substance concentration	: 7 – 9 µg/mL of buffer
chemical analysis	: extraction with petroleum ether; determination of dichlobenil in organic layer, using a GC method with Ni electron capture detector
sampling times	: after 16, 30, 60, 90 and 150 days

Results

Only the pH measurement on 4 February 1983 was made available (time of the test is not clear); the result is given in Table B.8.4.1.1a. The results of the analysis for the stability of dichlobenil in the buffered solutions are given in Table B.8.4.1.1b. The coefficient of variation for the duplicate analysis equals 1.6%. Decomposition was significant for all three pH levels. The DT₅₀ value at all pH levels was > 150 days. Any analysis for metabolites is not indicated.

Table B.8.4.1.1a Results of pH measurement in the hydrolysis test.

Intended value	5	7	9
Measured value ¹	6.84/6.81 ²	8.26/8.21 ²	8.18/2.50

1 duplicate measurements

2 turbidity observed

Table B.8.4.1.1b Results of chemical analysis of dichlobenil in buffered solutions

Analysis time in test days	Content of dichlobenil (mean of duplicate tests)					
	pH 5		pH 7		pH 9	
	µg/mL	% of t = 0	µg/mL	% of t = 0	µg/mL	% of t = 0
0	7.24		8.90		8.93	
16	7.16	98.9	8.55	96.1	8.68	97.2
30	7.14	98.6	8.64 ¹	97.1	8.65	96.9
60	7.04	97.2	8.57	96.3	8.55	95.7
90	7.20	99.4	8.58	96.4	8.30	92.9
150	6.83	94.3	8.24	92.6	8.18 ¹	91.6

1 based on one value, the other was regarded as an outlier

Acceptability of the test

With respect to the acceptability of the test, the following must be stated:

- Measurements of pH values are given only for one occasion in the raw data of the report addendum (two measurements for each buffer). At pH 5 the pH differs considerably from the intended value; at pH 9, one pH level is unacceptable (2.5 instead of ca. 9). Turbidity was observed in the buffered solutions of pH 5 and pH 7. It is therefore considered by RMS that the result of the study, a negligible potential for hydrolysis, is only convincingly shown for environments with a pH of 6.8 to 8.3. As this is the environmentally relevant range, the results are considered relevant.
- Identification of metabolites was no part of the study.
- The test was carried out in non-sterile glass vessels and not in sterile vessels, as necessary to prevent microbial degradation in an abiotic test and required according to the guidelines. As dichlobenil was almost completely stable in the present test, microbial degradation can be excluded, although the test did not follow one of the most important requirements.

Conclusion

The test does not meet the requirements with respect to the method and reliable reporting of raw data. It is very likely that the test substance is stable in aqueous solutions, however. Although the test deviates considerably from current guidelines, the results are considered environmentally relevant and can be used in further assessment.

B.8.4.1.2 Hydrolysis of the metabolite [^{14}C]-2,6-dichlorobenzamide (IIA 7.2.1.1/01)

Characteristics of the study

Reference	: Jacob and Fitzmaurice (2003)	Radiochemical purity	: 99.0%
Year of execution	: 2003	Specific activity	: 9.51 MBq/mg
Guideline	: EPA 161-1	Result	: the test substance is stable under the conditions of the test
GLP	: yes	Metabolites	: < 1.2% unidentified metabolites
Test substance	: [^{14}C]-2,6-dichlorobenzamide; lot no. SEL/1169; white solid	Acceptable	: yes

Study design

The purpose of the study was to investigate the hydrolysis rate constants, DT_{50} values of [^{14}C]-2,6-dichlorobenzamide in buffer solutions and the formation and identity of possible metabolites. Two experiments were carried out. The first experiment was a preliminary experiment and carried out to identify hydrolysis products at pH 4, 7, and 9 at a temperature of 50°C. The test set up of the final experiment was based on the first experiment. It was carried out at pH 5, 7, and 9 at a temperature of 25°C. The following study design was applied:

duration of the test	: 5 d at 50 30 d at 25°C 30 d at 50°C
temperatures	: 50 ± 2°C (preliminary experiment) and 25 ± 1 (final experiment)
light conditions	: darkness
type of buffers	: pH 4: 0.05 M citrate buffer pH 5: 0.015 M acetate buffer pH 7: 0.05 M phosphate buffer pH 9: 0.005 M disodium tetra borate buffer
type of test vessel and content	: 50-mL sterile, cylindrical, stoppered glass vessels
number of replicate test vessels	: 6 (50°C) and 14 (25°C)
dosing of test substance	: dissolved in deionised water and buffer solution
nominal test substance concentration	: 1.75 mg metabolite/L
chemical analysis	: HPLC, LSC, and LC-MS
sampling times	: at 50°C after 0, 2.4 h, and 5 d; at 25°C after 0, 5, 9, 14, 20, 26, and 30 d; duplicate samples for all time points, except for t = 0 for which one sample was taken

Results

Recoveries of the applied radioactivity were 97.8 – 101.6% at 50°C (preliminary test) and

95.9 - 100.2% at 25°C (final test). These recoveries show a complete ^{14}C mass balance without dissipation of radioactivity from the solutions, either by volatilisation or by adsorption onto the test vessels. The pH values in the four buffer solutions were 4.05, 5.05, 7.01, and 9.04 after sterilisation.

No significant degradation occurred in the preliminary experiment at 50°C. Two unidentified components were detected, but the total concentration of these components never exceeded 1.0% of the applied radioactivity. In the final experiment at 25°C, three unidentified components were detected, of which two were present at test initiation and one appeared after 14 d of incubation. No significant degradation was observed as the total concentration of these three components never exceeded 1.2% of the applied radioactivity. Therefore, it was concluded that, under the conditions of the test, [^{14}C]-2,6-dichlorobenzamide is hydrolytically stable at pH 4, 7, and 9 at 50°C for 5 d and at pH 5, 7, and 9 at 25°C for 30 d.

Acceptability of the test

The test is considered acceptable.

Conclusion

At 50°C the metabolite 2,6-dichlorobenzamide is hydrolytically stable at pH 4, 7, and 9 for 5 d and at pH 5, 7, and 9 at 25°C for 30 d.

B.8.4.2 Photolytic degradation

B.8.4.2.1 Calculation of the theoretical lifetime of the active substance in upper surface water (IIA 2.9.3/01 and IIA 2.9.3/02)

Characteristics of the study

Reference	: Harned (2003a); Harned (2003b)	Calculated first-order rate constant k	: $4.53\text{E-}05 \text{ sec}^{-1}$
Year of execution	: not indicated	Theoretical lifetime	: 6.24 h
Guideline	: no	Calculated DT_{50}	: 4.25 h
GLP	: not applicable	Acceptable	: yes
Test substance	: dichlobenil		

Study design

The theoretical lifetime (τ) of dichlobenil in upper surface water was calculated using the first-order rate constant (k) for direct phototransformation of dichlobenil in the surface layer of natural water.

This rate constant was calculated from the quantum yield (Φ , $1.5\text{E-}03 \text{ mole/Einstein}$), the UV/visible absorption spectrum of dichlobenil in aqueous solution (ca. 290 – 320 nm), and the solar light intensity available in the spectral range which coincides with the light absorption spectrum of

dichlobenil (k_a , 3.02E-02 Einstein/mole/sec). The quantum yield was calculated from the absorption spectrum, the experimentally determined first-order aqueous photodegradation rate constant (see IIA 2.9.2/01 and IIA 2.9.2), and the wavelength distribution and intensity of the simulated sunlight to which the sample was exposed.

The following formulas were used to calculate the first-rate constant and the theoretical lifetime:

$$k = \phi \times k_a \quad \text{and} \quad \tau = 1/k$$

Results

The first-order rate constant (k) was 4.53E-05 sec⁻¹. From the rate constant, the theoretical lifetime (τ) was calculated to be 0.26 d (6.24 h). RMS calculated a DT₅₀ value of 4.25 h.

Acceptability of the test

The test is considered acceptable.

Conclusions

The calculated first-order rate constant, theoretical lifetime, and DT₅₀ for direct phototransformation of dichlobenil in the surface layer of natural water are 4.53E-05 sec⁻¹, 6.24 and 4.25 h, respectively.

B.8.4.2.2 Photolytic degradation of the active substance in water (IIA 2.9.2/01 and IIA 2.9.2/02)

Characteristics of the study

Reference	: Boelhouwers et al. (1989)	Radiochemical purity	: 99.3%
Year of execution	: 1989	Specific activity	: 0.99 mCi/g
Guideline	: EPA 161-2	DT ₅₀ (pH 7)	: 15.1 (artificial sunlight) 10.2 (natural sunlight)
GLP	: yes	Metabolites	
Test substance	: [¹⁴ C]dichlobenil; batch no. AOI87L04A; appearance not indicated	Acceptable	: yes
Chemical purity	: 98.3%		

Study design

The purpose of the study was to determine the decrease of [¹⁴C]dichlobenil in aqueous solution, when exposed to xenon light. A comparison of the xenon-light source and natural sunlight at 40° North latitude (Joustra and Groeneveld (1987), IIA 2.9.2/02) revealed that the light intensities of both sources are similar at wavelengths from 350 to 400 nm. Below 350 nm, xenon light has a higher intensity than sunlight and *vice versa* above 400 nm. In this study, 24 h irradiation with xenon light equals 0.5 d of natural sunlight at 40° North latitude. The following study design was applied:

duration of the test	: 21 d
temperature	: $25 \pm 1^\circ\text{C}$
light conditions	: 24 h light/d; Atlas Fade-Ometer equipped with a xenon arc lamp with quartz inner and borosilicate outer filter (340 nm);
type of buffer	: sterile water buffered at pH 7
type of test vessel and content	: closed cylindrical Pyrex ampoules; 25 mL test solution
number of replicate test vessels	: 48 exposed to light and 10 dark controls
dosing of test substance	: stock solution in acetonitrile
nominal test substance concentration	: 5.749 mg a.s./L
determination of applied radioactivity, quantitative chemical analysis and identification photoproducts	: LSC, HPLC, MS, ^1H NMR, and IR
sampling times	: 0, 1, 3, 7, 15, and 21 d; 4 irradiated and 2 dark control vessels were analysed

Results

Recovery of the applied radioactivity in irradiated and dark control samples was 95 and 99%, respectively. These recoveries show a complete ^{14}C -mass balance, the pH remained constant at 7.0 during the study.

^{14}C -Dichlobenil was stable in the dark controls. However, after 15 and 21 days of continuous irradiation, the dichlobenil concentration had decreased to 51.7 and 39.8% of the initial concentration, respectively. The results are summarised in Table B.8.4.2.2a. The half-life of ^{14}C -dichlobenil was calculated to be 15.1 d, assuming first-order kinetics. This half-life corresponds to 10.2 d of natural sunlight at 40° North latitude. RMS recalculated the DT_{50} with TableCurve 2D version 4 and found similar results.

One of the degradation products found accounted for 14 and 17% of the applied radioactivity after 15 and 21 d, respectively. This compound was identified as 4-chloro-2(3H)benzoxazolone. Six polar compounds (acetamide, acetic acid, ethanol, 1,2-propanediol, 2-butanone and phenol) were formed as well, together representing 16 and 23% of the applied radioactivity, after 15 and 21 d, respectively. The two major components of this group were identified as acetamide and acetic acid. RMS recalculated the DT_{50} values and found similar results.

Table B.8.4.2.2a DT_{50} values for ^{14}C -dichlobenil as calculated by the authors and RMS

exposure	DT_{50} value (d) at 25°C
xenon light	15.1
natural sunlight 40° North ¹	10.2

¹ Calculated: 24 h irradiation with the xenon-light source used equals 0.675 d of natural sunlight at 40° North latitude.

Acceptability of the test

The test is considered acceptable.

Conclusions

The DT₅₀ of [¹⁴C]-dichlobenil in artificial sunlight was 15.1 d, which is equal to 10.2 d in natural sunlight. The degradation product 4-chloro-2(3H)benzoxazolone accounted for 14 and 17% of the applied radioactivity after 15 and 21 d, respectively; it must therefore be considered as a major metabolite.

B.8.4.2.3 Photolytic degradation of the metabolite [¹⁴C]-2,6-dichlorobenzamide in water (IIA 7.2.1.2/01 and 2.9.2/02)

Characteristics of the study

Reference	: Reynolds (2000)	Radiochemical purity	: ≥ 95% (radiolabelled metabolite)
Year of execution	: 2000	Specific activity	: 6.86 mCi/mmol
Guideline	: EPA 161-2	DT ₅₀ (pH 5)	: the test substance is stable under the conditions of the test
GLP	: yes	Acceptable	: yes
Test substance	: unlabeled 2,6-dichlorobenzamide; lot no. ARS-81C25N; purity 99.7%; appearance not indicated radiolabelled [¹⁴ C]-2,6-dichlorobenzamide; lot no. DUPH016; appearance not indicated		

Study design

The purpose of the study was to determine the photochemical reaction of the metabolite 2,6-dichlorobenzamide in water in sterilised water at pH of 5 and to assess the rates (half life), nature, and initial chromatographic profiling of degradation products.

duration of the test	: 31 d
temperature	: 25 – 26°C
light conditions	: 12 h light/12 h dark; xenon arc lamp with UV filter (λ ≥ 290 nm)
type of buffer	: pH 5: 0.01 M acetate
type of test vessel and content	: tubes sealed with Teflon®-lined caps and Teflon® tape, placed in two-compartment, stainless steel chambers with a flat Pyrex® glass window lid and coolant insulation; ca. 40 mL
number of replicate test vessels	: 16 exposed to light and 14 dark controls
dosing of test substance	:
nominal test substance concentration	:
determination of applied radioactivity, quantitative chemical analysis and identification photoproducts	: LSC, HPLC, and LC/MS
sampling times	: 0, 3, 7, 14, 21, and 31 d; duplicate samples for all time points

Results

Recovery of the applied radioactivity in irradiated and dark control samples ranged from 99.0 to 102%.

These recoveries show a complete ¹⁴C-mass balance without dissipation of radioactivity from the

solutions, either by volatilisation or by adsorption onto the test vessels. The pH of the buffer solution was determined after 0, 14, and 31 d and ranged from 5.03 to 5.04.

Throughout the study, the total amount of radioactivity that was identified as the parent compound ranged from 98.8 – 103% and from 98.7 – 104% of the total applied radioactivity in irradiated and dark control samples, respectively. The results show that, under the conditions of the test, [¹⁴C]-2,6-dichlorobenzamide is photolytically stable at pH 5 and 25°C for 31 d.

Acceptability of the test

The test is considered acceptable.

Conclusions

[¹⁴C]-2,6-dichlorobenzamide is photolytically stable at pH 5 and 25°C for 31 d.

B.8.4.3 Ready biodegradability

B.8.4.3.1 Ready biodegradability of the active substance in a manometric respirometry test (IIA 7.2.1.3.1/01)

Characteristics of the study

Reference	: Mead (2002)	Test substance	: dichlobenil; batch no. 42763011/MI-0246; white solid
Year of execution	: 2002	Purity	: not indicated
Guideline	: OECD 301F; EEC Commission Directive 92/69/EEC; OPPTS 835.3110	Test duration and	: 28 d; static
GLP	: yes	Degradation	: the test substance is stable under the conditions of the test
		Acceptable	: yes

Study design

In an initial experiment, 100 mg a.s./L was added to sewage sludge micro-organisms. No biodegradation was observed in the toxicity control (test material + reference substance) after 14 d of incubation. However, the standard material gave sufficient (68%) biodegradation after 14 days. Therefore, the final test was performed with a reduced test substance concentration of 50 mg a.s./L. The following test set up was applied:

species	: mixed population of micro-organisms (activated sludge) from a waste water treatment plant treating predominantly domestic sewage
inoculum	: 5 mL
test medium	: according to the guidelines
pre-treatment	: sludge was coarsely sieved and aerated in a temperature-controlled room at 21 ± 1°C

exposure temperature	: 21 ± 0.7°C
photoperiod	: 24 h/d dark
type of test vessel and content	: sample flasks sealed by a sensor head/CO ₂ trap immersed in a temperature-controlled water bath
number of replicate test vessels	: 3 (test substance), 4 (control with inoculum), 3 (reference compound), and 2 (reference compound with test substance (toxicity control))
concentration activated sludge	: 2.5 mL of inoculum/L test medium
aeration	: no
dosing	: directly dispersed in culture medium
exposure concentrations	: 0 (control) and 50 mg a.s./L
type of measurements	: oxygen consumption (BOD) at t = 7, 14 and 21 days, pH before the start and at the end of the test DOC at the start and end of the test, temperature daily
chemical analysis	: no
reference compound	: aniline

Results

The pH varied between 8.2 and 8.4. The control BOD was less than 60 mg O₂ after 28 d. The difference between replicate BOD values at the end of the test was less than 20%. The reference compound aniline was degraded by 66% after 14 d, which confirms the suitability of the inoculum and test conditions. The toxic control (aniline + test substance) attained 55% degradation after 28 d, thereby confirming that the test substance was not toxic to the sewage treatment plant micro-organisms.

After 28 d, BOD values were significantly lower in vessels with test substance than in control vessels. No degradation of the test substance was observed and therefore, dichlobenil cannot be considered to be readily biodegradable under the conditions of the test.

Acceptability of the test

The test substance contains a single nitrogen atom, but nitrate and nitrite were not analysed. The authors state that the method of analysis is not accurate enough to detect effects due to the small amount of nitrogen present. The test is considered acceptable.

Conclusions

Dichlobenil is not readily biodegradable in a manometric respiration test.

