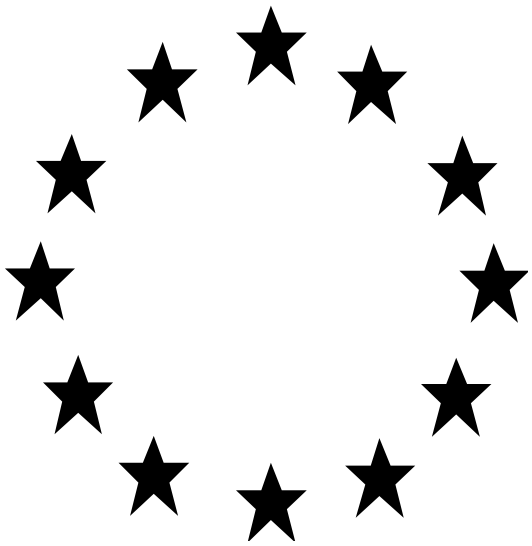


Draft Assessment Report (DAR)

- public version -

Initial risk assessment provided by the rapporteur Member State Germany for the existing active substance

CHLORIDAZON

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

Volume 3, Annex B, B.8

July 2005

Annex B

Chloridazon

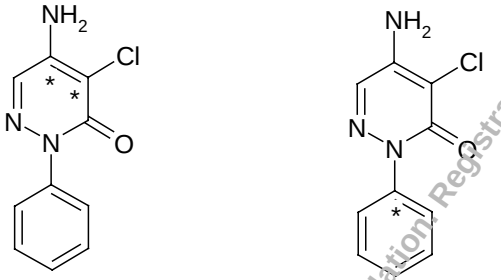
B-8: Environmental fate and behaviour

B.8 Environmental fate and behaviour

B.8.1 Route and rate of degradation in soil (Annex IIA 7.1.1; Annex IIIA 9.1.1)

All metabolic investigations were carried out with chloridazon (^{14}C-radiolabelled) in the pyridazinone ring Figure B.8.1-1, left). Additionally, the fate of the phenyl labelled chloridazon was elucidated in the aerobic soil metabolism study Figure B.8.1-1, right).

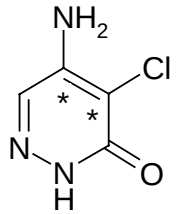
Figure B.8.1-1: Chloridazon (* designates positions of ^{14}C-labels)



5-amino-4-chloro-2-phenylpyridazine-3-one

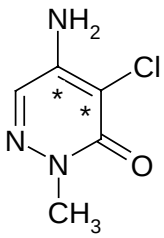
In the course of the metabolism studies, 2 metabolites of chloridazon were found. Both were dephenylated metabolites and the structures are given below (Figure B.8.1-2; Figure B.8.1-3). Throughout the environmental dossier these metabolites are named as given here, as metabolite B and metabolite B-1.

Figure B.8.1-2: Metabolite B



5-amino-4-chloro-pyridazine-3-one

Figure B.8.1-3: Metabolite B-1



5-amino-4-chloro-2-methylpyridazine-3-one

B.8.1.1 Route of degradation

B.8.1.1.1 Aerobic degradation

Reference number: II A 7.1.1.1.1/1

Report: Wood N.F., 1989; BOD 2000-841
Aerobic soil metabolism of pyrazon, 5-amino-4-chloro-2-phenyl-3(2H)-pyridazinone
BASF Corporation Agricultural Products Center, Research Triangle Park, NC 27709, USA, unpublished, BASF RegDoc# 1989/5165

Guidelines: EPA 162-1

GLP: No, studies were conducted prior to the implementation of GLP but are scientifically valid.

Reference number: II A 7.1.1.1.1/2

Report: Wood N.F., 1991; BOD 2001-593
Metabolic fate of the phenyl moiety in the aerobic soil metabolism of pyrazon - Addendum to BASF report No. M8910
BASF Corporation Agricultural Products Center, Research Triangle Park, NC 27709, USA, unpublished, BASF RegDoc# 1991/11618

Guidelines: EPA 162-1

GLP: No, studies were conducted prior to the implementation of GLP but are scientifically valid

In an amendment to the laboratory part of the study, a short review on the microbial metabolism of phenyl compounds was presented and especially the mineralisation rate of the phenyl labelled chloridazon was described.

Test system
The aerobic soil metabolism of [^{14}C]-chloridazon was investigated in two soils, a sandy loam soil and a sandy clay loam soil. The soil characteristics are summarised in Table B.8.1-1. The specific radioactivity of the pyridazinone-labelled test substance was 954000 dpm/µg or 96.6 mCi/mM (15.9 MBq/mg) with a radiochemical purity > 99 %. A nominal concentration of 3.95 mg [^{14}C]-chloridazon/kg soil was used. This is equivalent to the maximum single application rate of about 3.0 kg as/ha, assuming an equal distribution in the top 5 cm soil layer and a soil density of 1.5 g/cm^3.

Test samples of 25 g soil were housed in glass reactors in crystallising dishes. The incubation conditions were: aerobic, in the dark, 25 °C, the moisture content was 75 % of field capacity (1/3 bar). At intervals of one to three weeks, volatiles were collected by drawing air through the system and the volatile compounds were collected.

Table B.8.1-1: Aerobic soil metabolism of ^{14}C-chloridazon: Characterisation of the soils used

Soil designation	249-103	249-91
Origin	Dinuba (California)	Fuquay-Varina (North Carolina)
textural class	sandy loam	sandy clay loam
% sand	54	66.8
% silt	32	9.2
% clay	14	24.0
Bulk density [g/cm^3]	1.38	1.26
Organic matter [%]	0.5	2.2
pH (water)	7.7	5.9
CEC cation exchange capacity [meq/100 g]	14.4	8.15
Field capacity at 1/3 bar [g/100 g]	15.2	15.51

Soil samples were taken at timepoints as specified in the result section. They were extracted with methanol immediately after sampling, and then further fractionated. The sandy clay loam soil samples were extracted with methanol/HCl from day 17 on, whereas the sandy loam soil samples were extracted from day 65 on. This additional extract step explains the decrease of bound residues from day 30 to day 65. Some bound residue fractions were worked up according to a standard procedure to separate residues in humins, humic acids and fulvic acids.

The methanol and methanol/HCl extracts were analysed by TLC. Aliquots and reference standards of chloridazon and metabolite B were spotted onto the silicagel plates and developed. The chromatograms were quantitatively analysed using a Bioscan Imaging Scanner System.

In the amendment to the study (BASF RegDoc# 1991/11618) four studies (1 BASF internal study and 3 literature citations) are presented and summarised to demonstrate the fate of the phenyl moiety in soil. The BASF internal study elucidated the mineralisation rate of pyridazinone- and phenyl-^{14}C-labelled chloridazon in direct comparison. 200 g of active soil (pH 7.3, humus content 1.5 - 2 %, activated by the addition of chloridazon) was fortified with 400 mg of each labelled compound. This is a highly exaggerated rate and was only used for the investigation of the principal possibility of mineralisation of both rings of chloridazon. The soil was incubated in the dark at ca. 22 °C for 84 or 93 days. Air samples were taken to determine the amount of CO_2 released.
The discussed literature studies investigated the metabolism of chloridazon in soil and *in vitro* with bacteria isolated from soil. The mechanism of the chloridazon degradation was elucidated down to the level of isolated enzyme systems.

Findings
The following tables, Table B.8.1-2 and Table B.8.1-3, are a summary of results taken from different tables in the original report. The total residues represent the sum of the columns of the table.
In all cases, the material balance was good and significantly greater than 90 % of the total applied radioactivity (TAR). This clearly proves that no major metabolite remained undetected during the study.

Table B.8.1-2: Aerobic soil metabolism of ^{14}C-chloridazon in sandy clay loam: Recovery of radioactivity and distribution of active substance and metabolite B (% of applied radioactivity) determined by TLC analysis

DAT	$^{14}CO_2$	Chloridazon	Metabolite B	Bound Residues	Total
0	0	95.7	0	4.0	99.7
17	0.5	97.0	0.8	2.7	101.0
31	0.8	91.5	1.5	3.3	97.1
69	1.5	84.8	4.6	9.3	100.2
124	2.2	70.2	13.8	13.3	99.5
244	3.1	29.3	46.0	15.9	94.3
367	3.9	20.7	48.2	19.0	91.8

Table B.8.1-3: Aerobic soil metabolism of ^{14}C-chloridazon in sandy loam: Recovery of radioactivity and distribution of active substance and metabolite B (% of applied radioactivity) determined by TLC analysis

DAT	$^{14}CO_2$	Chloridazon	Metabolite B	Bound Residues	Total
0	0	100.8	0	2.2	103
17	1.4	87.3	1.1	8.6	98.4
30	1.8	87	1.9	12.4	103.1
65	3.2	88.7	6.7	4.7	103.3
120	5.6	74.3	16.9	9.3	106.1
240	12.1	19.2	51.5	10.8	93.6
373	18.6	7.1	55.9	12.7	94.3

In nearly all cases, only chloridazon and metabolite B were found. The only exceptions were a few methanol/HCl extracts from some soils sampled late in the study where polar metabolites amounting to about 2 % of applied radioactivity were detected. This means that the only metabolite resulting from chloridazon in major amounts up to > 51 % TAR after 240 days, resp. up to 56 % TAR after 373 days in soil is its stable metabolite B.

The overall amounts of bound residues were moderate and highest at the end of the study with 13 - 19 % TAR. Most of the radioactivity was associated with the humin and fulvic acid fractions with very little amounts detected in the humic acid fraction.

The mineralisation rate in both soils after 120 resp. 124 days was negligible, i.e. max. approx. 5 % TAR. After 373 days in the sandy clay loam merely 3.9 % and in the sandy loam soil 18.6 % of the radioactivity were released as CO_2. No volatile organic compounds except CO_2 were detected.
This soil metabolism study was performed only with the pyridazinone-labelled chloridazon and revealed that apart from minor amounts CO_2 the major transformation product of chloridazon in soil is metabolite B. This was sufficient to describe the fate of the active substance in soil, because the amendment to the soil metabolism study (BASF RegDoc# 1991/11618) reveals that the phenyl-part of the molecule is rapidly mineralised (76 % after 30 days, 81 % after 84 days) whereas in the same experiment the CO_2-formation from the pyridazone label was only 0.5 % after 93 days. The presence of metabolite B suggests, that the bond between the pyridazinone and the phenyl ring was broken.

Valid: yes

Reference number: II A 7.1.1.1.1/3

Report: Dams W., 1989; BOD 2000-839
Degradation behaviour of chloridazon in soil
BASF AG, Agrarzentrum Limburgerhof, Limburgerhof, Germany,
unpublished, BASF DocID 1989/10209

Guidelines: BBA IV 4-1

GLP: Yes

Test system
The degradation of chloridazon in 4 soils was investigated and in addition, the appearance of metabolite B was also followed. Non-radiolabelled chloridazon with a chemical purity of 99.85 % was used. The characterisation of the four soils is given in Table B.8.1-4.

Table B.8.1-4: Aerobic soil degradation of chloridazon: Characterisation of the soils used

Origin of soil BASF code	Ruchheim 87/068	Limburgerhof 87/062	Limburgerhof 88/061	LUFA Speyer 2.2 88/004
Soil type	loam	loamy sand	clay	loamy sand
Organic C [%]	1.44	0.54	2.84	2.75
Microbial biomass; start/end [mg/100 g dry soil]	24.5/24.5	16.8/10.9	58.0/89.1	40.4/53.8
pH	7.2	6.7	7.4	5.6
Water holding capacity [g/100 g]	49	40	44	40
CEC [mVal/100 g]	14.8	5.2	42.4	12.6

CEC = cation exchange capacity

Aliquots of sieved soils (50 g, sieved to 2 mm) were filled into Erlenmeyer flasks and 125 µg chloridazon was added in distilled water. The application rate corresponds to ca. 2.5 kg as/ha. The water content in the soils was adjusted to 40 % of the maximum water holding capacity. The flasks were loosely closed with cotton plugs and stored in a temperature controlled cabinet (dark) of 20 °C (± 2 °C). The water evaporation was controlled regularly and the volatiles were not collected. After 0, 2, 4, 8, 16, 32, 64 and 100 days, samples were taken and analysed for chloridazon and metabolite B. The analytical method was BASF method 285. Chloridazon and metabolite B were extracted from soil with methanol. After several clean up steps, the final determination was made by HPTLC as diazo dyes after diazotation and coupling to naphthol.

Limit of quantification: For both compounds, the limit of determination was 0.01 mg/kg. Soil 88/061 from Limburgerhof showed some background interferences of metabolite B of up to 0.17 mg/kg soil.

Recovery:
For chloridazon the average recoveries achieved during method development ranged between 76.9 % and 100.7 % and 67.0 and 100.6 % during the course of the study. Recoveries of the metabolite B were between 72.3 % and 94.3 % during method development.

Findings
The values given in the table below show the results of two measurements, both were corrected for the procedural recoveries of the method.

Table B.8.1-5: Degradation of chloridazon in 4 soils; values in mg/kg dry soil (HPTLC); results of two measurements

DAT	Soil Ruchheim		Soil Limburgerhof 87/062		Soil Limburgerhof 88/061		Soil LUFA 2.2	
	Value 1	Value 2	Value 1	Value 2	Value 1	Value 2	Value 1	Value 2
0	3.27	3.26	2.53	2.43	2.29	2.80	2.33	1.96
2	2.54	2.66	2.28	1.91	2.33	2.25	1.95	2.05
4	2.61	2.86	2.14	2.14	1.64	2.74	2.06	2.10
8	2.29	2.34	1.58	1.83	1.89	2.19	2.15	2.33
16	0.87	0.95	0.18	0.36	2.21	2.15	2.31	1.96
32	0.29	0.21	0.06	0.32	1.52	2.27	1.69	2.00
64	0.13	0.17	<0.05	<0.05	1.28	1.36	1.70	1.69
100	0.08	0.07	<0.05	0.06	0.96	1.07	0.23	0.42

Table B.8.1-6: Formation of metabolite B out of chloridazon in 4 soils; values in mg/kg dry soil (HPTLC); results of two measurements

DAT	Soil Ruchheim		Soil Limburgerhof 87/062		Soil Limburgerhof 88/061		Soil LUFA 2.2	
	Value 1	Value 2	Value 1	Value 2	Value 1	Value 2	Value 1	Value 2
0	<0.05	<0.05	<0.05	<0.05	0.16	0.22	<0.05	<0.05
2	<0.05	<0.05	0.05	<0.05	0.20	0.22	<0.05	<0.05
4	<0.05	<0.05	<0.05	0.05	0.22	0.14	<0.05	<0.05
8	<0.05	<0.05	0.06	0.07	0.22	0.20	<0.05	<0.05
16	1.23	1.13	1.72	1.36	0.22	0.20	<0.05	<0.05
32	1.40	1.30	1.78	1.44	0.19	0.28	0.167	<0.05
64	1.26	1.43	1.38	1.39	0.64	0.57	<0.05	0.1
100	1.40	1.39	1.25	1.43	1.12	1.02	1.53	1.25

Table B.8.1-7: Formation of metabolite B out of chloridazon in 4 soils; based on concentrations in µmol/kg dry soil

DAT		Soil Ruchheim		Soil Limburgerhof 87/062		Soil Limburgerhof 88/061		Soil LUFA 2.2	
		Value 1	Value 2	Value 1	Value 2	Value 1	Value 2	Value 1	Value 2
Chloridazon as									
0	µMol/kg	14.76	14.71	11.42	10.97	10.33	12.64	10.51	8.85
100	dry soil	0.36	0.32	0.23	0.27	4.33	4.83	1.04	1.90
100	% of DAT 0	2.45	2.15	1.98	2.47	41.9	38.2	9.87	21.4
Metabolite B									
100	µMol/kg dry soil	9.62	9.55	8.59	9.83	7.70	7.01	10.51	8.59
100	% of as DAT 0	65.2	64.9	75.2	89.6	74.5	55.5	100	97.1

Mostly, the results of the two measurements are in good agreement. Metabolite B reached very high concentrations. In 2 of the 4 soils a significant increase was measured between day 8 and day 16, whereas in the 2 other soils the increase appeared later, between day 64 and day 100. These results again prove the high importance of metabolite B as by far the most significant degradation product of chloridazon.
The measured concentration of metabolite B, expressed in mg/kg dry soil on day 100 in relation to the initial concentration of chloridazon at day 0, reaches a max. amount of 64.8 % in soil LUFA 2.2.

Valid: questionable

Comment of RMS
This mineralisation study was performed with unlabelled chloridazon with an analytical recovery during the study between 67 and 100 %. Evaluation of complete material balance is not possible, since CO_2 and bound residues were not investigated.
The recalculation of the data on molar weight shows that the formation of metabolite B out of chloridazon was between 65 and 100 %. Especially the high formation rates are questionable since formation of bound residues (13 - 19 %) was observed in the ^{14}C-labelled study.
This study can be used as additional information for the high formation rate of metabolite B out of chloridazon. For assessing the aerobic mineralisation of chloridazon the results of the completely balanced ^{14}C-labelled study are used.

Reference number: II A 7.1.1.1.1/4

Report: Bayer H., 2003(c); BOD 2003-307
Aerobic degradation of metabolite B (Metabolite of BAS 119 H, chloridazon) in 4 soils (DT_{50}/DT_{90})
BASF AG, Agrarzentrum Limburgerhof, Limburgerhof, Germany, unpublished, BASF DocID 2002/1004262

Guidelines: SETAC Procedures for assessing the environmental fate and ecotoxicity for pesticides (March 1995), BBA IV 4-1

GLP: Yes

Reference number: II A 7.1.1.1.1/5

Report: Bayer H., 2003(e); BOD 2003-276
Report Amendment No. 1 to final report: Aerobic degradation of Metabolite B (Metabolite of BAS 119 H, chloridazon) in 4 soils (DT50/DT90)
BASF AG, Agrarzentrum Limburgerhof, Limburgerhof, Germany, unpublished, BASF DocID 2003/1005450

Guidelines: SETAC Europe, BBA IV 4-1

GLP: Yes

Test system
The degradation of the predominant soil metabolite B of chloridazon was investigated in a laboratory study under aerobic conditions in 4 soils. ^{14}C-Radiolabelled metabolite B with a specific radioactivity of 6.05 MBq/mg and a radiochemical purity of 100 % was used. The soil parameters for the 4 soils are given in Table B.8.1-8. The soils cover a pH range ($CaCl_2$) from 5.8 to 7.3, a clay content (German scheme) from 6.3 % to 9.5 % and an organic carbon content from 1.0 % to 1.9 %. All soils had been passed through a 2 mm screen prior to use.

Table B.8.1-8: Aerobic degradation of metabolite B: Characterisation of soils used

Origin of soil BASF - Code	Limburgerhof Bruch West 98/060/03	Limburgerhof Schlag 35 b 98/145/03	LUFA 2.3 F 33398 98/570/03	LUFA 2.2 F 23598 98/736/03
Soil type				
USDA scheme	sandy loam	loamy sand	sandy loam	loamy sand
< 2 µm (clay) [%]	9.5	6.3	9.1	8.7
2-50 µm (silt) [%]	20.1	16.0	24.8	15.3
50-2000 µm (sand) [%]	70.4	77.7	66.1	76.0
German scheme	loamy sand	slight loamy sand	loamy sand	loamy sand
< 2 µm (Ton) [%]	9.5	6.3	9.1	8.7
2-63 µm (Schluff) [%]	23.2	19.3	26.5	17.2
63-2000 µm (Sand) [%]	67.3	74.4	64.4	74.1
Organic C [%]	1.60	0.99	1.18	1.87
pH [$CaCl_2$]	7.3	6.2	6.0	5.8
CEC [mVal/100 g]	13	6	10	10
MWC [g H_2O/100 g dry soil]	41.05	36.78	39.00	50.30
Field capacity at 1/3 bar [g H_2O/100 g dry soil]	16.1	12.7	14.4	16.3
Microbial biomass (mg C/100 g dry soil)	44.7	32.7	16.1	46.2

CEC = cation exchange capacity; MWC = maximum water holding capacity

The nominal application rate was 1.7 mg metabolite B/kg dry soil which corresponds to a concentration in the field of circa 1275 g metabolite B/ha (calculated on the basis of an equal distribution in the top 5 cm soil layer and a soil density of 1.5 g/cm^3).
For application, the 4 soils were treated with the treatment solution (3.457 mg metabolite B in 2.034 kg dry soil) each and the soils were thoroughly mixed by means of a hand mixer. Then

the soils were adjusted to 40 % of the respective maximum water holding capacity (MWC) and thoroughly mixed again.
Small portions of the soils (corresponding to 100 g dry soil) were filled into glass dishes. For the incubation, the glass dishes were placed on metal trays (8 dishes per tray). The metal trays were arranged in the stainless steel incubation tubes of the metabolism apparatus, which consists of an incubator with an open gas flow system. The incubation temperature was 20 °C in the dark. Throughout the study, the water content of the soils was checked periodically by weighing the glass dishes. The soil moisture was readjusted if necessary. During the study, the incubation tubes of the metabolism apparatus were aerated with a slight stream of moistened CO_2-free air. The volatiles were trapped in a set of 3 absorption traps containing (1) 40 mL 0.5 M NaOH, (2) 40 mL ethyleneglycole, and (3) 25 mL 0.5 M H_2SO_4 (one trapping system per incubation tube). The trapping solutions were collected and analysed for radioactivity. Sampling times were 0 (no sampling of volatiles), 3, 7, 14, 30, 62, 92 and 121 days after treatment (DAT).

From each sampling 50 g soil were worked up by extraction with methanol and methanol/water. After concentration the extracts were analysed by HPLC for the metabolite pattern. The bound residues after extraction were determined by combustion. Structure elucidation was performed by HPLC/MS and structure assignment was confirmed by comparison of the MS/MS spectra and the HPLC retention times of the respective reference substances.

Findings
The distribution of the radioactivity at different sampling times is shown in Table B.8.1-9.
The formation of CO_2 (mineralisation) was insignificant accounting for only 1.1 to 5.4 % TAR after 121 days. No other volatile compounds were detected.
In total, 3 peaks could be detected in the soil extracts. The parent peak of metabolite B decreased to around 36 – 51 % TAR at the end of the study after 121 days. Metabolite B-1 was formed in all four soils, however in somewhat varying amounts. It was detected earliest from 7 DAT onwards and steadily increased until the end of the study reaching maximum values between 1 % and 14 % TAR after 121 days. The third peak appearing only in soil Bruch West with 0.1 % TAR was not elucidated in structure.
Bound residues in all four soils were continuously formed in high amounts of up to 30.8 – 41.7 % TAR reaching their maximum after 62 - 121 days of incubation.
The material balance ranged from 83.0 % TAR to 100.1 % TAR in all samplings with average values of 93.3 % to 95.4 % TAR for each soil throughout the incubation period of 121 days.
From the results of this study it is concluded that the major reason for the decrease of metabolite B in aerobic soil consists of the steady formation of bound residues (maximum 30.8 - 41.7 % TAR). Moreover, small to moderate amounts of metabolite B are transformed into metabolite B-1 (1.0 – 14.1 % TAR after 121 days) by methylation of the pyridazinone nitrogen N-2. This process is reversible since a reaction from metabolite B-1 back to metabolite B is possible to some extent. The reaction sequence between methylation and demethylation is a well known physiological activity of soil microorganisms. Mineralisation plays only a minor role (maximum 1.1 – 5.4 % TAR) for the degradation of metabolite B.

As a result of this study, metabolite B-1 was recognised as a metabolite of chloridazon in soil present in amounts exceeding 10 %.
Therefore, the degradation of this soil metabolite was also investigated in detail in the following study.

Table B.8.1-9: Aerobic soil metabolism of ^{14}C-metabolite B in 4 soils: Recovery of radioactivity and distribution of test substance and metabolites (% of applied radioactivity) determined by HPLC analysis

Soil	DAT	CO_2	Metabolite B	Metabolite B-1	Unknown	Others	bound Residues	Total
Bruch West	0	n.d.	98.7	0	0	0	1.3	100.0
	3	0.1	85.8	0	0	0	9.0	95.0
	7	0.4	81.8	1.0	0	0	14.0	97.1
	14	0.7	78.3	2.6	0	0	17.0	98.7
	30	0.8	66.7	4.5	0	0	24.5	96.4
	62	1.6	51.5	8.6	0	0	33.2	95.0
	92	1.8	41.8	10.5	0.1	0	34.2	88.4
	121	2.4	36.2	14.1	0.1	0	35.0	87.9
Li 35 b	0	n.d.	99.1	0	0	0	0.9	100.0
	3	0.3	87.2	0	0	0	9.2	96.7
	7	0.6	80.6	0	0	0	18.9	100.1
	14	1.3	76.1	0.1	0	0	20.9	98.4
	30	2.3	64.4	1.5	0	0	24.2	92.4
	62	3.4	53.6	2.7	0	0	37.7	97.4
	92	4.1	44.2	3.3	0	0	36.6	88.3
	121	5.4	43.1	4.5	0	0	37.1	90.0
LUFA 2.3	0	n.d.	97.8	0	0	0	2.2	100.0
	3	0.2	79.1	0	0	0	9.9	89.2
	7	0.3	71.9	0	0	0	25.4	97.7
	14	0.6	69.6	0	0	0	24.7	94.9
	30	0.8	63.4	0.3	0	0	31.2	95.8
	62	1.4	55.2	0.7	0	0	35.4	92.6
	92	1.8	49.6	0.7	0	0	41.7	93.8
	121	2.2	50.9	1.0	0	0	39.0	93.1
LUFA 2.2	0	n.d.	99.4	0	0	0	0.6	100.0
	3	0.0	88.6	0	0	0	8.1	96.7
	7	0.1	83.6	0.9	0	0	13.0	97.6
	14	0.1	80.8	1.7	0	0	13.9	96.5
	30	0.5	71.3	3.4	0	0	18.8	93.8
	62	0.9	61.2	4.7	0	0	24.0	90.7
	92	1.0	50.2	5.7	0	0	30.8	87.7
	121	1.1	49.8	6.8	0	0	25.2	83.0

n.d. not determined

Valid: yes

Reference number: II A 7.1.1.1.1/6

Report: Bayer H., Erzgraeber B., 2003; BOD 2003-308
Aerobic degradation of metabolite B-1 (Metabolite of BAS 119 H, chloridazon) in 4 soils (DT_{50}/DT_{90})
BASF AG, Agrarzentrum Limburgerhof, Limburgerhof, Germany, unpublished, BASF DocID 2002/1004263

Guidelines: SETAC Procedures for assessing the environmental fate and behaviour and ecotoxicity of pesticides (March 1995), BBA IV 4-1

GLP: Yes

Test system
The degradation of metabolite B-1 was investigated in a laboratory study under aerobic conditions in 4 soils. ^{14}C-Radiolabelled metabolite B-1 with a specific radioactivity of 4.35 MBq/mg and a radiochemical purity of 100 % was used. The soils were the same as used in the previous study BASF RegDoc# 2002/1004262, above. The soil parameters for the 4 soils are given in Table B.8.1-8. The soils cover a pH range ($CaCl_2$) from 5.8 to 7.3, a clay content (German scheme) from 6.3 % to 9.5 % and an organic carbon content from 1.0 % to 1.9 %. All soils had been passed through a 2 mm screen prior to use.

The nominal application rate was 2.0 mg metabolite B-1/kg dry soil which corresponds to a concentration in the field of 1500 g metabolite B-1/ha (calculated on the basis of an equal distribution in the top 5 cm soil layer and a soil density of 1.5 g/cm^3).
The soils were adjusted to 40 % of the respective maximum water holding capacity. After treatment with the application solution (4 mg metabolite B-1 per 2 kg dry soil), the soils were thoroughly mixed by means of a hand mixer.
Small portions of the soils (corresponding to 100 g dry soil) were filled into glass dishes. For the incubation, the glass dishes were arranged in the stainless steel incubation tubes of the metabolism apparatus, which consists of an incubator with an open gas flow system. The incubation temperature was 20 °C in the dark. Throughout the study, the water content of the soils was checked periodically by weighing the glass dishes. The soil moisture was readjusted if necessary. During the study, the incubation tubes of the metabolism apparatus were aerated with a slight stream of moistened CO_2-free air. The volatiles were trapped in a set of 3 absorption traps containing (1) 25 mL 0.5M NaOH, (2) 25 mL 0.5M H_2SO_4 and (3) 25 mL ethylene glycol (one trapping system per incubation tube). The trapping solutions were collected and analysed for radioactivity. Sampling times were 0 (no sampling of volatiles), 3, 7, 14, 30, 59, 91 and 120 days after treatment (DAT).
From each sampling, 50 g of each soil were worked up by extraction with methanol and methanol/water. After concentration, the extracts were analysed by HPLC to obtain the metabolite pattern. The bound residues after extraction were determined by combustion.
Structure elucidation was performed by mass spectrometry and structure assignment was confirmed by comparison with the MS/MS spectra of the respective reference substances.

Findings
The distribution of the radioactivity at different sampling times is shown in Table B.8.1-10.
The formation of CO_2 (mineralisation) was insignificant accounting for only 1.3 to 6.4 % TAR after 120 days. No other volatile compounds were detected.
In total, only 2 significant peaks could be detected, the parent peak (metabolite B-1) which decreased to around 48 – 59 % TAR at the end of the study and metabolite B that was formed in all four soils. It was detected earliest from 3 DAT onwards and increased in the course of the study reaching maximum values between 2.9 and 10.5 % TAR mostly after 120 days.
Besides these 2 compounds, up to 9 different minor peaks were detected in the chromatograms of the soil extracts. These peaks (summarised in the column "Others") were formed only in trace amounts (≤ 1.2 % TAR) and most of them were only transient. None of these peaks appeared in all 4 soils. Due to the low amounts formed, the structures could not be elucidated.
Bound residues in all four soils were formed in moderate to high amounts of up to 24.8 – 36.8 % TAR reaching their maximum at the end of the study after 120 days of incubation.

The material balance ranged from 91.1 % TAR to 100.4 % TAR in all samplings with average values of 96.7 % to 97.5 % TAR for each soil throughout the incubation period of 120 days.

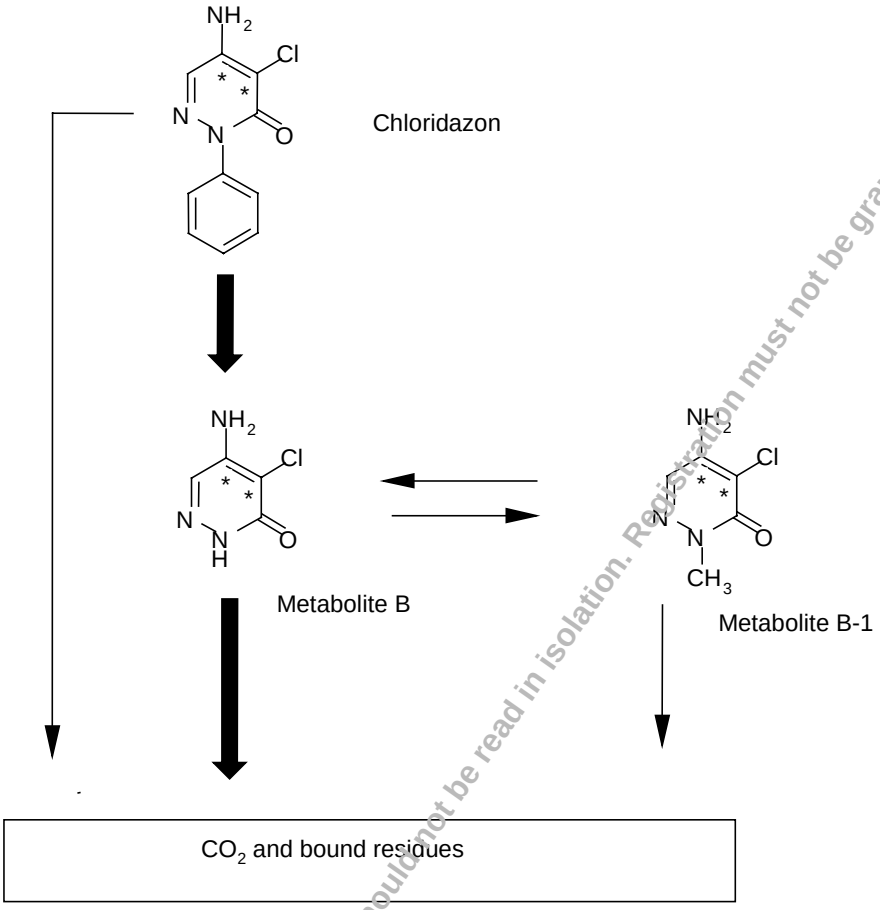
Table B.8.1-10: Aerobic soil metabolism of ^{14}C-metabolite B-1 in 4 soils: Recovery of radioactivity and distribution of test substance and metabolites (% of applied radioactivity) determined by HPLC analysis

Soil	DAT	CO_2	Metabolite B-1	Metabolite B	Others* (sum)	Bound Residues	Total
Bruch West	0	n.d.	99.5	0.0	0.0	0.5	100.0
	3	0.1	94.0	0.7	0.0	5.7	100.4
	7	0.3	86.5	1.3	0.0	8.6	96.6
	14	0.8	80.9	2.8	0.9	12.7	98.3
	30	1.8	75.0	5.4	0.0	16.6	98.8
	59	2.7	65.7	8.6	0.3	19.9	97.2
	91	3.5	56.8	9.4	0.0	24.0	93.7
	120	4.4	50.7	10.5	0.4	25.0	91.1
Li 35 b	0	n.d.	99.4	0.0	0.0	0.6	100.0
	3	0.1	90.6	0.7	0.0	8.1	99.5
	7	0.5	83.8	1.2	0.0	11.9	97.4
	14	1.2	76.4	2.2	0.5	18.0	98.3
	30	2.5	71.4	4.3	0.0	20.5	98.8
	59	4.2	63.3	5.1	0.3	24.3	97.2
	91	5.2	51.4	8.9	0.0	27.6	93.2
	120	6.4	47.7	9.0	0.1	32.4	95.6
LUFA 2.3	0	n.d.	98.7	0.0	0.0	1.3	100.0
	3	0.0	84.9	0.0	0.1	13.0	98.1
	7	0.1	78.3	0.1	0.0	18.7	97.2
	14	0.4	72.4	0.1	1.1	24.1	98.0
	30	0.7	67.6	1.0	0.8	28.1	98.2
	59	1.0	63.3	2.9	0.1	30.5	97.8
	91	1.1	57.3	1.8	0.9	34.1	95.2
	120	1.3	53.2	1.9	0.1	36.8	93.2
LUFA 2.2	0	n.d.	99.7	0.0	0.0	0.3	100.0
	3	0.2	91.6	0.0	0.0	4.8	96.6
	7	0.6	86.9	1.3	1.2	7.8	97.8
	14	1.3	80.9	1.6	1.1	11.4	96.4
	30	2.6	77.8	3.1	0.6	16.2	100.2
	59	3.5	68.2	3.7	0.0	18.8	94.7
	91	4.8	62.0	4.6	0.4	21.7	93.5
	120	5.6	59.3	4.7	0.5	24.8	94.8

n.d. not determined
* sum of up to 4 unknown peaks none of them exceeding 1.2 % TAR

From the results of this study it is concluded that the major reason for the decrease of metabolite B-1 in aerobic soil consists of the formation of bound residues (maximum 24.8 – 36.8 % TAR). Moreover, small to moderate amounts of metabolite B-1 (max. 2.9 – 10.5 % TAR) are transformed into metabolite B by demethylation of the methyl group at the pyridazinone nitrogen N-2. This process seems to be reversible since kinetic data from the modelling suggest that a reaction from metabolite B back to metabolite B-1 occurs to some extent which is well in line with the results obtained in the study conducted with metabolite B (BASF RegDoc# 2002/1004262). Mineralisation plays only a minor role (maximum 1.3 – 6.4 % TAR) for the degradation of metabolite B-1.

Figure B.8.1-4: Proposed aerobic degradation pathway for chloridazon in soil



Valid: yes

B.8.1.1.2 Anaerobic degradation

Reference number: II A 7.1.1.1.2/1

Report: Wood N.F., 1990; BOD 2001-594
Anaerobic soil metabolism of pyrazon
BASF Corporation Agricultural Products Center, Research Triangle Park, NC 27709, USA, unpublished, BASF RegDoc# 1989/5166

Guidelines: EPA 162-2

GLP: No, studies were conducted prior to the implementation of GLP but are scientifically valid

Test systems

The anaerobic soil metabolism of [^{14}C]-chloridazon was investigated according to the USA-EPA Guideline 162-2 in two soils, a sandy loam soil and a sandy clay loam soil. The soils were the same that were used for aerobic soil metabolism and the soil characteristics are summarised in Table B.8.1-1. The specific radioactivity of the test substance was 954000 dpm/µg

or 96.6 mCi/mM (15.9 MBq/mg) with a radiochemical purity > 99 %. A nominal concentration of 3.95 mg [^{14}C]-chloridazon/kg dry soil was used. This is equivalent to the maximum single application rate of about 3.0 kg as/ha, assuming an equal distribution in the top 5 cm soil layer and a soil density of 1.5 g/cm^3.

Test samples of 25 g soil were housed in glass reactors in crystallising dishes. The incubation conditions were: aerobic for 31 days, in the dark, 25 °C, the moisture content was 75 % of field capacity (1/3 bar). At intervals of one to three weeks, volatiles were collected by drawing air through the system and the volatile compounds were collected. After 31 days, the conditions were changed to anaerobic by flushing the system from that timepoint on with nitrogen. Anaerobicity was confirmed using an anaerobic indicator.

Soil samples were taken at time points specified in the result section. They were extracted with methanol immediately after sampling. The sandy clay loam soil samples were additionally extracted with methanol/HCl from day 17 on (of aerobic incubation), whereas the sandy loam soil samples were extracted from day 15 on (of anaerobic incubation). This explains for the sandy loam soil the decrease of bound residues after that sampling.

The methanol and methanol/HCl extracts were analysed by TLC. Aliquots and reference standards of chloridazon and metabolite B were spotted onto the silicagel plates and developed. The chromatograms were quantitatively analysed using a Bioscan Imaging Scanner System.

Findings

The following tables, Table B.8.1-11 and Table B.8.1-12, are a summary of results taken from different tables in the original report. The total residues represent the sum of the columns of the table.

In all cases, the material balance was good and significantly greater than 90 % of the total applied radioactivity (TAR). This clearly proves that no major metabolite remained undetected during the study.

No volatile organic compounds except CO_2 were detected. The mineralisation rate was negligible (< 4 % TAR) in both soils.

Table B.8.1-11: Anaerobic soil metabolism of ^{14}C-chloridazon in sandy clay loam: Recovery of radioactivity and distribution of active substance and metabolite B (% of applied radioactivity) determined by TLC analysis

DAT Total	DAT Aerobic	DAT Anaerobic	CO_2	Chloridazon	Metabolite B	Bound Residues	Total
0	0	0	0	95.7	0	4	99.7
17	17	0	0.5	97.0	0.8	2.7	101
31	31	0	0.8	91.5	1.5	3.3	97.1
46	31	15	0.8	89.6	1.8	3.3	95.5
61	31	30	0.9	91.1	3.9	6.6	102.5
91	31	60	1.2	81.5	8.8	9.7	101.2

Table B.8.1-12: Anaerobic soil metabolism of ^{14}C-chloridazon in sandy loam: Recovery of radioactivity and distribution of active substance and metabolite B (% of applied radioactivity) determined by TLC analysis

DAT Total	DAT Aerobic	DAT Anaerobic	CO_2	Chloridazon	Metabolite B	Bound Residues	Total
0	0	0	0	100.8	0	2.2	103
17	17	0	1.4	87.3	1.1	8.6	98.4
30	30	0	1.8	87	1.9	12.4	103.1
45	30	15	1.9	93.9	2.3	2.8	100.9
59	30	29	2.3	94.3	2.7	3.9	103.2
90	30	60	3.5	89.6	4.8	6.2	104.1

Only the unchanged parent substance chloridazon in extremely high amounts between 82 % and 90 % and metabolite B in small amounts not exceeding 9 % TAR were found. At the end of the test bound residues were low and CO_2-formation was below 4 % TAR. No other metabolites can be expected under the exclusion of oxygen.

Valid: yes

B.8.1.1.3 Soil photolysis

Reference number: II A 7.1.1.1.2/2

Report: Singh M.,Tanaka F., 1993; BOD 2001-596
Photolysis of ^{14}C-chloridazon (BAS 119 H) on soil
BASF Corporation Agricultural Products Center, Research Triangle Park, NC 27709, USA, unpublished, BASF DocID 1993/5008

Guidelines: EPA 161-3

GLP: Yes

Test system
Soil photolysis of chloridazon was performed with a Hanau Suntest photoreactor equipped with a xenon lamp. Light was filtered through a quartz filter and an UV-filter and so a cut-off for wavelengths < 290 nm was reached. The light intensity was 1900 µE/m^{2}s. The duration of the experiment was 350 hours employing a 12 h light/12 h dark photoperiod. Air dried and sieved (2 mm screen) soil was adjusted to a moisture content of 75 % of field capacity (1/3 bar). The soil characteristics are given in Table B.8.1-13.

Table B.8.1-13: Soil photolysis of chloridazon: Characterisation of the soils used

Soil designation	678-13-08
Origin	BASF field test site Holly Springs (North Carolina)
Soil series	Wagram
Soil classification	loamy sand
% sand	80
% silt	13.3
% clay	6.7
pH	6.8
Organic matter [%]	1.9
CEC [meq/100 g]	5.2
% moisture content at 1/3 bar	12.4
Bulk density [g/cm^3]	1.31

CEC = cation exchange capacity

^{14}C-Radiolabelled chloridazon with a radiochemical purity > 98 % and a specific radioactivity of 0.797 mCi/mmol (0.12 mBq/mg) was used. The purity was checked by HPLC. The solution with the test item was uniformly applied onto the soil surface. About 5 g of soil were weighed and placed into glass dishes. The application rate was equivalent to 7.6 lb as/A (corresponds to 8.5 kg/ha). The soil samples were placed into the photolysis vessels and irradiated. The incubation temperature was 25 °C ± 1 °C. A trapping systems for the collection of volatiles was connected. Soil samples were taken at approx. 82, 154, 240 and 350 hours of irradiation. Two sets of incubation systems were used and the sampling times were slightly different and therefore, the results for both sets were reported separately. Dark control samples were stored in a climatic chamber at the same temperature. Soil samples were extracted with solvents and final analysis was performed by TLC and comparison with reference material of chloridazon.

Findings

Although two sets of photolysis experiments were conducted, the overall results from both sets were nearly identical. Because the sampling times were slightly different, the data were not averaged and are given here in two separate tables. Balance data for "Total", "Bound Residues" and cumulated CO_2 values were taken from table 2 of the original report, data for chloridazon from table 6 and 7. The "Others" as a sum of the non-identified metabolites were calculated here in the dossier simply as the subtraction.

The material balance was always good and ranged from 93 to 104 %. Essentially, all of the volatile material was identified as CO_2 amounting up to 14 % TAR in the irradiated samples. The dark samples (data not shown in detail) showed only low mineralisation of less than 1 % of TAR. This shows that under the influence of light at soil surfaces chloridazon can be substantially degraded.

Table B.8.1-14: Soil photolysis of chloridazon: Recovery of radioactivity and degradation of active substance determined by TLC (in % of applied radioactivity), data set 1

Sampling time (hours)	CO_2	Chloridazon	Others*	Bound Residues	Total
82.25	3.29	77.89	16.43	3.89	101.5
154.35	6.54	71.08	15.88	5.84	99.34
240.27	9.76	66.28	22.10	5.46	103.6
349.54	14.01	57.03	17.08	5.84	93.96

* none of the individual peaks exceeding 5 % TAR

Table B.8.1-15: Soil photolysis of chloridazon: Recovery of radioactivity and degradation of active substance determined by TLC (in % of applied radioactivity), data set 2

Sampling time (hours)	CO_2	Chloridazon	Others*	bound Residues	Total
75.55	2.74	84.28	12.64	3.24	102.90
155.36	6.58	75.92	11.66	4.17	98.33
239.8	9.68	67.71	20.84	5.27	103.5
346.64	13.36	61.27	13.30	5.64	93.57

* none of the individual peaks exceeding 3.2 % TAR

The amounts of bound residues were generally low not exceeding 6 % TAR.

The methanol extracts of soil contained primarily chloridazon and up to four minor degradation products. The percent recovery of chloridazon in the soil extracts decreased with increasing time. The yield of each individual degradation product was less than 5 % TAR. The methanol/HCl extracts contained less radioactivity with maximum values up to 8 % TAR. Chloridazon was not found in these extracts, but three significant groups of peaks appeared, all at less than 4 % TAR.

Metabolite B, the only major degradation product in aerobic soil metabolism of chloridazon was not observed in any of soil extracts.

In the dark control soil samples after 30 days of incubation, nearly all of the radioactivity was in the methanol extracts and TLC analysis of these methanol extracts revealed, that the only product present was chloridazon. These data are consistent with the soil metabolism study in the US soils that showed, that after 30 days of incubation only tiny amounts of metabolite B were present.

Valid: yes

Conclusions – Route of degradation
Soil metabolism studies were performed with chloridazon and with its two metabolites, B and B-1.
Under aerobic conditions in soil chloridazon is primarily degraded to its main metabolite B which contains the pyridazinone ring part of the molecule. This metabolite can account for more than 50 % TAR at the end of the tests evaluated and is considered stable.

Whereas the phenyl ring part of chloridazon is microbially attacked, opened and mineralised to CO_2 (up to 76 % TAR after 30 days), the pyridazinone ring persists undergoing only negligible ultimate degradation of max. approx. 5 % TAR after 120 days. Bound residues reach a max. of 19 % TAR after 367 days.

In aerobic soil metabolism studies conducted with metabolite B, unchanged metabolite B accounted for up to 51 % TAR after 121 days. Apart from insignificant metabolism/ degradation the further fate of metabolite B consists predominantly in the formation of high amounts of bound residues, precisely up to 42 % TAR after 92 days, whereas only small to moderate amounts of metabolite B (max. 14 % TAR after 121 days) are converted into metabolite B-1 by methylation of the pyridazinone nitrogen N-2. This process is obviously reversible as it was shown in a separate metabolism study with metabolite B-1 that a partial conversion from metabolite B-1 back to metabolite B (max. 10.5 % TAR after 120 days) is possible. The reaction sequence between methylation and demethylation is a well known physiological activity of soil microorganisms.
As already described for the metabolite B, beside up to 59 % TAR unchanged metabolite B-1 identified after 120 days, the major portion of metabolite B-1 was also recovered by combustion as non-extractable radioactivity, precisely up to 37 % TAR after 120 days.
Ultimate aerobic degradation of both metabolite B and metabolite B-1 is negligible with max. CO_2-amounts of approx. 5 % TAR released from each molecule after 120 resp. 121 days of testing.

Under anaerobic conditions in soil, chloridazon is not metabolised to a significant extent, contrary to the behaviour under aerobic conditions. At study termination apart from a mean of approx. 86 % TAR unchanged chloridazon only one metabolite, precisely metabolite B was found, however in amounts not exceeding 9 % TAR. This metabolite was also found under aerobic conditions. Bound residues were also low, the mineralisation rate was negligible.

In conclusion, from the results of the metabolism studies performed, the behaviour of chloridazon in soil consists in the formation of one major metabolite, which under aerobic conditions is to a small extent further metabolised, and the extensive formation of bound residues, whereas mineralisation and hence ultimate biodegradation to CO_2 is insignificant. Thus chloridazon and its metabolites are considered highly persistent in soil.

At soil surfaces under the influence of light, chloridazon was photolysed to a number of polar and non polar products. No photoproduct was found to exceed 5 % TAR. Metabolite B could not be detected under the influence of light. Under the influence of light at soil surfaces chloridazon can be partly degraded to CO_2 with a maximum of 14 % TAR after 15 days.

B.8.1.2 Rate of degradation

B.8.1.2.1 Laboratory studies

Reference number: II A 7.1.1.2.1/1 (A II 7.1.1.1.1/1)

Report: Wood N.F., 1989; BOD 2000-841
Aerobic soil metabolism of pyrazon, 5-amino-4-chloro-2-phenyl-3(2H)-pyridazinone
BASF Corporation Agricultural Products Center, Research Triangle Park, NC 27709, USA, unpublished, BASF RegDoc# 1989/5165

Guidelines: EPA 162-1

GLP: No, studies were conducted prior to the implementation of GLP but are scientifically valid

Reference number: II A 7.1.1.2.1/2

Report: Dressel J., 2003; BOD 2003-309
Compilation of parameters characterising the environmental fate of BAS 119 H (chloridazon) and its metabolites
BASF AG, Agrarzentrum Limburgerhof, Limburgerhof, Germany, unpublished, BASF RegDoc# 2003/1001026

Guidelines: none

GLP: No, not subject to GLP regulations

Reference number: II A 7.1.1.2.1/3

Report: Dams W., 1989; BOD 2000-839
Degradation behaviour of chloridazon in soil
BASF AG, Agrarzentrum Limburgerhof, Limburgerhof, Germany, unpublished, BASF RegDoc# 1989/10209

Guidelines: BBA IV 4-1

GLP: Yes

Reference number: II A 7.1.1.2.1/4

Report: Platz K., 2001; BOD 2003-310
Estimation of half-lives of chloridazon in 4 soils from a laboratory degradation study
BASF AG, Agrarzentrum Limburgerhof, Limburgerhof, Germany, unpublished, BASF RegDoc# 2000/1017056

Guidelines: none

GLP: No, not subject to GLP regulations

Reference number: II A 7.1.1.2.1/5

Report: Bayer H., 2003(a); BOD 2003-307
Aerobic degradation of metabolite B (metabolite of BAS 119 H, chloridazon) in 4 soils (DT_{50}/DT_{90})
BASF AG, Agrarzentrum Limburgerhof, Limburgerhof, Germany, unpublished, BASF RegDoc# 2002/1004262

Guidelines: none

GLP: Yes

Reference number: II A 7.1.1.2.1/6

Report: Bayer H., 2003(e); BOD 2003-276
Report amendment No. 1 to final report: Aerobic degradation of metabolite B (metabolite of BAS 119 H, chloridazon) in 4 soils (DT_{50}/DT_{90})
BASF AG, Agrarzentrum Limburgerhof, Limburgerhof, Germany, unpublished, BASF DocID 2003/1005450

Guidelines: SETAC Europe, BBA IV 4-1

GLP: Yes

Reference number: II A 7.1.1.2.1/7

Report: Bayer H., Erzgraeber B., 2003; BOD 2003-308
Aerobic degradation of metabolite B-1 (Metabolite of BAS 119 H, chloridazon) in 4 soils (DT_{50}/DT_{90})
BASF AG, Agrarzentrum Limburgerhof, Limburgerhof, Germany, unpublished, BASF DocID 2002/1004263

Guidelines: SETAC Procedures for assessing the environmental fate and behaviour and ecotoxicity of pesticides (March 1995), BBA IV 4-1

GLP: Yes

Reference number: II A 7.1.1.2.1/8

Report: Wood N.F., 1990; BOD 2001-594
Anaerobic soil metabolism of pyrazon
BASF Corporation Agricultural Products Center, Research Triangle Park, NC 27709, USA, unpublished, BASF RegDoc# 1989/5166

Guidelines: EPA 162-2

GLP: No, studies were conducted prior to the implementation of GLP but are scientifically valid

All BASF internal laboratory studies measuring the degradation of chloridazon and its soil metabolites B and B-1 have already been described in the previous chapter in detail with regard to the test systems, the methods and the findings. Therefore, within this chapter only details of the calculation of the degradation rates will be given.

Findings

Chloridazon
In the aerobic soil metabolism study by Wood N., the aerobic DT_{50} of chloridazon in 2 soils was determined by first order linear regression analysis on log transformed data. The DT_{50} in the sandy clay loam was determined to be 152 d ($r^2 = 0.97$) and in the sandy loam soil 90 d ($r^2 = 0.96$). Using the Q10 factor for temperature correction from 25 °C to 20 °C results in DT_{50} values of 224.9 d and 133.2 d for the sandy clay loam and the sandy loam respectively.
A more recent kinetic evaluation of the data gained in this study with the software tool ModelMaker, version 4.0 (Cherwell Scientific, 2000) with a nonlinear curve fit algorithm was conducted (BASF RegDoc# 2003/1001026) by Dressel J. and yielded higher first order half-lives of 187.6 d ($r^2 = 0.970$) and 154.9 d ($r^2 = 0.945$) respectively. In the same study of Dressel J. (BASF RegDoc# 2003/1001026) these half–lives were furthermore also normalised to the reference conditions (20 °C, pF2) according to FOCUS and resulted in standardised half-lives of 173.9 d for the sandy clay loam and 157.1d for the sandy loam (Table B.8.1-16).

For the aerobic soil rate study with chloridazon conducted by Dams W. (BASF RegDoc# 1989/10209), the calculations were repeated according to the current knowledge of modeling by Platz K. (BASF RegDoc# 2000/1017056). This latter study does not contain any laboratory work and is merely an estimation of half-lives. The summarised results are given in Table B.8.1-17.

Table B.8.1-16: DT_{50} values of chloridazon in aerobic soils in days determined from the results of the study by Wood, N.F.

Soil	ModelMaker, version 4.0 Dressel, J. BASF RegDoc# 2003/1001026 25 °C	ModelMaker, version 4.0 Dressel, J. BASF RegDoc# 2003/1001026) 20 °C, pF2 normalised

	DT_{50}	r^2	DT_{50}	r^2
sandy clay loam	187.6	0.97	173.9	0.98
sandy loam	154.9	0.95	157.1	0.96

r^2 = coefficient of determination

Table B.8.1-17: DT_{50} and DT_{90} values of chloridazon in aerobic soils in days determined from the results of the study by Dams, W.

Soil	Timme and Frehse, best fit Dams, BASF RegDoc#1989/10209			ModelMaker, version 3.0.4 Platz, BASF RegDoc# 2000/1017056		ModelMaker, version 4.0 Dressel, BASF RegDoc# 2003/1001026 20 °C, pF2 normalised
	DT_{50}	DT_{90}	r^2	DT_{50}	r^2	DT_{50}
Ruchheim, loam, 87/068	10	50	0.98	10.7	0.98	9.0
Limburgerhof, loamy sand, 87/062	10	54	0.98	8.6	0.96	8.6
Limburgerhof, clay, 88/061	>100	>100	0.92	82.1	0.97	40.6
LUFA 2.2 Speyer, loamy sand	43	140	0.89	75.1	0.95	75.1

r^2 = coefficient of determination

Subsequent standardisation of these calculated values to reference conditions according to FOCUS by Dressel, 2003 (BASF RegDoc# 2003/1001026) are included in Table B.8.1-17.

Under anaerobic conditions chloridazon was more stable, as expected. The DT_{50} at 25 °C based on regression analysis resulted in the sandy clay soil in a value of 370 days and in the sandy loam soil in a value of 607 days.

Metabolites

The degradation rates in 4 soils at 20 °C and 40 % MWHC for the two identified soil metabolites of chloridazon, the major metabolite B and the minor metabolite B-1, are summarised in Table B.8.1-18. For the calculation of the degradation rates of these two compounds, the program ModelMaker, version 3.0.4 (Cherwell Scientific Publishing Limited, Oxford) was applied. Due to the complex compartment scheme, the DT_{50} values were assessed on the basis of a best fit estimation and determined graphically.