B.8.4.3.2 Ready biodegradability of the metabolite 2,6-dichlorobenzamide in a closed bottle test (IIA 7.2.1.3.1/02)

Characteristics of the study

Reference	: Van der Laan-Straathof and Philips-Van Loo (1996)	Purity	: > 99.5%
Year of execution	: 1996	Test duration and regime	: 28 d; static
Guideline	: OECD 301D; EEC C.4E	Degradation	: the test substance is stable under the conditions of the test
GLP	: yes	Acceptable	: yes
Test substance	: 2,6-dichlorobenzamide (BAM); batch no. ARS81C25N; white powder		

Study design

The following test set up was applied:

species	: mixed population of micro-organisms (activated sludge) from a waste water treatment plant treating predominantly domestic sewage
inoculum	: 2 mg dw/L test medium
test medium	: according to the guidelines, except that NH_4Cl was omitted to prevent nitrification and a two times higher concentration of $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$ was used
pre-treatment	: sludge (50 mg dw/L test medium) was aerated at $20 \pm 1^\circ\text{C}$ for one week, after which it was diluted to 2 mg dw/L
exposure temperature	: $19 - 21^\circ\text{C}$
photoperiod	: 24 h/d dark
type of test vessel and content	: 280-mL BOD bottles with glass stoppers, sealed with silicon paste
number of replicate test vessels	: 10 (test substance), 10 (control without inoculum), 10 (control with inoculum), 10 (reference compound)
concentration activated sludge	: 11.2 mL of inoculum/test vessel
dosing	: directly dispersed in culture medium
exposure concentrations	: 0 (control) and 2.0 mg metabolite/L
type of measurements	: dissolved oxygen content at $t = 0, 7, 14, 21$, and 28 d, pH at the beginning and at the end of the test, temperature continuously
chemical analysis	: no
reference compound	: sodium acetate

Results

The pH varied between 6.4 and 7.1. Oxygen depletion in the inoculum blank was less than 1.5 mg/L and the difference between replicate dissolved oxygen contents at the end of the test was less than 20%. The reference compound sodium acetate was degraded by 66% after 14 d, which confirms that the inoculum used for the test had sufficient activity. After 28 d, the test substance was degraded for 9.2%. A test substance is regarded readily biodegradable when 60% biodegradation has been achieved within a 10-day window. As this criterion is not met, 2,6-dichlorobenzamide is not classified as readily biodegradable in this test.

Acceptability of the test

The test is considered acceptable.

Conclusions

2,6-dichlorobenzamide is not readily biodegradable in a closed bottle test.

B.8.4.4 Water/sediment studies

B.8.4.4.1 Aerobic water/sediment study (IIA, 7.2.1.3.2/01)

Characteristics of the study

Reference	: Willems and Hoitink (2004)	DT ₅₀ (water)	: Goorven: 10.9 d	Engelse Dijk: 10.1 d
Year of execution	: 2003, 2004	DT ₅₀ (system)	: Goorven: 307 d	Engelse Dijk: 66 d
Guideline	: OECD 308	DT ₉₀ (water)	: Goorven: 36 d	Engelse Dijk: 34 d
GLP	: yes	DT ₉₀ (system)	: Goorven: 1020 d	Engelse Dijk: 218 d
Test substance	: [¹⁴ C]dichlobenil; batch no CFQ 11075	Metabolites	BAM, 2-chlorobenzoic acid	
Radiochemical purity	: > 99%	Acceptable	: yes	
Chemical purity	: 100.0%			

Study design

The test substance was [*ring-U*-¹⁴C]dichlobenil, radiochemical purity > 99%, specific activity 1.96 GBq/mmol). The radiolabeled dichlobenil was diluted with unlabeled dichlobenil (batch no. ARS-9108BA-B, purity 100.0%). The sediments and associated waters were collected from Goorven (a static pond near Oisterwijk, province Noord-Brabant, NL) and from Engelse Dijk (a static pond near 's-Hertogenbosch, province Noord-Brabant, NL). The characterisation of water and sediment is given in Table B.8.4.4.1a. Sediment was sampled from the upper 0-10 cm, sieved (2 mm) and stored for 5 days at 4°C. Water was taken from the upper 1 m layer, sieved (150 µm) and stored for 5 days at 4°C.

Table B.8.4.4.1a Relevant characteristics of waters and sediments

Location of collection	Goorven		Engelse Dijk	
	sediment	water	sediment	water
Texture class of sediment	Sand		Silty clay loam	
DOC (mg/L)		14.6		19.5
Organic carbon content (%)	0.8		6.3	
Organic matter content (%)	1.4 ¹⁾		10.8 ¹⁾	
pH	6.2 (water)	5.44	7.5 (water)	7.46
	5.2 (KCl)		7.3 (KCl)	
CEC (mEq/kg)	11		452	
Soil microbial biomass (mg C/kg soil)				
• day 0	79.6		1471	
• day 100	44.2		1201	
Mean redox potential (mV)		157		39
Mean oxygen concentration (mg/L)		7.9		7.19

¹⁾ Organic matter content (%) = Organic carbon content (%) x 1.72

Portions of sieved sediment (250 g wet weight for the Goorven system and 125 g wet weight for the Engelse Dijk system) were placed into cylindrical 1000-mL brown glass flasks. Aliquots of 470 mL of the corresponding sieved water were added to each flask. A sediment layer of about 2 cm and a water layer of about 6 cm were thus obtained. The flasks were then connected to an air stream which was allowed to bubble gently through the upper layer of the water. Prior to testing, the flasks were equilibrated at ca. 20°C, in the dark, for 12 days (Goorven) or 20 days (Engelse Dijk). pH, DO and redox potential were monitored twice weekly during the equilibration period. After the equilibration period the redox potential of the sediments were: Goorven: -235 mV, Engelse Dijk: -280 mV.

After equilibration, a 450 µL aliquot of a stock solution of [¹⁴C]dichlobenil in acetonitrile was added to the water phase in each test flask. The final concentration of dichlobenil in the water was 2.7 mg/L, corresponding to a field rate of 8.1 kg/ha assuming 100% overspray on a ditch with 30 cm water layer and homogeneous distribution.

Incubation was carried out at 19.0 – 21.1°C in the dark. Aeration of the flasks took place every day for half an hour in the morning and half an hour in the evening. An air stream was allowed to bubble gently through the upper layer of the water. The air left the flask through a polyurethane foam (PUF) plug and was led through a trap with 2-methoxyethanol and two traps with NaOH solution (2 mol/L). ¹⁴CO₂ in the NaOH traps was confirmed by precipitation as BaCO₃. During incubation, oxygen concentration, pH and redox potential of the water were determined on the day of sampling or at least once a week. The redox potential of the sediment was determined every two weeks. The ranges of these measurements for the sediments and waters are given in Table B.8.4.4.1b.

Table B.8.4.4.1b Physico-chemical characterisation of water and sediment during incubation with [¹⁴C]dichlobenil

System	Parameter	Water range	Sediment range
Goorven	O ₂ (mg/L)	6.4 – 8.7	-29 – -235
	pH	4.3 – 5.9	
	Redox potential (mV)	+77 – +233	
Engelse Dijk	O ₂ (mg/L)	6.1 – 8.7	-119 – -280
	pH	7.3 – 8.3	
	Redox potential (mV)	+55 – +175	

Two flasks of each system were harvested at 30 min after addition of the test compound and after 3, 7, 15, 30, 59, and 100 days. At sampling days, also foam plugs and liquid traps were analysed and replaced. Polyurethane foam (PUF) plugs were extracted with acetonitrile. The extract was analysed by LSC.

Sediment and water were separated by decantation. Duplicate samples of the decanted water were taken for LSC. Water was extracted twice with dichloromethane. Additionally, from day 30 onwards, a subsample of the post-extraction residual water of the Engelse Dijk system was acidified to pH 3 and two or three times extracted with dichloromethane in order to extract acid metabolites. To the combined dichloromethane layers, acetonitrile was added and the extract was concentrated to 10 mL. Radioactivity in all extracts and the remaining water was measured by LSC.

The remaining sediment was extracted three times with methanol. The soil residue that was remaining after the extraction was extracted with methanol in a Soxhlet apparatus. The soil residues remaining after solvent extraction were allowed to air-dry. Triplicate portions of 1 g were taken for combustion/LSC analysis.

All combined PUF extracts, concentrated water extracts and sediment extracts were subjected to HPLC in several solvent systems with UV/radio detection. TLC was performed on selected extracts (one solvent system). Metabolites were identified by co-chromatography. One unknown metabolite was identified by LC-MS.

Results

The results of the microbial biomass measurements showed sufficient viable conditions at the start of the experiment (microbial biomass $\geq 1\%$ of organic carbon). The sediment was sufficiently anaerobic during the experimental period and the water was sufficiently aerobic. In the Goorven system at all sampling times, the total average recovery of the radioactivity varied between 97.9% and 100.0%. The recovery of dichlobenil at $t = 0$ was 98.9%.

At the end of the incubation (after 100 days), 36.4% of the applied radioactivity was recovered from the PUF plug in the Goorven system. All radioactivity in the PUF plug consisted of dichlobenil. Hardly any radioactivity was found in the methoxyethanol trap.

On day 100, 0.63% of the applied radioactivity (a.r.) in the Goorven system was recovered as $^{14}\text{CO}_2$ in the NaOH traps, while 18.8% was recovered in the water phase. The major part of the radioactivity (42.3% a.r.) was recovered in the sediment (39.3% extractable and 3.0% unextractable). In Table B.8.4.4.1c the distribution and recovery of applied radioactivity for the Goorven system are given.

Table B.8.4.4.1c Distribution and recovery of applied radioactivity for the Goorven system

	% of applied radioactivity						
Sampling time (d)	Water phase	Sediment			Volatiles		Total
		Extracted	Bound	Total	PUF plug	CO ₂	
0	98.5	1.4	0.04	1.5	0	-	100.0
3	54.3	41.0	0.42	41.4	3.5	0.05	99.2
7	45.3	47.9	0.80	48.7	5.3	0.10	99.4
15	31.4	55.5	1.3	56.8	9.5	0.13	97.9
30	26.1	55.2	1.4	56.7	15.5	0.29	98.5
59	22.6	48.7	2.0	50.7	25.3	0.37	99.1
100	18.8	39.3	3.0	42.3	36.4	0.63	98.2

In the Engelse Dijk system at all sampling times, the total average recovery of the radioactivity varied between 98.6% and 101.4%. The recovery of dichlobenil at $t = 0$ was 100.4%. At the end of the incubation (after 100 days) 27.1% of the applied radioactivity was recovered from the PUF plug in the Engelse Dijk system. Almost all radioactivity in the PUF plug consisted of dichlobenil. Hardly any radioactivity was found in the methoxyethanol trap.

At the end of the incubation 4.5% of the applied radioactivity in the Engelse Dijk system was recovered as ¹⁴CO₂ in the NaOH traps, while 27.4% was recovered in the water phase. The major part of the radioactivity (39.8% a.r.) was recovered in the sediment (32.0% extractable and 7.8% unextractable). In Table B.8.4.4.1d the distribution and recovery of applied radioactivity for the Engelse Dijk system are given.

Table B.8.4.4.1d Distribution and recovery of applied radioactivity for the Engelse Dijk system

	% of applied radioactivity						
Sampling time (d)	Water phase	Sediment			Volatiles		Total
		Extracted	Bound	Total	PUF plug	CO ₂	
0	98.8	2.1	0.09	2.2	0.0	-	100.9
3	65.6	28.9	1.7	30.6	4.8	0.01	101.0
7	49.1	43.6	1.8	45.4	6.9	0.02	101.4
15	37.6	49.8	2.4	52.3	11.1	0.12	101.1
30	34.7	45.2	3.4	48.6	16.6	0.31	100.3
59	33.4	33.9	7.8	41.7	20.9	2.6	98.6
100	27.4	32.0	7.8	39.8	27.1	4.5	98.8

In the water phase of the Goorven system in addition to dichlobenil a total of five radioactive fractions were found. 2,6-Dichlorobenzamide (BAM) represented the largest fraction, with a maximum of 4.46% after 100 days. All other individual metabolites were $\leq 0.61\%$ at any time. In the sediment BAM was the only metabolite detected after 100 days.

In the water phase of the Engelse Dijk system in addition to dichlobenil a total of ten radioactive fractions were found, BAM representing a maximum of 5.32% a.r. after 100 days. An important unknown metabolite was identified by LC/MS as 2-chlorobenzoic acid and found in the Engelse Dijk system only, representing 9.13% and 7.91% a.r. at two subsequent sampling times at 59 and 100 days, respectively. All eight other metabolites were individually $\leq 10\%$ a.r. at any time point or $\leq 5\%$ a.r. at two consecutive time points. One of the minor fractions was identified as hydroxy-dichlobenil (max. 0.26%). In the sediment BAM was detected as a metabolite, representing a maximum of 2.04% after 100 days. Also four minor unidentified fractions were detected, individually not exceeding 10% a.r. at any time point and not exceeding 5% a.r. at two consecutive time points. In Table B.8.4.4.1e and Table B.8.4.4.1f data for both aquatic systems are summarised.

Table B.8.4.4.1e Proportions (% a.r.) of identified radioactive components in the water phase, sediment extracts and total of sediment extracts and water phase at several time points after application of [^{14}C]dichlobenil in the Goorven system

Compartment	Component	Time after application (days)						
		0	3	7	15	30	59	100
Water phase	dichlobenil	97.5	54.0	45.4	30.4	24.4	16.8	11.1
	BAM	0.0	0.0	0.0	0.43	1.17	2.82	4.46
	2-chlorobenzoic acid	0.0	0.0	0.0	0.0	0.0	0.0	0.0
	4 unidentified fractions	1.36	0.67	0.87	0.79	1.08	2.48	3.34
Sediment extracts	dichlobenil	1.4	41.0	47.9	55.6	55.2	48.7	37.6
	BAM	0.0	0.0	0.0	0.0	0.0	0.0	1.73
Volatile	dichlobenil	0.0	3.5	5.3	9.5	15.5	25.3	36.4
Total of sediment extracts and water phase	dichlobenil (without volat.)	98.9	95.0	93.3	86.0	79.6	65.5	48.7
	BAM	-	-	-	0.43	1.17	2.28	6.19
	2-chlorobenzoic acid	-	-	-	-	-	-	-
	others	1.36	0.67	0.87	0.79	1.08	2.48	3.34
	Total	100.3	95.7	94.2	87.2	81.9	70.3	58.2

Table B.8.4.4.1f Proportions (% a.r.) of identified radioactive components in the water phase, sediment extracts and total of sediment extracts and water phase, at several time points after application of [^{14}C]dichlobenil in the Engelse Dijk system

Compartment	Component	Time after application (days)						
		0	3	7	15	30	59	100
Water phase	dichlobenil	98.3	63.9	47.8	33.1	20.7	9.8	7.2
	BAM	0.0	0.0	0.31	0.70	3.38	4.12	5.32
	2-chlorobenzoic acid	0.0	0.0	0.0	0.0	3.35	9.13	7.91
	8 unidentified fractions	2.1	0.98	1.9	4.0	7.6	10.7	7.6
Sediment extracts	dichlobenil	2.07	26.8	42.4	47.1	40.0	25.2	22.7
	BAM	0.0	0.0	0.0	0.0	1.76	1.91	2.04
	4 unidentified fractions	0.0	2.0	1.2	2.8	3.4	6.8	7.3
Volatile	dichlobenil	0.0	4.7	6.9	10.5	16.6	20.9	25.9
Total of sediment extracts and water phase	dichlobenil (without volat.)	100.4	90.7	90.2	80.2	60.7	35.0	29.9
	BAM	0.00	0.00	0.31	0.70	5.14	6.03	7.36
	2-chlorobenzoic acid	0.0	0.0	0.0	0.0	3.35	9.13	7.91
	others	2.1	2.98	3.1	6.8	11.0	17.5	14.9
	Total	102.5	93.7	93.6	87.7	80.2	67.7	60.1

DT₅₀ values for dichlobenil were calculated using a single first order (SFO) kinetic model and non-linear regression. DT₅₀ values for water were based on dissipation (degradation, adsorption to sediment and volatilisation). DT₅₀ for the whole system was based on dichlobenil concentrations corrected for volatilised dichlobenil (^{14}C in PUF). Corrected dichlobenil was obtained from: $\text{dichlobenil}_{\text{water}} + \text{dichlobenil}_{\text{sediment}} / (\text{total mass balance } ^{14}\text{C in PUF})$. Results are shown in Table B.8.4.4.1h.

Table B.8.4.4.1h DT₅₀ values and DT₉₀ values for [^{14}C]dichlobenil in water/sediment systems (calculated using a SFO kinetic model).

	Goorven		Engelse Dijk	
	DT ₅₀ (d)	DT ₉₀ (d)	DT ₅₀ (d)	DT ₉₀ (d)
Water System	10.9 307 ¹⁾	36.1 1020 ¹⁾	10.1 66 ¹⁾	34 218 ¹⁾

¹⁾ Corrected for volatilised dichlobenil

The authors also applied a hockey stick degradation kinetic model. Because all calculations with SFO kinetics had a r^2 value > 0.81 there is no reason to accept DT₅₀ values obtained with a model other than SFO. A conceptual multi-compartment model was built by the authors taking into account all compartments (including volatile dichlobenil) and all identified metabolites. The degradation DT₅₀ values obtained for the water and the whole system confirmed the slow degradation of dichlobenil in an aerobic water/sediment system.

Remarks by RMS

- The redox potential during the equilibrium period was not reported.

- The FOMC model is not an option for refinement of level P-II approaches for water/sediment systems. Furthermore, it is unclear from the study if an Fsed check was performed. Moreover, in view of the very similar endpoints from both approaches, the PEC values calculated with the various endpoints are in the same order of magnitude in STEP 1 and 2. PEC calculations are therefore performed with the SFO endpoints.

Acceptability of the test

The study is considered acceptable.

Conclusion

Dichlobenil degraded slowly in two water/sediment systems, with DT₅₀ (system) values of 307 and 66 days. Major detected metabolites were 2,6-dichlorobenzamide (BAM) in water and sediment, and 2-chlorobenzoic acid in water (one system only), the latter at two subsequent sampling times in amounts > 5%. The formation of bound residue and CO₂ was slow.

B.8.4.4.2 Aerobic aquatic metabolism study (IIA, 7.2.1.3.2/02)

Characteristics of the study:

Reference	: Whitright (2001)	DT ₅₀ (water)	: none
Year of execution	: 2001	DT ₅₀ (system)	: none
Guideline	: EPA Subdiv. N, 160-4, 160-5, 162-4	DT ₉₀ (water)	: none
GLP	: yes	DT ₉₀ (system)	: none
Test substance	: [¹⁴ C]Dichlorobenzamide	Metabolites	: none
Radiochemical purity	: 96.34%	Acceptable	: no ¹⁾

¹⁾ This study is not a water/sediment study because upland soil was used

Study design

An aerobic aquatic metabolism study was conducted in one water/soil system, according to EPA Guidelines Subdiv. N, series 160-4, 160-5 and 162-4 in compliance with GLP. The test substance was [1-phenyl-¹⁴C]2,6-dichlorobenzamide (BAM) (lot no. DUPH016, radiochemical purity 96.34%, specific activity 254 MBq/mmol). The soil was collected from a cranberry bog in Long Beach, Washington (state), USA. The soil was very wet and probably almost saturated with water. Water was collected from a pond used to flood the bogs. The characterisation of water and soil is given in Table B.8.4.4.1a. Soil was wet-sieved (2 mm) before use.

Table B.8.4.4.2a. Relevant characteristics of water and soil

Location of collection	Long Beach, Washington (state), USA	
	Soil	Water
Texture class of soil	Sand	
DOC (mg/L)		10.8
Organic matter content (%)	7.1	
pH	4.9 (water)	7.6
CEC (mmol/kg)	85	
Redox potential at day 0 (mV)		283
Oxygen concentration at day 0 (mg/L)		7.85
Soil microbial biomass (mg C/kg soil)	518	
Plate counts (soil extract/nutrient agar) (CFU/mL)	110	

Portions of sieved soil (20 g dry weight) were placed into 150 mL Erlenmeyer flasks and water was added to a total of 80 mL (including the soil water) in each flask. The soil contained 44.96% moisture. The amount of wet soil placed in each flask was 36.34 g. Two flasks were used to measure redox potential and oxygen concentration. The flasks were not equilibrated before adding the test substance.

A 20.16 μL aliquot of a stock solution of [^{14}C]BAM in acetonitrile was added to the water phase in each test flask. The final concentration of BAM in the water was 0.074 mg/L. Incubation was carried out at 24.9-27.7°C in the dark. The flasks were connected to an air stream (0.5-3 mL/min) which was allowed to bubble into the water. The flow of air was as follows:

Pre-test system

- NaOH solution (1 mol/L) to remove CO_2
- A water bottle to humidify the gas flow

Test system

- Test flask

Post-test system

- An empty wash bottle
- Polyurethane foam plug
- A trap containing H_2SO_4 solution (1 mol/L)
- Two traps containing NaOH solution (1 mol/L) to trap $^{14}\text{CO}_2$

During incubation the oxygen concentration and redox potential of the water were determined on the day of sampling. The ranges of these measurements for sediment and water are given in Table B.8.4.4.2b.

Table B.8.4.4.2b Physico-chemical characterisation of water during incubation with [^{14}C]BAM

System	Parameter	Range
Long Beach	O ₂ (mg/L)	6.4-8.5
	Redox potential (mV)	+257 - +311

Two flasks were harvested 0, 7, 15, 22 and 30 days after treatment. At sampling days the associated foam plugs and liquid traps were also removed. Polyurethane foam (PUF) plugs were extracted with methanol. The extract was analysed by LSC.

Solids and water were separated by centrifugation. Duplicate samples of the filtered decanted water were taken for LSC. The water was analysed by HPLC (one system) and UV detection. Eluting fractions were collected and measured by LSC. The remaining solids were extracted twice with methanol, followed by water and finally acetonitrile. The combined extracts were concentrated and radioactivity determined by LSC. The concentrate was analysed by HPLC (one system) and UV detection. Eluting fractions were collected and measured by LSC. The 30-days post-extraction solids were also Soxhlet extracted exhaustively with methanol and water. The soil residues remaining after solvent extraction were allowed to air-dry. Six replicate portions of 0.2 g were taken for combustion/LSC analysis.

Results

The results of the microbial biomass measurements showed sufficient viable conditions at the start of the experiment (microbial biomass $\geq 1\%$ of organic carbon). The water was sufficiently aerobic. No data were available about the redox state of the soil sediment.

At all sampling times the total average recovery of the radioactivity varied between 95.2% and 102.0%. The recovery of BAM at $t = 0$ was 87.2.5%.

At the end of the incubation (after 30 days) no radioactivity was recovered from the PUF plug and no radioactivity was found in the H₂SO₄ trap. By that time 2.61% of the applied radioactivity was recovered as $^{14}\text{CO}_2$ in the NaOH traps, while 39.7% was recovered in the water phase. The major part of the radioactivity (59.7% a.r.) was recovered in the sediment (57.1% extractable and 2.6% unextractable). In Table B.8.4.4.2c the distribution and recovery of applied radioactivity are given.

Table B.8.4.4.2c Distribution and recovery of applied radioactivity (average of duplicates)

	% of applied radioactivity						
Sampling time (d)	Water phase	Sediment			Volatiles		Total
		Extracted	Bound	Total	PUF plug, H ₂ SO ₄ trap	CO ₂	
0	54.6	39.0	1.5	40.5	-	-	95.2
7	43.1	53.3	6.4	59.7	0.0	0.96	103.8
15	45.5	40.7	5.5	46.2	0.0	0.39	92.1
22	36.7	49.5	6.7	56.3	0.0	0.91	93.9
30	39.7	57.1 ¹⁾	2.6 ¹⁾	59.7	0.0	2.61	102.0

¹⁾ Extraction included exhaustive Soxhlet extraction

BAM was the only significant radioactive residue observed in all water fractions throughout the 30-day incubation period. BAM was also the only significant radioactive residue observed in all soil extracts throughout the 30-day incubation period. The identity of BAM was established by HPLC with MS. DT₅₀ values could not be calculated.

Remarks by RMS

The study was not carried out according to OECD Guideline 308. The study was carried out with a bog soil instead of sediment. The history of the soil was not described. The system was not equilibrated before addition of the test substance. Based on the high percentage water in the soil, it was probably (almost) saturated and it may be presumed that the bog soil was anaerobic during incubation. However, proof for this presumption (e.g. measurement of the redox potential of the soil) is lacking.

Acceptability of the test

The study is not considered acceptable.

Conclusion

The study is not considered acceptable.

B.8.4.4.3 Anaerobic water/sediment study (IIA, 7.2.1.3.2/02)

Characteristics of the study:

Reference	: Saxena (1989)	Chemical purity	: 99.9%
Year of execution	: 1988, 1989	DT ₅₀ (water)	: no reliable value
Guideline	: EPA, Subdiv. N, 162-3	DT ₅₀ (system)	: no reliable value
GLP	: yes	Metabolites	: not reliable
Radiochemical purity	: 95.2%	Acceptable	: no

Study design

A water/sediment study was conducted in one water/sediment system, according to EPA Guideline Subdiv. N, series 162-3 in compliance with GLP. The test substance was [*ring*-U-¹⁴C]dichlobenil (batch no. AOI87A30B, radiochemical purity 95.2%, specific activity 692 MBq/mg). The radiolabeled dichlobenil was diluted with unlabeled dichlobenil (batch no. ARS-82I01N, purity 99.9%). The sediments and associated waters were collected from Lake Mendota, Dane County, Wisconsin, USA. The characterisation of water and sediment is given in Table B.8.4.4.3a.

Table B.8.4.4.3a. Relevant characteristics of water and sediment

Location of collection	Lake Mendota, Dane County, Wisconsin, USA	
	Sediment	Water
Texture class of sediment	sand	
Organic matter content (%)	0.8	
pH	7.8	8.5
CEC (mmol/kg)	66	
Aerobic plate count (mL ⁻¹)	390	
Aerobic spore count (mL ⁻¹)	8	
Anaerobic plate count (mL ⁻¹)	1100	
Anaerobic spore count (mL ⁻¹)	< 1	
Oxygen concentration (mg/L)		2.2

Sediment was sieved at 2 mm. Portions of sieved sediment (2 g dry weight) were placed into glass containers. Aliquots of 20 mL of the corresponding water that had been purged with a stream of nitrogen were added to each flask. The total weight of sediment + water was 22.61 g. The containers were closed with a septum, placed in a glass chamber flushed with nitrogen and incubated in the dark at ca. 25°C. After a period of 2 weeks 250 mg of a 25% glucose solution was added to each container, which was then equilibrated for another 2 weeks.

After equilibration an aliquot of 101.4 µL of a stock solution of [¹⁴C]dichlobenil in methanol was added to the water phase in each test flask. The final concentration of dichlobenil in the water was 1.15 mg/L, corresponding to a field rate of 3.45 kg/ha assuming 100% overspray on a ditch with 30 cm water layer and homogeneous distribution. Incubation was carried out at 24-25°C in the dark.

Two containers were harvested after 0, 6, 14, 27, 60, 90, 122, 154, 192, 217, 248, 290, 339 and 370 days. At sampling days (except for day 0) the headspace of the containers was purged for 10 min with nitrogen, which was led through three traps: a trap with xylene, a trap with KOH solution (1 mol/L) and a trap with ethylene glycol. The contents of the traps were analysed by LSC.

Sediment and water were separated after centrifugation. Samples of the water layer were taken for LSC. The water was further analysed by HPLC. The remaining sediment was extracted twice with methanol. The extract was further analysed by LSC and HPLC (two systems). Eluting fractions were collected and measured by LSC. The soil residues remaining after solvent extraction were allowed to air-dry. Duplicate portions of 0.1-0.4 g were taken for combustion/LSC analysis.

The presence of undegraded dichlobenil was confirmed by GC/MS.

Samples which showed metabolites were analysed by another HPLC system. Metabolites were confirmed by co-chromatography.

Results

The results of the cell counts showed sufficient viable conditions at the start of the experiment. At all sampling times the total average recovery of the radioactivity varied between 76.9% and 100.1%. The total recovery of dichlobenil at t=0 was 97.8%.

At the end of the incubation (after 370 days) hardly any radioactivity was found in the ethylene glycol trap and in the CO₂ trap. The xylene trap contained 4.0% a.r. The major part was recovered in the water phase (69.7%). The sediment contained 14.4 % a.r. (10.5% extractable and 3.9% unextractable). In Table B.8.4.4.3b the distribution and recovery of applied radioactivity are given.

Table B.8.4.4.3b Distribution and recovery of applied radioactivity (average of duplicates)

	% of applied radioactivity							
Sampling time (d)	Water phase	Sediment			Volatiles			Total
		Extracted	Bound	Total	Ethylene glycol	Xylene	CO ₂	
0 ¹⁾	96.8	3.3	n.d.	3.3	-	-	-	100.1
6	84.0	12.7	0.9	13.6	0.0	2.2	0.1	99.9
14	83.8	12.4	1.8	14.2	0.0	1.0	0.1	99.1
27	85.4	11.2	1.1	12.3	0.0	1.5	0.0	99.2
60	80.7	13.1	2.9	16.0	0.0	0.7	0.0	97.4
90	78.5	11.5	4.6	16.1	0.0	0.6	0.0	95.2
122	77.3	10.5	2.1	12.4	0.0	0.6	0.1	90.6
154	62.1	13.8	2.5	16.3	0.0	0.1	0.0	78.5
192	77.6	12.5	2.9	15.4	0.0	0.9	0.0	93.9
217	65.1	8.7	4.3	13.0	0.0	0.2	0.1	78.4
248	52.6	22.2	1.8	24.0	0.0	0.3	0.0	76.9
290	75.9	10.5	1.8	12.3	0.0	0.0	0.0	88.2
339	73.5	10.6	4.8	15.4	0.3	0.8	0.3	90.2
370	69.7	10.5	3.9	14.4	0.2	4.0	0.0	88.3

¹⁾ One replicate

In most samples dichlobenil was the only compound detected in the water phase and in the sediment extract. At the day 217 sampling point metabolites were found in the water phase (18% a.r.) and the sediment extract (2.2% a.r.) of one replicate. These metabolites were co-chromatographically identified as 2,6-dichlorobenzamide, 2,6-dichlorobenzoic acid and 2-chlorobenzonitrile. At the day 339 sampling point metabolites were found only in the water phase of one replicate (14% a.r.). In Table B.8.4.4.3c data on identified radioactive components are summarised.

Table B.8.4.4.3c Proportions (% a.r.) of identified radioactive components in the water phase, sediment extracts and total of sediment extracts and water phase at several time points after application of [^{14}C]dichlobenil (average of duplicates)

Sampling time (d)	Water phase		Sediment extract		Total water+ sediment	
	Dichlobenil	Metabolites	Dichlobenil	Metabolites	Dichlobenil	Metabolites
0 ¹⁾	98	0.0	0.0	0.0	98	0.0
6	85	0.0	13	0.0	98	0.0
14	86	0.0	12	0.0	98	0.0
27	95	0.0	5.5	0.0	101	0.0
60	76	0.0	12	0.0	88	0.0
90	80	0.0	11	0.0	91	0.0
122	77	0.0	9.5	0.0	87	0.0
154	67	0.0	12	0.0	79	0.0
192	74	0.0	11	0.0	85	0.0
217	78, 19 ²⁾	0.0, 18 ²⁾	5.3	0.0, 2.2 ²⁾	84	0.0, 22 ²⁾
248	56	0.0	22	0.0	78	0.0
290	73	0.0	11	0.0	84	0.0
339	68, 24 ²⁾	0.0, 14 ²⁾	8.4	0.0	76.4	0.0, 14 ²⁾
370	66	0.0	10	0.0	76	0.0

¹⁾ One replicate; ²⁾ Duplicates

The authors calculated from the data a DT_{50} value of 1040 days for dichlobenil in this anaerobic aquatic system (SFO kinetic model, log-linear regression, $r^2 = 0.81$).

Acceptability of the test

The DT_{50} calculation of the authors does not take into account the gradually decreasing material balance. If this is considered, the DT_{50} is probably longer. No reliable value for the DT_{50} can be given. The design of the study does not fulfil the requirements of the OECD 308 guideline for an anaerobic water/sediment study. Moreover, a fully anaerobic water/sediment system is not representative for most surface waters. Therefore, the study is not considered acceptable.

Conclusions

The study is considered not acceptable.

B.8.4.5 Monitoring of dichlobenil in surface water and groundwater

Monitoring of dichlobenil in surface water

No data available.

Monitoring of dichlobenil in groundwater in the Netherlands (IIA 7.4/01)

Characteristics of the study

Reference	: Wyma-Teitsma and Kerkdijk (2004)	Test substance	: dichlobenil; batch no. and appearance not applicable
Year of execution	: 2003	Purity	: not applicable
Guideline	: no	Measured dichlobenil	: < LOQ (= 0.05 µg/L)
GLP	: yes	Acceptable	: yes

The study was performed to assess whether the commercial use(s) of dichlobenil has resulted in its presence in groundwater in the Netherlands under realistic worst-case conditions. Dichlobenil can be used on uncultivated areas, such as roadsides, along railway tracks and on industrial areas. Based on this information, as well as confidential sales information, application areas were selected in the east and south-east of the Netherlands.

Groundwater samples were taken from 65 relevant wells located in Pleistocene sandy areas with low organic content (< 0.5%) near the above mentioned application areas. Field spikes, field blanks, and wipe samples (from the outer cap of the well) were also taken. The samples were analysed with GC-MS. Results revealed that dichlobenil concentrations in all wells were below the LOQ of 0.05 µg/L. Therefore, the Dutch criterion for leaching of pesticides to groundwater (0.1 µg/L) is fulfilled.

Acceptability of the test

According to the Dutch authority for pesticide registration (CTB), the test set should consist of a minimum of 80 wells instead of 65 wells. However, as the concentration dichlobenil was below the LOQ in all samples, it is unlikely that different results would have been found when the test set was expanded to 80 wells. Therefore, the study is considered acceptable.

Conclusions

Dichlobenil concentrations in samples taken from 65 relevant wells were below the LOQ of 0.05 µg/L. The Dutch criterion for leaching of pesticides to groundwater (0.1 µg/L) is fulfilled.

B.8.4.6 Summary

Hydrolysis

Although it is very likely that the parent compound is hydrolytically stable, the study provided deviated considerably from guidelines. However, it is considered by RMS that the result of the study, a negligible potential for hydrolysis, is convincingly shown for environments with a pH of 6.8 to 8.3. As this is the environmentally relevant range, the results are considered relevant.

A hydrolysis experiment with the metabolite 2,6-dichlorobenzamide in sterile buffers at a temperature of 50°C at three pH levels showed that the metabolite was hydrolytically stable at pH 4, 7, and 9 for 5 d and at pH 5, 7, and 9 at 25°C for 30 d. Three unidentified degradation products, < 1.2% a.r. were observed.

Photolysis

The stability of dichlobenil in aqueous solution, when exposed to xenon light, was determined and compared with the stability under sunlight conditions. Dichlobenil was stable in the dark controls. After 15 and 21 days of continuous irradiation, the dichlobenil concentration had decreased to 51.7 and 39.8% of the initial concentration, respectively. The results are summarised in Table B.8.4.6a. The DT₅₀ value of [¹⁴C]-dichlobenil was calculated to be 15.1 d; this corresponds to 10.2 d of natural sunlight.

Table B.8.4.6a DT₅₀ values for [¹⁴C]-dichlobenil

exposure	DT ₅₀ value (d) at 25 °C
xenon light	15.1
natural sunlight 40° North ¹	10.2

¹ Calculated: 24 h irradiation with the xenon-light source equals 0.675 d of natural sunlight at 40° North latitude.

One of the degradation products found accounted for 14 and 17% of the applied radioactivity after 15 and 21 d, respectively. This compound was identified as 4-chloro-2(3H)benzoxazolone and is a major degradation product.

A photolysis study with 2,6-dichlorobenzamide showed that the metabolite was stable at pH 5 and 25°C for 31 d.

Ready Biodegradability

No degradation of dichlobenil was observed in a manometric respiration test. Therefore, dichlobenil is not considered to be readily biodegradable. The metabolite 2,6-dichlorobenzamide (BAM) was degraded for 9.2% after 28 d in a closed bottle test and is therefore considered to be not ready biodegradable as well.

Water/sediment study

An aerobic water/sediment study with two sediment systems was performed. The sediment systems were collected from Goorven (a static pond near Oisterwijk, province Noord-Brabant, NL) and from Engelse Dijk (a static pond near 's-Hertogenbosch, province Noord-Brabant, NL). dichlobenil degraded slowly with DT_{50} (system) values of 307 and 66 days. The DT_{50} and DT_{90} values based on SFO kinetics for the water phase and the whole systems are summarised in Table B.8.4.6b.

Table B.8.4.6b DT_{50} values and DT_{90} values for [^{14}C]dichlobenil in water/sediment systems (calculated using a SFO kinetic model).

	Goorven		Engelse Dijk	
	DT_{50} (d)	DT_{90} (d)	DT_{50} (d)	DT_{90} (d)
Water	10.9	36.1	10.1	34
System	307 ¹	1020 ¹	66 ¹	218 ¹

¹ Corrected for volatilised dichlobenil

In the Goorven system, after 100 days, the metabolite 2,6-Dichlorobenzamide (BAM) represented the largest fraction, with a maximum of 4.46%, 1.73% and 6.19% in water, sediment and system, respectively. In the water phase of the Goorven system, a total of 5 radioactive fractions were found in addition to dichlobenil. All other individual metabolites were $\leq 0.61\%$ at any time. In the sediment BAM was the only metabolite detected after 100 days.