Table B.8.1-18: Degradation rates of metabolite B and metabolite B-1 as determined by the aerobic soil degradation rate studies with both compounds

Soil	Metabolite B				Metabolite B-1			
	DT_{50} [d]	**DT_{90} [d]**	**r^2**	**DT_{50} [d] normalised[1]**	**DT_{50} [d]**	**DT_{90} [d]**	**r^2**	**DT_{50} [d] normalised[2]**
Bruch West	80	*	0.97	92.9	135	*	0.97	139.5
Li 35 b	93	*	0.94	97.3	118	*	0.95	131
LUFA 2.3	132	*	0.79	116.9	152	*	0.84	135.4
LUFA 2.2	120	*	0.95	128.7	170	*	0.94	176.8

r^2 = coefficient of determination

* calculated value greater than 2 times study duration and therefore considered to be beyond the period of reliable extrapolation
[1] re-calculated by Dressel J., 2003, (BASF RegDoc# 2003/1001026) considering only the rate constant representing the flux from compartment "metabolite B" to compartment "elimination"
[2] kinetic equilibrium between metabolite B and metabolite B-1 was not taken into account.

For the metabolite B, Dressel J., 2003, (BASF RegDoc# 2003/1001026) recalculated the DT_{50}-values listed in the table above, considering only the rate constant representing the flux from compartment "metabolite B" to compartment "elimination" (i.e. CO_2 and bound residues), thus not considering the formation/dissipation of metabolite B-1. These slightly higher DT_{50} are: Bruch West: 103 days, Li 35b: 97.3 days, LUFA 2.3: 134.2 days and LUFA 2.2: 128.7 days. Subsequently in the same study these values were standardised to reference conditions according to FOCUS resulting in the following values: Bruch West: 92.9 days, Li 35b: 97.3 days, LUFA 2.3: 116.9 days and LUFA 2.2: 128.7 days.

In addition to the DT_{50} reported in the table presented above for metabolite B-1, half –lives for the flux from compartment "metabolite B-1" to compartment "elimination" were also recalculated by Dressel, 2003, (BASF RegDoc# 2003/1001026). Subsequently, half-lives were standardised to reference conditions according to FOCUS: Bruch West: 154.7 days, post standardisation 139.5 days; Li 35b: pre- and post standardisation 131 days, LUFA 2.3: 155.4 days, post standardisation to 135.4 days and LUFA 2.2: pre- and post standardisation 176. 8 days. It must be noted however that the apparent relevant kinetic equilibrium between metabolite B and metabolite B-1, as shown in the proposed degradation pathway (cf. Figure B.8.1-4) was not taken into account.

Valid: yes

Reference number: II A 7.1.1.2.1/10

Report: Capri E. et al, 1995; BOD 2001-598
Metamitron and chloridazon dissipation in a silty clay loam soil
Instituto di Chimica Agraria ed Ambientale - Universita Cattolica del Sacre Cuore, Piacenza, Italy, BASF RegDoc# 1995/10446
J. Agric. Food Chem. 1995, 43, 247-253

Guidelines: not relevant, Literature

GLP: No, not subject of GLP regulations

Test system
In this non-GLP university study, the fate of chloridazon was investigated under a variety of conditions in the laboratory and under field conditions. Only the laboratory results of the study at 10, 20 and 30 °C at 22 % soil moisture are summarised here. The soil used was a silty clay loam.

Table B.8.1-19: Soil parameters for the investigations of the degradation rate of chloridazon under laboratory conditions

Soil parameter	Value
pH [H_2O]	7.8

Soil parameter	Value
Organic matter [%]	2.21
CEC [meq/100 g]	28.6
% clay	35.8
% silt	47.3
% sand	17
Bulk density [kg/L]	1.6
Field capacity (at 0.05 bar) [g/100 g]	26
Wilting point (at 15 bar) [g/100 g]	18.7

CEC = cation exchange capacity

Fresh soil samples were incubated in loosely capped glass containers. For each treatment, a water suspension was added to obtain a final concentration of 2 mg/kg dry soil. The soils were incubated at 15, 22 and 29 % soil moisture and 10, 20 and 30 °C. Samples were taken at 1, 3, 7, 14, 28, 45 and 60 days after treatment and analysed for chloridazon by HPLC analysis with diode array detector. The detection limit was 0.025 mg/kg.
Half-lives and dissipation times were calculated by assuming that degradation follows first-order-kinetics.

Findings
Within the literature article, the results for the concentration of chloridazon were not reported in tables, but as graphs. The resulting degradation rates are given in Table B.8.1-20. The degradation followed a first order kinetic with regression coefficients, that are always statistically significant.

Table B.8.1-20: Degradation rates of chloridazon at different temperature and 22 % soil moisture in a silty clay loam under laboratory conditions

Temperature [°C]	DT_{50} [d]	r^2
10	75.6	0.85
20	21.3	0.82
30	13.6	0.94

r^2 = coefficient of determination

Increasing the temperature to 30 °C strongly accelerates degradation, but the main increase occurs with a temperature variation from 10 to 20 °C by a factor of 3.5. At 10 °C an increase of soil moisture to 29 % results in a DT_{50} of 41 days, whereas a reduction of the soil moisture to 15 % retards degradation, i.e. lengthens the DT_{50} of 134 days.

Valid: no

Comment of the RMS:
The study was not performed according to standardised guidelines and the results can not be validated due to the lack of the raw data (literature). The study can not be used for the risk assessment.

B.8.1.2.2 Field studies

The laboratory rate studies showed that in European soils the DT_{50} values can be far greater than 60 days, which is the trigger value given by EEC Directive 91/414 amended by EC Di-

rective 95/36 that requires the performance of field soil studies. During the field soil dissipation studies, the soil residues of chloridazon and its soil metabolites metabolite B and metabolite B-1 were determined.

Reference number: II A 7.1.1.2.2/1

Report: Hesse B., Sasturain J., 1993; BOD 2003-400
Investigation into the dissipation behaviour of chloridazon in the soil under field conditions
BASF AG, Agrarzentrum Limburgerhof, Limburgerhof, Germany, unpublished, BASF RegDoc# 1993/11484

Guidelines: BBA IV 4-1, IVA guidelines on residue studies part V. Studies on degradation in soil

GLP: Yes

Reference number: II A 7.1.1.2.2/2

Report: Eubanks M.W., Clark J.R., 1989; BOD 2001-602
Pyramin herbicide (chloridazon) field soil dissipation studies for fall and spring use: summary report
Pan-Agricultural Laboratories Inc., Madera, California 93638, United States of America, unpublished, BASF RegDoc# 1989/5154

Guidelines: EPA 164-1

GLP: Yes

Reference number: II A 7.1.1.2.2/3

Report: Sasturain J., Kellner O., 1998; BOD 2001-603
Study of the dissipation of chloridazon in the soil under field conditions
BASF AG, Agrarzentrum Limburgerhof, Limburgerhof, Germany, unpublished, BASF DocID 1998/1000787

Guidelines: BBA IV 4-1, IVA guidelines on residue studies part V

GLP: Yes

Reference number: II A 7.1.1.2.2/4

Report: Kellner O. et al., 2003; BOD 2003-312
Field soil dissipation of BAS 119 H (Formulation BAS 119 33 H) on bare soil in Sweden 2000-2001

BASF AG, Agrarzentrum Limburgerhof, Limburgerhof, Germany, unpublished, BASF RegDoc# 2003/1001009

Guidelines: BBA IV 4-1, SETAC, IVA-Leitlinie fuer Rueckstandsversuche Teil V (1993), Guidance Document on Residue Analytial Methods (SANCO/825/00rev.6)

GLP: Yes

Reference number: II A 7.1.1.2.2/5

Report: Domenichini P., 2003; BOD 2003-313
Terrestrial field degradation of chloridazon applied to bare soil in Southern Europe (Italy and Spain in the year 2000)
SIPCAM, Laboratorio Chimico, Solerano sul Lambro, Italy
unpublished, BASF RegDoc# 2003/1001025

Guidelines: BBA IV 4-1, SETAC

GLP: Yes

Test system
Four field soil dissipation studies were performed in Europe and 1 in the USA to investigate the degradation and dissipation of chloridazon in soil and to determine the concentrations of metabolite B and metabolite B-1. In total, 10 trials were performed at 10 locations: 5 in Germany, 1 in Sweden, 1 in Spain, 1 in Italy and 2 in the USA in California (USA without determination of metabolite B-1).
A range of soils with organic C contents from 0.2 to 2.4 % (partially calculated from org. matter content) and pH values from 4.6 to 8.08 was covered. The geographical distribution of the trial locations and a summary of the relevant soil parameters of all trials is given in Table B.8.1-21.
All European trials were performed with the formulated product BAS 119 33 H. This is the typical product used against weeds in sugar beets. It is known as "Pyramin WG" or "Pyramin DF" and is a 65 % WG formulation. The use rate of 2.6 kg as/ha is the maximum recommended use rate in agricultural practice in Europe and therefore, the degradation of chloridazon and the formation and degradation of metabolites under field conditions is represented by these trials. The product BAS 119 16 H used in the US trials is known as Pyramin FL, it is a FL formulation with an as content of 40 %. The use rates for the US trials were higher but were nevertheless in a range that will not influence the degradation behaviour to a significant extent. A summary of the application parameters is shown in Table B.8.1-22.

The formulations in the European trials were applied as homogeneous spray mixtures onto non-cropped bare soil with broadcast spray equipment. The trials were kept free of vegetation throughout the study period. In the US trials, sugar beets were sown a few days before chloridazon was sprayed as pre-emergence herbicide.

Table B.8.1-21: Characterisation of the fields used in the field dissipation studies with chloridazon

BASF RegDoc#	Trial No.	Location	Soil type	Soil Properties	
				% org. C	pH
2003/1001009	HUS/08/00	Sweden, 23791 Bjärred	Silty sand	1.35	6.0 ($CaCl_2$)
1998/1000787	DU2/58/92	Germany, 7103 Niederhofen	Sandy loam	2.4	6.5 ($CaCl_2$)
1998/1000787	DU3/24/92	Germany, 6701 Birkenheide	Clayey sand	1.2	4.6 ($CaCl_2$)
1993/11484	D05/97	Germany, 24250 Bothkamp	Heavy loamy sand	1.4	5.1 ($CaCl_2$)
1993/11484	D07/95	Germany, 84051 Holzen	Loam	1.3	7.1 ($CaCl_2$)
1993/11484	VTU/83	Germany, 74193 Stetten	Loam	1.2	6.8 ($CaCl_2$)
1989/5154	RCN88056	USA; Chico, California	Varies	1.3 - 1.5*	6.7 - 7.0
1989/5154	RCN88057	USA, Madera, California	Sandy loam	0.2 - 0.3*	5.9 - 6.4
2003/1001025	CLZ/1-1	Italy, Chignolo, Po, PV	Sandy loam	1.2*	6.53
2003/1001025	CLZ/1-2	Spain, Elburgo, Alava	Clay, silt loam	1.2*	8.08

* org. C content was calculated from org. matter content: % org. C = % org. matter / 1.72

Table B.8.1-22: Application parameters of the field soil dissipation studies with chloridazon

BASF RegDoc#	Trial No.	Formulation	Application date	Application rate nominal [g as/ha]	Day 0 (% recovery)
2003/1001009	HUS/08/00	BAS 119 33 H	19.06.2000	2600	71*
1998/1000787	DU2/58/92	BAS 119 33 H	19.05.1992	2600	82**
1998/1000787	DU3/24/92	BAS 119 33 H	27.05.1992	2600	34***
1993/11484	D05/97	BAS 119 33 H	30.04.1990	2600	85****
1993/11484	D07/95	BAS 119 33 H	03.05.1990	2600	30****
1993/11484	VTU/83	BAS 119 33 H	25.04.1990	2600	109****
1989/5154	RCN88056	BAS 119 16 H	04.05.1988	4400	198***
1989/5154	RCN88057	BAS 119 16 H	13.09.1988	4400	75**
2003/1001025	CLZ/1-1	BAS 119 33 H	22.03.2000	2600	113*
2003/1001025	CLZ/1-2	BAS 119 33 H	16.05.2000	2600	103*

* based on application verification samples
** based on day 7 sampling, soil cores
*** based on day 0 soil cores
**** based on day 6 - 8 sampling, soil cores

The recoveries at day 0 were determined by a variety of different ways, the results are given in Table B.8.1-22. Especially the day 0 recovery based on the results of soil cores show a high variability.

Whereas all European trials covered the spring application, the two US trials covered spring and autumn application.

The soil samples were analysed with different methods:

BASF method 285
Chloridazon, metabolite B and metabolite B-1 were extracted from 50 g soil with methanol and the methanol was removed by a rotary evaporator. Chloridazon and metabolite B-1 were separated from metabolite B on an Extrelut column. After elution and further clean up, the determination was carried out on precoated HPTLC plates. After development, the compounds were rendered visible as azo dyes on HPTLC after diazotation and coupling with naphthol. The evaluation was performed densitometrically with a thin layer scanner at 500 nm. The lower limit of the practical working range was defined as 0.01 mg/kg.

BASF method 8904
This method is able to determine chloridazon and the metabolite B. The soil was extracted with 0.1N HCl in methanol. The extract was concentrated, neutralised and filtered. An extrelut column was used to isolate the compounds from the aqueous solution. The column eluate was concentrated and derivatised with pentafluorobenzyl bromide. After silica gel flash chromatography the quantitation was done by gas chromatography (DB 17 capillary column) and thermoionic specific detection.

BASF method 464/0
This is the most recent method for the determination of chloridazon and its metabolites B and B-1. A 25 g soil or sediment sample aliquot was extracted with 80 % aqueous methanol. After centrifugation, acidic acid and sodium chloride were added to the supernatant. The extract was concentrated to the aqueous phase by evaporation of methanol and filled up with pure water. The aqueous sample was soaked into an Extrelut column. Chloridazon and metabolite B-1 were extracted from the Extrelut column with dichloromethane (DCM) (eluate 1) and metabolite B was extracted with a DCM/propanol-2 mixture (eluate 2). The eluate 1 is washed with sodium hydroxide and further cleaned up on an alumina SPE column. The eluate 2 is cleaned up on a silica gel SPE column. The final chromatographic analysis of chloridazon and its metabolites B and B-1 was performed by HPLC/DAD or UV detection. The results of the validation study of BASF method 464/0 as well as the procedural recovery results obtained demonstrate that chloridazon and its metabolites B and B-1 can be accurately determined in soil with a limit of quantitation (LOQ) of 0.01 mg/kg.

Findings
The results of the trials and the soil residues detected in the individual soil layers are given in Table B.8.1-23 to Table B.8.1-32.

Under field conditions chloridazon is also primarily transformed to its more stable major metabolite B with reported dissipation half lives up to max. 78.5 days found in trial HUS/08/00 in Sweden. Chloridazon was in all trials mainly found in the top soil layers of 0 – 10 cm and 10 – 25 cm. In deeper layers, max. recovery was 0.04 mg/kg in 61-91 cm soil depth on 90 DAT in California (trial RCN88057).

Metabolite B appeared in the different trials in the top soil layers from 0-10 cm in amounts of $\leq$ 0.01 up to max. 0.448 mg/kg, the highest value found in trial HUS/08/00 in Sweden in the top 10 cm after 64 DAT. In trial CLZ/1-1 in Italy 0.305 mg/kg were still found in the top 10 cm after 182 DAT. It was often still found after longer periods of time, e.g. 0.07 – 0.1 mg/kg after 6 or 12 months in trial HUS/08/00 in Sweden. At the end of the studies metabolite B was still recovered in amounts of 0.01 mg/kg in a soil depth of 87-100 cm (trial D07/95 in Holzen, Germany) and in a depth of 91-122 cm (in trial RCN88057 in Madera,

California), thus demonstrating the tendency of this metabolite, as also shown for metabolite B-1, to move into deeper layers of soil.
Although statistically debatable, the DT_{50} values available for the metabolite B from different climatic regions (Sweden vs. California) indicate a retarded dissipation under field conditions when compared with those obtained under laboratory conditions.

Metabolite B-1 is generally found only in minor quantities in some samples, mostly after longer time periods after application, e.g. in study SIP 1296 in Italy in trial CLZ/1-1 accounting for max. 0.033 mg/kg at 182 DAT resp. 0.027 mg/kg 555 days after application in the 0 – 10 cm soil layer. In trial VTU/83 in Stetten, Germany, 0.01mg/kg was detected in the lowest soil depth analysed, i.e. in the 87-100 cm layer, 100 and 188 days after application. A calculation of field degradation rates was not possible.

Valid: yes

Table B.8.1-23: Field soil dissipation results from trial HUS/08/00 in Bjärred, Sweden, in study SE/HA/057/00; summary results of the residues in mg/kg dry soil

Soil depth [cm]	DAT	Chloridazon [mg/kg]	Metabolite B [mg/kg]	Metabolite B-1 [mg/kg]
0 - 10	7	1.350	0.012	<0.01
10 - 25	7	0.011	<0.01	<0.01
0 - 10	14	1.280	0.023	<0.01
10 - 25	14	0.021	<0.01	<0.01
0 - 10	29	0.988	0.055	<0.01
10 - 25	29	0.011	<0.01	<0.01
0 - 10	64	0.111	0.448	<0.01
10 - 25	64	<0.01	0.020	<0.01
25 - 37.5	64	<0.01	<0.01	<0.01
37.5 - 50	64	<0.01	<0.01	<0.01
0 - 10	100	0.022	0.445	0.011
10 - 25	100	<0.01	0.125	<0.01
25 - 37.5	100	<0.01	0.023	<0.01
37.5 - 50	100	<0.01	<0.01	<0.01
0 - 10	183	0.014	0.070	<0.01
10 - 25	183	<0.01	0.072	<0.01
25 - 37.5	183	<0.01	0.026	<0.01
37.5 - 50	183	<0.01	<0.01	<0.01
0 - 10	360	0.011	0.119	0.013
10 - 25	360	<0.01	0.109	0.012
25 - 37.5	360	<0.01	0.027	<0.01
37.5 - 50	360	<0.01	<0.01	<0.01

Table B.8.1-24: Field soil dissipation results from trial DU2/58/92 in Niederhofen, Germany, in study DE/HA/027/92; summary results of the residues in mg/kg dry soil

Soil depth [cm]	DAT	Chloridazon [mg/kg]	Metabolite B [mg/kg]	Metabolite B-1 [mg/kg]
0 - 10	0	0.93	<0.01	<0.01
10 - 25	0	<0.01	<0.01	0.01
0 - 10	7	<0.01	<0.01	<0.01

Soil depth [cm]	DAT	Chloridazon [mg/kg]	Metabolite B [mg/kg]	Metabolite B-1 [mg/kg]
10 - 25	7	0.95	0.01	<0.01
0 - 10	14	0.67	0.02	<0.01
10 - 25	14	<0.01	<0.01	<0.01
0 - 10	58	0.02	0.12	<0.01
10 -25	58	0.02	0.02	<0.01
25 - 37	58	0.02	<0.01	<0.01
37 - 50	58	0.01	<0.01	<0.01
0 - 10	106	0.04	0.06	<0.01
10 - 25	106	<0.01	0.01	<0.01
25 - 37	106	<0.01	<0.01	<0.01
37 - 50	106	<0.01	<0.01	<0.01
50 - 62	106	<0.01	<0.01	<0.01
62 - 75	106	<0.01	<0.01	<0.01
75 - 87	106	<0.01	<0.01	<0.01
87 - 100	106	<0.01	<0.01	<0.01
0 - 10	182	<0.01	0.03	<0.01
10 -25	182	0.03	0.03	<0.01
25 - 37	182	<0.01	<0.01	<0.01
37 - 50	182	<0.01	<0.01	<0.01
50 - 62	182	<0.01	<0.01	<0.01
62 - 75	182	<0.01	<0.01	<0.01
75 - 87	182	<0.01	<0.01	<0.01
87 - 100	182	<0.01	<0.01	<0.01

Table B.8.1-25: Field soil dissipation results from trial DU3/24/92 in Birkenheide, Germany, in study DE/HA/027/92; summary results of the residues in mg/kg dry soil

Soil depth [cm]	DAT	Chloridazon [mg/kg]	Metabolite B [mg/kg]	Metabolite B-1 [mg/kg]
0 - 10	0	0.59	<0.01	<0.01
10 - 25	0	<0.01	0.01	<0.01
0 - 10	7	0.06	<0.01	<0.01
10 - 25	7	0.04	<0.01	<0.01
0 - 10	15	0.20	0.01	<0.01
10 - 25	15	0.18	<0.01	<0.01
0 - 10	28	0.10	<0.01	<0.01
10 - 25	28	0.22	<0.01	<0.01
25 - 37	28	0.04	<0.01	<0.01
37 - 50	28	0.03	<0.01	<0.01
0 - 10	62	0.27	<0.01	<0.01
10 - 25	62	0.02	0.04	<0.01
25 - 37	62	0.04	0.02	<0.01
37 - 50	62	<0.01	<0.01	<0.01
0 - 10	105	0.06	0.02	<0.01
10 - 25	105	0.07	0.04	<0.01
25 - 37	105	0.03	0.04	<0.01
37 - 50	105	<0.01	<0.01	<0.01
50 - 62	105	<0.01	<0.01	<0.01
62 - 75	105	<0.01	<0.01	<0.01
75 - 87	105	<0.01	<0.01	<0.01
87 - 100	105	<0.01	<0.01	<0.01
0 - 10	180	0.04	0.02	<0.01
10 - 25	180	0.01	0.03	<0.01
25 - 37	180	<0.01	0.03	<0.01

Soil depth [cm]	DAT	Chloridazon [mg/kg]	Metabolite B [mg/kg]	Metabolite B-1 [mg/kg]
37 - 50	180	<0.01	<0.01	<0.01
50 - 62	180	<0.01	<0.01	<0.01
62 - 75	180	<0.01	<0.01	<0.01
75 - 87	180	<0.01	<0.01	<0.01
87 - 100	180	<0.01	<0.01	<0.01

Table B.8.1-26: Field soil dissipation results from trial D05/97 in Bottkamp, Germany, in study DE/HA/013/90; summary results of the residues in mg/kg dry soil

Soil depth [cm]	DAT	Chloridazon [mg/kg]	Metabolite B [mg/kg]	Metabolite B-1 [mg/kg]
0 - 10	0	0.73	0.01	<0.01
10 - 25	0	0.01	<0.01	<0.01
0 - 10	7	1.42	0.01	<0.01
10 - 25	7	<0.01	<0.01	<0.01
0 - 10	15	0.35	0.01	<0.01
10 - 25	15	<0.01	<0.01	<0.01
0 - 10	29	0.39	0.02	<0.01
10 - 25	29	<0.01	<0.01	<0.01
25 - 37	29	<0.01	<0.01	<0.01
37 - 50	29	<0.01	<0.01	<0.01
0 - 10	56	0.16	0.07	<0.01
10 - 25	56	<0.01	<0.01	<0.01
25 - 37	56	<0.01	<0.01	<0.01
37 - 50	56	<0.01	<0.01	<0.01
0 - 10	98	<0.01	0.13	<0.01
10 - 25	98	<0.01	0.09	<0.01
25 - 37	98	<0.01	<0.01	<0.01
37 - 50	98	<0.01	0.01	<0.01
50 - 62	98	<0.01	<0.01	<0.01
62 - 75	98	<0.01	<0.01	<0.01
75 - 87	98	<0.01	<0.01	<0.01
87 - 100	98	<0.01	<0.01	<0.01
0 - 10	190	<0.01	0.02	<0.01
10 - 25	190	<0.01	0.05	<0.01
25 - 37	190	<0.01	0.04	<0.01
37 - 50	190	<0.01	0.02	<0.01
50 - 62	190	<0.01	0.01	<0.01
62 - 75	190	<0.01	0.01	<0.01
75 - 87	190	<0.01	<0.01	<0.01
87 - 100	190	<0.01	<0.01	<0.01

Table B.8.1-27: Field soil dissipation results from trial D07/95 in Holzen, Germany, in study DE/HA/013/90; summary results of the residues in mg/kg dry soil

Soil depth [cm]	DAT	Chloridazon [mg/kg]	Metabolite B [mg/kg]	Metabolite B1 [mg/kg]
0 - 10	0	0.08	0.03	<0.01
10 - 25	0	0.02	0.01	0.01
0 - 10	6	0.52	0.03	<0.01
10 - 25	6	0.01	0.01	<0.01
0 - 10	13	0.14	0.02	<0.01
10 - 25	13	0.09	0.01	<0.01
0 - 10	29	0.16	0.07	0.02
10 -25	29	0.01	0.01	0.01
25 - 37	29	<0.01	0.01	<0.01
37 - 50	29	<0.01	<0.01	<0.01
0 - 10	60	0.06	0.10	0.02
10 - 25	60	<0.01	0.03	0.01
25 - 37	60	<0.01	0.02	0.02
37 - 50	60	<0.01	0.01	0.01
0 - 10	102	0.01	0.07	0.01
10 -25	102	<0.01	0.02	0.02
25 - 37	102	<0.01	0.01	0.01
37 - 50	102	<0.01	<0.01	<0.01
50 - 62	102	<0.01	<0.01	<0.01
62 - 75	102	<0.01	<0.01	<0.01
75 - 87	102	<0.01	<0.01	<0.01
87 - 100	102	<0.01	<0.01	<0.01
0 - 10	186	0.01	0.08	0.02
10 - 25	186	0.07	0.03	0.02
25 - 37	186	<0.01	0.04	0.02
37 - 50	186	<0.01	0.02	0.02
50 - 62	186	<0.01	0.01	0.01
62 - 75	186	<0.01	<0.01	<0.01
75 - 87	186	<0.01	0.01	<0.01
87 - 100	186	<0.01	0.01	<0.01

Table B.8.1-28: Field soil dissipation results from trial VTU/83 in Stetten, Germany, in study DE/HA/013/90; summary results of the residues in mg/kg dry soil

Soil depth [cm]	DAT	Chloridazon [mg/kg]	Metabolite B [mg/kg]	Metabolite B-1 [mg/kg]
0 - 10	0	0.13	0.03	<0.01
10 - 25	0	0.06	0.01	<0.01
0 - 10	8	1.76	0.02	<0.01
10 - 25	8	<0.01	<0.01	<0.01
0 - 10	14	0.62	0.02	<0.01
10 - 25	14	<0.01	0.01	<0.01
0 - 10	30	0.42	0.31	<0.01
10 - 25	30	<0.01	0.01	0.01
25 - 37	30	<0.01	0.01	<0.01
37 - 50	30	<0.01	0.01	0.01
0 - 10	61	<0.01	0.03	0.18
10 - 25	61	<0.01	0.01	<0.01
25 - 37	61	<0.01	<0.01	<0.01
37 - 50	61	<0.01	<0.01	<0.01
0 - 10	100	0.06	0.21	0.01
10 - 25	100	0.02	0.02	<0.01
25 - 37	100	<0.01	0.01	0.01
37 - 50	100	<0.01	<0.01	0.01
50 - 62	100	<0.01	<0.01	<0.01
62 - 75	100	<0.01	<0.01	<0.01
75 - 87	100	<0.01	<0.01	0.01
87 - 100	100	<0.01	<0.01	0.01
0 - 10	188	0.02	0.05	<0.01
10 - 25	188	<0.01	0.01	<0.01
25 - 37	188	<0.01	<0.01	0.01
37 - 50	188	<0.01	0.01	0.01
50 - 62	188	<0.01	0.01	<0.01
62 - 75	188	<0.01	<0.01	0.01
75 - 87	188	<0.01	<0.01	0.01
87 - 100	188	<0.01	<0.01	0.01

Table B.8.1-29: Field soil dissipation results from trial RCN88056 in Chico, California, USA, in study E8950; summary results of the residues in mg/kg dry soil (metabolite B-1 was not determined)