In the Engelse Dijk system, after 100 days, 2,6-Dichlorobenzamide (BAM) represented the largest fraction, with a maximum of 5.32, 2.04 and 7.36% in water, sediment and system, respectively. An important unknown metabolite was identified by LC/MS as 2-chlorobenzoic acid and found in the water phase of Engelse Dijk system only, representing 9.13% and 7.91% a.r., at two subsequent sampling times after 59 and 100 days, respectively. All eight other metabolites were individually $\leq 10\%$ a.r. at any time point or $\leq 5\%$ a.r. at two consecutive time points. Also four minor unidentified fractions were detected in the sediment, individually not exceeding 10% a.r. at any time point and not exceeding 5% a.r. at two consecutive time points.

An anaerobic water/sediment study was performed as well. However, this study was not considered acceptable.

Monitoring of surface water

There are no data available.

Monitoring of groundwater

Dichlobenil concentrations in samples taken from 65 relevant wells were below the LOQ of 0.05 µg/L. The Dutch criterion for leaching of pesticides to groundwater (0.1 µg/L) is fulfilled.

B.8.4.7 Assessment

Dichlobenil is most likely hydrolytically stable at three pH levels. However, additional information from the notifier is required to draw a definite conclusion. The degradation product 2,6-dichlorobenzamide was hydrolytically stable at three pH levels. In a photolysis test, the half-life of [¹⁴C]-dichlobenil was calculated to be 15.1 d; this corresponds to 10.2 d of natural sunlight. In this photolysis test, the degradation product 4-chloro-2(3H)benzoxazolone accounted for 14 and 17% of the applied radioactivity after 15 and 21 days, respectively; it must therefore be considered as a major degradation product. The degradation product 2,6-dichlorobenzamide was photolytically stable at pH 5 and 25°C for 31 days. Dichlobenil and its metabolite 2,6-dichlorobenzamide were not readily biodegradable. Dichlobenil degraded slowly in two water/sediment systems, with DT₅₀ (system) values of 307 and 66 days. Major metabolites were 2,6-dichlorobenzamide (BAM) in water and sediment, and 2-chlorobenzoic acid in water (one system only). The overall fate and the metabolic pathway of dichlobenil in water/sediment systems is given in Figure B.8.4.7a and B.8.4.7b, respectively.

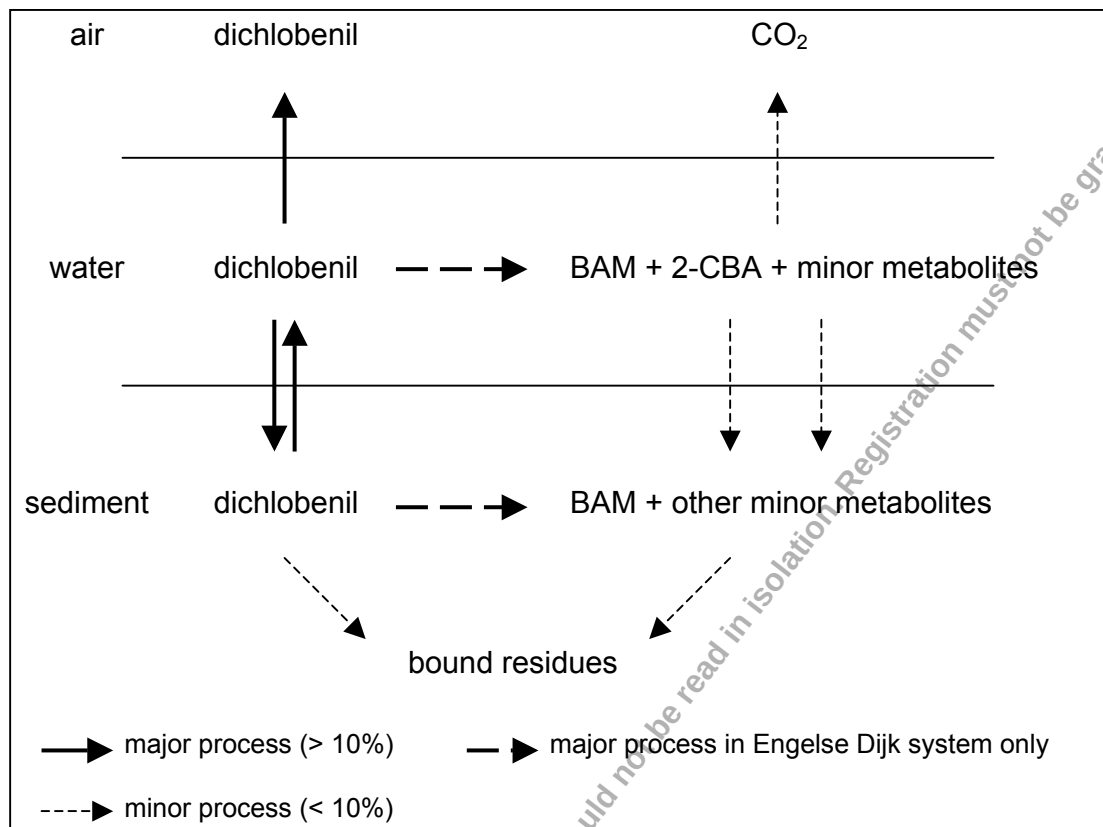


Figure B.8.4.7a Overall fate of dichlobenil in water/sediment systems.

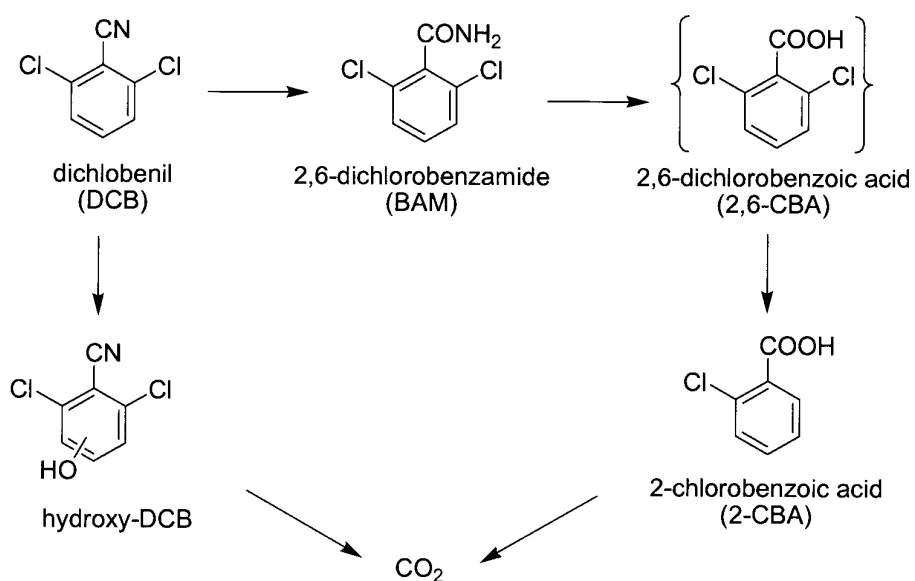


Figure B.8.4.7b Metabolic pathway of dichlobenil in water/sediment systems.

B.8.5 IMPACT ON WATER TREATMENT PROCEDURES

Given the nature of the proposed uses, it is unlikely that dichlobenil will reach sewage treatment works in significant levels to have an impact on water treatment procedures (taking into consideration 3 hour EC50 values for bacterial respiration of > 21 mg a.s./L.).

WARNING: This document forms part of an EC evaluation data package and should not be read in isolation. Registration must not be granted on the basis of this document.

B.8.6 PREDICTED ENVIRONMENTAL CONCENTRATIONS IN SURFACE WATER, GROUNDWATER AND IN SEDIMENT

B.8.6.1 Predicted environmental concentrations in surface water (PEC_{SW})

Actual and TWA PEC_{SW}: dichlobenil and metabolites

According to the official guidance document of FOCUS Surface Water Scenarios⁴ in the context of 91/414/EEC predicted concentrations in surface water need to be calculated for broadcast spreading of granules in the field. Actual and TWA PEC_{SW} estimations for treatment of vines with dichlobenil and the use in non-crop situations were calculated with FOCUS Step 1, Step 2 and Step 3 approach.

Actual and TWA PEC_{SW} according to FOCUS Step 1 & 2: dichlobenil and 2,6-dichlorobenzamide

Actual and TWA PEC_{SW} estimations for dichlobenil and BAM were performed by using the following assumptions for Step 1 and 2:

Input data	dichlobenil	2,6-dichlorobenzamide (BAM)
Application rate (g/ha) of a.s.	5400	69.4 % * rel. MW * dose = 4140 g/ha
Crop Interception	None	None
Application/crop type	Vines and non-crops	Vines and non-crops
Number of applications per season	1	-
Region and season of application	South and North Europe early spring (Mar–May)	South and North Europe early spring (Mar–May)
Water solubility (mg/L)	21.2	1830
KOC (L/kg)	237	41
DT ₅₀ water/sediment (d)	186.5 (step 1)	1000
DT ₅₀ water(d)	186.5 (step 2)	1000 (step 2)
DT ₅₀ sediment (d)	1000 (step 2)	1000 (step 2)
DT ₅₀ soil (d)	40.5 (step 2)	125 (step 2)
Distance to the water body (m)	1.00	1.00
Spray drift (% of application)	0	0
Runoff + drainage (% of	10.00 (step 1)	10.00 (step 1)

⁴ FOCUS (2001). "FOCUS Surface Water Scenarios in the EU Evaluation Process under 91/414/EEC". Report of the FOCUS Working Group on Surface Water Scenarios, EC Document Reference SANCO/4802/2001-rev.2. 245 pp.

application)	2.00 (step 2, N-Europe)	2.00 (step 2, N-Europe)
	4.00 (step 2, S-Europe)	4.00 (step 2, S-Europe)
Ratio of field to water body:	10.00	10.00
Water depth (cm)	30.00	30.00
Sediment depth (cm)	5.00	5.00
Effective sediment depth for sorption (cm)	1.00	1.00
Sediment OC (%)	5.00	5.00
Sed. bulk density (kg/L)	0.80	0.80

* the value for the metabolite BAM is unknown but essential for the calculation, therefore a worst case value is taken as input

The calculations at Step 1 and Step 2 were performed with the software tool STEPS 1-2 in FOCUS, developed by the FOCUS Surface Water Scenarios Group (FOCUS, 2004).

The results for surface water of the Step 1 calculation are listed in Table B.8.6.1a-b.

Table B.8.6.1a Actual and TWA PEC_{SW} (µg/L) of dichlobenil following application at maximum dose (5400 g a.s./ha) in the field according to FOCUS step 1

Days after application	Actual and TWA PEC _{SW} of dichlobenil (µg/L)	
	Actual PEC _{SW}	TWA PEC _{SW}
0	1370	-
1	1360	1370
2	1360	1360
4	1350	1360
7	1330E+03	1350
14	1300	1330
21	1270	1320
28	1230	13003
42	1170	1270
50	1140	1250
100	943.2	1140

Table B.8.6.1b Actual and TWA PEC_{SW} ($\mu\text{g/L}$) of the soil metabolite 2,6-dichlorobenzamide following application at maximum dose (5400 g a.s./ha equivalent to 4140 g BAM/ha) in the field according to FOCUS step 1

Days after application	Actual and TWA PEC_{SW} of 2,6-dichlorobenzamide ($\mu\text{g/L}$)	
	Actual PEC_{SW}	TWA PEC_{SW}
0	1310	
1	1310	1310
2	1310	1310
4	1300	1310
7	1300	1310
14	1300	1300
21	1290	1300
28	1280E+03	1300
42	1270	1290
50	1260	1290
100	1220	1260

The results for surface water of the Step 2 calculations are listed in table B.8.6.1c-f

Table B.8.6.1c Actual and TWA PEC_{SW} ($\mu\text{g/L}$) of dichlobenil following application at maximum dose (5400 g a.s./ha) to vines and non-crops in the field according to FOCUS step 2, early application (March-May) in North Europe

Days after application	Actual and TWA PEC_{SW} of dichlobenil ($\mu\text{g/L}$)	
	Actual PEC_{SW}	TWA PEC_{SW}
0	255.5	---
1	254.5	255.0
2	253.7	254.6
4	252.2	253.8
7	250.0	252.6
14	244.8	250.0
21	239.7	247.4
28	234.8	244.9
42	225.1	239.9
50	219.8	237.1
100	189.3	220.6

Table B.8.6.1d Actual and TWA PEC_{SW} (µg/L) of the soil metabolite 2,6-dichlorobenzamide following application at maximum dose (5400 g a.s./ha equivalent to 4140 g BAM/ha) to vines and non-crops in the field according to FOCUS step 2, early application (March-May) in North Europe

Days after application	Actual and TWA PEC _{SW} of 2,6-dichlorobenzamide (µg/L)	
	Actual PEC _{SW}	TWA PEC _{SW}
0	256.0	---
1	255.8	255.9
2	255.6	255.8
4	255.2	255.6
7	254.7	255.3
14	253.5	254.7
21	252.3	254.1
28	251.0	253.5
42	248.6	252.3
50	247.2	251.6
100	238.8	247.3

Table B.8.6.1e Actual and TWA PEC_{SW} (µg/L) of dichlobenil following application at maximum dose (5400 g a.s./ha) to vines and non-crops in the field according to FOCUS step 2, early application (March-May) application in South Europe

Days after application	Actual and TWA PEC _{SW} of dichlobenil (µg/L)	
	Actual PEC _{SW}	TWA PEC _{SW}
0	510.9	---
1	509.0	510.0
2	507.5	509.1
4	504.5	507.5
7	500.0	505.3
14	489.6	500.0
21	479.5	494.9
28	469.5	489.8
42	450.3	479.8
50	439.7	474.2
100	378.6	441.3

Table B.8.6.1f Actual and TWA PEC_{SW} (µg/L) of the soil metabolite 2,6-dichlorobenzamide following application at maximum dose (5400 g a.s./ha equivalent to 4140 g BAM/ha) to vines and non-crops in the field according to FOCUS step 2, early (March-May) application in South Europe

Days after application	Actual and TWA PEC _{SW} of 2,6-dichlorobenzamide (µg/L)	
	Actual PEC _{SW}	TWA PEC _{SW}
0	511.9	---
1	511.6	511.7
2	511.2	511.6
4	510.5	511.2
7	509.4	510.7
14	507.0	509.4
21	504.5	508.2
28	502.1	507.0
50	497.2	504.5
100	494.5	503.1

Actual and TWA PEC_{SW} according to FOCUS Step 3: dichlobenil and 2,6-dichlorobenzamide

For Step 3 the SWASH tool was applied. This tool is supported by the models: TOXSWA, MACRO and PRZM using the following assumptions (FOCUS Surface Water Scenarios SANCO/4802/2001-rev.2 final (March 2004), Step 3 assumptions):

- (i) Single application of a maximum dose of 5400 g a.s./ha to vines and non-crops in the field. The actual and TWA PEC_{SW} values were calculated for a single application in North and South Europe.
- (ii) No entry into surface water via drift and no interception by the crop, based on the type of application (broadcast spreading of granules). Entry into surface water is via run-off, erosion and drainage, as taken from the FOCUS surface water scenarios. Application on soil was assumed for dichlobenil in the simulations with MACRO and PRZM.
- (iii) PEC_{SW} calculations for the scenario's D6, R1, R2, R3 and R4 characterised by among others vines:

D6 (Thiva, Greece): Field ditches, entry via drainage;

R1 (Weiherbach, Germany): First order streams and ponds, entry via run-off;

R2 (Porto, Portugal): First order streams, entry via run-off;

R3 (Bologna, Italy): First order streams, entry via run-off.

R4 (Roujan, France): First order streams, entry via run-off.

For the scenarios D1, D3, D4, D5, and R1, characterised by non-crop applications, PEC_{SW} values were calculated by using spring oil seed rape as representative for non-crop applications. These are not available in FOCUS surface water scenarios and therefore, a crop with no irrigation and relatively little transpiration was chosen as a substitute.

D1 (Lanna, Sweden): Field ditches and first order streams, entry via drainage;

D3 (Vredepeel, Netherlands): Field ditches, entry via drainage;

D4 (Skousbo, Denmark): First order streams and ponds, entry via drainage;

D5 (La Jailliere, France): First order streams and ponds, entry via drainage;

R1 (Weiherbach, Germany): First order streams and ponds, entry via run-off.

- (iv) The input values for dichlobenil and 2,6-dichlorobenzamide used for the FOCUS Step 3 calculations are shown in the next table.

	dichlobenil	2,6-dichlorobenzamide
Molar mass (g/mol)	172	190
Water solubility (mg/L)	21.2	1830
Saturated vapour pressure (Pa)	0.14	0.00024
Formation from a.s. in soil (%)	-	69.41
Half-life in water (d)	186.5	n.d. (1000)*
Half-life in sediment (d)	1000	n.d.(1000)*
Half-life in soil (d)	40.5	125
K _{OM} suspended solids (L/kg)	137.47	24
Freundlich exponent (-)	0.90	0.90
K _{OM} sediment (L/kg)	137.47	24
Freundlich exponent (-)	0.90	0.90

* half-life of 2,6-dichlorobenzamide is not determined, therefore the maximum DT₅₀ value for FOCUS Step 3 is taken as input value (1000 days)

In the SCP opinion of 14 december 2004⁵, the procedure of modelling surface water concentrations with FOCUS surface water for non-spray applications was discussed. For broad-cast spreading of granules, like the proposed application of dichlobenil as CASORON GR, this opinion may have consequences regarding the model parameterisation in STEP 3. Main changes towards the default model input settings are:

- In TOXSWA, input via dust drift should be considered for the broadcast application of granules (as a non-FOCUS run in TOXSWA shell, Appendix 2 SCP opinion) dependent on particle size characterisation
- In PRZM, the run-off input parameters need redefinition (CAM=1 should be CAM=6; DEPI=4 should be DEPI=1).
- In MACRO, the drainage input parameter for the mixing depth may need to be redefined.

In this section, the potential consequences needed for the calculation of surface water and sediment concentrations of dichlobenil on the basis of this opinion are described.

⁵ Opinion of the Scientific Panel on Plant Health, Plant Protection Products and their Residues on a request of EFSA related to FOCUS sw scenarios. *The EFSA Journal* (2004)145, 1-31.

- TOXSWA: The product is nearly dust-free (see Table B.2.2). Particle size distribution is as follows: >2.0 mm 0%; 1.25-2.0 mm <4%; 1.0-1.25 mm <25%; 0.5-1.0 mm >60%; 0.25-0.5 mm >10%; 0.1-0.25 mm <0.1%; <0.1 mm <0.1%; Number of particles/gram: 2500-3000. Content of dust/fines according to CIPAC Method MT 171 is: Dust content at start: 0.3 mg; Dust content at end (3 years): 0.2 mg (of a test weight of 30 grammes). The product is nearly dust-free (category 1 of CIPAC Method MT 171). This means that the criteria in the proposed calculation pathway (App 2 and 4 of the SCP opinion) are not exceeded. Therefore assessing the contribution of spray drift is not considered necessary.
- PRZM: as the drainage scenarios provide a much worse case assessment (see results below), the expected small influence of changing the parameter settings will not affect the overall aquatic risk assessment.
- MACRO: for broadcast spreading, no adjustments are necessary (0.1 mm default mixing depth for broadcast spreading of granules, category 2b).

In conclusion, the SCP opinion for non-spray applications has no consequences for the FOCUS surface water calculations for dichlobenil.

Under the above assumptions, application of dichlobenil leads to actual and TWA PEC_{SW} values of dichlobenil and the metabolite 2,6-dichlorobenzamide as listed in Tables B.8.6.1g – B.8.6.1zj. Tables B.8.6.1g – B.8.6.1r correspond with applications at vines and Tables B.8.6.1s-B.8.6.1zj correspond with applications to non-crop (bare soil).

Table B.8.6.1g Actual and TWA PEC_{SW} ($\mu\text{g/L}$) of dichlobenil following early application at maximum dose (5400 g a.s./ha) of dichlobenil to vines in the field according to FOCUS step 3, scenario D6 (Thiva, ditches)

Days after application	Actual and TWA PEC_{SW} of dichlobenil ($\mu\text{g/L}$)	
	Actual PEC_{SW}	TWA PEC_{SW}
0	240.486	-
1	123.350	195.714
2	93.901	158.912
4	65.293	120.669
7	50.625	91.760
14	14.213	63.295
21	8.032	46.810
28	6.058	37.234
42	4.098	27.471
50	6.796	23.902
100	0.081	13.362

Table B.8.6.1h Actual and TWA PEC_{SW} (µg/L) of the soil metabolite 2,6-dichlorobenzamide following early application at maximum dose (5400 g a.s./ha) of dichlobenil to vines in the field according to FOCUS step 3, scenario D6 (Thiva, ditches)

Days after application	Actual and TWA PEC _{SW} of 2,6-dichlorobenzamide (µg/L)	
	Actual PEC _{SW}	TWA PEC _{SW}
0	72.034	-
1	51.538	65.298
2	48.706	59.899
4	46.401	54.168
7	47.286	49.501
14	35.042	45.338
21	28.769	41.572
28	25.487	38.264
42	20.543	37.055
50	29.036	36.869
100	0.151	35.813

Table B.8.6.1i Actual and TWA PEC_{SW} (µg/L) of dichlobenil following early application at maximum dose (5400 g a.s./ha) of dichlobenil to vines in the field according to FOCUS step 3, scenario R1 (Germany, streams)

Days after application	Actual and TWA PEC _{SW} of dichlobenil (µg/L)	
	Actual PEC _{SW}	TWA PEC _{SW}
0	16.269	-
1	0.011	7.539
2	0.004	3.775
4	0.001	1.889
7	0.001	1.080
14	0.001	0.649
21	0.000	0.433
28	0.000	0.325
42	0.000	0.231
50	0.000	0.194
100	0.000	0.097

Table B.8.6.1j Actual and TWA PEC_{SW} (µg/L) of the soil metabolite 2,6-dichlorobenzamide following early application at maximum dose (5400 g a.s./ha) of dichlobenil to vines in the field according to FOCUS step 3, scenario R1 (Germany, streams)

Days after application	Actual and TWA PEC _{SW} of 2,6-dichlorobenzamide (µg/L)	
	Actual PEC _{SW}	TWA PEC _{SW}
0	1.160	-
1	0.000	0.537
2	0.000	0.269
4	0.000	0.134
7	0.000	0.077
14	0.000	0.043
21	0.000	0.029
28	0.000	0.022
42	0.000	0.017
50	0.000	0.015
100	0.000	0.007

Table B.8.6.1k Actual and TWA PEC_{SW} (µg/L) of dichlobenil following early application at maximum dose (5400 g a.s./ha) of dichlobenil to vines in the field according to FOCUS step 3, scenario R1 (Germany, ponds)

Days after application	Actual and TWA PEC _{SW} of dichlobenil (µg/L)	
	Actual PEC _{SW}	TWA PEC _{SW}
0	0.098	-
1	0.093	0.095
2	0.089	0.093
4	0.082	0.089
7	0.073	0.084
14	0.078	0.082
21	0.057	0.077
28	0.041	0.070
42	0.029	0.059
50	0.019	0.053
100	0.002	0.030

Table B.8.6.1l Actual and TWA PEC_{SW} (µg/L) of the soil metabolite 2,6-dichlorobenzamide following early application at maximum dose (5400 g a.s./ha) of dichlobenil to vines in the field according to FOCUS step 3, scenario R1 (Germany, ponds)

Days after application	Actual and TWA PEC _{SW} of 2,6-dichlorobenzamide (µg/L)	
	Actual PEC _{SW}	TWA PEC _{SW}
0	0.008	-
1	0.008	0.008
2	0.008	0.008
4	0.008	0.008
7	0.008	0.008
14	0.007	0.008
21	0.007	0.008
28	0.007	0.008
42	0.006	0.007
50	0.006	0.007
100	0.004	0.007

Table B.8.6.1m Actual and TWA PEC_{SW} (µg/L) of dichlobenil following early application at maximum dose (5400 g a.s./ha) of dichlobenil to vines in the field according to FOCUS step 3, scenario R2 (Portugal, streams)

Days after application	Actual and TWA PEC _{SW} of dichlobenil (µg/L)	
	Actual PEC _{SW}	TWA PEC _{SW}
0	10.557	-
1	0.007	5.890
2	0.003	2.950
4	0.001	1.476
7	0.000	0.844
14	0.000	0.422
21	0.000	0.281
28	0.001	0.352
42	0.000	0.235
50	0.000	0.197
100	0.000	0.102

Table B.8.6.1n Actual and TWA PEC_{SW} (µg/L) of the soil metabolite 2,6-dichlorobenzamide following early application at maximum dose (5400 g a.s./ha) of dichlobenil to vines in the field according to FOCUS step 3, scenario R2 (Portugal, streams)

Days after application	Actual and TWA PEC _{SW} of 2,6-dichlorobenzamide (µg/L)	
	Actual PEC _{SW}	TWA PEC _{SW}
0	1.816	-
1	0.001	1.013
2	0.000	0.507
4	0.000	0.253
7	0.000	0.145
14	0.000	0.072
21	0.000	0.048
28	0.000	0.047
42	0.000	0.031
50	0.000	0.026
100	0.000	0.014

Table B.8.6.1o Actual and TWA PEC_{SW} (µg/L) of dichlobenil following early application at maximum dose (5400 g a.s./ha) of dichlobenil to vines in the field according to FOCUS step 3, scenario R3 (Italy, streams)

Days after application	Actual and TWA PEC _{SW} of dichlobenil (µg/L)	
	Actual PEC _{SW}	TWA PEC _{SW}
0	49.280	-
1	0.244	44.173
2	0.071	23.575
4	0.025	11.823
7	0.011	6.765
14	0.003	3.386
21	0.002	2.258
28	0.001	1.694
42	0.001	1.130
50	0.001	0.949
100	0.000	0.475

Table B.8.6.1p Actual and TWA PEC_{SW} (µg/L) of the soil metabolite 2,6-dichlorobenzamide following early application at maximum dose (5400 g a.s./ha) of dichlobenil to vines in the field according to FOCUS step 3, scenario R3 (Italy, streams)

Days after application	Actual and TWA PEC _{SW} of 2,6-dichlorobenzamide (µg/L)	
	Actual PEC _{SW}	TWA PEC _{SW}
0	7.501	-
1	0.018	6.731
2	0.005	3.588
4	0.002	1.796
7	0.001	1.027
14	0.000	0.514
21	0.000	0.343
28	0.000	0.257
42	0.000	0.171
50	0.000	0.144
100	0.000	0.072

Table B.8.6.1q Actual and TWA PEC_{SW} ($\mu\text{g/L}$) of dichlobenil following early application at maximum dose (5400 g a.s./ha) of dichlobenil to vines in the field according to FOCUS step 3, scenario R4 (France, streams)

Days after application	Actual and TWA PEC_{SW} of dichlobenil ($\mu\text{g/L}$)	
	Actual PEC_{SW}	TWA PEC_{SW}
0	55.549	-
1	0.056	37.084
2	0.019	18.585
4	0.007	9.301
7	0.003	5.317
14	0.001	2.660
21	0.001	1.773
28	0.008	1.430
42	0.000	0.958
50	0.000	0.805
100	0.000	0.402

Table B.8.6.1r Actual and TWA PEC_{SW} ($\mu\text{g/L}$) of the soil metabolite 2,6-dichlorobenzamide following early application at maximum dose (5400 g a.s./ha) of dichlobenil to vines in the field according to FOCUS step 3, scenario R4 (France, streams)

Days after application	Actual and TWA PEC_{SW} of 2,6-dichlorobenzamide ($\mu\text{g/L}$)	
	Actual PEC_{SW}	TWA PEC_{SW}
0	2.932	-
1	0.001	1.957
2	0.000	0.980
4	0.000	0.490
7	0.000	0.280
14	0.000	0.140
21	0.000	0.093
28	0.000	0.077
42	0.000	0.052
50	0.000	0.043
100	0.000	0.022

Spring oil seed rape as example for non-crop application

Table B.8.6.1s Actual and TWA PEC_{SW} ($\mu\text{g/L}$) of dichlobenil following early application at maximum dose (5400 g a.s./ha) of dichlobenil to spring oil seed rape in the field according to FOCUS step 3, scenario R1 (Germany, streams)

Days after application	Actual and TWA PEC_{SW} of dichlobenil ($\mu\text{g/L}$)	
	Actual PEC_{SW}	TWA PEC_{SW}
0	36.589	-
1	0.080	19.771
2	0.018	9.907
4	0.053	4.958
7	0.017	3.477
14	0.072	1.936
21	0.001	1.308
28	0.000	0.981
42	0.000	0.673
50	0.000	0.565
100	0.000	0.285

Table B.8.6.1t Actual and TWA PEC_{SW} (µg/L) of the soil metabolite 2,6-dichlorobenzamide following early application at maximum dose (5400 g a.s./ha) of dichlobenil to spring oil seed rape in the field according to FOCUS step 3, scenario R1 (Germany, streams)

Days after application	Actual and TWA PEC _{SW} of 2,6-dichlorobenzamide (µg/L)	
	Actual PEC _{SW}	TWA PEC _{SW}
0	2.590	-
1	0.003	1.401
2	0.001	0.701
4	0.002	0.351
7	0.000	0.228
14	0.006	0.123
21	0.000	0.083
28	0.000	0.063
42	0.000	0.045
50	0.000	0.038
100	0.000	0.019

Table B.8.6.1u Actual and TWA PEC_{SW} (µg/L) of dichlobenil following early application at maximum dose (5400 g a.s./ha) of dichlobenil to spring oil seed rape in the field according to FOCUS step 3, scenario R1 (Germany, ponds)

Days after application	Actual and TWA PEC _{SW} of dichlobenil (µg/L)	
	Actual PEC _{SW}	TWA PEC _{SW}
0	1.592	-
1	1.518	1.554
2	1.456	1.521
4	1.351	1.463
7	1.343	1.409
14	1.252	1.373
21	0.909	1.275
28	0.665	1.153
42	0.406	0.950
50	0.268	0.852
100	0.025	0.477

Table B.8.6.1v Actual and TWA PEC_{SW} (µg/L) of the soil metabolite 2,6-dichlorobenzamide following early application at maximum dose (5400 g a.s./ha) of dichlobenil to spring oil seed rape in the field according to FOCUS step 3, scenario R1 (Germany, ponds)

Days after application	Actual and TWA PEC _{SW} of 2,6-dichlorobenzamide (µg/L)	
	Actual PEC _{SW}	TWA PEC _{SW}
0	0.121	-
1	0.120	0.120
2	0.119	0.120
4	0.117	0.119
7	0.114	0.118
14	0.108	0.115
21	0.102	0.113
28	0.110	0.112
42	0.100	0.111
50	0.094	0.110
100	0.067	0.098

Table B.8.6.1w Actual and TWA PEC_{SW} (µg/L) of dichlobenil following early application at maximum dose (5400 g a.s./ha) of dichlobenil to spring oil seed rape in the field according to FOCUS step 3, scenario D1 (Lanna, streams)

Days after application	Actual and TWA PEC _{SW} of dichlobenil (µg/L)	
	Actual PEC _{SW}	TWA PEC _{SW}
0	39.194	-
1	23.965	34.758
2	1.936	34.121
4	0.113	33.713
7	0.043	33.170
14	0.018	30.718
21	25.930	28.266
28	32.993	26.357
42	21.243	23.508
50	18.069	22.208
100	10.873	16.782

Table B.8.6.1x Actual and TWA PEC_{SW} (µg/L) of the soil metabolite 2,6-dichlorobenzamide following early application at maximum dose (5400 g a.s./ha) of dichlobenil to spring oil seed rape in the field according to FOCUS step 3, scenario D1 (Lanna, streams)

Days after application	Actual and TWA PEC _{SW} of 2,6-dichlorobenzamide (µg/L)	
	Actual PEC _{SW}	TWA PEC _{SW}
0	138.618	-
1	137.547	138.442
2	135.595	138.009
4	129.460	136.145
7	117.277	131.887
14	113.770	123.539
21	106.168	120.153
28	105.262	118.071
42	101.161	111.611
50	103.073	109.598
100	85.387	105.100

Table B.8.6.1y Actual and TWA PEC_{SW} (µg/L) of dichlobenil following early application at maximum dose (5400 g a.s./ha) of dichlobenil to spring oil seed rape in the field according to FOCUS step 3, scenario D1 (Lanna, ditch)

Days after application	Actual and TWA PEC _{SW} of dichlobenil (µg/L)	
	Actual PEC _{SW}	TWA PEC _{SW}
0	53.565	-
1	52.830	53.437
2	52.437	53.135
4	51.985	52.829
7	46.800	51.773
14	37.165	47.432
21	30.850	44.357
28	27.392	41.633
42	23.225	37.221
50	20.543	35.188
100	11.181	26.543

Table B.8.6.1z Actual and TWA PEC_{SW} (µg/L) of the soil metabolite 2,6-dichlorobenzamide following early application at maximum dose (5400 g a.s./ha) of dichlobenil to spring oil seed rape in the field according to FOCUS step 3, scenario D1 (Lanna, ditch)

Days after application	Actual and TWA PEC _{SW} of 2,6-dichlorobenzamide (µg/L)	
	Actual PEC _{SW}	TWA PEC _{SW}
0	138.618	-
1	137.547	138.442
2	135.595	138.009
4	129.460	136.145
7	117.277	131.887
14	113.770	123.539
21	106.168	120.153
28	105.262	118.071
42	101.161	111.611
50	103.073	109.598
100	85.387	105.100

Table B.8.6.1za Actual and TWA PEC_{SW} (µg/L) of dichlobenil following early application at maximum dose (5400 g a.s./ha) of dichlobenil to spring oil seed rape in the field according to FOCUS step 3, scenario D3 (Vredepeel, ditch)

Days after application	Actual and TWA PEC _{SW} of dichlobenil (µg/L)	
	Actual PEC _{SW}	TWA PEC _{SW}
0	0.001	-
1	0.001	0.001
2	0.001	0.001
4	0.001	0.001
7	0.001	0.001
14	0.001	0.001
21	0.001	0.001
28	0.001	0.001
42	0.001	0.001
50	0.001	0.001
100	n.c.	0.001

n.c. = not calculable

Table B.8.6.1zb Actual and TWA PEC_{SW} (µg/L) of the soil metabolite 2,6-dichlorobenzamide following early application at maximum dose (5400 g a.s./ha) of dichlobenil to spring oil seed rape in the field according to FOCUS step 3, scenario D3 (Vredepeel, ditch)

Days after application	Actual and TWA PEC _{SW} of 2,6-dichlorobenzamide (µg/L)	
	Actual PEC _{SW}	TWA PEC _{SW}
0	89.744	-
1	89.624	89.671
2	89.656	89.669
4	89.665	89.660
7	89.616	89.645
14	89.377	89.605
21	88.915	89.538
28	88.737	89.485
42	88.391	89.409
50	88.274	89.367
100	85.205	89.035

Table B.8.6.1zc Actual and TWA PEC_{SW} ($\mu\text{g/L}$) of dichlobenil following early application at maximum dose (5400 g a.s./ha) of dichlobenil to spring oil seed rape in the field according to FOCUS step 3, scenario D4 (Skousbo, stream)

Days after application	Actual and TWA PEC_{SW} of dichlobenil ($\mu\text{g/L}$)	
	Actual PEC_{SW}	TWA PEC_{SW}
0	6.051	-
1	4.432	5.290
2	5.591	5.067
4	4.268	4.921
7	3.599	4.746
14	2.379	4.063
21	1.270	3.415
28	0.657	2.863
42	0.300	2.075
50	0.811	1.823
100	0.082	1.049

Table B.8.6.1zd Actual and TWA PEC_{SW} ($\mu\text{g/L}$) of the soil metabolite 2,6-dichlorobenzamide following early application at maximum dose (5400 g a.s./ha) of dichlobenil to spring oil seed rape in the field according to FOCUS step 3, scenario D4 (Skousbo, stream)

Days after application	Actual and TWA PEC_{SW} of 2,6-dichlorobenzamide ($\mu\text{g/L}$)	
	Actual PEC_{SW}	TWA PEC_{SW}
0	93.717	-
1	90.683	92.234
2	91.905	91.582
4	86.462	91.190
7	83.019	90.732
14	75.299	89.240
21	63.976	87.451
28	64.607	84.598
42	79.140	77.678
50	65.925	77.688
100	38.912	66.761

Table B.8.6.1ze Actual and TWA PEC_{SW} ($\mu\text{g/L}$) of dichlobenil following early application at maximum dose (5400 g a.s./ha) of dichlobenil to spring oil seed rape in the field according to FOCUS step 3, scenario D4 (Skousbo, pond)

Days after application	Actual and TWA PEC_{SW} of dichlobenil ($\mu\text{g/L}$)	
	Actual PEC_{SW}	TWA PEC_{SW}
0	4.176	-
1	4.164	4.175
2	4.135	4.171
4	4.054	4.157
7	3.904	4.123
14	3.467	4.033
21	3.059	3.922
28	2.693	3.796
42	2.259	3.519
50	1.977	3.364
100	0.881	2.542

Table B.8.6.1zf Actual and TWA PEC_{SW} ($\mu\text{g/L}$) of the soil metabolite 2,6-dichlorobenzamide following early application at maximum dose (5400 g a.s./ha) of dichlobenil to spring oil seed rape in the field according to FOCUS step 3, scenario D4 (Skousbo, pond)