Soil depth [cm]	DAT	Chloridazon [mg/kg]	Metabolite B [mg/kg]
0 – 15	0	3.85	<0.01
15 - 30	0	0.57	<0.01
30 - 91	0	<0.01	<0.01
0 - 15	3	2.61	<0.01
15 - 30	3	0.31	<0.01
30 - 91	3	<0.01	<0.01
0 - 15	7	2.71	<0.01
15 - 30	7	0.13	<0.01
30 - 61	7	<0.01	<0.01
61 - 91	7	0.01	<0.01
91 - 122	7	<0.01	<0.01
0 - 15	14	2.69	0.01
15 - 30	14	0.10	<0.01
30 - 61	14	0.01	<0.01
61 - 91	14	<0.01	<0.01
91 - 122	14	<0.01	<0.01
0 - 15	30	2.37	0.01
15 - 30	30	0.18	<0.01
30 - 61	30	<0.01	<0.01
61 - 91	30	<0.01	<0.01
0 - 15	58	2.39	0.03
15 - 30	58	0.28	<0.01
30 - 61	58	0.01	<0.01
61 - 91	58	<0.01	<0.01
91 - 122	58	<0.01	<0.01
0 - 15	89	3.02	0.04
15 - 30	89	0.22	0.01
30 - 61	89	0.02	<0.01
61 - 91	89	0.02	<0.01
91 - 122	89	<0.01	<0.01
0 - 15	153pre	0.68	0.07
15 - 30	153pre	0.08	0.01
30 - 61	153pre	0.01	<0.01
61 - 91	153pre	<0.01	<0.01
0 - 15	153harv	0.80	0.08
15 - 30	153harv	0.15	0.01
30 - 61	153harv	0.01	<0.01
61 - 91	153harv	<0.01	<0.01
0 - 15	182	0.47	0.05
15 - 30	182	0.07	0.03
30 - 61	182	0.01	<0.01
61 - 91	182	<0.01	<0.01
0 - 15	363	0.07	0.02
15 - 30	363	0.01	0.02
30 - 61	363	<0.01	<0.01
61 - 91	363	<0.01	<0.01

153 harv = 153 days, after harvest
153 pre = 153 days, before harvest

Table B.8.1-30: Field soil dissipation results from trial RCN88057 in Madera, California, USA, in study E8950; summary results of the residues in mg/kg dry soil (metabolite B-1 was not determined)

Soil depth [cm]	DAT	Chloridazon [mg/kg]	Metabolite B [mg/kg]
0 - 15	0	0.61	<0.01
15 - 91	0	<0.01	<0.01
0 - 15	3	0.78	0.01
15 - 30	3	0.01	<0.01
30 - 122	3	<0.01	<0.01
0 - 15	7	1.46	<0.01
15 - 30	7	<0.01	<0.01
30 - 61	7	<0.01	<0.01
61 - 91	7	0.01	<0.01
0 - 15	14	0.87	0.02
15 -30	14	0.10	<0.01
30 - 61	14	0.01	0.01
61 - 91	14	<0.01	<0.01
91 - 122	14	0.01	<0.01
0 - 15	30	0.69	0.02
15 - 30	30	0.01	<0.01
30 - 91	30	<0.01	<0.01
0 - 15	59	0.35	0.04
15 -30	59	0.03	<0.01
30 - 61	59	0.02	<0.01
61 - 91	59	<0.01	<0.01
91 - 122	59	<0.01	<0.01
0 - 15	90	0.35	0.01
15 -30	90	0.18	<0.01
30 - 61	90	0.03	<0.01
61 - 91	90	0.04	<0.01
91 - 122	90	<0.01	<0.01
0 - 15	181	0.25	0.11
15 - 30	181	0.05	0.03
30 - 61	181	<0.01	<0.01
61 - 122	181	<0.01	<0.01
0 - 15	251pre	0.03	0.05
15 -30	251pre	0.02	0.09
30 - 61	251pre	0.01	0.08
61 - 91	251pre	<0.01	<0.01
91 - 122	251pre	<0.01	<0.01
0 - 15	251harv	0.01	0.03
15 -30	251harv	0.01	0.03
30 - 61	251harv	<0.01	0.02
61 - 91	251harv	<0.01	<0.01
91 - 122	251harv	<0.01	<0.01
0 - 15	360	<0.01	<0.01
15 -30	360	<0.01	<0.01
30 - 61	360	<0.01	<0.01
61 - 91	360	<0.01	<0.01
91 - 122	360	<0.01	0.01

251 harv = 251 days, after harvest
251 pre = 251 days, before harvest

Table B.8.1-31: Field soil dissipation results from trial CLZ/1-1 in Chignolo, Italy, in study SIP1296; summary results of the residues in mg/kg dry soil

Soil depth [cm]	DAT	Chloridazon [mg/kg]	Metabolite B [mg/kg]	Metabolite B-1 [mg/kg]
0 - 10	0	2.332	<0.01	<0.01
10 - 20	0	<0.01	<0.01	<0.01
20 - 30	0	<0.01	<0.01	<0.01
0 - 10	7	0.904	<0.01	<0.01
10 - 20	7	<0.01	<0.01	<0.01
20 - 30	7	<0.01	<0.01	<0.01
0 - 10	15	1.241	<0.01	<0.01
10 - 20	15	<0.01	<0.01	<0.01
20 - 30	15	<0.01	<0.01	<0.01
0 - 10	30	0.721	0.010	<0.01
10 - 20	30	0.026	<0.01	<0.01
20 - 30	30	0.019	<0.01	<0.01
0 - 10	61	0.184	0.297	0.014
10 - 20	61	0.035	0.032	<0.01
20 - 30	61	<0.01	0.018	<0.01
0 - 10	100	0.122	0.296	0.029
10 - 20	100	0.011	0.027	<0.01
20 - 30	100	<0.01	<0.01	<0.01
0 - 10	182	0.122	0.305	0.033
10 - 20	182	<0.01	0.015	<0.01
20 - 30	182	<0.01	<0.01	<0.01
0 - 10	371	0.012	0.062	0.021
10 - 20	371	<0.01	0.060	0.017
20 - 30	371	<0.01	0.018	<0.01
0 - 10	555	0.013	0.062	0.027
10 - 20	555	<0.01	0.029	0.021
20 - 30	555	<0.01	0.010	<0.01

Table B.8.1-32: Field soil dissipation results from trial CLZ/1-2 in Elburgo, Spain, in study SIP1296; summary results of the residues in mg/kg dry soil

Soil depth [cm]	DAT	Chloridazon [mg/kg]	Metabolite B [mg/kg]	Metabolite B-1 [mg/kg]
0 - 10	0	1.611	<0.01	<0.01
10 - 20	0	0.012	<0.01	<0.01
20 - 30	0	<0..1	<0.01	<0.01
0 - 10	7	1.076	0.012	<0.01
10 - 20	7	0.014	<0.01	<0.01
20 - 30	7	<0.01	<0.01	<0.01
0 - 10	14	0.579	0.010	<0.01
10 - 20	14	<0.01	<0.01	<0.01
20 - 30	14	<0.01	<0.01	<0.01
0 - 10	29	0.953	0.024	<0.01
10 - 20	29	<0.01	<0.01	<0.01
20 - 30	29	<0.01	<0.01	<0.01
0 - 10	59	0.520	0.031	<0.01
10 - 20	59	<0.01	<0.01	<0.01
20 - 30	59	<0.01	<0.01	<0.01
0 - 10	98	0.121	0.225	<0.010
10 - 20	98	<0.01	<0.01	<0.01
20 - 30	98	<0.01	<0.01	<0.01
0 - 10	182	0.024	0.056	<0.01
10 - 20	182	<0.01	<0.01	<0.01
20 - 30	182	<0.01	<0.01	<0.01
0 - 10	363	0.025	0.048	<0.01
10 - 20	363	<0.01	0.018	<0.01
20 - 30	363	<0.01	<0.01	<0.01
0 - 10	540	0.013	0.062	0.013
10 - 20	540	<0.01	0.048	0.025
20 - 30	540	<0.01	<0.01	0.010

The results of the calculation of the degradation rates are reported here (chloridazon: Table B.8.1-33, metabolite B: Table B.8.1-34) as they are given in the original reports. At that time, these calculations were performed according to the existing knowledge and accepted methods and the resulting values were not normalised to standardised conditions according to FOCUS.

The amounts of metabolite B-1 were generally so low, that degradation rates could not be calculated.

In study 2003/1001009 with the trial HUS/08/00, a compartment model was developed and the degradation of chloridazon and its metabolite B were calculated according to first order.

In study 1998/1000787 with the trials DU2/58/92 and DU3/24/92, the calculations were performed according to Timme and Frehse (best fit), but because the day 0 recoveries were low, the 6 to 8 days figures were used as starting values. Only the degradation rate for chloridazon was calculated.

In study 1993/11484 with the trials D05/97, D07/95 and VTU/83, again only the degradation of chloridazon was calculated according to Timme and Frehse (best fit). Corrected values were used and an outlier was eliminated.

In the US study 1989/5154, the degradation rate for chloridazon and metabolite B was calculated with an SAS statistical program and the slope of the degradation curve was calculated.

In study 2003/1001025 in Italy and Spain, due to the fairly low concentrations of metabolite B-1 an estimation of reliable kinetic parameters for formation and degradation could not be expected and was therefore not conducted. For metabolite B, a kinetic evaluation was conducted, but no reliable, statistically significant parameters could be obtained and thus were not reported. For chloridazon, the available soil concentrations in different soil depths were cumulated and transformed into areic molar soil concentrations (mol/ha), which served as model input. The dissipation of chloridazon in the field was assumed to follow first order kinetics. The estimation of first order rate constants was performed with the calculation tool ModelMaker, version 3.0.4 employing a compartment model.

Table B.8.1-33: Degradation rates for chloridazon as given in the study reports

BASF RegDoc#	Trial No.	DT_{50} (days)	DT_{90} (days)	r^2
2003/1001009	HUS/08/00	78.5	214	0.85
1998/1000787	DU2/58/92	5	53	0.74
1998/1000787	DU3/24/92	53	178	0.91
1993/11484	D05/97	22	74	0.66
1993/11484	D07/95	11	118	0.75
1993/11484	VTU/83	3	35	0.64
1989/5154	RCN88056	68	not calculated	0.827
1989/5154	RCN88057	59	not calculated	0.758
2003/1001025	CLZ/1-1	16.8	55.7	0.885
2003/1001025	CLZ/1-2	30.1	99.9	0.885

r^2 = coefficient of determination

Table B.8.1-34: Degradation rates for metabolite B as given in the study reports

BASF RegDoc#	Trial No.	DT_{50} (days)	r^2
2003/1001009	HUS/08/00	359.5	0.85 (high type-1-error rate of 0.448)
1989/5154	RCN88056	217	0.661
1989/5154	RCN88057	130	0.394

r^2 = coefficient of determination

All DT_{50} values derived for metabolite B within the field dissipation studies conducted with chloridazon are statistically unreliable as can be seen in Table B.8.1-34. The good r^2 of 0.85 for trial HUS/08/00 indicates the goodness of fit for the whole model including the degradation of the parent compound and formation and degradation of metabolite B. The t-test that was conducted for the single parameters revealed a high grade of uncertainty for the half-life estimation of metabolite B which is expressed by a type-1-error rate = 0.448. This means the parameter explained the variation of the data by chance with a probability of 45 %.

B.8.1.2.3 Soil residue study

Comment of RMS:
The study is not triggered. Though DT_{50lab} values of chloridazon can be higher than one third of the time period between application and harvest of beets, the study is not triggered since the possible residues, the active substance and metabolite B, are not phytotoxic, not acutely

toxic to earthworms and had no negative effects on soil micro-organisms at test concentrations, which were higher than the maximum yearly application rate (see B.9).
The geometric mean value of the DT_{50lab} values is calculated to be 43.1 days and shorter than one third of the vegetation period of beets.

B.8.1.2.4 Soil accumulation study

Comment of RMS:
The study is not triggered, though it cannot be excluded that the $DT_{90field}$ value of metabolite B is greater than one year.
The PEC_{soil} calculations for metabolite B resulted in a maximum initial soil concentration of metabolite B of 0.6 mg/kg soil or in a $PEC_{soil, act}$. of 0.521 mg/kg after around 100 days (see Table B.8.3-4).
It could be shown that the metabolite B was not acutely toxic to earthworms and had no negative effects on soil micro-organisms at clearly higher test concentrations than obtained after application of the maximum field rate of 2600 g as/ha. The latter results in a PEC_{ini} of 3.47 mg as/kg soil. This is clearly lower than the NOEC of 1000 mg as/kg soil or 1132 mg metabolite B/kg soil for earthworms and 26 mg as/kg soil or 8.53 mg metabolite B/kg soil for microorganisms. Furthermore, the metabolite had no herbicidal activity. Therefore, a soil accumulation study is not triggered.

Conclusions - Rate of degradation
From the two laboratory studies performed in compliance with current EPA resp. BBA guidelines, aerobic half-lives for chloridazon derived using ModelMaker software ranged between 8.6 days (20 °C) and 187.6 days (25 °C) and thus cover a wide spectrum. The corresponding half-lives for chloridazon normalised to reference conditions according to FOCUS are in a similar order of magnitude, ranging from 8.6 to 173.9 days.
For the metabolites B and B-1, half-lives derived using ModelMaker software on the basis of a best fit estimation and determined graphically, range between 80 days and 132 days, and 118 days and 170 days respectively. Here, the covered range is smaller than for the parent substance.
Under anaerobic conditions, as expected, very much longer half lives for chloridazon between 370 and 607 days were determined in the laboratory.

From the field degradation rates presented in the tables above it is confirmed that the major metabolite B is more stable in soil than chloridazon itself, as already shown in the laboratory. For chloridazon, the DT_{50} of 78.5 days observed in Sweden is proposed as a realistic worst-case field half life. In all trials chloridazon was mainly found in the top soil layers of 0 - 10 cm and 10 - 25 cm, in deeper layers max. recovery was 0.04 mg/kg in 61 - 91 cm soil depth.

Metabolite B appeared in the different trials in the top soil layers from 0 - 10 cm in max. amounts of 0.448 mg/kg after 64 DAT. In this soil layer it was still found in amounts of 0.07 and 0.1 mg/kg after 6 and 12 months in Sweden. At the end of the resp. studies metabolite B was detected in amounts of 0.01 mg/kg in a soil depth of 87 – 100 cm in Germany and in a depth of 91 - 122 cm in California. Although statistically unreliable, the DT_{50} values available for the metabolite B from different climatic regions (Sweden vs. California) indicate a retarded dissipation under field conditions when compared with those obtained under laboratory conditions.

In the field the minor metabolite B-1 is generally found only in lower quantities of max. 0.033 mg/kg in the 0 – 10 cm soil layer in some samples and mostly after longer periods of time after application. However, in Germany, 0.01 mg/kg was detected in the 87 - 100 cm soil layer 100 and 188 days after application, thus demonstrating the tendency of this metabolite, as also proven for metabolite B-1, to move into deeper layers of soil. A calculation of field degradation rates for this metabolite B was not possible.

According to the results of the rate studies, it is concluded that worst-case primary degradation of chloridazon and its two metabolites in soil can be very slow.
Together with the data from the route studies, chloridazon is overall assessed to be relatively persistent to non-biodegradable in soil.

B.8.2 Adsorption, desorption and mobility in soil (Annex IIA 7.1.2, 7.1.3; Annex IIIA 9.1.2)

B.8.2.1 Adsorption and desorption

Reference number: II A 7.1.2/1

Report: Ellenson J.L., 1987; BOD 2000-845
Soil adsorption/desorption of pyrazon
BASF Corporation Agricultural Products Center, Research Triangle Park, NC 27709, USA, unpublished. BASF RegDoc# 1987/5074

Guidelines: EPA 163-1, OECD 106

GLP: No, studies were conducted prior to the implementation of GLP but are scientifically valid

Reference number: II A 7.1.2/2

Report: Keller W., 1980; BOD 2003-315
Adsorption behaviour of crop protection products in the system soil/water
BASF AG, Agrarzentrum Limburgerhof, Limburgerhof, Germany, unpublished. BASF RegDoc# 1980/1000066

Guidelines: none

GLP: No

Reference number: II A 7.1.2/3

Report: Daum A., 1998; BOD 2003-316
Determination of the pKa of Reg. No. 014 456 (BH 119 Metabolite B) in water at 20 °C
BASF AG, Agrarzentrum Limburgerhof, Limburgerhof, Germany, unpublished. BASF DocID 1998/11081

Guidelines: OECD 112

GLP: Yes

Reference number: II A 7.1.2/4

Report: Seher A., 1999; BOD 2003-358
Soil adsorption/desorption study of 035 375 (BH 119-B-Me) on soils
BASF AG, Agrarzentrum Limburgerhof, Limburgerhof, Germany, unpublished. BASF RegDoc# 1999/11086

Guidelines: OECD 106, EPA 163-1

GLP: Yes

Test system
Adsorption and desorption of chloridazon, metabolite B and metabolite B-1 has been investigated in three studies using batch equilibrium procedures. Characteristics of the soils are provided in Table B.8.2-1 to Table B.8.2-3.

In the study of Ellenson (1987), ^{14}C-chloridazon with a specific radioactivity of 2.3 MBq/mg and a radiochemical purity of 98.8 % was used. In the study of Keller W. (1980), ^{14}C-labelled metabolite B was investigated. No further details of the test substance are given in the report. In the study with metabolite B-1 (Seher, 1999), ^{14}C-labelled test substance with a specific radioactivity of 4.35 MBq/mg and a radiochemical purity of > 99 % was used.

Four different concentrations in the range of approx. 0.04 to 5 mg as/L were tested with chloridazon and metabolite B-1. The soil:liquid ratio was 1:5. For metabolite B, three concentrations were tested with a soil:liquid ratio of 1:4.

Solutions of the test substance in 0.01 M $CaCl_2$ ($CaSO_4$ for metabolite B) were prepared, the respective soil was added and the suspension was shaken for 16 - 24 hours. Then, an aliquot of the supernatant was radioassayed. The number of soils tested was five with chloridazon, four with metabolite B and six with metabolite B-1. Using the empirical Freundlich equation, K_f and 1/n were determined from the experimental data. Additionally, normalisation to the organic carbon content of the soils was performed resulting in the $K_{f,oc}$.

Table B.8.2-1: Soils used to investigate adsorption and desorption of chloridazon

Soil designation	Soil I	Soil II	Soil III	Soil IV	Soil V
Origin	Fuquay Varina, NC, USA	Fuquay Varina, NC, USA	Greenville, MS, USA	Woodland, CA, USA	Dinuba, CA, USA
Textural class (USDA scheme)	sand	sand-loam	silt-loam	clay	sand-loam
Particle size distribution [%] (USDA scheme):					
0.050 - 2 mm	93.2	85.6	23.2	33.6	62.4
0.002 - 0.050 mm	2.0	9.6	60.8	29.6	24.0
< 0.002 mm	4.8	4.8	16.0	36.8	13.6
Organic carbon [%]	0.1	0.2	0.5	1.1	0.5
Organic matter [%]	0.2	0.4	0.8	1.9	0.9
CEC [mVal/100 g]	0.83	1.49	10.8	31.1	7.5
pH [H_2O]	6.6	6.0	7.0	6.6	6.8

CEC = cation exchange capacity

Table B.8.2-2: Soils used to investigate adsorption and desorption of metabolite B of chloridazon

Soil designation	Standard soil 2.1	Standard soil 2.2	Standard soil 2.3	Pfungstadt
Origin	Germany	Germany	Germany	Germany
Soil particles < 0.02 mm	10.7	14.3	23.2	40.0
Organic carbon [%]	0.7	2.4	0.9	0.6
Organic matter [%]	1.2	4.2	1.6	1.0
CEC [mVal/100 g]	5.0	10.0	9.0	13.0
pH [$CaCl_2$]	7.0	6.0	7.3	7.3

CEC = cation exchange capacity

Table B.8.2-3: Soils used to investigate adsorption and desorption of metabolite B-1 of chloridazon

Soil designation	Lufa 2.2	Bruch West	Li 35b	USA 538-30-5	USA 538-31-2	Canada 95024
Origin	Germany	Germany	Germany	USA	USA	Canada
Textural class (German scheme)	sand/ loamy sand	loamy sand	loamy sand	loamy sand	silty loamy sand	sandy loam
Textural class (USDA scheme)	sand/ loamy sand	sandy loam	loamy sand	loamy sand	loam	sandy clay loam
Particle size distribution [%] (German scheme):						
0.063 - 2 mm	85	72	81	81	40	46
0.002 - 0.063 mm	10	18	12	11	47	31
< 0.002 mm	5	10	7	8	13	23
Particle size distribution [%] (USDA scheme):						
0.050 - 2 mm	86	73	83	83	44	49
0.002 - 0.050 mm	9	17	10	9	43	28
< 0.002 mm	5	10	7	8	13	23
Organic carbon [%]	2.5	1.5	1.1	0.4	0.5	3.4
Organic matter [%]	4.3	2.6	1.9	0.7	0.9	5.8
CEC [mVal/100 g]	11.2	12.1	7.2	4	10	26
pH [$CaCl_2$]	5.8	7.5	6.5	5.8	5.2	7.5

CEC = cation exchange capacity

Desorption was investigated with the adsorbed residues remaining from the adsorption determination. A 0.01 M $CaCl_2$ solution was added to the soil samples at a ratio of 1:5 and the desorbed amount of radioactivity in the supernatant was determined after 16 - 24 hours of shaking. For chloridazon, only two of the soils (soil III, Greenville and soil IV, Woodland) adsorbed enough test substance to allow a full desorption isotherm study. For the other soils that showed little adsorption, the ratio of desorbed chloridazon to soil-adsorbed chloridazon R_{des} was reported as an indicator of the desorption tendency of the compound. Desorption of metabolite B was not investigated.

Findings

The adsorption and desorption constants of chloridazon and its metabolites for the different soils are presented in Table B.8.2-4 - Table B.8.2-6.

Moderately high adsorption with K_f values in the range of 0.2 - 3.6 mL/g and $K_{f,oc}$ values in the range of 89 – 340 mL/g were observed for chloridazon. Reasonable Freundlich adsorption exponents 1/n between 0.84 and 1.03 were determined with the exception of soil II for which a very low 1/n of 0.57 was calculated. Desorption constants could be derived only for two soils since the amount adsorbed was too low in the other soils. Instead, for these soils the desorption coefficient R_{des} is given.

In an attempt to correlate the adsorption behaviour of chloridazon to known soil characteristics, cross-correlation statistics are given in the report. Strong positive correlation was found between the K_f and the soil organic matter content. It must be stated however that also a strong correlation between CEC, organic matter and clay content exists which makes it difficult to confine the adsorption properties to any of these factors individually. No dependence of the adsorption on the soil pH was found.

Table B.8.2-4: Adsorption and desorption of ^{14}C-chloridazon

Soil designation	Textural class	Adsorption constant K_f [mL/g]	Adsorption exponent 1/n	Adsorption constant $K_{f,oc}$ [mL/g]	Desorption constant $K_{f,des}$ [mL/g]	Desorption coefficient R_{des}*
Soil I	sand	0.25	1.0301	220	-	0.3
Soil II	sand-loam	0.2	0.5681	89	-	<0.1
Soil III	silt-loam	1.0	0.8355	220	1.42	0.63
Soil IV	clay	3.6	0.8774	340	0.41	0.44
Soil V	sand-loam	0.69	0.9143	128	-	0.47
Arithmetic mean			0.845	199		

* possible values [0,…,1]

Table B.8.2-5: Adsorption of ^{14}C-labelled metabolite B of chloridazon

Soil designation	Adsorption constant K_f [mL/g]	Adsorption exponent 1/n	Adsorption constant $K_{f,oc}$ [mL/g]
Standard soil 2.1	0.3400	0.8043	49*
Standard soil 2.2	0.7055	0.8679	29*
Standard soil 2.3	0.4224	0.8191	46*
Pfungstadt soil	0.4277	0.8435	74*
Arithmetic mean		0.834	50

*recalculated from data in the report

Table B.8.2-6: Adsorption and desorption of ^{14}C-labelled metabolite B-1 of chloridazon

Soil designation	Textural class	Adsorption constant K_f [mL/g]	Adsorption exponent 1/n	Adsorption constant $K_{f,oc}$ [mL/g]	Desorption constant $K_{f, des}$ [mL/g] step 1	step 2
LUFA 2.2	sand/loamy sand	0.682	0.907	27	2.44	3.46
Bruch West	sandy loam	0.499	0.851	33	1.79	1.76
Li 35b	loamy sand	0.429	0.861	39	1.88	2.60
USA 538-30-5	loamy sand	0.399	0.794	100	1.99	1.66
USA 538-31-2	loam	0.681	0.915	136	4.02	4.34
CAN 95024	sandy clay loam	7.337	0.871	216	19.58	21.26
Arithmetic mean			0.8665	91.8		

Only weak adsorption of metabolite B to soil was observed with $K_{f,oc}$ values ranging from 29 to 74 with Freundlich adsorption exponents 1/n in the range of about 0.80 - 0.87.
From the study of Daum A. (1998), which is not discussed in further detail here, it became clear that metabolite B does not dissociate in water. Therefore, a dependence of the adsorption of metabolite B on the soil pH is not to be expected.

Weak to moderate adsorption to soil was observed for metabolite B-1 with K_f values below 1 mL/g except for the Canadian soil for which a higher K_f of about 7.3 mL/g was determined. Upon standardisation to the organic carbon content of the soils $K_{f,oc}$ values between 27 and 136 mL/g and 216 mL/g for the Canadian soil were calculated. Freundlich adsorption exponents 1/n ranged from 0.79 to 0.92. The desorption constants $K_{f,des}$ for the two desorption steps were in the range of 1.66 - 21.26 mL/g.
The absence of dissociation in water of metabolite B is expected to apply also for metabolite B-1, its methylated derivative. Therefore, a dependence of the adsorption on the soil pH is also not expected for metabolite B-1. This was also supported by the results of the adsorption study.

Valid: yes

Comment of the RMS:
The K_{oc} value of soil V (Table B.8.2-4) was recalculated by the RMS due to a calculation error regarding this soil in the original report (AII 7.1.2/1, DOC#1987/5074). The provided value is corrected from 180 to 128 and the resulting K_{oc} arithmetic mean is changed from 210 to 199.
The OECD TG 106 recommends to exclude soils with an organic carbon content < 0.3 %. Though the organic carbon content of the soils I and II are below 0.3 %, they were considered in the calculation due to the good correlation coefficient between oc- and kf-values (0.95).

Conclusion
Adsorption of chloridazon to soil is moderately strong with $K_{f,oc}$ values ranging from 89 to 340 mL/g. The adsorption of the metabolites of chloridazon is weaker with $K_{f,oc}$ values of 29 - 74 mL/g for metabolite B and 27 – 216 mL/g for metabolite B-1. There is no indication of a pH dependence of the adsorption.

B.8.2.2 Mobility in soil

Reference number: II A 7.1.3.1/1

Report: Keller W., 1985; BOD 2001-605
Leaching behaviour of pesticides - BAS 119 33 H
BASF AG, Agrarzentrum Limburgerhof, Limburgerhof, Germany, unpublished. BASF RegDoc# 1985/10062

Guidelines: BBA Merkblatt Nr. 37

GLP: No, studies were conducted prior to the implementation of GLP but are scientifically valid

Test system:
Soil column leaching was investigated with German standard soils 2.1, 2.2 and 2.3. No further details of the soils are given in the report. An amount of 0.784 mg/20 cm^2 of formulation BAS 119 33 H corresponding to 0.510 mg/20 cm^2 or 2.6 kg/ha chloridazon was applied to the column filled with the respective soil. Water was applied to simulate 200 mm rainfall (393 mL). The leachate water was extracted with extrelut columns, cleaned up with silicagel columns and measured by HPTLC equipped with an UV-densitometer.

Findings
128.4 µg, < 4 µg and 82.4 µg of chloridazon corresponding to 25.18 %, < 0.8 % and 16.16 % of the applied amount were found in the leachate water of the columns filled with standard soils 2.1, 2.2 and 2.3, respectively. No degradates were detected.

Valid: yes

B.8.2.2.1 Aged residue column leaching studies

Reference number: II A 7.1.3.2/1

Report: Keller E., 1988; BOD 2001-606
The leaching of ^{14}C-chloridazon after aerobic aging
BASF AG, Agrarzentrum Limburgerhof, Limburgerhof, Germany, unpublished. BASF RegDoc# 1988/10126

Guidelines: BBA IV 4-2

GLP: Yes

Test system:
The leaching of aged residues of chloridazon was studied in German standard soil 2.1. Characteristics of the soil are given in Table B.8.2-7. Soil samples containing ^{14}C-chloridazon at a rate of 3 mg/kg soil (nominal) were incubated in the dark for 30 days at 22 ^{o}C and 40 % MWC. The radiochemical purity of the test substance was > 99 % with a specific radioactivity of 2.27 MBq/mg. 100 g of treated, aged soil was transferred to the top of a column (inner diameter 5 cm) containing untreated soil to a height of 28 cm. Water was applied to simulate 200 mm rainfall (393 mL in two days). The leachate water was collected

in four fractions of about 100 mL and analysed for radioactive residues. Soil samples were extracted with methanol and methanol/water and the extracts were analysed by radio-TLC and radio-HPLC.

Table B.8.2-7: Soil used to investigate the leaching of residues of chloridazon after aerobic ageing

Soil designation	Standard soil 2.1
Origin	Germany
Textural class (German scheme)	sand
Particle size distribution [%] (German scheme): 0.063 - 2 mm 0.002 - 0.063 mm < 0.002 mm	 85.9 10.2 3.9
Organic carbon [%]	0.75
Organic matter [%]	1.29
Microbial biomass [mg C/100g dry soil]	10.1
CEC [mVal/100 g]	5.0
pH (CaCl2)	5.9

Organic matter = organic carbon x 1.72
CEC = cation exchange capacity

Findings

During the 30 day ageing period, a mineralisation rate of 1.4 % of the total radioactivity at day 0 was recorded. That means that the amount of radioactivity that was loaded onto the column after ageing was almost equivalent to the initial total radioactivity. The results of the leaching experiment are summarised in Table B.8.2-8.

Table B.8.2-8: Leaching behaviour of residues of ^{14}C-chloridazon after aerobic ageing (values in % of the total radioactive residues after 30 days ageing = % TRR)

	Total	ERR	RRR
segment 1 - top	14.7	12.5	4.7
segment 2	16.2	10.3	8.3
segment 3	13.0	7.2	2.2
segment 4	17.1	9.2	2.6
segment 5	19.1	10.5	2.3
segment 6	11.1	6.4	1.5
segment 7	1.8	0.9	0.2
segment 8 (sand) - bottom	0		
soil (total)	93.0		
leachate fraction 1	0		
leachate fraction 2	0		
leachate fraction 3	0.2		
leachate fraction 4	0.1		
leachate (total)	0.3		
Total	93.3		

Only very low amounts of radioactivity (0.3 % of the TRR) were found in the leachate. Almost all of the radioactivity (93 % TRR) was retained in the soil column.

The radioactive residues were only partially extractable (ERR) from the soil segments of the column. Up to 8.3 % TRR of bound residues (RRR) were found in the individual soil segments. Analysis of the extracts of the soil segments revealed that almost exclusively chloridazon was extractable. Besides chloridazon, very minor amounts of metabolite B (< 1 % TRR in total) were detected.

Chloridazon and metabolite B were also detected in low amounts in leachate fractions 3 and 4. Fractions 1 and 2 were not analysed due to very low radioactivity.

valid: yes

Conclusion
The results of the non-aged column leaching study show that chloridazon is potentially mobile. In the aged leaching study only small amounts of radioactivity were found in the leachate indicating that ageing of the residues greatly reduces the leaching potential.

B.8.2.2.2 Lysimeter studies or field leaching studies

The leaching behaviour of chloridazon and its metabolites was investigated in an outdoor lysimeter study using ^{14}C-chloridazon. Additional data are taken from a second lysimeter study in which non-radiolabelled chloridazon was applied along with ^{14}C-quinmerac and analysed with the "cold" residue method.

Reference number: II A 7.1.3.3/1

Report: Gatzweiler E. et al., 1992; BOD 2003-317
Field lysimeter study with (4,5-^{14}C)chloridazon
Forschungszentrum Jülich GmbH, Jülich, Germany, unpublished
BASF RegDoc# 1992/11927

Guidelines: none

GLP: No

Test system:
In this study two different soils were used: A typical "Parabraunerde" according to the German nomenclature from Jülich-Merzenhausen ("LY-TP", lysimeter 211) and a sandy "Pseudogley-Parabraunerde" from Niederkrüchten-Overhetfeld ("LY-SPB", lysimeter 206). The characteristics of these soils are listed in Table B.8.2-9.

Table B.8.2-9: Characterisation of soils used in the outdoor lysimeter study BASF RegDoc# 1992/11927

LY-TP, Jülich-Merzenhausen					
Horizon	A_p	A_1	B_{t1}	B_{t2}	B_{t3}
soil depth [cm]	0 - 39	39 - 52	55 - 77	77 - 98	98 - 119
Particle size distribution [%]					
Sand	6.4	1.0	0.1	0.8	0.7
Silt	78.2	77.1	73.4	74.1	72.7
Clay	15.4	21.9	26.5	25.1	26.6
Organic C [%]	1.05	0.35	0.30	0.30	0.25
pH (KCl)	7.2	6.9	6.8	6.7	6.5
LY-SPB, Niederkrüchten-Overhetfeld					
Horizon	A_p	B_v / A_h	S_w / B_v	S_d / B_{t1}	C_v / B_v
soil depth [cm]	0 - 30	30 - 41	41 - 52	52 - 70	70 - 115
Particle size distribution [%]					
Sand	74.1	75.6	76.2	49.5	93.7
Silt	21.7	21.5	21.2	36.7	4.6
Clay	4.2	2.9	2.6	13.8	1.7
Organic C [%]	0.90	0.20	0.15	0.20	0.20
pH ($CaCl_2$)	6.9	6.8	6.6	3.8	3.9

Although this study was started already in 1989, prior to the release of the BBA guideline IV, 4-3, soil LY-SPB was chosen in order to comply with the soil specification as given in a precursor of this guideline. Soil LY-TP with its higher silt and clay content does not meet the soil specification of the BBA guideline, but nevertheless gives valid information on the behaviour of chloridazon in an undisturbed soil monolith. The lysimeter with soil LY-TP had a surface of 1 m^2, the lysimeter with soil LY-SPB a surface of 0.5 m^2, both with a depth of 1.1 m. The lysimeters and their surrounding control plots of about 9 m^2 (for each lysimeter) were planted with the same crops in order to establish growth conditions that are very similar to the situation found in a cropped field.
The application in the first experimental year was carried out preemergence on sugar beets on 26 April, 1989. The target application rate was 2.6 kg as/ha (= 260 mg as/m^2). Actual application rates (after determination of losses) were 2.96 kg/ha on soil LY-TP and 2.5 kg/ha on soil LY-SPB. The specific radioactivity of the test substance was 5.34 MBq/mg at a radiochemical purity of 98 %. The radiolabelled test substance was mixed with non-radioabeled chloridazon in a ratio of 17.32 mg + 307.68 mg. The treatment was done with the test substance as a wettable powder (WP) formulation. Rotational crops were winter wheat followed by winter barley. The study was conducted outdoors for two years at the Institute of Radioagronomy, Jülich Research Centre, Jülich, Nordrhein-Westfalen, Germany.

Leachate was sampled in intervals of 3 - 4 weeks, provided that any leachate had been formed. After determination of $^{14}CO_2$ and other volatile derivatives, the radioactive residues were adsorbed on Extrelut columns and subsequently desorbed from the columns with dichloromethane/2-propanol.
The soil was sampled after the harvest of the sugar beets (6 months after application) down to a depth of 60 cm and after the harvest of the winter wheat (16 months after application) to a depth of 30 cm. Two years after application the soil cores were disassembled: The upper soil layers of soil LY-SPB down to a depth of 80 cm were removed in layers of 10 cm. The remaining soil layers of LY-SPB and the entire soil core of LY-TP were sampled using a Humax soil drill of 10 cm diameter and were divided into 10 cm segments. The soil samples were extracted with methanol.

Leachate and soil extracts were analysed by LSC and radio-TLC. Soil and plant samples were combusted and analysed by LSC.
The total amount of precipitation (incl. additional irrigation) in the first year was 772.9 mm for soil LY-TP and 784.9 mm for soil LY-SPB. In the second year the respective total precipitation was 820.3 mm for soil LY-TP and 808.3 mm for soil LY-SPB. The differences in precipitation between the two soils originate from different amounts of irrigation. Although the precipitation in the first year was slightly lower than 800 mm as required by the BBA guideline (which had not been released at that time), this represents realistic worst case field conditions to assess the potential groundwater contamination.

Findings

Leachate
The total amount of leachate in the first year was 112.5 L/m^2 for soil LY-TP and 130.2 L/m^2 for soil LY-SPB. In the second year, the respective amounts were 126.9 L/m^2 for soil LY-TP and 200.2 L/m^2 for soil LY-SPB. The results of leachate analysis are summarised in Table B.8.2-10. Identification of metabolites was done by comparison of their retention times with those of co-chromatographed reference compounds.

The active substance chloridazon was detected only at the first sampling of soil LY-TP in a concentration of 0.048 µg/L. In all subsequent leachate samples from soil LY-TP and in all leachate samples from soil LY-SPB, the active substance was below the LOQ of 0.024 µg/L.

Metabolite concentrations were generally higher in the leachates from soil LY-SPB than from soil LY-TP. With soil LY-TP moderate concentrations of metabolite B (max. yearly average 2.13 µg/L) and only low concentrations of metabolite B-1 were observed (max. yearly average 0.10 µg/L). The maximum concentration of metabolite B of 3.00 µg/L in individual samples was reached already in the first year (March 1990). With soil LY-SPB much higher concentrations were determined: Max. yearly average 40.56 µg/L for metabolite B and 2.12 µg/L for metabolite B-1. The maximum concentration of metabolite B of 54.57 µg/L was reached in the second experimental year in March 1991. Additionally, remarkable concentrations of non-identified radioactivity are to be noted with soil LY-SPB.

Table B.8.2-10: Yearly average concentrations of chloridazon and its metabolites in lysimeter leachates [µg/L]

Study period	Amount of leachate [L/m²]	Chloridazon	Metabolite B	Metabolite B-1	CO_2 incl. other volatiles*	NIR*
Soil LY-TP, Jülich-Merzenhausen						
1st study year 1989 – 1990	112.5	0.009	2.13	0.08	0.049	1.12
2nd study year 1990 – 1991	126.9	0	1.47	0.10	0.398	0.74
Total study period 1989 – 1991	239.4	0.004	1.78	0.09	0.234	0.92
Soil LY-SPB, Niederkrüchten-Overhetfeld						
1st study year 1989 – 1990	130.2	n.d.	6.57	0.13	0.038	7.58
2nd study year 1990 – 1991	200.2	n.d.	40.56	2.12	0.528	11.26
Total study period 1989 – 1991	330.4	n.d.	27.17	1.34	0.335	9.81

* as equivalents of active substance
NIR = not identified radioactivity
n.d. not detectable, i.e. below the LOQ of 0.024 µg/L

Soil

The results of the soil analyses are shown in Table B.8.2-11. Remarkable concentrations of radioactivity were determined in the soil after disassembling. The maximum concentration was found in the upper two soil layers. The radioactivity strongly decreased from about 40 – 50 cm downwards.

Chloridazon was found in moderate concentrations in the soil segments with max. 0.099 µg/g in soil LY-TP in a depth of 10 - 20 cm and with max. 0.065 µg/g in soil LY-SPB in a depth of 20 - 30 cm. The concentrations of metabolites in the soil were moderate to low. By far the highest proportion of radioactivity in the soil comprised bound residues. The bound residues were fractionated into fulvic acids, humic acids and humins.

Plants

After harvest of the crops, the plant fractions were combusted and analysed for radioactivity by LSC. The total residues taken up by plants during the study are listed in Table B.8.2-12.

Table B.8.2-11: Distribution of radioactivity in soil layers after disassembling of ^{14}C-chloridazon-treated lysimeter soil cores [µg/g dry soil]

Soil layer [cm]	Total radioactivity [µg/g]	Chloridazon [µg/g]	Metabolite B [µg/g]	Metabolite B-1 [µg/g]	NIR [µg/g]	Bound residues [µg/g]
Soil LY-TP, Jülich-Merzenhausen						
0 - 10	0.554	0.060	0.032	0.004	0.002	0.485
10 - 20	0.607	0.099	0.053	0.008	0.004	0.474
20 - 30	0.301	0.078	0.043	0.007	0.003	0.204
30 - 40	0.097	0.026	0.014	0.003	0.001	0.059
40 - 50	0.024	0.008	0.004	0.001	0.001	n.a.
50 - 60	0.014	0.003	0.0015	0.0006	<0.001	n.a.
60 - 70	0.011	n.a.	n.a.	n.a.	n.a.	n.a.
70 - 80	0.007	n.a.	n.a.	n.a.	n.a.	n.a.
80 - 90	0.005	n.a.	n.a.	n.a.	n.a.	n.a.
90 -100	n.d.	n.a.	n.a.	n.a.	n.a.	n.a.
100 -110	n.d.	n.a.	n.a.	n.a.	n.a.	n.a.
Soil LY-SPB, Niederkrüchten-Overhetfeld						
0 - 10	0.333	0.027	0.013	0.001	0.002	0.297
10 - 20	0.345	0.045	0.024	0.002	0.003	0.281
20 - 30	0.211	0.065	0.037	0.004	0.003	0.130
30 - 40	0.165	0.060	0.032	0.003	0.007	0.097
40 - 50	0.046	0.015	0.006	0.001	0.005	n.a.
50 - 60	0.019	0.005	0.003	0.0002	0.001	n.a.
60 - 70	0.020	0.008	0.004	0.0004	0.001	n.a.
70 - 80	0.020	0.011	0.005	0.0005	0.002	n.a.
80 - 90	0.015	0.008	0.004	0.0005	0.001	n.a.
90 -100	0.011	0.008	0.003	0.0004	0.001	n.a.
100 -110	0.012	0.006	0.004	0.0003	<0.001	n.a.

NIR = not identified radioactivity
n.d. = not detectable
n.a. = not analysed

Table B.8.2-12: Residues in plants (total uptake in % of total applied radioactivity)

Study period	Crop	% Total radioactivity
Soil LY-TP, Jülich-Merzenhausen		
1st study year 1989 – 1990	sugar beet	0.98
2nd study year 1990 – 1991	winter wheat	0.76
end of the study	winter barley*	0.30
Soil LY-SPB, Niederkrüchten-Overhetfeld		
1st study year 1989 – 1990	sugar beet	0.79
2nd study year 1990 – 1991	winter wheat	2.05
end of the study	winter barley*	0.16

* harvested as green matter

Material Balance

The overall balance of radioactivity of the two lysimeters (LY-TP and LY-SPB) is shown in Table B.8.2-13. The major portion of the radioactivity was found in the soil, mostly as bound residues. Losses - most probably by mineralisation to $^{14}CO_2$ - are the second significant fraction of the applied radioactivity. The portion of radioactivity found in the leachate and the crops was low.

Table B.8.2-13: Overall balance of radioactivity (% of total applied radioactivity)

	Soil	Leachate	Plants	Losses (mineralisation)*
Soil LY-TP, Jülich-Merzenhausen	76.7	0.32	2.03	20.95
Soil LY-SPB, Niederkrüchten-Overhetfeld	64.4	7.05	3.00	25.55

* determined by calculating the difference to 100 %

Valid: The study is plausible. The study was started prior to the release of the BBA guideline (February 1990).

Comment of the RMS:
Following conditions of the BBA guideline IV 4-3 are kept in the lysimeter study:

Conditon BBA IV 4-3	Lysimeter LY-TP (No 211)	Lysimeter LY-SPB (no 206)
thickness 1 – 1.3 m	yes	yes
area 0.5 – 1 m²	yes	yes
loamy silty sand	not specified	not specified
sum of silt and clay max. 30 %	no	yes
clay 10 %	no	yes
organic carbon max 1.5 %	yes	yes
max. application rate	yes	yes
annual average rainfall min 800 mm/a	773 - 820	785 - 808

The soil texture of lysimeter LY-TP 211 is not as conservative as required in the current BBA guideline, reflected by the low leachate concentrations of the metabolites.
The metabolite concentrations of lysimeter LY-SPB which is relevant for the evaluation clearly exceed 0.1 µg/L.
The analysis of the soil layers reveal that the active substance and the metabolite B preferably remains in the upper soil layers down to 30 - 40 cm depth.

Reference number: II A 7.1.3.3/2

Report: Mittelstaedt W., Führ F., 1993; BOD 2001-607
Field lysimeter study with ^{14}C-quinmerac
Forschungszentrum Jülich GmbH, Jülich, Germany, unpublished,
BASF RegDoc# 1993/11386

Guidelines: BBA IV 4-3

GLP: No

Reference number: II A 7.1.3.3/3

Report: Nicolaisen R.K., 1993; BOD 2001-608
Note from the translator on discrepencies between the original German report and the English translation
Translation office Nicolaisen, Otterstadt, Germany, unpublished,
BASF RegDoc# 1993/11384

Guidelines: none

GLP: No, not subject of GLP regulations

Test system:
In this lysimeter study, non-radiolabelled chloridazon was applied along with ^{14}C-labelled quinmerac (corresponding to formulation BAS 523 03 H). Only data related to chloridazon are reported here.
A sandy "Pseudogley-Parabraunerde" from Niederkrüchten-Overhetfeld ("LY-SPB", lysimeter 210) was used. This soil was from the same origin as the "LY-SPB" used in the study reported above (BASF RegDoc# 1992/11927), but from another spot of the field. Characteristics of this soil are given in Table B.8.2-14. The soil meets the specifications of BBA guideline IV, 4-3.
The lysimeter had a surface area of 0.5 m^2 and depth of the soil column of 1.10 m. The lysimeter and the surrounding control plot of about 9 m^2 was planted with the same crop in order to establish growth conditions on the lysimeter that are very similar to the situation found in a cropped field.

Table B.8.2-14: Characterisation of the soil used in the outdoor lysimeter study BASF RegDoc# 1993/11386

LY-SPB, Niederkrüchten-Overhetfeld					
horizon soil depth [cm]	A_p 0 - 30	S_w / B_{v1} 30 - 50/55	S_d / B_t 50/55 - 77	S_w / B_{v2} 77 - 100	S_w / B_{v3} 100 - 120/140
Particle size distribution [%]					
Sand	71.0	72.8	72.2	72.9	91.2
Silt	23.7	22.8	25.1	23.6	5.9
Clay	5.2	4.4	2.7	3.5	2.9
Organic C [%]	1.15	0.45	0.20	0.15	0.10
pH (KCl)	6.85	6.87	6.77	6.55	6.47

The application was made preemergence on sugar beets on 16 May, 1990. The actual application rate of chloridazon (after calculation of losses) was 1820 g/ha with the test substance applied in the BAS 119 33 H formulation (65 % active substance as a wettable powder). The study was conducted outdoors for two years at the Institute of Radioagronomy, Jülich Research Centre, Jülich, Nordrhein-Westfalen, Germany.
Leachate was sampled in intervals of 3 - 4 weeks, provided that any leachate had been formed. Aliquots of the individual leachate samples were shipped to BASF AG, Limburgerhof and the leachate was analysed for chloridazon and metabolite B with the "cold" residue method. No further details of the analysis are given in the report. Soil and plant samples were not analysed for chloridazon.
The amount of precipitation including irrigation was 839.8 mm in the first year and 780.3 mm in the second year. The total precipitation in the two trial years was 1620.1 mm.

Findings
The total amount of leachate was 59.5 L/m^2 in the first year and 261.2 L/m^2 in the second year. The results of the leachate analysis are given in Table B.8.2-15. Not all of the leachate samples could be analysed for chloridazon due to the limited amount of leachate, mainly in the first experimental year. Chloridazon was never detected above the LOQ of 0.05 µg/L. Moderate to high concentrations of metabolite B were measured in the leachate. From the data in the report, the yearly average concentrations of metabolite B were calculated based only on these leachate samples, in which metabolite B was actually measured. This is considered to be a conservative estimation since from the course of the concentrations of metabolite B in the individual samples it can be deduced that the peak concentrations are clearly found in the measured samples but not in those, which have not been analysed. Based on this calculation, the yearly average of metabolite B in the leachate was 4.06 µg/L in the first year and 12.18 µg/L in the second year. The maximum concentration of metabolite B in individual samples was 22.8 µg/L in the last leachate sample in April 1992.

In this study with the same sandy soil as in the previously described study (BASF RegDoc# 1992/11927), considerably lower concentrations of metabolite B were observed: 12.18 µg/L vs. 40.56 µg/L (max. yearly averages). This is considered to be only partly due to the different application rate which was 2.5 kg/ha (on soil LY-SPB) in the first study and 1.82 kg/ha in the second study.

Table B.8.2-15: Concentrations of chloridazon and metabolite B in lysimeter leachates (µg/L)

Percolate measurement date	Days after application	Chloridazon [µg/L]	Metabolite B [µg/L]
6 Nov 1990	174	-	-
7 Jan 1991	236	n.a.	5.40
4 Feb 1991	264	n.a.	1.13
21 Mar 1991	309	n.a.	n.a.
11 Apr 1991	330	n.a.	n.a.
Average 1990/1991		**n.a.**	**4.06***
4 Jul 1991	414	n.a.	n.a.
14 Oct 1991	516	n.a.	n.a.
11 Nov 1991	544	< 0.05	6.17
3 Dec 1991	566	< 0.05	6.76
8 Jan 1992	602	< 0.05	9.72
11 Feb 1992	636	< 0.05	14.80
16 Mar 1992	670	< 0.05	19.00
6 Apr 1992	691	< 0.05	22.80
Average 1991/1992		**< 0.05***	**12.18***

n.a. = not analysed
* average calculated only with actually measured samples

Valid: The study is plausible but does not fullfil the validity criteria of the guideline.

Comment of the RMS:
Though the study is performed according to the BBA guideline, the requirements of the guideline is not fulfilled regarding the use of lysimeters in parallel. However, the study confirms the results of the previous lysimter study where concentrations of metabolite B exceeding 0.1 µg/L were found in the leachate.

Conclusion
From the results of the two outdoor lysimeter studies, it is concluded that the application of chloridazon is safe with regard to groundwater. Only one measureable detect of chloridazon and yearly average concentrations far below 0.1 µg/L were determined in the lysimeter leachates.

The chloridazon metabolites B resp. metabolite B-1 have a high leaching potential. Yearly average concentrations of metabolite B exceeded 0.1 µg/L in both years with maximum concentration of 40 µg/L in the second year.
For the concentrations of the metabolites in the leachate, a dependency on the soil was observed. Whereas high concentrations of metabolite B were observed with the sandy soil LY-SPB with the maximum concentration of 40 µg/L in the second year after application, concentrations formed with the loamy soil LY-TP were between 1.47 and 2.13 with its maximum in the first year after application. According to current guidelines the loamy sand is too conservative for an assessment of the leachate behaviour this further evaluations are based on the results obtained with the sandy soil.
Metabolite B-1 was generally detected in much lower concentrations than metabolite B ranging between 0.08 and 0.1 in loamy soil and 0.13 and 2.12 in the sandy soil.

B.8.3 Predicted environmental concentrations in soil (PECS) (Annex IIIA 9.1.3)

Reference number: III A 9.1.3/1

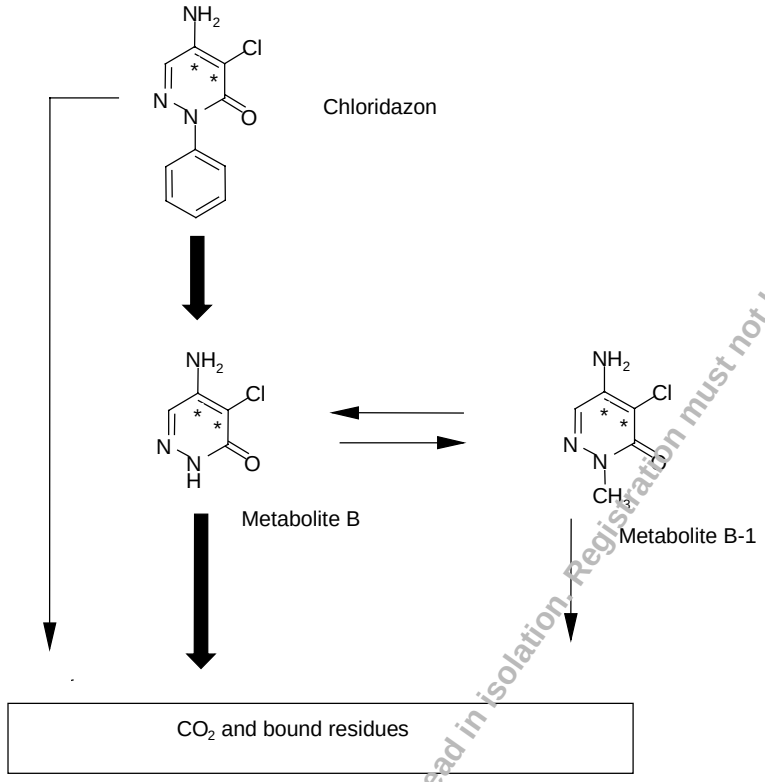
Report: Dressel J., 2003(e); BOD 2003-309
Compilation of parameters characterising the environmental fate of BAS 119 H (chloridazon) and its metabolites
BASF AG, Agrarzentrum Limburgerhof, Limburgerhof, Germany, unpublished, BASF DocID 2003/1001026

Guidelines: not applicable

GLP: no, not subject to GLP regulations

A compilation of all relevant studies and a selection of parameters for the calculation of predicted environmental concentrations (PEC) in soil, groundwater, surface water and sediment was conducted. In the following only the results related to PEC calculations for soil (PEC_{soil}) are presented. In Figure B.8.3-1 the principal soil metabolism scheme of chloridazon is shown which was parameterised as follows (summary in Table B.8.3-1).

Figure B.8.3-1: Proposed degradation pathway for chloridazon in soil



1. Chloridazon degrades to metabolite B. The average molar formation fraction of metabolite B was estimated from the soil metabolism study (2 soils) to be 0.648 (64.8 %). The degradation kinetics was assumed to follow first order kinetics with the worst case field half-life of 78.5 d observed in the far north of Europe (Sweden).

2. Metabolite B-1 is formed from metabolite B in a kinetic equilibrium. Metabolite B degrades to bound residues and CO_2, whereas the only way of degradation of metabolite B-1 is the back-reaction to metabolite B. The first order rate constants characterising the kinetic equilibrium were selected from the laboratory soil degradation study of metabolite B. As a worst case assumption, the parameter combination that was able to describe the highest formation of metabolite B-1 was chosen. For the degradation of metabolite B the uncorrected worst case laboratory uncorrected half-life was chosen (132 d) since the field half-lives are statistically unreliable.

Table B.8.3-1: Parameters suitable for the calculation of predicted environmental concentrations (PEC) in soil (PEC_{soil})

Parameter	Unit	Selected for	Chloridazon	Metabolite B	Metabolite B-1
Molar formation fraction	-	PEC_{gw}/ PEC_{soil}	-	**0.648**	-
Worst case soil half life	d	PEC_{soil}	**78.5** (field)	**132** (laboratory, uncorrected)	-
Worst case parameters for kinetic equilibrium between metabolite B and metabolite B-1	1/d	PEC_{soil}	-	-	**k_{12}=0.00329** **k_{21}=0.0105**

Valid: yes

Reference number: III A 9.1.3/2

Report: Hauck T., 2003; BOD 2003-320
Predicted environmental concentrations of BAS 119 H (chloridazon) and its metabolites in soil (PECsoil) after field application of BAS 119 33 H
BASF AG, Agrarzentrum Limburgerhof, Limburgerhof, Germany, unpublished, BASF DocID 2003/1001029

Guidelines: not applicable

GLP: no, not subject to GLP regulations

Introduction
Predicted Environmental Concentrations (PEC) are calculated for initial, short-term and long-term actual and time weighted average concentrations in soil for chloridazon and its soil metabolites 'metabolite B' and 'metabolite B-1'.

Materials and methods
Application rates, number of applications and crop interception
The formulated product BAS 119 33 H is proposed to be applied to beta beets at a maximum rate of 2.6 kg as/ha. One single application per annum is to be made prior to or after crop emergence. To consider the worst case exposure of soil organisms to chloridazon the calculations were conducted for a pre-emergence application. Therefore, the full application rate, without interception by a crop canopy, reaches the soil surface.
The application rates, growth stages, interception values and resulting amounts applied reaching the soil surface are summarised in Table B.8.3-2.