Days after application	Actual and TWA PEC_{SW} of 2,6-dichlorobenzamide ($\mu\text{g/L}$)	
	Actual PEC_{SW}	TWA PEC_{SW}
0	185.381	-
1	185.346	185.378
2	185.242	185.369
4	184.850	185.333
7	183.856	185.225
14	180.769	184.712
21	177.261	183.883
28	173.525	182.830
42	165.917	180.300
50	161.661	178.699
100	n.c.	171.136

n.c. = not calculable

Table B.8.6.1zg Actual and TWA PEC_{SW} ($\mu\text{g/L}$) of dichlobenil following early application at maximum dose (5400 g a.s./ha) of dichlobenil to spring oil seed rape in the field according to FOCUS step 3, scenario D5 (France, streams)

Days after application	Actual and TWA PEC_{SW} of dichlobenil ($\mu\text{g/L}$)	
	Actual PEC_{SW}	TWA PEC_{SW}
0	1.180	-
1	0.661	0.880
2	0.771	0.871
4	0.841	0.834
7	0.888	0.814
14	0.373	0.759
21	0.264	0.735
28	0.221	0.724
42	0.259	0.710
50	0.230	0.695
100	n.c.	0.636

n.c. = not calculable

Table B.8.6.1zh Actual and TWA PEC_{SW} ($\mu\text{g/L}$) of the soil metabolite 2,6-dichlorobenzamide following early application at maximum dose (5400 g a.s./ha) of dichlobenil to spring oil seed rape in the field according to FOCUS step 3, scenario D5 (France, streams)

Days after application	Actual and TWA PEC_{SW} of 2,6-dichlorobenzamide ($\mu\text{g/L}$)	
	Actual PEC_{SW}	TWA PEC_{SW}
0	47.618	-
1	46.961	45.759
2	44.363	45.580
4	39.841	45.026
7	34.979	43.851
14	30.714	41.478
21	27.957	39.014
28	25.869	37.318
42	33.678	36.485
50	34.467	35.869
100	n.c.	34.110

n.c. = not calculable

Table B.8.6.1zi Actual and TWA PEC_{SW} (µg/L) of dichlobenil following early application at maximum dose (5400 g a.s./ha) of dichlobenil to spring oil seed rape in the field according to FOCUS step 3, scenario D5 (France, ponds)

Days after application	Actual and TWA PEC _{SW} of dichlobenil (µg/L)	
	Actual PEC _{SW}	TWA PEC _{SW}
0	1.237	-
1	1.230	1.236
2	1.216	1.234
4	1.178	1.226
7	1.116	1.209
14	0.978	1.157
21	0.845	1.101
28	0.733	1.094
42	0.611	1.058
50	0.545	1.029
100	n.c.	0.847

n.c. = not calculable

Table B.8.6.1zj Actual and TWA PEC_{SW} (µg/L) of the soil metabolite 2,6-dichlorobenzamide following early application at maximum dose (5400 g a.s./ha) of dichlobenil to spring oil seed rape in the field according to FOCUS step 3, scenario D5 (France, ponds)

Days after application	Actual and TWA PEC _{SW} of 2,6-dichlorobenzamide (µg/L)	
	Actual PEC _{SW}	TWA PEC _{SW}
0	114.400	-
1	114.379	114.398
2	114.326	114.392
4	114.118	114.368
7	113.652	114.295
14	112.134	114.007
21	110.267	113.747
28	n.c.	113.362
42	n.c.	112.316
50	n.c.	111.700
100	n.c.	102.139

n.c. = not calculable

Total maximum PEC_{SW} for 2,6-dichlorobenzamide (BAM) in each scenario

The *in situ* formation of BAM in the water-sediment is small compared to the amount of BAM entering the system via the soil (drainage/runoff), as the maximum percentage of *in situ* formed BAM is 5.32 % and 2.04 % in water and sediment (both at day 100/end of study), respectively.

The FOCUS surface water report⁶ (page 134) provides the following guidance on the need to model metabolites formed in a water-sediment study: the maximum formation mass should be compared to the monthly averaged hydraulic residence time of the FOCUS surface water bodies (τ). The monthly averaged

⁶ FOCUS (2001). "FOCUS Surface Water Scenarios in the EU Evaluation Process under 91/414/EEC".

Report of the FOCUS Working Group on Surface Water Scenarios, EC Document Reference

SANCO/4802/2001-rev.2. 245 pp.

residence time is approximately 0.1, 5 and 150 d for a stream, ditch and pond, respectively. It is then considered that if the time needed for maximum formation is larger than the residence time, the formation of metabolites in the FOCUS surface water body is negligible, (nearly all substance has flowed out before a considerable metabolite mass has been formed).

As the formation percentage at day 100 still can be considered minor, and the maximum residence time of 150 days (pond) is in the same order of magnitude, it is considered unnecessary to take the *in situ* formation of BAM into account. Moreover, the amount of soil derived BAM is more than ten times higher than the *in situ* formed amount. Therefore RMS considers that additional PEC calculations for the *in situ* formation of BAM can be considered superfluous.

Actual PEC_{SW} for the major metabolites 2-chlorobenzoic acid and 4-chloro-2(3H)benzoxazolone formed by degradation of dichlobenil in surface water

These metabolites can be formed by transformation of dichlobenil in the surface water.

For the metabolites 2-chlorobenzoic acid and 4-chloro-2(3H)benzoxazolone (*photolysis metabolite*) only the maximum percentage of formation is known and no other parameters. The PEC_{SW} of these metabolites are calculated on basis of the maximum PEC_{SW} of the parent and the corresponding percentage of formation: 9.13% and 17% respectively.

Table B.8.6.1zk Actual PEC_{SW} (µg/L) of the metabolites 2-chlorobenzoic acid and 4-chloro-2(3H)benzoxazolone following application at maximum dose (5400 g a.s./ha) of dichlobenil to vines and spring oil seed rape in the field according to FOCUS step 3, based on *in situ* formation rates only.

Crop	Scenario	Maximum PEC _{SW} (µg/L)	
		2-chlorobenzoic acid	4-chloro-2(3H)benzoxazolone
Vines	D6 ditch	21.917	40.809
	R1 stream	1.475	2.747
	R1 pond	0.009	0.016
	R2 stream	0.957	1.782
	R3 stream	4.479	8.339
	R4 stream	5.051	9.405
Non-crop (oil seed rape)	D1 stream	3.568	6.644
	D1 ditch	4.775	8.891
	D3 ditch	0.000	0.000
	D4 stream	0.552	1.028
	D4 pond	0.292	0.543
	D5 stream	0.108	0.201
	D5 pond	0.092	0.172
	R1 stream	3.338	6.216
	R1 pond	0.144	0.268

B.8.6.2 Predicted environmental concentrations in groundwater

Annual applications were simulated for a period of 20 years with a six-year "warm-up period", using FOCUS PEARL version 3.3.3. Simulations were performed for vines and non-crop (fallow soil) situations in the North and South of Europe.

The maximum dose of 5.4 kg a.s./ha was not corrected for the interception by the crop (0% for treatment with granules) and the fraction of the dose on soil was assumed to be 1 (100%). Application was set to a yearly dosage. Since the application date was not specified, the date of application was chosen to be 25th May for both North Europe and South Europe. The average lab DT_{50} value (40.5 days), average K_{OM} value (137.5 L/kg) and a default 1/n value (0.9) were used for modelling. Sorption was assumed to be pH-independent. One metabolite > 10%, 2,6-dichlorobenzamide, was detected in soil. It is assumed that the metabolite is formed at a maximum of 69.41% of the applied dose. An average DT_{50} (field) value of 125.0 days was determined for the metabolite 2,6-dichlorobenzamide assuming SFO kinetics. The average K_{OC} value for this metabolite amounts to 41 L/kg corresponding with an average K_{OM} value of 24 L/kg. Physico-chemical parameters of dichlobenil and BAM are shown in Table B.8.6.2a.

Table B.8.6.2a Physico-chemical parameters of dichlobenil and BAM used for modelling

Substance	Parameter	Value	Unit
Dichlobenil	molecular mass	172	g/mol
	vapour pressure	0.135	Pa (25°C)
	water solubility	21.2	mg/L (pH 7, 25°C)
2,6-dichlorobenzamide (BAM)	molecular mass	190	g/mol
	vapour pressure	2 E-05	Pa (25°C)
	water solubility	1830	mg/L (pH 7, 25°C)

All other substance parameters in PEARL were set at the default values recommended by the FOCUS working group. The results of the modelling are shown in Table B.8.6.2b and c.

Table B.8.6.2b FOCUS-PEARL estimations of concentrations in groundwater (80th percentile, µg/L) of dichlobenil and the metabolite 2,6-dichlorobenzamide after single application to vines

FOCUS scenario	80th percentile concentration in groundwater (µg/L) of dichlobenil	80th percentile concentration in groundwater (µg/L) of 2,6-dichlorobenzamide
Location	Single application (May)	Single application (May)
Chateaudun	0.288	340.961
Hamburg	0.191	380.348
Kremsmünster	0.107	302.933
Piacenza	2.693	290.500
Porto	< 0.001	84.149
Sevilla	0.180	278.559
Thiva	0.3174	262.178

Table B.8.6.2c FOCUS-PEARL estimations of concentrations in groundwater (80th percentile, µg/L) of dichlobenil and the metabolite 2,6-dichlorobenzamide after single application on bare soil

FOCUS scenario	80th percentile concentration in groundwater (µg/L) of dichlobenil	80th percentile concentration in groundwater (µg/L) of 2,6-dichlorobenzamide
Location	Single application (May)	Single application (May)
Chateaudun	< 0.001	284.050
Hamburg	0.061	364.929
Jokioinen	< 0.0012	324.477
Kremsmünster	0.033	293.002
Okehampton	0.0742	287.690
Piacenza	0.327	284.115
Porto	< 0.001	80.079
Sevilla	< 0.001	180.728
Thiva	< 0.001	183.314

For crop type vines estimated 80th percentile dichlobenil concentrations in groundwater were < 0.1 µg/L for the scenario Porto, but ≥ 0.1 µg/L for the scenarios Chateaudun, Hamburg, Kremsmünster, Piacenza, Sevilla and Thiva. For the metabolite 2,6-dichlorobenzamide concentrations ≥ 0.1 µg/L were found in all relevant scenarios.

In case of application on bare soil (non-crop) dichlobenil concentrations in groundwater were < 0.1 µg/L for 8 of the 9 scenarios. For scenario Piacenza ≥ 0.1 µg/L for dichlobenil was found. For the metabolite 2,6-dichlorobenzamide concentrations ≥ 0.1 µg/L were found in all 9 scenarios.

It can be concluded that a safe use with regard to the leaching potential has been demonstrated for dichlobenil in some scenarios. A potential for leaching is demonstrated for 2,6-dichlorobenzamide in all scenarios.

See for the assessment of non-relevance Volume 1, appendix 4.

B.8.6.3 Predicted environmental concentrations in sediment (PEC_{SED})

Water/sediment studies were conducted in two water/sediment systems. The average DT₅₀ for the whole water/sediment system was 186.5 days and 10.5 days for water (dissipation half-life). As no DegT₅₀ was derived for the water phase, the average system value was used to calculate the PEC values in surface water. For sediment a DT₅₀ value of 1000 d was used for the PEC_{SED} calculations. Dichlobenil is found to be hydrolytically stable.

The PEC_{SED} values are calculated by use of the FOCUS Step 1, Step 2 and Step 3 approach (FOCUS, 2001). No major metabolites (> 10%, > 5% at two consecutive time points, or increasing towards the end of the study) were detected in sediment. Although the *in situ* formation of 2,6-dichlorobenzamide (BAM) in sediment is negligible, input via soil is considered relevant. Therefore, PEC_{SED} values are also determined for BAM.

The results of the Step 1 calculation are listed in Table 8.6.3a-b.

Table B.8.6.3a Actual and TWA PEC_{SED} ($\mu\text{g/kg}$ dry sediment) of dichlobenil following application at maximum dose (5400 g a.s./ha) in the field according to FOCUS step 1

Days after application	Actual and TWA PEC_{SED} of dichlobenil ($\mu\text{g/kg}$ dw)	
	Actual PEC_{SED}	TWA PEC_{SED}
0	3240	
1	3230	3240
2	3220	3230
4	3190	3220
7	3160	3200
14	3080	3160
21	3000	3120
28	2920	3080
42	2770	3000
50	2690	2960
100	2240	2710

Table B.8.6.3b Actual and TWA PEC_{SED} ($\mu\text{g/kg}$ dry sediment) of the soil metabolite 2,6-dichlorobenzamide following application at maximum dose (5400 g a.s./ha) in the field according to FOCUS step 1

Days after application	Actual and TWA PEC_{SED} of 2,6-dichlorobenzamide ($\mu\text{g/kg}$ dw)	
	Actual PEC_{SED}	TWA PEC_{SED}
0	536.4728	-
1	536.1011	536.2870
2	535.7296	536.1011
4	534.9875	535.7298
7	533.8761	535.1734
14	531.2920	533.8782
21	528.7204	532.5872
28	526.1613	531.3004
42	521.0801	528.7391
50	518.1986	527.2829
100	500.5468	518.3023

The results for sediment of the Step 2 calculations are listed in Table B.8.6.3c-f.

Table B.8.6.3c Actual and TWA PEC_{SED} (µg/kg dry sediment) of dichlobenil following application at maximum dose (5400 g a.s./ha) in the field according to FOCUS step 2, early (March-May) application in North Europe

Days after application	Actual and TWA PEC _{SED} of dichlobenil (µg/kg dw)	
	Actual PEC _{SED}	TWA PEC _{SED}
0	605.4295	---
1	605.0100	605.2198
2	603.2039	604.6634
4	599.6078	603.0339
7	594.2537	600.4167
14	581.9462	594.2478
21	569.8935	588.1316
28	558.0905	582.0917
42	535.2127	570.2519
50	522.5633	563.6297
100	450.0044	524.5052

Table B.8.6.3d Actual and TWA PEC_{SED} (µg/kg dry sediment) of dichlobenil following application at maximum dose (5400 g a.s./ha) in the field according to FOCUS step 2, early (March-May) application in South Europe

Days after application	Actual and TWA PEC _{SED} of dichlobenil (µg/kg dw)	
	Actual PEC _{SED}	TWA PEC _{SED}
0	1.21E+03	---
1	1.21E+03	1.21E+03
2	1.21E+03	1.21E+03
4	1.2E+03	1.21E+03
7	1.19E+03	1.2E+03
14	1.16E+03	1.19E+03
21	1.14E+03	1.18E+03
28	1.12E+03	1.16E+03
42	1.07E+03	1.14E+03
50	1.05E+03	1.13E+03
100	900.0088	1.05E+03

Table B.8.6.3e Actual and TWA PEC_{SED} (µg/kg dry sediment) of the soil metabolite 2,6-dichlorobenzamide following application at maximum dose (5400 g a.s./ha) in the field according to FOCUS step 2, early (March-May) application in North Europe

Days after application	Actual and TWA PEC _{SED} of 2,6-dichlorobenzamide (µg/kg dw)	
	Actual PEC _{SED}	TWA PEC _{SED}
0	104.9409	---
1	104.8682	104.9045
2	104.7955	104.8682
4	104.6503	104.7956
7	104.4330	104.6867
14	103.9275	104.4334
21	103.4244	104.1808
28	102.9238	103.9291
42	101.9299	103.4281
50	101.3662	103.1432
100	97.9133	101.3865

Table B.8.6.3f Actual and TWA PEC_{SED} ($\mu\text{g/kg}$ dry sediment) of the soil metabolite 2,6-dichlorobenzamide following application at maximum dose (5400 g a.s./ha) in the field according to FOCUS step 2, early (March-May) application in South Europe

Days after application	Actual and TWA PEC_{SED} of 2,6-dichlorobenzamide ($\mu\text{g/kg dw}$)	
	Actual PEC_{SED}	TWA PEC_{SED}
0	209.8818	---
1	209.7364	209.8091
2	209.5910	209.7364
4	209.3007	209.5911
7	208.8659	209.3734
14	207.8549	208.8667
21	206.8489	208.3617
28	205.8477	207.8582
42	203.8598	206.8562
50	202.7324	206.2865
100	195.8266	202.7730

The results of the Step 3 calculations are listed in the Tables B.8.6.3g-zj. Tables B.8.6.3g – B.8.6.3r correspond with applications at vines and Tables B.8.6.3s – B.8.6.3zj correspond with applications to non-crop (bare soil).

Table B.8.6.3g Actual and TWA PEC_{SED} ($\mu\text{g/kg}$) of dichlobenil following early application at maximum dose (5400 g a.s./ha) of dichlobenil to vines in the field according to FOCUS step 3, scenario D6 (Thiva, ditches)

Days after application	Actual and TWA PEC_{SED} of dichlobenil ($\mu\text{g/kg}$)	
	Actual PEC_{SED}	TWA PEC_{SED}
0	97.806	-
1	96.380	97.381
2	96.359	96.644
4	88.465	95.783
7	87.882	92.898
14	70.796	87.726
21	61.026	81.243
28	54.911	75.809
42	47.784	67.923
50	47.416	64.598
100	30.698	51.928

Table B.8.6.3h Actual and TWA PEC_{SED} ($\mu\text{g/kg}$) of the soil metabolite 2,6-dichlorobenzamide following early application at maximum dose (5400 g a.s./ha) of dichlobenil to vines in the field according to FOCUS step 3, scenario D6 (Thiva, ditches)

Days after application	Actual and TWA PEC_{SED} of 2,6-dichlorobenzamide ($\mu\text{g/kg}$)	
	Actual PEC_{SED}	TWA PEC_{SED}
0	68.868	-
1	68.835	68.864
2	68.801	68.855
4	68.838	68.833
7	67.982	68.818
14	61.011	68.459
21	52.693	68.010
28	n.c.	67.296
42	n.c.	65.912

50	n.c.	65.132
100	n.c.	58.610

n.c. Not calculable.