Table B.8.3-2: The worst-case application scenario of chloridazon - BAS 119 H

Crop	Sugar beet
Growth stage [BBCH]	Prior to crop emergence
Number of applications / year	1
Application rate [g as/ha]	2600
Interception by crop canopy [%]	0
Amount reaching the soil surface [g as/ha]	2600

Initial PEC_{soil} values were calculated assuming an even distribution to a depth of 5 cm in soil with a bulk density of 1.5 g/cm³.

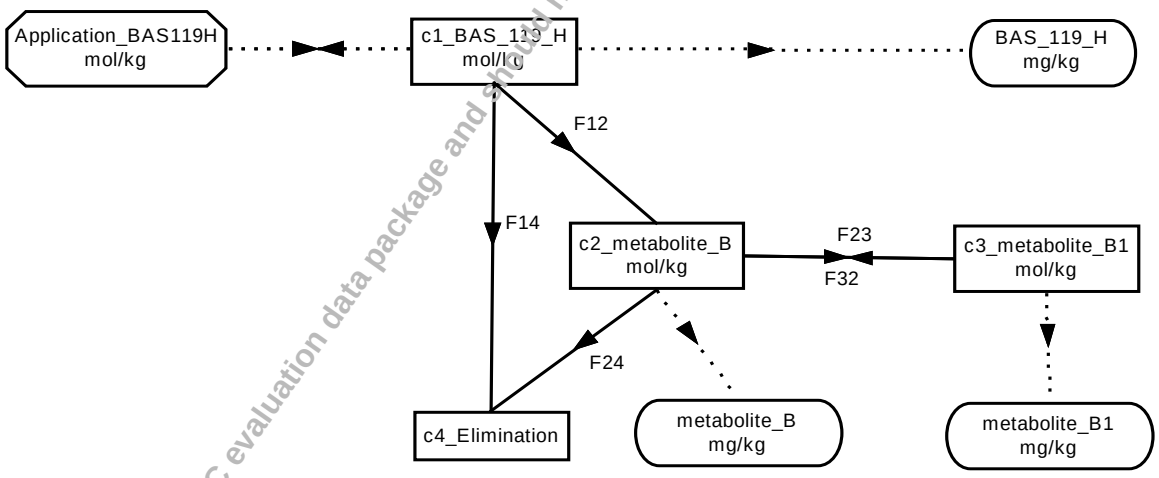
Metabolism of chloridazon in soil
The degradation pathway for chloridazon in soil deduced from studies describing the route and the rate of degradation (Table B.8.3-1) was used and parameterised as described above.

Calculation procedure of initial and actual PEC values
As mentioned earlier small amounts of metabolite B are transformed into metabolite B-1 by a reversible methylation, forming a kinetic equilibrium between the two substances. Therefore, standard approaches for calculating the PEC_{soil} are not appropriate. Following the recommen-

dations of Kloskowski et al. (1999), a compartment model was used to describe the behaviour of BAS 119 H and its metabolites in soil.
The compartment model including the parent as well as the metabolites B and B-1 was set up with the software ModelMaker version 4.0 in order to calculate the expected time course of the concentrations of BAS 119 H and its metabolites in soil. The model is shown in Table B.8.3-2. All fluxes F_{xy} were parameterised with first order rate constants. Corrections for the differences in molar weight of the active substance and its metabolites were included in the compartment model.
The initial PEC value in soil ($PEC_{soil,ini}$) was calculated considering the application rate (2600 g/ha), the crop interception (0 %), a soil bulk density of 1.5 kg/dm^3 and a thickness of the soil layer of 5 cm.

The actual Predicted Environmental Concentrations ($PEC_{soil,act}$) for given time points after application of the active substance were calculated with ModelMaker. The reported values are the concentrations of the compound after the day of maximum concentration of each compound which for chloridazon is the day of treatment. For the metabolites the day of the maximum calculated soil concentration is reached during the period the calculations are conducted for.

Figure B.8.3-2: Model to predict the environmental concentration of BAS 119 H and its metabolites B and B-1 in soil (square boxes = compartments, octagonal box = application event, round-edged boxes = variable for the calculation of actual soil concentration (mg/kg) from molar concentrations)



Calculation of time weighted average PEC values
The time weighted average concentration in soil of BAS 119 H for each time interval Δt = 0, 1, 2, 3, 4, 7, 14, 21, 28, 42, 100, 200 and 365 days were determined in the spreadsheet software Excel using the output of the ModelMaker model consisting of actual soil concentrations for chloridazon and its two metabolites in a 0.1 d resolution. The concept of a moving time frame (moving average) was applied. For all possible realisations of the time intervals Δt average concentration values were calculated (arithmetic mean of all actual concentrations within the interval = numerical integration). The $PEC_{soil,twa}$ was then defined as the maximum value for each time interval Δt.

Results

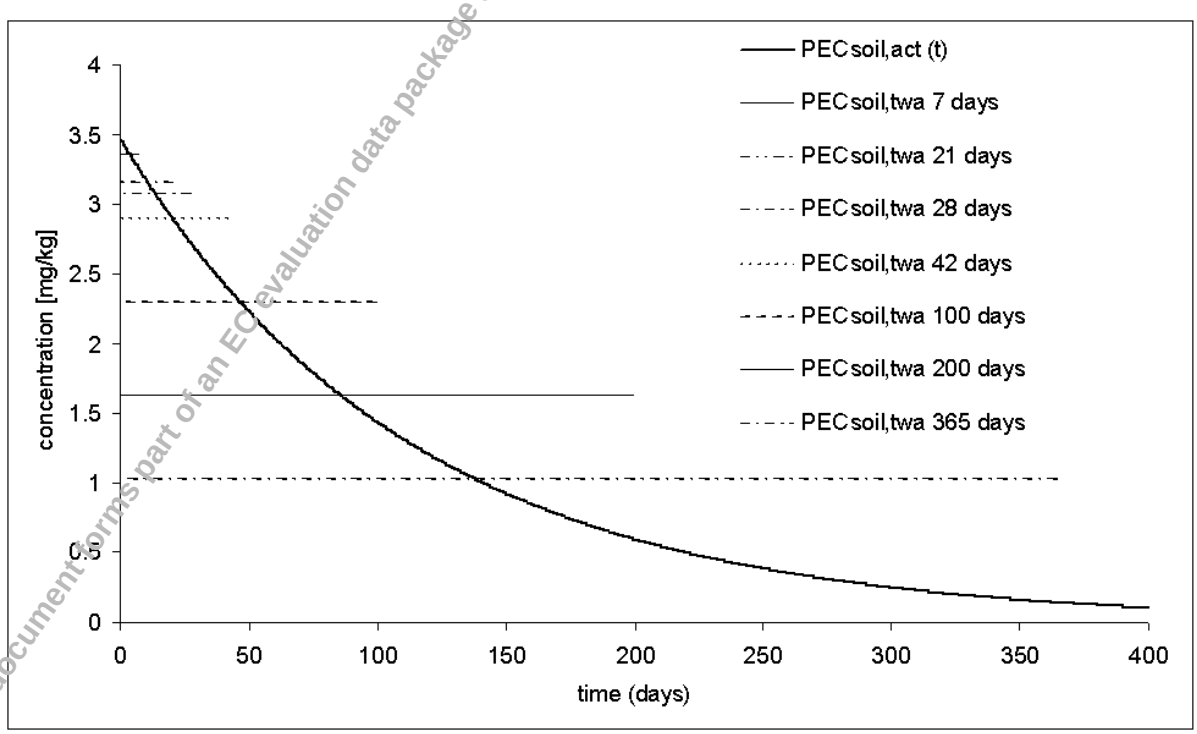
PEC_{soil} of BAS 119 H

The actual and the time weighted average Predicted Environmental Concentrations for BAS 119 H in soil ($PEC_{soil,act}$ and $PEC_{soil,twa}$) are shown in Table B.8.3-3. The course of the actual concentrations as well as the level of the time-weighted average concentrations are shown in Figure B.8.3-3.

Table B.8.3-3: $PEC_{soil,act}$ and $PEC_{soil,twa}$ of BAS 119 H

	Day after last application [d]	$PEC_{soil,act}$ [mg kg^{-1}]	$PEC_{soil,twa}$ [mg kg^{-1}]
Initial	0	3.467	
Short-term	1	3.436	3.451
	2	3.406	3.436
	3	3.376	3.421
	4	3.346	3.406
Long-term	7	3.259	3.362
	14	3.064	3.261
	21	2.880	3.164
	28	2.707	3.071
	42	2.392	2.897
	100	1.434	2.303
	200	0.593	1.627
	365	0.135	1.033

Figure B.8.3-3: $PEC_{soil,act}$ and $PEC_{soil,twa}$ of BAS 119 H after application of the formulated product BAS 119 33 H (the horizontal lines show the concentration level and the averaging period of the calculated $PEC_{soil,twa}$)



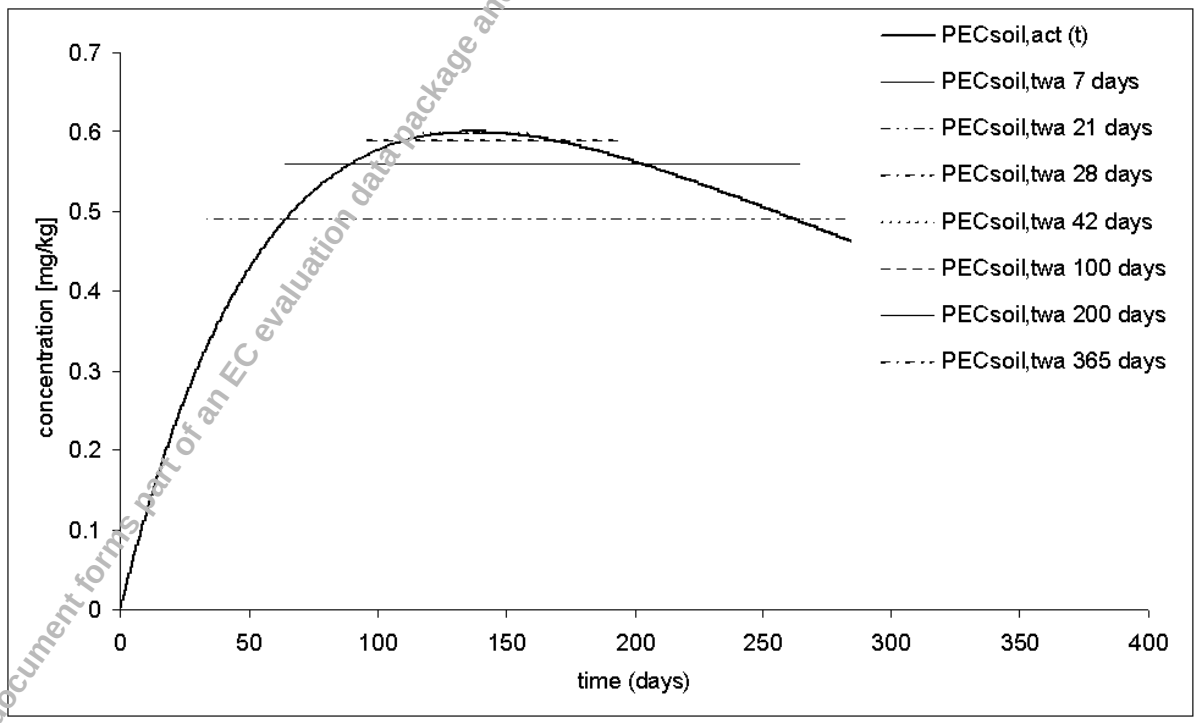
PEC_{soil} of Metabolite B

The actual and the time weighted average predicted environmental concentrations for metabolite B in soil ($PEC_{soil,act}$ and $PEC_{soil,twa}$) are shown in Table B.8.3-4. The course of the actual concentrations as well as the level of the time-weighted average concentrations are shown in Figure B.8.3-4.

Table B.8.3-4: $PEC_{soil,act}$ and $PEC_{soil,twa}$ of metabolite B

	Day after maximum concentration [d]	$PEC_{soil,act}$ [mg kg^{-1}]	$PEC_{soil,twa}$ [mg kg^{-1}]
Maximum	0	0.600	
Short-term	1	0.600	0.600
	2	0.600	0.600
	3	0.600	0.600
	4	0.600	0.600
Long-term	7	0.600	0.600
	14	0.598	0.600
	21	0.595	0.600
	28	0.591	0.599
	42	0.582	0.598
	100	0.521	0.589
	200	0.397	0.560
	365	0.233	0.491

Figure B.8.3-4: $PEC_{soil,act}$ and $PEC_{soil,twa}$ of metabolite B after application of BAS 119 H (the horizontal lines show the concentration level of the calculated $PEC_{soil,twa}$)



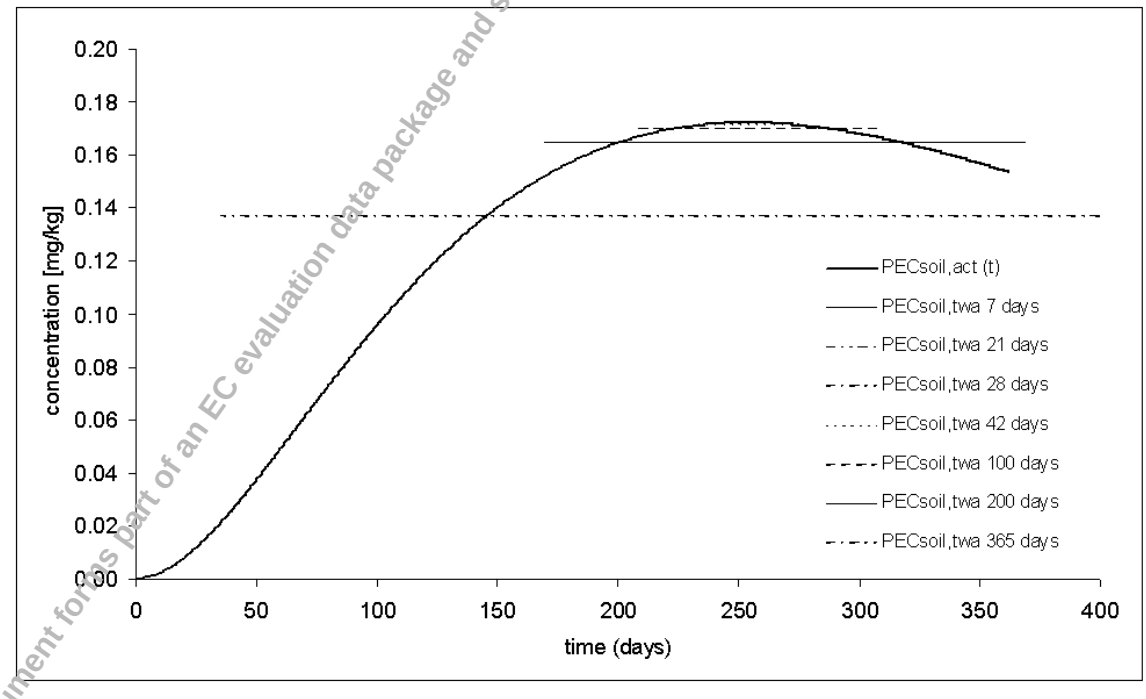
PEC_{soil} of metabolite B-1

The actual and the time weighted average predicted environmental concentrations for metabolite B-1 in soil ($PEC_{soil,act}$ and $PEC_{soil,twa}$) are shown in Table B.8.3-5 and the course of the actual concentrations as well as the level of the time-weighted average concentrations are shown in Figure B.8.3-5.

Table B.8.3-5: $PEC_{soil,act}$ and $PEC_{soil,twa}$ of metabolite B-1

	Day after maximum concentration [d]	$PEC_{soil,act}$ [mg kg^{-1}]	$PEC_{soil,twa}$ [mg kg^{-1}]
Maximum	0	**0.172**	
Short-term	1	0.172	0.172
	2	0.172	0.172
	3	0.172	0.172
	4	0.172	0.172
Long-term	7	0.172	0.172
	14	0.172	0.172
	21	0.171	0.172
	28	0.171	0.172
	42	0.169	0.172
	100	0.156	0.170
	200	0.125	0.165
	365	0.077	0.137

Figure B.8.3-5: $PEC_{soil,act}$ and $PEC_{soil,twa}$ of metabolite B-1 after application of BAS 119 H (the horizontal lines show the concentration level of the calculated $PEC_{soil,twa}$)



Comment of the RMS:

The calculations are acceptable.

B.8.4 Fate and behaviour in water (Annex IIA 7.2.1; Annex IIIA 9.2.1, 9.2.3)

B.8.4.1 Hydrolytic degradation

Reference number: II A 7.2.1.1/1

Report: Ellenson J., Brem G., 1988; WAS 2001-267
Hydrolysis of ^{14}C-pyrazon in pH 5, 7, and 9 solutions at 25 degrees Celsius
BASF Corporation Agricultural Products Center, Research Triangle Park, NC 27709, USA, unpublished, BASF RegDoc# 1988/5518

Guidelines: EPA 161-1

GLP: No, studies were conducted prior to the implementation of GLP but are scientifically valid

Test system
Hydrolysis of [^{14}C]-chloridazon was tested in aqueous buffer solutions at three different pH-values (pH 5, 7 and 9) at 25 °C $\pm$ 1 °C using the [pyridazinone-4,5-^{14}C]-labelled compound. The specific radioactivity of the labelled substance was 15.89 MBq/mg (radiochemical purity $\geq$ 97.7 %). The concentration of the labelled chloridazon in the buffer solutions was about 50 mg/L for each test. The hydrolysis at pH 5,7 and pH 9 was followed for 30 days. Analysis of the samples was performed by radio-HPLC and radio-TLC.

Findings
The amounts of chloridazon found by radio-HPLC at the beginning of the test and 30 days after test initiation are shown in Table B.8.4-1. No degradation occurred. Chloridazon was found to be hydrolytically stable at pH 5,7 and 9 during an incubation period of 30 days. From the obtained results and the chemical structure of chloridazon degradation is also not to be expected at pH 4.

Table B.8.4-1: Hydrolysis of chloridazon at pH 5, 7 and 9. Quantitative evaluation by radio-HPLC

Sample	Chloridazon	
	mg/kg	% TRR
pH 5; 0 days	54.51	100
pH 5; 30 days	56.00	103
pH 7; 0 days	45.10	100
pH 7; 30 days	49.02	109
pH 9; 0 days	47.33	100
pH 9; 30 days	51.40	109

* TRR = total radioactive residues

Conclusion:
Chloridazon is hydrolytically stable at acidic, neutral and basic pH.

Valid: yes

B.8.4.2 Photochemical degradation

Active substance

Reference number: II A 7.2.1.2/1

Report: Ellenson J., Jordan J., Wickler V., 1989; LUF 2001-228
Photolysis of BAS 119 H in pH 7 aqueous solution at 25 degrees Celsius
BASF Corporation Agricultural Products Center, Research Triangle Park, NC 27709, USA, unpublished, BASF DocID 1989/5090

Guidelines: EPA 161-2

GLP: No, studies were conducted prior to the implementation of GLP but scientifically valided

Reference number: II A 7.2.1.2/2

Report: Tanaka F.S., 1992; LUF 2001-229
Aqueous photolysis of ^{14}C-chloridazon at pH 7
BASF Corporation Agricultural Products Center, Research Triangle Park, NC 27709, USA, unpublished. BASF RegDoc# 1992/5090

Guidelines: EPA 161-2

GLP: Yes

The direct photolysis was performed because the absorption coefficients of chloridazon for wavelengths above 290 nm were ≥ 10 L/(mol cm). Since chloridazon is stable at acidic, neutral and basic pH, direct photolysis was conducted only at one pH, i.e. pH 7. Two studies were performed. The second study [see II A 7.2.1.2/2] was conducted to upgrade the earlier photolysis study [see II A 7.2.1.2/1] regarding identification of volatile photoproducts and the measurement of a chloridazon absorption spectrum.

Test system
Photolysis of [^{14}C]-chloridazon at a concentration of about 50 mg/L was performed with a Hanau Suntest photoreactor equipped with a xenon lamp. Sterilised glass vessels used for this study were custom-fabricated and consisted of a water-jacketed glass chamber covered with a quartz plate. Each vessel had an air inlet and an air outlet. The incoming air was sterilised and the CO_2 was removed. A trapping system for volatiles was connected to each vessel. The temperature of the aqueous solution under photolysis was maintained at 25 °C. The vessels were located under a xenon lamp with a light intensity of about 1900-2100 µE/(m^2 s) and a cut-off for wavelengths < 290 nm to simulate natural sunlight. The duration of the experiment was 30 days with an approximate 12 h light/12 h dark cycle.
The specific radioactivity of the radiolabelled test substance was 15.9 MBq/mg and 20.9 MBq/mg respectively, with a radiochemical purity of ≥ 97.7 %.

Dark control samples of the test solution were stored in a climatic chamber. The temperature was 25 ± 1 °C during the experiment.

Samples were analysed for chloridazon and degradation products by radio-TLC and radio-HPLC.

Findings
In general, the reversed phase TLC analyses of sample solutions were consistent with results shown by HPLC [see II A 7.2.1.2/1]. Three major non-polar degradation products (TLC zone 3, 4 and 6 with R_f-values of 0.28, 0.44 and 0.67) were resolved. The major non-polar components (TLC-zone 3 and 4) reached a maximum of 9 % TAR after about 150 hours, respectively, but subsequently declined. A similar pattern is seen for TLC-zone 6 except that the maximum level occurred at 260 hours. The amount of the most polar compound (TLC-zone 8) increased during the photolysis period and accounted for approximately 14 % TAR at the end of the study. However, it was demonstrated that this TLC-peak can be separated into a mixture of products ranging from 1 to 7 % TAR. MS analysis of the isolated products was performed but no unambiguous identification could be obtained. However, since each of the individual degradation products accounted for less than 10 % TAR, no additional structure elucidation was done. Approximately 17 % TAR were determined to be carbon dioxide and/or other organic volatiles. Results are given in Table B.8.4-2.

Table B.8.4-2: Distribution of radioactivity during aqueous photolysis at pH 7 (mean values of two test vessels in % TAR, see II A 7.2.1.2/1)

TAT	Volatiles	Chloridazon	TLC zone	TLC zone	TLC zone	TLC zone	TLC zone	Balance
			1 + 2 + 7	3	4	6	8*	
0	0	100	0	0	0	0	0	100
15 h	0.8	90.2	1.7	2.0	3.4	1.3	1.3	100.7
42 h	2.7	76.9	3.7	4.5	7.3	2.5	2.7	100.3
89 h	5.1	62.3	4.9	8.0	6.0	4.9	5.4	96.6
152 h	8.7	53.6	4.8	8.8	9.2	4.9	7.4	97.4
213 h	11.6	40.8	4.7	8.5	8.3	9.2	9.1	92.2
260 h	14.0	32.4	5.9	8.0	8.5	8.3	12.1	89.2
343 h	17.4	26.3	4.8	8.6	6.0	8.2	13.8	85.1

* consists of several peaks

A semi-log plot of the concentration of chloridazon versus time indicated that the reaction followed first order kinetics resulting in a half-life of chloridazon of 151 h (= **6.3 days**) under continuous irradiation. This values corresponds to a half-life of **12.5 days** under real conditions of a clear summer day (12 h/12 d day/night cycle).

In the second study [see II A 7.2.1.2/2] it was demonstrated that more than 98 % of volatile radioactivity corresponded to radiolabelled carbon dioxide. However, the amount of $^{14}CO_2$ after 30 days was significantly higher (51 %) as compared with the previous study (17 %). The significant increase in the amount of $^{14}CO_2$ was probably due to the presence of co-solvent acetonitrile (0.8 %) resulting in a more equal distribution of chloridazon in the test system and a higher availability for photolytical degradation.

Radio-TLC analysis of the aqueous phase as well as of ethylacetate extracts of the 30 day-sample resulted in several peaks that could not be identified. One large peak representing 19 % TAR appeared to be an unresolved mixture of highly polar products. None of the other

peaks could be assigned to any specific compound with equal or more than 10 % TAR. No further structure elucidation was achieved.

Analysis of the dark control showed that the no radioactivity was lost during photolysis and the test substance remained stable during the study period.

Valid: yes

Reference number: II A 7.2.1.2/3

Report: Sarafin R., 1991; LUF 2003-57
Chloridazon (BAS 119 H) - Absorption coefficients at pH 4, pH 7 and pH 9
BASF AG, Agrarzentrum Limburgerhof, Limburgerhof, Germany.
unpublished, BASF RegDoc# 1991/10347

Guidelines: BBA IV 6-1

GLP: Yes

Reference number: II A 7.2.1.2/4

Report: Sarafin R., 1992(a); LUF 98-00155
Chloridazon - Determination of quantum yield
BASF AG, Agrarzentrum Limburgerhof, Limburgerhof, Germany,
unpublished, BASF RegDoc# 1992/10441

Guidelines: BBA IV 6-1, OECD Draft Test Guideline Phototransformation of Chemicals in Water (January 1990)

GLP: Yes

Test system
For the determination of the quantum yield of chloridazon, aqueous solutions of [^{14}C]-labelled chloridazon were irradiated at 305 nm. Degradation of the test substance was quantified by LSC, TLC and HPLC. Simultaneous measurement of the amount of quanta absorbed by the test solution allowed the calculation of the quantum yield. The specific radioactivity of the test substance was 2.26 MBq/mg, the radiochemical purity 98.9 %. Two experiments with irradiations of 72 h each were performed in a Quantacount apparatus with a xenon lamp and at a wavelength of 305 nm. The concentration of the test substance in the aqueous test solution was 14 µg/mL and 12.5 µg/mL, respectively. The pH of the solutions was basically neutral (pH 6.8 and 7.6). Since the UV-spectra of chloridazon above 290 nm are identical between pH 4 and pH 9, the determination of the quantum yield at different pH is not required.
Calibration of the Quantacount was performed by irradiation of a chemical actinometer simultaneously with each sample irradiation. Iron(III)oxalate was used as actinometer. Analyses were performed by LSC, TLC and HPLC measurements.

Findings

No loss of radioactivity during irradiation occurred. TLC and HPLC analyses revealed the formation of both polar and unpolar photodegradates and a corresponding decrease of chloridazon in the test solutions. No attempt to identify and quantify the metabolites was made. The quantum yield of chloridazon was calculated to be 2.0×10^{-4} mol/Einstein.

Valid: yes

Reference number: II A 7.2.1.2/5

Report: Scharf J., 1999(a); LUF 2001-225
Photolytical halflife of chloridazon in the top layer of aqueous systems
BASF AG, Agrarzentrum Limburgerhof, Limburgerhof, Germany, unpublished, BASF RegDoc# 1999/10693

Guidelines: EEC 94/37

GLP: No, not subject to GLP regulations

With quantum yield, absorption spectrum and with the help of a program which uses the algorithms developed by Frank and Klöpffer (1985) for the direct photochemical transformation of chemicals in water (Frank, R. and Klöpffer, W. (1985), Ermittlung von Strahlungsdaten und Entwicklung eines Programms zur Abschätzung der abiotischen Transformation von Chemikalien in natürlichen Gewässern, Forschungsbericht Nr. 106 020 46), the theoretical photolytical half-life of chloridazon in the top layer of aqueous systems was calculated for the main application periods. The values are given in Table B.8.4-3.

Table B.8.4-3: Theoretical photolytical half-life of chloridazon in the top layer of aqueous systems

month of application	Environmental half-life [d irradiation]
March	75.6
April	36.8
May	25.9
June	21.6

Valid: yes

Metabolite

Reference number: II A 7.2.1.2/6

Report: von Goetz N., 2000(b); WAS 2004-250
Aqueous photolysis of the metabolite B of chloridazon (BAS 119 H), unpublished, BASF RegDoc# 2000/1000147

Guidelines: FAO Revised Guidelines on Environmental Criteria for the Registration of Pesticides Revision 3 (28 August 1993), EPA 161-2

GLP: Yes

In order to assess the environmental behaviour of chloridazon metabolite B, information on the photolytical degradation in water and on the amount and nature of degradation products formed by photolysis is provided as supplementary information.