Table B.8.6.3i Actual and TWA PEC_{SED} ($\mu\text{g/kg}$) of dichlobenil following early application at maximum dose (5400 g a.s./ha) of dichlobenil to vines in the field according to FOCUS step 3, scenario R1 (Germany, streams)

Days after application	Actual and TWA PEC_{SED} of dichlobenil ($\mu\text{g/kg}$)	
	Actual PEC_{SED}	TWA PEC_{SED}
0	3.908	-
1	1.794	2.901
2	1.306	2.291
4	0.950	1.728
7	0.732	1.354
14	0.729	1.095
21	0.561	0.944
28	0.480	0.838
42	0.441	0.727
50	0.394	0.678
100	0.267	0.499

Table B.8.6.3j Actual and TWA PEC_{SED} ($\mu\text{g/kg}$) of the soil metabolite 2,6-dichlorobenzamide following early application at maximum dose (5400 g a.s./ha) of dichlobenil to vines in the field according to FOCUS step 3, scenario R1 (Germany, streams)

Days after application	Actual and TWA PEC_{SED} of 2,6-dichlorobenzamide ($\mu\text{g/kg}$)	
	Actual PEC_{SED}	TWA PEC_{SED}
0	0.160	-
1	0.060	0.108
2	0.044	0.083
4	0.033	0.062
7	0.026	0.048
14	0.023	0.037
21	0.018	0.032
28	0.015	0.028
42	0.018	0.026
50	0.015	0.024
100	0.010	0.018

Table B.8.6.3k Actual and TWA PEC_{SED} ($\mu\text{g/kg}$) of dichlobenil following early application at maximum dose (5400 g a.s./ha) of dichlobenil to vines in the field according to FOCUS step 3, scenario R1 (Germany, ponds)

Days after application	Actual and TWA PEC_{SED} of dichlobenil ($\mu\text{g/kg}$)	
	Actual PEC_{SED}	TWA PEC_{SED}
0	0.190	-
1	0.190	0.190
2	0.190	0.190
4	0.189	0.190
7	0.186	0.189
14	0.189	0.188
21	0.182	0.188
28	0.171	0.188
42	0.149	0.183
50	0.138	0.180
100	0.096	0.154

Table B.8.6.3l Actual and TWA PEC_{SED} ($\mu\text{g/kg}$) of the soil metabolite 2,6-dichlorobenzamide following early application at maximum dose (5400 g a.s./ha) of dichlobenil to vines in the field according to FOCUS step 3, scenario R1 (Germany, ponds)

Days after application	Actual and TWA PEC_{SED} of 2,6-dichlorobenzamide ($\mu\text{g/kg}$)	
	Actual PEC_{SED}	TWA PEC_{SED}
0	0.017	-
1	0.017	0.017
2	0.017	0.017
4	0.017	0.017
7	0.017	0.017
14	0.017	0.017
21	0.017	0.017
28	0.017	0.017
42	0.017	0.017
50	0.016	0.017
100	0.015	0.017

Table B.8.6.3m Actual and TWA PEC_{SED} ($\mu\text{g/kg}$) of dichlobenil following early application at maximum dose (5400 g a.s./ha) of dichlobenil to vines in the field according to FOCUS step 3, scenario R2 (Portugal, streams)

Days after application	Actual and TWA PEC_{SED} of dichlobenil ($\mu\text{g/kg}$)	
	Actual PEC_{SED}	TWA PEC_{SED}
0	2.980	-
1	1.40	2.252
2	1.026	1.796
4	0.749	1.362
7	0.579	1.070
14	0.421	0.817
21	0.350	0.714
28	0.893	0.681
42	0.506	0.668
50	0.443	0.638
100	0.316	0.499

Table B.8.6.3n Actual and TWA PEC_{SED} ($\mu\text{g/kg}$) of the soil metabolite 2,6-dichlorobenzamide following early application at maximum dose (5400 g a.s./ha) of dichlobenil to vines in the field according to FOCUS step 3, scenario R2 (Portugal, streams)

Days after application	Actual and TWA PEC_{SED} of 2,6-dichlorobenzamide ($\mu\text{g/kg}$)	
	Actual PEC_{SED}	TWA PEC_{SED}
0	0.279	-
1	0.107	0.195
2	0.081	0.151
4	0.060	0.112
7	0.047	0.088
14	0.034	0.064
21	0.028	0.053
28	0.045	0.050
42	0.029	0.045
50	0.026	0.042
100	0.021	0.032

Table B.8.6.3o Actual and TWA PEC_{SED} ($\mu\text{g/kg}$) of dichlobenil following early application at maximum dose (5400 g a.s./ha) of dichlobenil to vines in the field according to FOCUS step 3, scenario R3 (Italy, streams)

Days after application	Actual and TWA PEC_{SED} of dichlobenil ($\mu\text{g/kg}$)	
	Actual PEC_{SED}	TWA PEC_{SED}
0	17.127	-
1	9.509	14.932
2	7.161	12.453
4	5.313	9.672
7	4.138	7.667
14	3.035	5.652
21	2.524	4.708
28	2.208	4.130
42	1.818	3.426
50	1.668	3.159
100	1.173	2.275

Table B.8.6.3p Actual and TWA PEC_{SED} ($\mu\text{g/kg}$) of the soil metabolite 2,6-dichlorobenzamide following early application at maximum dose (5400 g a.s./ha) of dichlobenil to vines in the field according to FOCUS step 3, scenario R3 (Italy, streams)

Days after application	Actual and TWA PEC_{SED} of 2,6-dichlorobenzamide ($\mu\text{g/kg}$)	
	Actual PEC_{SED}	TWA PEC_{SED}
0	1.328	-
1	0.677	1.141
2	0.515	0.936
4	0.386	0.718
7	0.301	0.566
14	0.219	0.415
21	0.181	0.344
28	0.158	0.301
42	0.129	0.249
50	0.118	0.229
100	0.076	0.162

Table B.8.6.3q Actual and TWA PEC_{SED} ($\mu\text{g/kg}$) of dichlobenil following early application at maximum dose (5400 g a.s./ha) of dichlobenil to vines in the field according to FOCUS step 3, scenario R4 (France, streams)

Days after application	Actual and TWA PEC_{SED} of dichlobenil ($\mu\text{g/kg}$)	
	Actual PEC_{SED}	TWA PEC_{SED}
0	16.238	-
1	7.737	12.797
2	5.776	10.272
4	4.258	7.817
7	3.304	6.146
14	2.418	4.507
21	2.012	3.749
28	2.533	3.317
42	1.647	2.862
50	1.492	2.656
100	1.031	1.942

Table B.8.6.3r Actual and TWA PEC_{SED} ($\mu\text{g/kg}$) of the soil metabolite 2,6-dichlorobenzamide following early application at maximum dose (5400 g a.s./ha) of dichlobenil to vines in the field according to FOCUS step 3, scenario R4 (France, streams)

Days after application	Actual and TWA PEC_{SED} of 2,6-dichlorobenzamide ($\mu\text{g/kg}$)	
	Actual PEC_{SED}	TWA PEC_{SED}
0	0.473	-
1	0.200	0.357
2	0.151	0.280
4	0.112	0.211
7	0.088	0.165
14	0.064	0.120
21	0.053	0.100
28	0.071	0.088
42	0.045	0.077
50	0.040	0.071
100	0.026	0.052

Spring oil seed rape as example for non-crop application (bare soil)

Table B.8.6.3s Actual and TWA PEC_{SED} ($\mu\text{g/kg}$) of dichlobenil following early application at maximum dose (5400 g a.s./ha) of dichlobenil to spring oil seed rape in the field according to FOCUS step 3, scenario R1 (Germany, streams)

Days after application	Actual and TWA PEC_{SED} of dichlobenil ($\mu\text{g/kg}$)	
	Actual PEC_{SED}	TWA PEC_{SED}
0	9.142	-
1	4.373	7.181
2	3.225	5.708
4	2.586	4.322
7	2.810	3.666
14	2.230	3.096
21	1.625	2.692
28	1.387	2.397
42	1.186	2.045
50	1.070	1.899
100	0.743	1.393

Table B.8.6.3t Actual and TWA PEC_{SED} ($\mu\text{g/kg}$) of the soil metabolite 2,6-dichlorobenzamide following early application at maximum dose (5400 g a.s./ha) of dichlobenil to spring oil seed rape in the field according to FOCUS step 3, scenario R1 (Germany, streams)

Days after application	Actual and TWA PEC_{SED} of 2,6-dichlorobenzamide ($\mu\text{g/kg}$)	
	Actual PEC_{SED}	TWA PEC_{SED}
0	0.357	-
1	0.151	0.266
2	0.112	0.206
4	0.089	0.154
7	0.084	0.126
14	0.071	0.101
21	0.050	0.087
28	0.043	0.077
42	0.041	0.067
50	0.036	0.062
100	0.024	0.046

Table B.8.6.3u Actual and TWA PEC_{SED} (µg/kg) of dichlobenil following early application at maximum dose (5400 g a.s./ha) of dichlobenil to spring oil seed rape in the field according to FOCUS step 3, scenario R1 (Germany, ponds)

Days after application	Actual and TWA PEC _{SED} of dichlobenil (µg/kg)	
	Actual PEC _{SED}	TWA PEC _{SED}
0	2.706	-
1	2.705	2.706
2	2.701	2.706
4	2.687	2.704
7	2.653	2.700
14	2.606	2.683
21	2.483	2.665
28	2.323	2.640
42	2.018	2.562
50	1.871	2.504
100	1.316	2.128

Table B.8.6.3v Actual and TWA PEC_{SED} (µg/kg) of the soil metabolite 2,6-dichlorobenzamide following early application at maximum dose (5400 g a.s./ha) of dichlobenil to spring oil seed rape in the field according to FOCUS step 3, scenario R1 (Germany, ponds)

Days after application	Actual and TWA PEC _{SED} of 2,6-dichlorobenzamide (µg/kg)	
	Actual PEC _{SED}	TWA PEC _{SED}
0	0.215	-
1	0.215	0.215
2	0.215	0.215
4	0.214	0.215
7	0.214	0.215
14	0.213	0.215
21	0.211	0.215
28	0.209	0.214
42	0.205	0.214
50	0.202	0.214
100	0.179	0.210

Table B.8.6.3w Actual and TWA PEC_{SED} (µg/kg) of dichlobenil following early application at maximum dose (5400 g a.s./ha) of dichlobenil to spring oil seed rape in the field according to FOCUS step 3, scenario D1 (Lanna, streams)

Days after application	Actual and TWA PEC _{SED} of dichlobenil (µg/kg)	
	Actual PEC _{SED}	TWA PEC _{SED}
0	87.808	-
1	n.c.	87.728
2	n.c.	87.697
4	n.c.	87.671
7	n.c.	87.614
14	n.c.	87.252
21	n.c.	86.939
28	n.c.	86.668
42	n.c.	85.812
50	n.c.	85.138
100	n.c.	83.488

n.c. Not calculable.

Table B.8.6.3x Actual and TWA PEC_{SED} ($\mu\text{g/kg}$) of the soil metabolite 2,6-dichlorobenzamide following early application at maximum dose (5400 g a.s./ha) of dichlobenil to spring oil seed rape in the field according to FOCUS step 3, scenario D1 (Lanna, streams)

Days after application	Actual and TWA PEC_{SED} of 2,6-dichlorobenzamide ($\mu\text{g/kg}$)	
	Actual PEC_{SED}	TWA PEC_{SED}
0	212.779	-
1	n.c.	212.629
2	n.c.	212.513
4	n.c.	212.300
7	n.c.	211.998
14	n.c.	211.780
21	n.c.	211.252
28	n.c.	210.458
42	n.c.	208.944
50	n.c.	208.180
100	n.c.	202.644

n.c. Not calculable.

Table B.8.6.3y Actual and TWA PEC_{SED} ($\mu\text{g/kg}$) of dichlobenil following early application at maximum dose (5400 g a.s./ha) of dichlobenil to spring oil seed rape in the field according to FOCUS step 3, scenario D1 (Lanna, ditch)

Days after application	Actual and TWA PEC_{SED} of dichlobenil ($\mu\text{g/kg}$)	
	Actual PEC_{SED}	TWA PEC_{SED}
0	137.564	-
1	n.c.	137.474
2	n.c.	137.470
4	n.c.	137.466
7	n.c.	137.419
14	n.c.	136.859
21	n.c.	136.429
28	n.c.	136.092
42	n.c.	134.923
50	n.c.	134.000
100	n.c.	131.806

n.c. Not calculable.

Table B.8.6.3z Actual and TWA PEC_{SED} ($\mu\text{g/kg}$) of the soil metabolite 2,6-dichlorobenzamide following early application at maximum dose (5400 g a.s./ha) of dichlobenil to spring oil seed rape in the field according to FOCUS step 3, scenario D1 (Lanna, ditch)

Days after application	Actual and TWA PEC_{SED} of 2,6-dichlorobenzamide ($\mu\text{g/kg}$)	
	Actual PEC_{SED}	TWA PEC_{SED}
0	212.779	-
1	n.c.	212.629
2	n.c.	212.513
4	n.c.	212.300
7	n.c.	211.998
14	n.c.	211.780
21	n.c.	211.252
28	n.c.	210.458
42	n.c.	208.944
50	n.c.	208.180
100	n.c.	202.644

n.c. Not calculable.

Table B.8.6.3za Actual and TWA PEC_{SED} ($\mu\text{g/kg}$) of dichlobenil following early application at maximum dose (5400 g a.s./ha) of dichlobenil to spring oil seed rape in the field according to FOCUS step 3, scenario D3 (Vredepeel, ditch)

Days after application	Actual and TWA PEC_{SED} of dichlobenil ($\mu\text{g/kg}$)	
	Actual PEC_{SED}	TWA PEC_{SED}
0	0.009	-
1	n.c.	0.009
2	n.c.	0.009
4	n.c.	0.009
7	n.c.	0.009
14	n.c.	0.009
21	n.c.	0.009
28	n.c.	0.009
42	n.c.	0.009
50	n.c.	0.009
100	n.c.	0.008

n.c. Not calculable.

Table B.8.6.3zb Actual and TWA PEC_{SED} ($\mu\text{g/kg}$) of the soil metabolite 2,6-dichlorobenzamide following early application at maximum dose (5400 g a.s./ha) of dichlobenil to spring oil seed rape in the field according to FOCUS step 3, scenario D3 (Vredepeel, ditch)

Days after application	Actual and TWA PEC_{SED} of 2,6-dichlorobenzamide ($\mu\text{g/kg}$)	
	Actual PEC_{SED}	TWA PEC_{SED}
0	219.226	-
1	n.c.	219.199
2	n.c.	219.172
4	n.c.	219.118
7	n.c.	219.037
14	n.c.	218.849
21	n.c.	218.668
28	n.c.	218.497
42	n.c.	218.091
50	n.c.	217.799
100	n.c.	215.496

n.c. Not calculable.

Table B.8.6.3zc Actual and TWA PEC_{SED} ($\mu\text{g/kg}$) of dichlobenil following early application at maximum dose (5400 g a.s./ha) of dichlobenil to spring oil seed rape in the field according to FOCUS step 3, scenario D4 (Skousbo, stream)

Days after application	Actual and TWA PEC_{SED} of dichlobenil ($\mu\text{g/kg}$)	
	Actual PEC_{SED}	TWA PEC_{SED}
0	7.065	-
1	7.011	7.060
2	6.941	7.052
4	6.767	7.042
7	6.533	7.036
14	5.826	6.939
21	5.219	6.778
28	4.810	6.566
42	4.987	6.099
50	4.634	5.921
100	3.399	5.107

Table B.8.6.3zd Actual and TWA PEC_{SED} ($\mu\text{g/kg}$) of the soil metabolite 2,6-dichlorobenzamide following early application at maximum dose (5400 g a.s./ha) of dichlobenil to spring oil seed rape in the field according to FOCUS step 3, scenario D4 (Skousbo, stream)

Days after application	Actual and TWA PEC_{SED} of 2,6-dichlorobenzamide ($\mu\text{g/kg}$)	
	Actual PEC_{SED}	TWA PEC_{SED}
0	133.650	-
1	133.618	133.648
2	133.524	133.644
4	133.157	133.628
7	132.050	133.552
14	129.629	133.123
21	127.043	132.410
28	124.226	131.595
42	119.034	129.704
50	116.393	128.520
100	n.c.	123.693

n.c. Not calculable.

Table B.8.6.3ze Actual and TWA PEC_{SED} ($\mu\text{g/kg}$) of dichlobenil following early application at maximum dose (5400 g a.s./ha) of dichlobenil to spring oil seed rape in the field according to FOCUS step 3, scenario D4 (Skousbo, pond)

Days after application	Actual and TWA PEC_{SED} of dichlobenil ($\mu\text{g/kg}$)	
	Actual PEC_{SED}	TWA PEC_{SED}
0	11.270	-
1	11.270	11.270
2	11.267	11.270
4	11.256	11.269
7	11.229	11.266
14	11.125	11.255
21	10.981	11.235
28	10.809	11.208
42	10.419	11.138
50	10.182	11.094
100	n.c.	10.697

n.c. Not calculable.

Table B.8.6.3zf Actual and TWA PEC_{SED} ($\mu\text{g/kg}$) of the soil metabolite 2,6-dichlorobenzamide following early application at maximum dose (5400 g a.s./ha) of dichlobenil to spring oil seed rape in the field according to FOCUS step 3, scenario D4 (Skousbo, pond)

Days after application	Actual and TWA PEC_{SED} of 2,6-dichlorobenzamide ($\mu\text{g/kg}$)	
	Actual PEC_{SED}	TWA PEC_{SED}
0	349.769	-
1	349.764	349.768
2	349.751	349.767
4	349.698	349.763
7	349.594	349.751
14	n.c.	349.699
21	n.c.	349.634
28	n.c.	349.449
42	n.c.	348.702
50	n.c.	347.973
100	n.c.	333.413

n.c. Not calculable.

Table B.8.6.3zg Actual and TWA PEC_{SED} ($\mu\text{g/kg}$) of dichlobenil following early application at maximum dose (5400 g a.s./ha) of dichlobenil to spring oil seed rape in the field according to FOCUS step 3, scenario D5 (France, streams)

Days after application	Actual and TWA PEC_{SED} of dichlobenil ($\mu\text{g/kg}$)	
	Actual PEC_{SED}	TWA PEC_{SED}
0	3.109	-
1	3.109	3.109
2	3.107	3.109
4	3.101	3.108
7	3.092	3.106
14	3.103	3.100
21	3.079	3.100
28	2.921	3.097
42	2.428	3.086
50	2.265	3.076
100	1.723	2.931

Table B.8.6.3zh Actual and TWA PEC_{SED} ($\mu\text{g/kg}$) of the soil metabolite 2,6-dichlorobenzamide following early application at maximum dose (5400 g a.s./ha) of dichlobenil to spring oil seed rape in the field according to FOCUS step 3, scenario D5 (France, streams)

Days after application	Actual and TWA PEC_{SED} of 2,6-dichlorobenzamide ($\mu\text{g/kg}$)	
	Actual PEC_{SED}	TWA PEC_{SED}
0	66.063	-
1	65.940	66.058
2	65.882	66.054
4	65.747	66.045
7	65.374	66.024
14	n.c.	65.935
21	n.c.	65.774
28	n.c.	65.506
42	n.c.	64.351
50	n.c.	63.197
100	n.c.	56.593

n.c. Not calculable.

Table B.8.6.3zi Actual and TWA PEC_{SED} ($\mu\text{g/kg}$) of dichlobenil following early application at maximum dose (5400 g a.s./ha) of dichlobenil to spring oil seed rape in the field according to FOCUS step 3, scenario D5 (France, ponds)

Days after application	Actual and TWA PEC_{SED} of dichlobenil ($\mu\text{g/kg}$)	
	Actual PEC_{SED}	TWA PEC_{SED}
0	4.321	-
1	4.321	4.321
2	4.319	4.321
4	4.312	4.320
7	4.302	4.319
14	4.258	4.315
21	4.193	4.311
28	4.113	4.306
42	n.c.	4.289
50	n.c.	4.276
100	n.c.	3.707

n.c. Not calculable.

Table B.8.6.3zj Actual and TWA PEC_{SED} ($\mu\text{g/kg}$) of the soil metabolite 2,6-dichlorobenzamide following early application at maximum dose (5400 g a.s./ha) of dichlobenil to spring oil seed rape in the field according to FOCUS step 3, scenario D5 (France, ponds)

Days after application	Actual and TWA PEC_{SED} of 2,6-dichlorobenzamide ($\mu\text{g/kg}$)	
	Actual PEC_{SED}	TWA PEC_{SED}
0	236.977	-
1	n.c.	236.816
2	n.c.	236.648
4	n.c.	236.297
7	n.c.	235.735
14	n.c.	234.239
21	n.c.	232.452
28	n.c.	230.335
42	n.c.	225.355
50	n.c.	222.345
100	n.c.	196.281

n.c. Not calculable.

B.8.7 FATE AND BEHAVIOUR IN AIR

B.8.7.1 Photolysis

B.8.7.1.1 Photolytic degradation of the active substance in air (IIA 2.10/01 and IIA 7.2.2/01)

Characteristics of the study

Reference	: Joustra <i>et al.</i> (1993)	Radiochemical purity	: 98.8%
Year of execution	: 1989	Specific activity	: 16.9 mCi/g
Guideline	: EPA 161-4	Test substance 2	: dichlobenil; batch no. ARS2I01N; appearance and purity not indicated
GLP	: yes	DT ₅₀ (pH 7)	: 2.8 d (artificial sunlight) 1.4 d (natural sunlight)
Test substance 1	: [U- ¹⁴ C]-2,6-dichlorobenzonitrile (dichlobenil); batch no. AOI87H05A; appearance not indicated	Metabolites	: 2,6-dichlorobenzamide
Chemical purity	: 98.9%	Acceptable	: yes

Study design

The purpose of the study was to determine the half life of [¹⁴C]dichlobenil in air when exposed to xenon light and to identify possible degradation products. After the incubation period, the test substance and possible degradation products were condensed before analysis. Unlabeled test material was used to identify very volatile photodegradation products that could not be recovered by condensation. In this study, 24 h irradiation with xenon light equals 0.5 d of natural sunlight at 50° North latitude.

Study design

duration of the test	: 10 d
temperature	: 25°C
light conditions	: 24 h light/d; xenon lamp (average light intensity was half that of natural sunlight)
relative humidity	: 35 – 50%
Photolysis equipment	: SUNTEST apparatus from Heraeus Instruments; average intensity of SUNTEST light at the specimen plane is half that of natural light
type of test vessel and content	: closed 10-L Pyrex ampoules; 0.5 mL test solution; one ampoule each sampling time
dosing of test substance	: stock solution in acetonitrile; 0.4 ml water was added to created a moisture saturated gas phase
nominal test substance concentration	: 12.5 µg a.s.per ampoule
Relative humidity in laboratory	: 35 – 50%
irradiation	: continuously during 1, 2, 4, 6 or 10 days
determination of applied radioactivity, quantitative chemical analysis and	: HPLC, LSC, GC-MS

identification photoproducts

sampling times : 1, 2, 4, 6 and 10 d for irradiated vessels and 4 and 10 d for dark controls

Results

The recovery of the applied radioactivity in irradiated and dark control samples was 99%, respectively. However, the recovery decreased in time from 89.5% after 1 d to 22.0% after 10 d of irradiation. Because of the incomplete ^{14}C -mass balance, an additional experiment was performed to analyse volatile photodegradation products.

There was no photodegradation of [^{14}C]-dichlobenil in the dark controls, which was shown by the high recovery of the test substance in the condensate (99%). After 10 d of continuous irradiation, only 10.3% of the initially added amount of test substance was recovered. The results are summarised in Table B.8.7.1.1a; DT_{50} values are given in Table B.8.7.1.1b. The calculated half-life of [^{14}C]-dichlobenil in air is 2.8 d, which equals 1.4 d of natural sunlight at 50° North latitude. RMS found a similar result using TableCurve 2D version 4.

One major metabolite was 2,6-dichlorobenzamide (BAM), which accounted for ca. 15% of the initial amount of radioactivity after 10 d of irradiation. At least five minor metabolites were formed, each comprising for ca. 1 – 4% of the initially applied radioactivity.

Table B.8.7.1.1a Results of the photolysis study with [^{14}C]-dichlobenil in air, expressed in μg in peaks as % of initial

Sample	Measured $\mu\text{g}/\text{ml}$ total C^{14}	% of initial	Mg dichlobenil in peak	Mg BAM in peak
starting solution	13.24			
4 days dark	0.132	99.5	0.132	-
10 days dark	0.132	98.6	0.131	-
1 day irradiated	0.110	89.5	0.115	0.003
2 days irradiated	0.083	62.4	0.074	0.010
4 days irradiated	0.042	31.9	0.033	0.011
6 days irradiated	0.038	28.3	0.021	0.015
10 days irradiated	0.029	22.0	0.014	0.019
Starting solution (20x diluted)	0.655		0.663	

Table B.8.7.1b DT_{50} values for [^{14}C]-dichlobenil

exposure	DT_{50} value (d)
xenon light	2.8
natural sunlight 50° North ¹	1.4

¹ Calculated: 24 h irradiation with the xenon-light source used equals 0.5 d of natural sunlight at 50° North latitude.

Acceptability of the test

The DT₅₀ in natural sunlight at 50° instead of 40° North latitude was calculated. As this represents less favourable conditions for photolysis (i.e. worst case), the test is considered acceptable.

Conclusions

The DT₅₀ of [¹⁴C]-dichlobenil in artificial sunlight was 2.8 d, which is equal to 1.4 d in natural sunlight. After 10 d irradiation, the metabolite 2,6-dichlorobenzamide, accounted for ca. 15% of the initial amount of radioactivity.

B.8.7.1.2 Prediction of gas-phase oxidation rate and half-life of the active substance in air (IIA 2.10)

Characteristics of the study

Reference	: Schocken (2001)	Test substance	: dichlobenil
Year of execution	: 2001	DT ₅₀	: 62.78 days (assuming a 12 h light/day)
Method	: AOPWIN ¹	Overall rate constant	: 0.1704 E-12 cm ³ /molecule/sec
GLP	: not applicable	Acceptable	: yes

¹ Atmospheric Oxidation Program for Microsoft Windows

Study design

The estimation methods used by the AOPWIN program are based on the structure activity relation methods of Atkinson^{7,8}.

Result

A theoretical calculation of the photo-oxidation of dichlobenil in the atmosphere, based on a hydroxyl concentration of 1.56 x 10⁶ molecules per cubic cm, resulted in a DT₅₀ of 62.78 days, assuming 12 hour light per day. The overall rate constant is 0.1704 E-12 cm³/molecule/sec.

⁷ Atkinson, R. (1989). *Kinetics and mechanisms of the gas-phase reactions of the hydroxyl radical with organic compounds*. J. Phys. Chem. Ref. Data Monograph No. 1, 1-246. NY: Amer. Inst. Physics & Amer. Chem. Soc.

⁸ Kwok, E.S.C. and Atkinson, R. (1995). *Estimation of Hydroxyl Radical Reaction Rate Constants for Gas-Phase Organic Compounds Using a Structure-Reactivity Relationship: An Update*. Atmospheric Environment 29: 1685-95. [adapted from Final Report to CMA Contract No. ARC-8.0-OR, Statewide Air Pollution Research Centre Univ. of CA, Riverside, CA 92521].

B.8.8 PREDICTED ENVIRONMENTAL CONCENTRATIONS IN AIR (PECA)

Based on a vapour pressure of 1.4×10^{-1} Pa at 25°C and a water solubility of 21.2 mg/L at 25°C the Henry's Law Constant of dichlobenil was calculated to be $1.317 \text{ Pa} \cdot \text{m}^3 \cdot \text{mol}^{-1}$ at 25°C (see B.2.1.6). Results for direct photolysis in air of dichlobenil (DT_{50} is 1.4 d) and the Henry's Law constant of $1.317 \text{ Pa} \cdot \text{m}^3 \cdot \text{mol}^{-1}$ suggest that the concentrations of dichlobenil in air are likely to be negligible.

WARNING: This document forms part of an EC evaluation data package and should not be read in isolation. Registration must not be granted on the basis of this document.

B.8.9 DEFINITION OF THE RESIDUE

The residue definition for assessment is as follows:

Soil:	dichlobenil, 2,6-dichlorobenzamide
Surface water:	dichlobenil, 2,6-dichlorobenzamide (entry route through soil); 4-chloro-2(3H)benzoxazolone and 2-chlorobenzoic acid (these metabolites could not be assessed, ecotox data are required)
Groundwater:	dichlobenil, 2,6-dichlorobenzamide
Sediment:	dichlobenil, 2,6-dichlorobenzamide (entry route through soil)
Air:	dichlobenil

The residue definitions for monitoring (i.e. ecotoxicologically relevant metabolites according to SANCO/3268/2001) are as follows:

Soil:	dichlobenil
Surface water:	dichlobenil; 4-chloro-2(3H)benzoxazolone and 2-chlorobenzoic acid (these metabolites could not be assessed, ecotox data are required).
Groundwater:	dichlobenil
Sediment	-
Air:	dichlobenil

B.8.10 REFERENCES RELIED ON

Annex point/ reference no.	Author(s)	Year	Title Company Report No. Source (where different from company) GLP or GEP status Published or not	Data protection claimed Yes/No	Owner
2.8/01	Thus, J.	1985	Determination by HPLC of the log P value of Dichlobenil and its main metabolite Report Duphar B.V., The Netherlands No.56635/12/1985 CA - 2294	Y	CHEM
2.8/02	Riggs, A.S.	2000	The partition coefficient (n-octanol/water) of 2,6-dichlorobenzamide Report Uniroyal Chemical Research Laboratory Ontario, Canada No.GRL-FR-11654 CA - 3913 GLP, Unpublished	Y	CHEM
2.9.1/01	Buisman, P.	1987	Stability and solubility of Dichlobenil in water Report Duphar B.V., The Netherlands No.56630/207/1987 CA - 2649 GLP, Unpublished	Y	CHEM
2.9.1/02	Oevelen, W.A.M.Van	2005	Stability and solubility of Dichlobenil in water: addendum to Duphar report no. 56630/207/87 Report Crompton Europe B.V., The Netherlands, No.AM950/059/2005 CA - 2649 Non-GLP, unpublished	Y	CHEM
2.9.2/01	Boelhouwers, E.J., Joustra, K.D., Klein, G. Et Al .	1989	Photodegradation of [¹⁴ C]Dichlobenil in water Report Duphar B.V., The Netherlands No.56630/58/1989 CA - 2829 GLP, Unpublished	Y	CHEM
2.9.2/02	Joustra, K.D., Groeneveld, D.J.	1987	Apparatus for photolysis studies. A comparison of the Xenon-light source and natural sunlight Report Duphar B.V., The Netherlands, No.56630/254/87 MIS – 51 Non-GLP, unpublished	Y	CHEM
2.9.3/01	Harned, W.H.	2003	Quantum yield calculation for Dichlobenil Report Crompton Co. Uniroyal Chemical Division, Middlebury, U.S.A. No.2001-060 CA - 4112 GLP, Unpublished	Y	CHEM
2.9.3/02	Harned, W.H.	2003	Calculation of the theoretical lifetime of Dichlobenil in upper surface waters Report Crompton Co. Uniroyal	Y	CHEM

Annex point/ reference no.	Author(s)	Year	Title Company Report No. Source (where different from company) GLP or GEP status Published or not	Data protection claimed Yes/No	Owner
			Chemical Division, Middlebury, U.S.A. No.2001-157 CA - 4111 GLP, Unpublished		
2.10	Schocken, M.J.	2001	Gas-phase oxidation rate and half-life of Dichlobenil in the troposphere Uniroyla Chemical Co. Inc., Middlebury, USA Report no. 2001-54 GLP, unpublished	N	CHEM
7.1.1.1.2/02	Kabler, K., Carpenter, M.	1989	Photodegradation study of 14C- Dichlobenil on soil surface Report Analytical Bio-Chemistry Laboratories, Inc., U.S.A. No.37135 CA - 2853 GLP, Unpublished	Y	CHEM
7.1.1.2.1/01	Lynn, R. Mccorquodale, G. Paterson, K.	2003	[14C]-Dichlobenil: the degradation of [14C]-Dichlobenil in agricultural soils under aerobic conditions Report Inveresk Research 22440 (Inveresk Project Number 802835) CA - 4152 GLP, Unpublished	Y	CHEM
7.1.1.2.1/02	Griffen, D.S.	2002	Aerobic soil metabolism of 14C-2,6- dichlorobenzamide (BAM) Report Uniroyal Chemical Co. Inc., Middlebury, U.S.A. No.2000-103 CA – 4070 GLP, Unpublished	Y	CHEM
7.1.1.2.2/01	Pouwelse, A.V., Loo, T.M.W. van	1991	2,6-dichlorobenzonitrile and 2,6- dichlorobenzamide residues in soil from 4 terrestrial field dissipation trials with Casoron G (Germany 1989/1990) Report Duphar B.V., The Netherlands No.56630/87/1991 CA – 2944 GLP, Unpublished	Y	CHEM
7.1.1.2.2/02	B. Schmidt; T. Butzbach	2003	Aerobic outdoor field dissipation of the fungicide AE C638206 in a clay loam soil	Y	BCS
7.1.1.2.2/02	T. Butzbach	2003	Field soil dissipation of AE C638206 following single application to bare soil in Northern Germany	Y	BCS
7.1.1.2.2/02	B.Pollmann	2003	Field Soil Dissipation of AE C638206 following a Single Application and Multiple Applications to bare Soil Plots at 1 Location in France, 2000	Y	BCS
7.1.1.2.2/02	D.P. Eyre	2003	Field soil dissipation of ae c638206 following single application to bare soil plots at two locations in europe in 1999 (with amendment)	Y	BCS

Annex point/ reference no.	Author(s)	Year	Title Company Report No. Source (where different from company) GLP or GEP status Published or not	Data protection claimed Yes/No	Owner
7.1.2/01	Thus, J.L.G., Laan, J.M.T., van der	1995	Adsorption/desorption test with Dichlobenil in four different agricultural soils and one hydrosol Report solvay Duphar B.V., The Netherlands No. 56835/53/1994 CA - 3115 GLP, Unpublished	Y	CHEM
7.1.2/02a	Dzialo, D.G.	2001	Adsorption/desorption of [14C]2,6- dichlorobenzamide Report Uniroyal Chemical Co. Inc. Middlebury, U.S.A. No.2001-001 CA - 4061 GLP, Unpublished	Y	CHEM
7.1.2/02b	Hardy, I.A.J.	2003	[14C]-AE C653711: re-evaluation of freundlich adsorption isotherm of AE C653711 (BAM) Report Battelle Agrifood Ltd., United Kingdom No.CX/03/002A CA - 4061 GLP, Unpublished	Y	CHEM
7.1.3.3/01a	Traub-Eberhard, U.	1992	Dichlobenil: mobility and degradation in soil in outdoor lysimeters Report Fraunhofer Institut, Germany No.DUP-001/7-11 CA - 2960 GLP, Unpublished	Y	CHEM
7.1.3.3/01b	Traub-Eberhard, U.	1994	Characterization of the 'unidentified radioactive material' in the leachate from an outdoor lysimeter study with Dichlobenil Report Fraunhofer Institut, Germany No. DUP-001/7-99 CA - 2960 GLP, Unpublished	Y	CHEM
7.2.1.1/01	Jacob, O., Fitzmaurice, M.	2003	[14C]-AE C653711: hydrolysis at pH 4, 5, 7 and 9 Report Battelle Agrifood Ltd., United Kingdom No.CX/03/030 CA - 4188 GLP, Unpublished	Y	CHEM
7.2.1.2/01	Reynolds, J.L.	2000	Photolysis of [14C] 2,6- dichlorobenzamide in water buffered at pH 5 Report Xenobiotic Laboratories Inc., U.S.A. No.XBL00041 (Uniroyal Chemical Company, Middlebury Study No. 2000-088) CA - 4043 GLP, Unpublished	Y	CHEM
7.2.1.3.1/01	Mead, C.	2002	Dichlobenil: assessment of ready biodegradability; manometric respirometry test Report Safepharm Laboratories Ltd.,	Y	CHEM

Annex point/ reference no.	Author(s)	Year	Title Company Report No. Source (where different from company) GLP or GEP status Published or not	Data protection claimed Yes/No	Owner
			United Kingdom No. 1133/016 CA - 4105 GLP, Unpublished		
7.2.1.3.1/02	Laan-Straathof, J.M.T.van der, Philips-van Loo, T.M.W.	1996	Determination of the ready biodegradability of 2,6- dichlorobenzamide in the closed bottle test Report Solvay Duphar B.V., The Netherlands No.56834/52/1996 CA - 3188 GLP, Unpublished	Y	CHEM
7.2.1.3.2/01	Willems, H., Hoitink, M.	2004	Aerobic degradation of 14-C- Dichlobenil in two water/sediment systems Report Notox B.V., The Netherlands No.388092 CA - 4171 GLP, Unpublished	Y	CHEM
7.2.2/01	Joustra, K.D., Stegman, K.H., Voorden, E. van de et al .	1993	Photolysis of [14C]-Dichlobenil in air Report Solvay Duphar B.V., The Netherlands No.56630/117/1992 CA - 3027 GLP, Unpublished	Y	CHEM
7.4/01	Wyma-Teitsma, G.R., Kerkdijk, H.	2004	Monitoring of Dichlobenil in groundwater in The Netherlands Report TNO, The Netherlands No.V5418 CA - 4166 GLP, Unpublished	Y	CHEM