Test system
The direct photolysis was performed at pH 5 using the [pyridazin-4,5-^{14}C]-label of metabolite B. The specific radioactivity was 6.05 MBq/mg (radiochemical purity 99.6 %). The overall concentration of the labelled active substance in the sterile aqueous buffer solution was 1.2 mg/L.
Sterilised glass vessels with quartz glass caps containing 20 mL test solution were irradiated in a thermostated block. Each vessel had an air inlet and an air outlet. The incoming air was moistened, sterilised, and the CO_2 was removed. A trapping system for volatiles was connected to each vessel. The thermostated vessels were located under a xenon lamp with a light intensity of about 3 mW/cm^2 and a cut-off for wavelengths < 290 nm to simulate natural sunlight. The duration of the experiment was 15 days under continuous irradiation.

Appropriate volumes of each test solution were stored in a climatic chamber to be used as dark control. The temperature was 22 ± 1 °C during the experiments.

For the determination of the quantum yield of metabolite B, a mixture of p-nitroanisol (1 x 10^{-5} M) and pyridine (1.84 x 10^{-4} M) was used as chemical actinometer according to DULIN and MILL (D. Dulin and T. Mill (1982), Development and Evaluation of Sunlight Actinometers, Environ.Sci.Technol. 16, 815 - 820). During each irradiation experiment, two vessels with the actinometer solution were irradiated simultaneously with the test solutions.
All samples were directly analysed by LSC and HPLC without work-up.

Findings
Except small amounts of $^{14}CO_2$ detected in the trapping system for volatiles, the major part of the radioactivity remained in the water. Table B.8.4-4 shows the overall material balance in the direct photolysis tests and in the dark control.

Table B.8.4-4: Distribution of radioactivity during aqueous photolysis and in dark control at pH 5 (mean values of 2 measurements)

DAT	Photolysis			Dark Control
	Water %TAR	Volatiles* %TAR	Sum %TAR	Water %TAR
0	100.0	0.0	100.0	100.0
1	93.9	0.1	94.0	94.8
2	95.5	0.8	96.2	92.7
4	93.4	0.8	94.2	94.6
7	84.5	5.1	89.6	93.8
10	87.8	6.0	93.8	95.5
15	79.4	7.4	86.8	97.8

* radioactivity was found only in the NaOH-traps

The components found by radio-HPLC are shown in Table B.8.4-5. Several minor degradation products and one major metabolite are formed during direct photolysis of metabolite B. Only the minor degradation products that at least exceeded 5 % TAR once are listed in this Table. All other peaks are summarised in the colums "others". The major degradation product with a molar

mass of 254 g/mol occurred with up to 13.5 % TAR at the end of the study. Based on the MS structure elucidation it can be concluded that this photolysis product results from the condensation of two molecules of metabolite B with HCl elimination, yielding three possible structures. The other metabolites occurred with less than 10 % TAR and were therefore not identified. In the dark control no degradation of metabolite B occurred.

Table B.8.4-5: HPLC peak distribution for photolysis at pH 5 (mean values of two test vessels in % TAR)

DAT	Metabolite B	Mass 254	Unknown (HPLC - 4.5 min)	Unknown (HPLC - 3.9 min)	Unknown (HPLC - 3.2 min)	Others (<5 %)*	Sum
0	100.0	0.0	0.0	0.0	0.0	0.0	100.0
1	93.9	0.0	0.0	0.0	0.0	0.0	93.9
2	87.9	2.0	0.8	0.5	1.7	2.7	95.6
4	76.8	5.5	2.6	0.9	2.5	5.3	93.5
7	49.3	9.1	5.8	3.0	5.3	11.8	84.3
10	57.4	8.3	2.1	5.1	4.1	10.7	87.8
15	34.9	13.5	2.5	4.6	7.1	16.9	79.4

* sum of individual peaks with less than 5 % at any sampling time

For the calculation of the half-life of metabolite B, the program ModelMaker Version 3.0.4 (Cherwell Scientific Publishing, Oxford, UK) was used. The resulting **half-life was 9.7 d** (r^2 = 0.9436) under continuous irradiation. Under real conditions of a clear summer day (12 h/12 d day/night cycle) the half-life would be approximately twice as long (19.4 days).
The determination of the quantum yield was based on the following equation:

$$\Phi_{ts} = \frac{\Phi_{ac} \times \Sigma(\varepsilon_{(\lambda)ac}\, I_{(\lambda)ac}) \times DT50_{ac}}{\Sigma(\varepsilon_{(\lambda)ts}\, I_{(\lambda)ts}) \times DT50_{ts}}$$

Φ_{ts}: quantum yield of the test substance
Φ_{ac}: quantum yield of the actinometer
$\varepsilon_{(\lambda)ts}$: absorption coefficient of the test substance
$\varepsilon_{(\lambda)ac}$ absorption coefficient of the actinometer
$DT50_{ac}$: half life of the actinometer
$I_{(\lambda)ts}$: light intensity of the used irradiation source during irradiation of the test substance
$I_{(\lambda)ac}$: light intensity of the used irradiation source during irradiation of the actinometer
$DT50_{ts}$: half life of the test substance

The quantum yield of metabolite B was calculated to be 1.7×10^{-5}.

With quantum yield, absorption spectrum, and with the help of a program which uses the algorithms developed by Frank and Klöpffer (1985) for the direct photochemical transformation of chemicals in water (Frank, R. and Klöpffer, W. 1985: Ermittlung von Strahlungsdaten und Entwicklung eines Programms zur Abschätzung der abiotischen Transformation von Chemikalien in natürlichen Gewässern, Forschungsbericht Nr. 106 020 46), the theoretical photolytical half-life of metabolite B in the top layer of aqueous systems was calculated for the main application periods of chloridazon. The values are given in Table B.8.4-6. The photolytical half-life of metabolite B in aqueous systems under outdoor conditions was smallest in June with 6.3 calender days.

Table B.8.4-6: Theoretical photolytical half life of chloridazon metabolite B in the top layer of aqueous systems

Month of application	Environmental half-life [d irradiation]
April	8.72

Month of application	Environmental half-life [d irradiation]
May	6.96
June	6.25
July	6.95
August	7.00

Valid: yes

Reference number: II A 7.2.1.2/7

Report: Scharf J., 1998; LUF 2003-39
Photolysis of chloridazon and its metabolite B in a natural water
BASF AG, Agrarzentrum Limburgerhof, Limburgerhof, Germany, unpublished, BASF RegDoc# 1998/10128

Guidelines: FAO Revised Guidelines on Environmental Criteria for the Registration of Pesticides Revision 3 (28 August 1993), EEC 94/37

GLP: Yes

Reference number: II A 7.2.1.2/8

Report: Scharf J., 1999(b); LUF 2003-40
Photolysis of metabolite BH 119-B-Me (BI) of chloridazon in a natural water
BASF AG, Ludwigshafen/Rhein, Germany, unpublished,.BASF RegDoc# 1999/10696

Guidelines: EEC 94/37

GLP: Yes

Additional information on the photolysis of chloridazon and metabolites B and B-1 is provided with a study on their photolytical degradation in a natural water under environmentally relevant conditions.

Test System
Natural water was obtained from a pond (Kleiner Waldsee) located in a forest west of Schifferstadt, Germany. The water had a pH of about 8, a TOC content of 12 - 13 mg/L and a nitrate content of less than 0.5 mg/L and 2 mg/L, respectively. The studies were performed with unlabelled test substances (purities > 99 %).
Each test substance was dissolved in 50 mL pond water at a concentration of 10 mg/L (chloridazon), 5 mg/L (metabolite B) and 5 mg/L (metabolite B-1). Each test solution was irradiated in glass vessels with quartz glass caps. The thermostated vessels were located under a xenon lamp with a light intensity of about 3 mW/cm^2 and a cut-off for wavelengths < 290 nm to simulate natural sunlight. The duration of the experiment was 15 days under continuous irradiation.
Dark control samples were stored in a climatic chamber together with the test solution. The temperature was 22 °C during the experiments.

Findings
From the results of HPLC-analysis DT_{50}-values were calculated for chloridazon, metabolite B and metabolite B-1 according to Timme, Frehse and Laska (1. order) and using the program Model Maker Version 3.0.3 (Cherwill Scientific Publishing, Oxfrod, UK). Results are shown in Table B.8.4-7.

Table B.8.4-7: Half-lives for chloridazon, metabolite B and metabolite B-1 that occurred during sensitised photolysis

	DT_{50} (related to permanent irradiation)	DT_{50} (related to 12 h/12 h day/night cycle)
Chloridazon*	23.3 d	46.6
Metabolite B*	5.9 d	11.8
Metabolite B-1**	1.2 d	2.4 d

*calculated according to Timme, Frehse and Laska (first order)
**calculated with Model Maker (first order)

Chloridazon and its metabolites B and B-1 can be degraded in natural water bodies like a pond. Sensitised photolytical degradation presents an essential sink under relevant environmental conditions, especially for metabolites B and B-1. In the case of metabolite B the photolytical half-life in natural water (5.9 days under continuous irradiation) was less than the half-life obtained in the direct photolysis using sterilised buffer (9.7 days under continuous irradiation; see II A 7.2.1.2/6).

Furthermore, it can be assumed that only a limited amount of photosensitisers like humic acids, nitrate or oxygen was available in the 50 mL-test system. Due to the almost constant available concentrations of all sensitisers in natural water bodies (ponds, lakes, streams, rivers), the environmental half-life of chloridazon and metabolites B and B-1 in natural water matrices can be assumed to be even lower than determined in the laboratory.

Valid: yes

Conclusion
Chloridazon can be degraded by direct photolysis. The photolytical half-life in aqueous systems decreased from 76 to 22 days from March to June.

Both metabolites B and B-1 degrade faster than the parent compound under the influence of light. The half-life of metabolite B in the direct photolysis was determined to be 10 days under continuous irradiation and even faster in natural water (6 days). Degradation of metabolite B-1 in natural water was even more rapid with a half-life of 1.2 days under continuous irradiation.

B.8.4.3 Biological degradation

B.8.4.3.1 Ready biodegradability of the active substance

From the summary of the results of the environmental behaviour of chloridazon it was assumed, that the compound does not fulfil the requirements for ready biodegradability. Therefore, the higher tiered water/sediment study described below was performed.

B.8.4.3.2 Water/sediment study

Reference number: II A 7.2.1.3.2/1

Report: Bieber W.-D., 1998; WAS 1999-7
Degradation of (^{14}C)chloridazon in two aerobic water/sediment systems
NATEC Institut für naturwissenschaftlich-technische Dienste, Hamburg, Germany, unpublished, BASF RegDoc# 1998/10916

Guidelines: BBA IV 5-1, EPA 162-4, SETAC Europe

GLP: Yes

Reference number: II A 7.2.1.3.2/2

Report: Dressel J., 2003
Compilation of parameters characterising the environmental fate of BAS 119 H (chloridazon) and its metabolites
BASF AG, Agrarzentrum Limburgerhof, Limburgerhof, Germany, unpublished, BASF RegDoc# 2003/1001026

GLP: No, not subject to GLP regulations

Test System
The distribution and degradation of chloridazon was studied in two natural systems of water and sediment. The water/sediment systems were taken from two streams (System A "Krempe" and System B "Ohlau") in the North-West and North of Hamburg, Germany.

The specific radioactivity of the [pyridazinone-4,5-^{14}C]-labelled active substance was 2.26 MBq/mg with a radiochemical purity of > 99 %.

Characteristics of the water/sediment systems are given in Table B.8.4-8. Chloridazon was applied to the water resulting in a concentration of 0.84 mg/L and 0.87 mg/L in system A and B, respectively. Assuming 100 % overspray of a 30 cm deep water body, the application rate is almost equivalent to the recommended field application rate of 2.5 kg/ha chloridazon.
Experiments under sterile conditions were also carried out in both water/sediment systems. Each incubation flask was equipped with a device for slow stirring the water only, a trap for volatile components and a septum allowing the introduction of air. The test vessels were incubated in the dark at a temperature of 20 ± 2 °C for up to 100 days. Aeration was achieved by a slow stirring of the water.
Water samples were directly analysed by radio-TLC. Sediment samples were extracted with methanol/water (1:1) and methanol, the extracts were combined and analysed by radio-TLC.

Table B.8.4-8: Characterisation of the water/sediment systems

Designation Origin		System A "Krempe" Hamburg, FRG	System B "Ohlau" Hamburg, FRG
Sediment	sand [%]	22.0	98.7
	silt [%]	50.4	< 0.5
	clay [%]	27.6	1.0
	textural class (German scheme)	silty loam	sand
	testural class (USDA)	clay loam	sand
	pH ($CaCl_2$)	6.7	6.7
	organic C [%]	3.6	0.19
	total N [%]	0.3	< 0.02
	total P [%]	0.19	0.02
	CEC [mVal/100 g]	19	3
	Dry matter [%]	39	83
	ATP [µg/kg]	1.44 (begin) 1.16 (end)	0.17 (begin) 0.08 (end)
	redox potential [mV]	-23 (begin) -45 (end)	-5 (begin) -17 (end)
Water	Temperature [°C]*	10	8
	pH	8.5 (begin) 7.9 (end)	8.0 (begin) 8.3 (end)
	redox potential [mV]	252 (begin) 279 (end)	245 (begin) 182 (end)
	O_2 content [mg/L]	7.3 (begin) 8.2 (end)	8.1 (begin) 8.3 (end)
	total N [mg/L]	8.1 (begin) 1.1 (end)	6.5 (begin) 1.3 (end)
	total P [mg/L]	0.05 (begin) 0.1 (end)	0.1 (begin) 0.1 (end)
	DOC [mg/L]	13	6
	hardness [mmol/L]	1.9	1.5

*Temperature of the water was determined at the sampling site

Findings

The distribution and recovery of radioactivity from water/sediment system A is shown in Table B.8.4-9, the corresponding results from system B are presented in Table B.8.4-10.

The radioactivity slowly moved from the water to the sediment. The radioactivity in the water decreased within 100 days to 40 % TAR in system A and to 50 % TAR in system B. In the sediment, the radioactivity correspondingly increased and accounted for about 49/31 % TAR (system A/B) at the end of the incubation period. Mineralisation was negligible in both systems (≤ 8 % TAR). The bound residues in the sediment increased with time and reached 21 % in both systems. The bound residues of the 100 DAT samples of system A and B were fractionated into humins, humic acids and fulvic acids. Roughly 9-10 % TAR was associated with the fulvic acid fraction. The remaining radioactivity (max. 7 % TAR) was located in the humic acids and humins. The fulvic acids fractions of samples were further partitioned with ethyl acetate. By radio-TLC analysis of these extracts containing 5 - 8 % TAR it was shown that most of the radioactivity consisted of parent chloridazon. Additionally, minor amounts of metabolite B were detected in the 100 DAT fulvic acid fraction of system B.

Table B.8.4-9: Distribution of radioactivity and material balance in the water/sediment system after application of [^{14}C]-chloridazon to water/sediment system A ("Krempe")

DAT	% TAR					
	Water	Sediment extractable residues	Sediment bound residues	Sediment total	CO_2	Material balance
0	94.7	0.7	0.2	0.9	-	95.6
0.25	90.1	5.4	0.7	6.1	-	96.1
1	81.7	11.2	1.9	13.1	-	94.8
2	78.5	13.4	3.2	16.6	0.1	95.2
7	67.9	22.4	4.1	26.5	0.2	94.6
14	61.2	26.1	7.0	33.1	0.3	94.6
30	51.1	30.6	10.7	41.2	1.2	93.5
60	41.2	34.5	15.8	50.3	2.3	93.8
100	39.8	27.4	21.4	48.8	3.4	92.0
100 (sterile)	48.2	28.7	14.3	43.0	< 0.1	91.2

Table B.8.4-10: Distribution of radioactivity and material balance in the water/sediment system after application of [^{14}C]-chloridazon to water/sediment system B ("Ohlau")

DAT	% TAR					
	Water	Sediment extractable residues	Sediment bound residues	Sediment total	CO_2	Material balance
0	90.7	2.9	1.1	4.0	-	94.7
0.25	87.6	5.7	0.8	6.5	-	94.1
1	81.0	10.3	2.6	12.9	-	93.9
2	79.7	9.0	3.9	12.9	0.1	92.7
7	75.5	13.6	4.2	17.8	0.2	93.6
14	73.4	12.9	6.8	19.7	0.4	93.4
30	66.2	17.1	7.8	24.9	1.6	92.7
60	62.4	16.4	10.3	26.7	2.7	91.8
100	49.9	10.1	20.7	30.7	8.1	88.7
100 (sterile)	64.2	13.9	13.1	27.0	< 0.1	91.3

Summaries of the radio-TLC results of the water and of the sediment extracts are shown in Table B.8.4-11 and Table B.8.4-12 for both systems, respectively.
Chloridazon steadily disappeared from the water phase, reaching about 37 % TAR in system A and nearly completely disappeared in system B after 100 days. The sudden drop of chloridazon from 39 % to 0.3 % TAR observed in the water phase of system B between day 60 and day 100 is however concurrent with an abrupt increase from 2.3 % to 43 % TAR of metabolite B. In the sediment, the amount of chloridazon increased to a maximum of about 34 % TAR at day 60 in system A and decreased to 27 % at the end of the study. In system B, chloridazon was detected in the sediment with max. 17 % TAR at day 30, but only 2 % TAR were present at the end of the study.

In both water/sediment systems, the same metabolites were detected (metabolite B and metabolite B-1).

Metabolite B was detected with less than 2 % TAR in the water and sediment of system A. In the system B, metabolite B occurred with ≤ 2 % in both water and sediment until 60 DAT, but significantly increased to 43 % TAR in the water and to 7 % in the sediment at 100 DAT. This may be interpreted as enhanced degradation of chloridazon in system B to the stable metabolite B after a very long lag phase.
Metabolite B-1 never reached more than 0.2 % TAR in the water or in the sediment of both systems at any sampling time.

Table B.8.4-11: Radio-TLC analysis of the water and the extracts of the sediment of system A ("Krempe") after application of [^{14}C]-chloridazon

DAT	% TAR				
	Chloridazon	Metabolite B	Metabolite B-1*	Others [a]	Sum
Water					
0	93.6	< 0.1	< 0.1 [a]	1.1	94.7
0.25	89.6	< 0.1	< 0.1 [a]	0.5	90.1
1	80.6	< 0.1	< 0.1 [a]	1.3	81.9
2	77.2	< 0.1	< 0.1 [a]	1.5	78.7
7	66.8	< 0.1	< 0.1 [a]	1.2	68.0
14	59.9	< 0.1	< 0.1 [a]	1.5	61.4
30	47.9	1.0	< 0.1 [a]	2.4	51.3
60	38.5	0.8	0.2 [a]	1.9	41.4
100	37.1	1.4	< 0.1 [a]	1.4	39.9
100 (sterile)	46.5	0.7	< 0.1*	1.0	48.2
Sediment					
0	0.6	< 0.1 [b]	-	-	0.6
0.25	5.3	< 0.1 [b]	-	-	5.3
1	10.8	< 0.1 [b]	-	-	10.8
2	13.2	< 0.1 [b]	-	-	13.2
7	22.3	< 0.1 [b]	-	-	22.3
14	25.9	< 0.1 [b]	-	-	25.9
30	29.7	0.6 [b]	-	-	30.3
60	34.0	0.3 [b]	-	-	34.3
100	27.1	0.3 [b]	-	-	27.4
100 (sterile)	28.2	0.5 [b]	-	-	28.7

[a] Total amount (water + sediment)
[b] Calculated for dossier (difference of total amount and amount in water phase)

Table B.8.4-12: Radio-TLC analysis of the water and the extracts of the sediment of system B ("Ohlau") after application of [^{14}C]-chloridazon

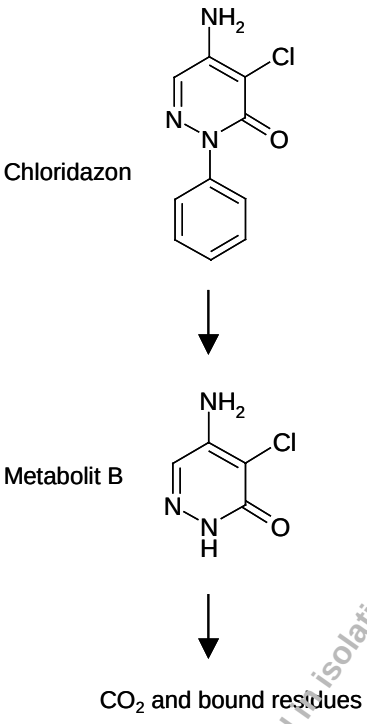
DAT	% TAR				
	Chloridazon	Metabolite B	Metabolite B-1[a]	Others[a]	Sum
Water					
0	89.3	< 0.1	< 0.1	1.5	90.8
0.25	87.0	< 0.1	< 0.1	0.8	87.8
1	80.0	< 0.1	< 0.1	1.2	81.2
2	78.5	< 0.1	< 0.1	1.2	79.7
7	74.2	< 0.1	< 0.1	1.4	75.6
14	72.0	< 0.1	< 0.1	1.5	73.5
30	64.6	0.5	< 0.1	1.4	66.5
60	59.1	2.3	< 0.1	1.1	62.5
100	0.3	42.6	< 0.1	7.5[c]	50.4
100 (sterile)	63.4	< 0.1	< 0.1	1.0	64.4
Sediment					
0	2.8	< 0.1[b]	-	-	2.8
0.25	5.5	< 0.1[b]	-	-	5.5
1	10.0	< 0.1[b]	-	-	10.0
2	8.9	< 0.1[b]	-	-	8.9
7	13.3	0.2[b]	-	-	13.5
14	12.6	0.1[b]	-	-	12.7
30	16.5	0.2[b]	-	-	16.7
60	15.8	0.5[b]	-	-	16.3
100	2.2	7.3[b]	-	-	9.5
100 (sterile)	13.8	< 0.1[b]	-	-	13.8

[a] Total amount (water + sediment)
[b] Calculated for dossier (difference of total amount and amount in water phase)
[c] Radioactive material remaining at TLC start region that can not be associated to any specific compound

In the sterilised vessels the distribution of radioactivity at the end of the study was comparable to the viable trials (100 DAT system A, 60 DAT system B). However, degradation of chloridazon to metabolite B did not occur under sterile conditions at 100 DAT in system B. The amount of bound residues were 14 % and 13 % TAR in system A and B, respectively, and thus only slightly lower than under biologically active conditions, i.e. 21 % TAR at study end. No mineralisation was observed.

The proposed route of degradation is given in Table B.8.4-1.

Figure B.8.4-1: Proposed route of degradation of chloridazon in water/sediment



Disappearance times were calculated for the active substance in the water phase and in the total system (water and sediment). The results are given in Table B.8.4-13.

Table B.8.4-13: DT_{50} and DT_{90} values in water/sediment systems under laboratory conditions

System	DT_{50} [days]		DT_{90} [days]	
	1. Order	Best fit	1. Order	Best fit
System A ("Krempe") [a]				
Chloridazon (water)	76 / 57.6[c]	35	> 200	> 200
Chloridazon (total)	182	> 200	> 200	> 200
System B ("Ohlau")				
Chloridazon (water)	- / 104.5[c]	66[b]	-	93[b]
Chloridazon (total)	-	74[b]	-	96[b]

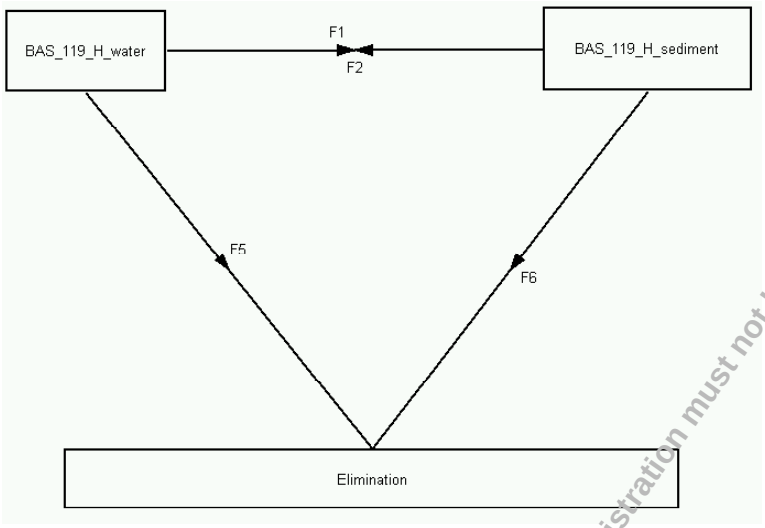
[a] values calculated according to Timme, Frehse, Laska; due to the abrupt drop of chloridazon between day 60 and day 100, a resp. calculation for system B was not possible.
[b] values obtained by interpolation from experimental data, see Table B.8.4-12.
[c] value calculated according to ModelMaker version 3.0.4 in Dressel (Reg.Doc. 2003/1001026)

Valid: yes

Amendment of the RMS

The data of the water–sediment study were used by the RMS to calculate the disappearance time for the active substance in the water phase related to biological degradation (more precisely: processes beside adsorption) using ModelMaker 4.0. These DT_{50} values are required for FOCUS surface calculations. The compartment model as used in the simulation is shown in Figure B.8.4-2.

Figure B.8.4-2: Compartment model as used in ModelMaker 4.0



Compartments:
BAS_119_H_sediment Unconditional; dBAS_119_H_sediment/dt = +F1-F6-F2. Initial Value = Start_Sediment
BAS_119_H_water Unconditional; dBAS_119_H_water/dt = -F1-F5+F2. Initial Value = Start_Wasser
Elimination Unconditional. dElimination/dt = +F5+F6. Initial Value = 0.0

Flow
flow: F1 Unconditional: Flow from BAS_421_F_water to BAS_421_F_sediment.
F1 = k_sorption × BAS_119_H_water
flow: F2 Unconditional: Flow from BAS_119_H_sediment to BAS_119_H_water.
F2 = k_desorption × BAS_119_H_sediment
flow: F5 Unconditional: Flow from BAS_421_F_water to Elimination. F5 = k_elim_water × BAS_119_H_water
flow: F6 Unconditional: Flow from BAS_421_F_sediment to Elimination.
F6 = k_elim_sediment × BAS_119_H_sediment

Summary of results

The results of the ModelMaker 4.0 calculation with Marquardt Optimisation (Weighted Least Squares) is summarised in the following table:

Table B.8.4-14: Results of the ModelMaker 4.0 calculation for determination of DT50 for degradation

Parameter	Name (ModelMaker 4.0)	Study A	Study B* (without t=100 d)	Unit
Sorption rate	k_sorption	0.042649	0.096944	1/d
Start concentration in sediment	Start_Sediment	4.2504	2.8997	%
Start concentration in water	Start_Wasser	88.337	88.059	%
Degradation rate in water	k_elim_water	0.0064086	0.0047595	1/d
Desorption rate	k_desorption	0.060578	0.45896	1/d
Adegradation rate in sediment	k_elim_sediment	0	0	1/d
Correlation coefficient	r^2	0.9900827	0.9972014	d
Half life in water (only degradation)		108.16	145.63	d
Half life in sediment (only degradation)		-	-	d

*Due to the low correlation coefficient r^2 if all data of study B were used, the calculation of the input parameter for the FOCUS modelling were performed without t = 100 d.

The input parameter for the FOCUS modelling are as follows:

Parameter	StudyA (d)	Study B (d)	Geometric mean (d)
Half life in water (only degradation)	108.2	145.6	125.5
Half life in sediment (only degradation)	-	-	-

Conclusions

The distribution and degradation of chloridazon was studied in two natural systems of water and sediment.

Primary degradation of chloridazon in the water phase is slow with first-order half-lives of 58 days (ModelMaker, version 3.0.4) and 76 days (according to Timme et al.) in one system and 105 days (ModelMaker version 3.0.4) in the second one investigated. Best fit half-lives of chloridazon for the water phase are 35 days (according to Timme et al.) for the first system resp. 66 days (interpolation from experimental data) for the second test system.

Metabolism of chloridazon is modest, only in one of the two water/sediment systems investigated an enhanced degradation of chloridazon after 60 days results in the formation of the main metabolite B in the water, accounting for 42.6 % TAR at the end of the test and which must therefore be considered as stable. No further individual metabolites were observed in significant amounts. Ultimate biodegradation was negligible with max. degrees of mineralisation up to 3 – 8 % TAR. Bound residues in the sediment reached 21 % TAR in both systems at study end.

After application of ^{14}C-chloridazon an overall comparison of the distribution of total radioactivity at study end after 100 days in both systems investigated with their corresponding systems sterilised before application of test substance results in values in a similar order of magnitude as to decline of in the water phase, both sediment extractable and bound residues and carbon dioxide evolution. Thus the fate of chloridazon in the aquatic ecosystem is obviously principally governed by abiotic distribution processes with biological processes playing only a minor role.

Taking all the data available into account – slow primary degradation in the water phase, negligible ultimate degradation, moderate transformation to bound residues together with a limited metabolism - it must be concluded that chloridazon is persistent to non-biodegradable in aquatic systems.

B.8.5 Impact on water treatment procedures (Annex IIIA 9.2.2)

B.8.5.1 Effects on biological methods for sewage treatment

Reference number: II A 8.7/1

Report: Bachner H., 2001; WAT 2001-542
Reg.Nr. 130 33 - Determination of the inhibition of oxygen consumption by activated sludge in the activated sludge respiration inhibition test
BASF AG, Ludwigshafen/Rhein, Germany, unpublished,
BASF RegDoc# 2001/1005967

Guidelines: EEC 88/302, OECD 209, ISO 8192-1986 (E) (Method B)

GLP: Yes

Material and methods:

Test substance: Chloridazon (BAS 119 H, Reg. No. 13 033), batch no. N198; purity: 93.5 %

Test species: Activated sludge from laboratory wastewater plants treating municipal sewage. Concentration of dry substance 1 g/L.

Test design: Assessment of the inhibitory effect of the test substance on the oxygen consumption rate of aerobic micro-organisms (activated sludge) after short-term exposure of 30 min; the inoculum was brought to a concentration of 5 g/L dry substance and aerated during the night. 50 mL were added to obtain a concentration of 1 g/L; 1 replicate each for test substance and reference substance and 3 replicates for non-treated control.

Test rates: Control, 250, 500, 1000 mg as/L

Reference substance: 3,5-dichlorophenol.

Test conditions: Temperature: 20 °C ± 2 °C; 250 mL Erlenmeyer test vessels, 8 mL/vessel 100-fold concentrated OECD medium; oxygen concentration during aeration > 2.5 mg/L.

Analytics: Not applicable.

Findings:
29 % inhibition of respiration was measured at the highest tested concentration of 1000 mg as/L (nominal). At a concentration of 500 mg as/L the inhibition was smaller than 20 % (precisely 19 %), the derived NOEC is therefore calculated to be 500 mg as/L.
The EC_{50} of the reference substance was about 9 mg as/L.

Valid yes

Conclusions:
The NOEC is calculated to be 500 mg as/L.

B.8.6 Predicted environmental concentrations in surface water and in ground water (PEC_{SW}, PEC_{GW}) (Annex IIIA 9.2.1, 9.2.3)

B.8.6.1 PEC in surface water and sediment

Predicted environmental concentrations of chloridazon in surface water (PEC_{sw}) and sediment (PEC_{sed}) resulting from pre-emergence spray application on sugar beet fields were calculated by the RMS using the STEP 1 - 3 approach of the European surface water assessment of Plant Protection Products (FOCUS, 2001). Simulations were run using the tool FOCUS SWASH 1.1 and European surface water scenarios as proposed by FOCUS (2001). In these scenarios, different entry routes of the substance into surface water like spray drift, run-off and drainage are considered.

B.8.6.1.1 Input parameters

B.8.6.1.1.1 Agricultural use pattern

Chloridazon is used in sugar beets (1 application per year, application rate: 2600 g/ha). No interception by the crop canopy can be assumed because the product can optionally be used pre-emergence. Thus, 2600 g/ha reach the soil surface.

Table B.8.6-1: Application pattern of chloridazon used for the simulations

Crop	FOCUS Scenario	FOCUS Site	Application window *	Application date (year)	Crop emergence
Sugar beets pre-emergence	D3	Vredepeel, Netherlands	11. April – 11. May	10. April	25. April
	D4	Skousbo, Denmark	20. April – 20. May	20. April	4. May
	R1**	Weiherbach, Germany	2. April – 2. May	26. April	16. April
	R3**	Bologna, Italy	6. March – 6. April	10. March	20. March

* set by FOCUS SWASH shell
** application model: soil linear, incorporation depth 4 cm

B.8.6.1.1.2 Substance properties of chloridazon and its metabolites

Two water-sediment studies were performed with chloridazon. The studies were analysed using the program ModelMaker (see water/sediment study). No degradation was found for chloridazon in the sediment phase. The degradation rate was set to 1000 days (maximum number that can be considered according to FOCUS SWASH). The results are summarised in Table B.8.6-3. For the simulations the geometric mean values was considered.

Table B.8.6-2: DT_{50}-values of chloridazon in water and sediment

Parameter	Study A (d)	Study B (d)	geom. mean (d)
chloridazon water	108.2	145.6	**125.5**
chloridazon sediment	-*	-*	
chloridazon total	**182**	-	

(*: set to 1000 d for the simulations)

The results for the 2 metabolites B and B-1 that were analysed in the water-sediment-study were as follows:
Formation and degradation of the metabolites in the water sediment systems could not be evaluated in a kinetic model. Thus, the initial PEC_{SW} was calculated based on the maximum percentage observed. No further degradation in the water-sediment system was considered (worst case assumption). As the maximum occurrence of metabolite B-1 was only 0.2 % (total amount in water and sediment) it was not considered for the surface water simulations.

DT_{50} values in soil after standardisation to reference conditions as proposed in FOCUS were found for chloridazon between 8.6 days and 173.9 days (see Table B.8.6-3). For the simulations the geometric mean was used (43.2 d).

Table B.8.6-3: Standardised DT_{50}-values (pF2, 20 °C) of chloridazon

Soil	Chloridazon DT_{50} standardised
Sandy clay loam	173.9
Sandy loam	157.6
Ruchheim, loam	9.0
Limburgerhof, loamy sand	8.6
Limburgerhof, clay	40.6
LUFA 2.2 Speyer, loamy sand	75.1
geometric mean	**43.2**

DT_{50} values in soil after standardisation to reference conditions as proposed in FOCUS were found for metabolite B between 92.9 days and 128.7 days (Table B.8.6-4). For the simulations the geometric mean of these soils was used (108.0 d).

Table B.8.6-4: Standardised DT_{50}-values (pF2, 20 °C) of metabolite B

Soil	Metabolite B DT_{50} [d] standardised
Bruch West	92.9
Li 35 b	97.3
LUFA 2.3	116.9
LUFA 2.2	128.7
Geometric mean	**108.0**

Chloridazon is a compound moderately sorbed to soil. The results of five studies could be considered (Table B.8.6-5). The arithmetic mean K_{OC} (201 L/kg) and Freundlich exponent (0.845) were selected according to the FOCUS-recommendations.

Table B.8.6-5 : Adsorption of chloridazon in different soils

Soil designation	Textural class	Adsorption constant Kf [mL/g]	Adsorption exponent 1/n	Adsorption constant Kf,oc [mL/g]
Soil I	sand	0.25	1.0301	220
Soil II	sand-loam	0.2	0.5681	89
Soil III	silt-loam	1.0	0.8355	220
Soil IV	clay	3.6	0.8774	340
Soil V	sand-loam	0.69	0.9143	128
Arithmetic mean			**0.845**	**199**

Metabolite B is a compound moderately to weakly sorbed to soil. The results of four studies could be considered (Table B.8.6-6). The arithmetic mean K_{OC} (50 L/kg) and Freundlich exponent (0.834) were selected according to the FOCUS-recommendations.

Table B.8.6-6: Adsorption of metabolite B in different soils

Soil designation	Adsorption constant Kf [mL/g]	Adsorption exponent 1/n	Adsorption constant Kf,oc [mL/g]
Standard soil 2.1	0.3400	0.8043	49*
Standard soil 2.2	0.7055	0.8679	29*
Standard soil 2.3	0.4224	0.8191	46*
Pfungstadt soil	0.4277	0.8435	74*
Arithmetic mean		**0.834**	**50**

* recalculated from data in the report

The remaining input parameters used for the simulations are summarised in Table B.8.6-7 for chloridazon and Table B.8.6-8 for metabolite B.

Table B.8.6-7: Other input parameters used for the simulations of chloridazon

Parameter	Value	Unit	Origin of data
molar mass	221.65	g/mol	Monograph, 1.7 PEC in groundwater
vapour pressure (20 °C)	10^{-9}	Pa	Monograph, 1.7 PEC in groundwater
molar enthalpy of vaporisation	95000	J/mol	FOCUSsw report chapter 7.3.4
solubility in water (20 ° C; pH 4.4)	422	mg/L	Monograph, 1.7 PEC in groundwater
molar enthalpy of dissolution	2700	J/mol	FOCUSsw report chapter 7.3.7
diffusion coefficient in water	$4.3\ 10^{-5}$	m^2/d	FOCUSsw report chapter 7.3.5
diffusion coefficient in air	0.43	m^2/d	FOCUSsw report chapter 7.3.6

Table B.8.6-8: Other input parameters used for the simulations of metabolite B

Parameter	Value	Unit	Origin of data
molar mass	145.55	g/mol	Monograph, 1.7 PEC in groundwater
maximum occurrence in soil	0,648	%	Monograph, 1.7 PEC in groundwater
maximum occruence in water	0,426	%	Monograph, 1.4.3.2 PEC in water/sediment
vapour pressure (20 °C)	10^{-9}*	Pa	Monograph, 1.7 PEC in groundwater
molar enthalpy of vaporisation	95000	J/mol	FOCUSsw report chapter 7.3.4
solubility in water (20 ° C; pH 4.4)	422*	mg/L	Monograph, 1.7 PEC in groundwater
molar enthalpy of dissolution	2700	J/mol	FOCUSsw report chapter 7.3.7
diffusion coefficient in water	$4.3\ 10^{-5}$	m^2/d	FOCUSsw report chapter 7.3.5
diffusion coefficient in air	0.43	m^2/d	FOCUSsw report chapter 7.3.6

(*: not measured, value of parent substance used)

B.8.6.1.2 Results of the simulations on STEP 1

The distance between treated area and water body is automatically defined by the modelling programme. In STEP 1 the distance of the edge nearest field is 1 m.

Table B.8.6-9: Results for chloridazon on STEP 1 (sugar beet, 2600 g/ha)

	PECsw (µg/L)		PECsed (µg/kg dry sediment)	
Time (d)	Actual	TWA	Actual	TWA
0	708.8428		1.36E+03	
1	701.1533	704.9981	1.4E+03	1.38E+03
2	698.4881	702.4090	1.39E+03	1.39E+03
4	693.1879	699.1218	1.38E+03	1.39E+03
7	685.3129	694.8880	1.36E+03	1.38E+03
14	667.2842	685.5733	1.33E+03	1.36E+03
21	649.7298	676.5382	1.29E+03	1.35E+03
28	632.6372	667.6900	1.26E+03	1.33E+03
42	599.7891	650.4824	1.19E+03	1.29E+03
50	581.7903	640.9243	1.16E+03	1.27E+03
100	480.9123	585.3379	957.0155	1.16E+03

Table B.8.6-10: Results for metabolite B on STEP 1

	PECsw (µg/L)		PECsed (µg/kg dry sediment)	
Time (d)	Actual	TWA	Actual	TWA
0	353.4601		173.3757	
1	352.7962	353.1281	176.3981	174.8869
2	352.5517	352.9010	176.2759	175.6119
4	352.0633	352.6043	176.0317	175.8828
7	351.3320	352.2157	175.6660	175.8682
14	349.6314	351.3483	174.8157	175.5544
21	347.9391	350.4938	173.9696	175.1670
28	346.2550	349.6444	173.1275	174.7623
42	342.9112	347.9564	171.4556	173.9383
50	341.0149	346.9973	170.5075	173.4651
100	329.3987	341.0853	164.6994	170.5259

B.8.6.1.3 Results of the simulations on STEP 2

The distance between treated area and water body is automatically defined by the modelling programme. In STEP 2 the distance of the edge nearest field is 1 m.

Table B.8.6-11: Maximum concentrations in water and sediment for chloridazon (STEP 2)

	North Europe	South Europe
water (µg/L)	276.86	148.39
sediment (µg/kg)	547.82	292.34

Table B.8.6-12: Detailed results for chloridazon on STEP 2 (in South Europe)

Time after max. peak (d)	PECsw (µg/L)		PECsed (µg/kg dry sediment)	
	Actual	TWA	Actual	TWA
0	276.8561	---	547.8225	---
1	273.9613	275.4087	545.3583	546.5904
2	272.7289	274.3769	542.9051	545.3610
4	270.2809	272.9402	538.0319	542.9134
7	266.6499	271.0209	530.8040	539.2694
14	258.3663	266.7538	514.3143	530.8930
21	250.3400	262.6134	498.3368	522.6902
28	242.5630	258.5679	482.8557	514.6567
42	227.7264	250.7343	453.3213	499.0824
50	219.6594	246.4038	437.2628	490.4684
100	175.3285	221.5330	349.0159	440.9760

Table B.8.6-13: Detailed results for chloridazon on STEP 2 (in North Europe)

Time after max. peak (d)	PECsw (µg/L)		PECsed (µg/kg dry sediment)	
	Actual	TWA	Actual	TWA
0	148.3855	---	292.3430	---
1	146.1982	147.2918	291.0280	291.6855
2	145.5406	146.5806	289.7189	291.0295
4	144.2342	145.7336	287.1183	289.7233
7	142.2965	144.6750	283.2612	287.7787
14	137.8760	142.3749	274.4615	283.3087
21	133.5928	140.1577	265.9352	278.9312
28	129.4427	137.9951	257.6737	274.6442
42	121.5252	133.8109	241.9128	266.3331
50	117.2202	131.4987	233.3433	261.7362
100	93.5632	118.2233	186.2507	235.3249

Table B.8.6-14: Maximum concentrations in water and sediment for metabolite B (STEP 2)

	North Europe	South Europe
water (µg/L)	73.9979	141.5905
sediment (µg/kg)	36.9067	70.6795

Table B.8.6-15: Detailed results for metabolite B on STEP 2 (in South Europe)

Time after max. peak (d)	PECsw (µg/L)		PECsed (µg/kg dry sediment)	
	Actual	TWA	Actual	TWA
0	141.5905	---	70.6795	---
1	141.3591	141.4748	70.6306	70.6550
2	141.2611	141.3924	70.5816	70.6306
4	141.0654	141.2779	70.4838	70.5816
7	140.7724	141.1240	70.3374	70.5083
14	140.0910	140.7777	69.9970	70.3377
21	139.4129	140.4357	69.6582	70.1676
28	138.7381	140.0956	69.3210	69.9981
42	137.3983	139.4195	68.6516	69.6606
50	136.6385	139.0352	68.2719	69.4688
100	131.9841	136.6666	65.9463	68.2856

Table B.8.6-16: Detailed results for metabolite B on STEP 2 (in North Europe)

Time after max. peak (d)	PECsw (µg/L)		PECsed (µg/kg dry sediment)	
	Actual	TWA	Actual	TWA
0	73.9979	---	36.9067	---
1	73.8133	73.9056	36.8811	36.8939
2	73.7622	73.8467	36.8555	36.8811
4	73.6600	73.7789	36.8045	36.8555
7	73.5070	73.6951	36.7280	36.8173
14	73.1512	73.5120	36.5502	36.7282
21	72.7971	73.3327	36.3733	36.6394
28	72.4448	73.1547	36.1973	36.5508
42	71.7451	72.8013	35.8477	36.3746
50	71.3484	72.6005	35.6495	36.2744
100	68.9180	71.3634	34.4351	35.6566

B.8.6.1.4 Results of the simulations on STEP 3

Maximum PEC_{sw} and PEC_{sed} values were extracted from the output of the STEP 3 calculations representing realistic worst case peak exposures of water bodies like ponds, streams and ditches for the investigated uses of chloridazon.
Crop specific distances between treated area and water bodies are automatically defined by the modelling programme SWASH. Regarding sugar beets the distances between the edge nearest field and farest from field are 1.3 m and 2 m for ditch, 1.8 m and 2.8 m for stream and 3.8 m and 33 m for pond scenarios.

Chloridazon
For the use of chloridazon in sugar beets these maximum PEC_{sw} and PEC_{sed} values calculated with the standard STEP 3 approach are given in Table B.8.6-17 and Table B.8.6-18. The worst case global maximum concentrations for chloridazon in the water phase are 13.62 µg/L (scenario D3, ditch) and 130.87 µg/L (scenario R3, stream), respectively. The worst case global maximum concentrations for chloridazon in sediment are 10.73 µg/kg (scenario D4, pond) and 27.61 µg/kg (scenario R3, stream), respectively.

Initial, short term and long-term PEC values (time weighted average) in surface water and sediment obtained at certain days after the peak concentrations were calculated for all scenarios. The PEC values of the two scenarios with the highest concentrations in stream and ditch or pond are compiled in Table B.8.6-19.

Table B.8.6-17: Maximum PEC_{sw} of chloridazon in different water bodies after pre-emergence use in sugar beets

FOCUS scenario*	FOCUS Site	Water body type	Global max. PEC_{sw} [µg/L]	Global max. incl. susp. solids [µg/L]	Date
D3	Vredepeel, Netherlands	ditch	13.62	13.63	10-Apr-1992
D4	Skousbo, Denmark	pond	2.082	2.083	27-Dec-1985
D4	Skousbo, Denmark	stream	11.46	11.47	20-Apr-1985
R1	Weiherbach, Germany	pond	1.332	1.333	30-May-1984
R1	Weiherbach, Germany	stream	19.26	19.26	20-May-1984
R3	Bologna, Italy	stream	130.9	130.9	15-Mar-1980

* D scenarios: main routes of entry are spray drift and drainage
R scenarios: main routes of entry are spray drift and run-off

Table B.8.6-18: Maximum PEC_{sed} of chloridazon in sediments of different water bodies after pre-emergence use in sugar beets

FOCUS scenario	FOCUS Site	Water body type	Global max. PEC_{sed} [µg/kg]	Date
D3	Vredepeel, Netherlands	ditch	4.340	11-Apr-1992
D4	Skousbo, Denmark	pond	10.73	17-Apr-1986
D4	Skousbo, Denmark	stream	4.069	21-Dec-1985
R1	Weiherbach, Germany	pond	4.469	31-Jul-1984
R1	Weiherbach, Germany	stream	5.523	20-May-1984
R3	Bologna, Italy	stream	27.61	16-Mar-1980

Table B.8.6-19: Actual and time weighted average PEC_{sw} and PEC_{sed} of chloridazon on certain days after peak concentration after pre-emergence use in sugar beets in Europe (maximal values)

Scenario / Site	PEC of chloridazon at certain days after maximum concentration									
	1 d	2 d	4 d	7 d	14 d	21 d	28 d	42 d	50 d	100 d
Surface water (PEC_{sw}) [µg as/L]										
D3 ditch										
PEC actual	6.132	0.782	0.040	0.004	0.002	0.001	0.001	0.001	0.001	0.000
PEC twa	10.45	6.663	3.438	1.974	0.990	0.661	0.496	0.331	0.278	0.139
R3 stream										
PEC actual	94.37	0.318	0.055	43.42	0.013	0.007	0.004	0.004	0.002	0.001
PEC twa	51.49	42.71	21.44	12.80	8.214	5.483	4.114	2.806	2.358	1.182
Sediment (PEC_{sw}) [µg as/kg]										
D4 pond										
PEC actual	10.73	10.73	10.73	10.72	*	*	*	*	*	*
PEC twa	10.73	10.73	10.73	10.73	10.73	10.72	10.72	10.70	10.69	10.39
R3 stream										
PEC actual	3.339	2.514	1.841	1.437	1.061	0.891	0.785	0.654	0.604	0.433
PEC twa	4.150	3.756	3.081	2.504	1.885	1.587	1.402	1.176	1.089	0.798

* simulated period too short for calculation of PEC_{twa}

Metabolite B

For the use of chloridazon in sugar beets maximum PEC_{sw} and PEC_{sed} values for the metabolite B calculated with the standard STEP 3 approach are given in Table B.8.6-20 and Table B.8.6-21. The worst case global maximum concentrations for metabolite B in the water phase are 28.57 µg/L (scenario D4, pond) and 2.28 µg/L (scenario R3, stream), respectively. The worst case global maximum concentrations for metabolite B in sediment are 81.58 µg/kg (scenario D4, pond) and 0.35 µg/kg (scenario R3, stream), respectively.

Initial, short term and long-term PEC values (time weighted average) in surface water and sediment obtained at certain days after the peak concentrations were calculated for all scenarios. The PEC values of the two scenarios with the highest concentrations in stream and ditch or pond are compiled in Table B.8.6-22.

Table B.8.6-20: Maximum PEC_{sw} of metabolite B in different water bodies after pre-emergence use in sugar beets

FOCUS scenario*	FOCUS Site	Water body type	Global max. PEC_{sw} [µg/L]	Global max. incl. susp. solids [µg/L]	Date
D3	Vredepeel, Netherlands	ditch	7.426	7.427	10-Apr-1992
D4	Skousbo, Denmark	pond	28.57	28.50	27-Dec-1985
D4	Skousbo, Denmark	stream	14.99	14.99	20-Apr-1985
R1	Weiherbach, Germany	pond	0.043	0.043	30-May-1984
R1	Weiherbach, Germany	stream	0.858	0.858	20-May-1984
R3	Bologna, Italy	stream	2.281	2.282	15-Mar-1980

* D scenarios: main routes of entry are spray drift and drainage
R scenarios: main routes of entry are spray drift and run-off

Table B.8.6-21: Maximum PEC_{sed} of metabolite B in different water bodies after pre-emergence use in sugar beets

FOCUS scenario	FOCUS Site	Water body type	Global max. PEC_{sed} [µg/kg]	Date
D3	Vredepeel, Netherlands	ditch	31.32	11-Apr-1992
D4	Skousbo, Denmark	pond	81.58	17-Apr-1986
D4	Skousbo, Denmark	stream	32.21	21-Dec-1985
R1	Weiherbach, Germany	pond	0.119	31-Jul-1984
R1	Weiherbach, Germany	stream	0.179	20-May-1984
R3	Bologna, Italy	stream	0.350	16-Mar-1980

Table B.8.6-22: Actual and time weighted average PEC_{sw} and PEC_{sed} of metabolite B on certain days after peak concentration after pre-emergence use in sugar beets in Europe (maximal values)

Scenario / Site	PEC of metabolite B at certain days after maximum concentration									
	1 d	2 d	4 d	7 d	14 d	21 d	28 d	42 d	50 d	100 d
Surface water (PEC_{sw}) [µg /L]										
D4 pond										
PEC actual	28.56	28.54	28.46	28.28	27.71	27.08	26.43	25.15	24.45	-
PEC twa	28.57	28.57	28.56	28.53	28.43	28.26	28.06	27.60	27.34	26.39
R3 stream										
PEC actual	1.633	0.004	0.001	1.280	0	0	0	0	0	0
PEC twa	0.899	0.743	0.373	0.213	0.159	0.106	0.08	0.059	0.049	0.025
Sediment (PEC_{sw}) [µg /kg]										
D4 pond										
PEC actual	81.58	81.57	81.57	81.56	81.56	-	-	-	-	-
PEC twa	81.58	81.57	81.57	81.57	81.57	81.54	81.50	81.31	81.15	78.40
R3 stream										
PEC actual	0.206	0.162	0.126	0.229	0.123	0.099	0.086	0.089	0.078	0.053
PEC twa	0.298	0.273	0.223	0.188	0.182	0.159	0.143	0.127	0.120	0.092

- no data

Conclusion

Predicted environmental concentrations of chloridazon in surface water (PEC_{sw}) and sediment (PEC_{sed}) resulting from pre-emergence spray application of chloridazon (1 x 2.6 kg as/ha) on sugar beet fields were calculated by the RMS using the STEP 1 - 3 approach of the European surface water assessment of Plant Protection Products (FOCUS, 2001). Simulations were run using the tool FOCUS SWASH 1.1 and European surface water scenarios as proposed by FOCUS (2001). In these 6 scenarios, different entry routes of the substance into surface water like spray drift, run-off and drainage are considered.

At STEP 3, the initial PEC of chloridazon in surface water (i.e. global maximum concentration) ranged from 1.332 to 130.9 µg/L. The initial PEC of chloridazon in sediment ranged from 4.340 to 27.61 µg/kg dry sediment. The actual and time weighted average exposure concentrations for all use scenarios were also calculated.

The worst case global maximum concentrations for chloridazon in the water phase are 130.87 µg/L (scenario R3, stream) and 13.62 µg/L (scenario D3, ditch), respectively. The worst case global maximum concentrations for chloridazon in sediment are 27.61 µg/kg (scenario R3, stream) and 10.73 µg/kg (scenario D4, pond), respectively.

The worst case global maximum concentrations for metabolite B in the water phase are 28.57 µg/L (scenario D4, pond) and 2.28 µg/L (scenario R3, stream), respectively. The worst case global maximum concentrations for metabolite B in sediment are 81.58 µg/kg (scenario D4, pond) and 0.35 µg/kg (scenario R3, stream), respectively.

B.8.6.2 PEC in groundwater

Introduction

Environmental concentrations of chloridazon and its metabolites B and B-1 in groundwater (PEC_{gw}) after application on sugar beets were calculated using the different FOCUS scenarios.

Calculations of PEC_{gw}-values were performed according to recommendations of the FOCUS Groundwater Scenarios Workgroup ($FOCUS_{gw}$) for the selection of scenarios and for the selection of pesticide parameters.
PEC_{gw} calculations for chloridazon and its metabolites were provided by the notifier (IIIA 9.2.1/2; Dressel J. 2003a) using FOCUS Pearl version 1.1.1 based on field half-lives from three field studies representing 3 agroclimatic regions of Europe (far north = Scandinavia: 78.5 d, north = northern central Europe: 53 d, south = southern Europe 30.1 d, taken from Table B.8.1-33).
The metabolism scheme and the information on the metabolism of metabolite B and reliable transformation rates were obtained from the laboratory soil metabolism studies. Therefore, a PEC_{gw} calculation based on the standardised DT_{50} values from the laboratory studies is preferred and was performed by the RMS using the validated FOCUS-PELMO 3.3.2. The PEC_{gw} calculated by the notifier are additionally presented at the end of the chapter for comparison.

Material and methods

Rate, number of applications and factors contributing to soil residues
Chloridazon is assumed to be sprayed at a rate of 2600 g/ha once per year or every third year pre- or post-emergence. According to good agricultural practice beta beets would typically not occur more frequent than every third year in a crop rotation in most parts of Europe due to otherwise accumulating soil-borne phytopathogenic potential. No interception by the crop canopy can be assumed because the product can optionally be used pre-emergence. Thus, 2600 g/ha reach the soil surface. The crop applications were simulated 7 d before emergence of the crop in each scenario. The resulting actual application dates are summarised in Table B.8.6-23.

Table B.8.6-23: Crop- or scenario- related data

Input parameter	Unit	Scenario	
Crop		Maize	
Application dates	-	Châteaudun:	April, 9th
		Hamburg:	April, 8th
		Jokioinen	May, 18th
		Kremsmünster:	April, 8th
		Okehampton:	April, 18th
		Piacenza:	March, 13th
		Porto:	March, 8th
		Sevilla:	November, 11th
		Thiva:	April, 23th
Application rate	g/ha	2600	
Crop interception	%	0	
Amount reaching soil	g/ha	2600	
Assignment of FOCUS scenario to agroclimatic region (see text)	-	Châteaudun:	north
		Hamburg:	north
		Jokioinen	far north
		Kremsmünster:	north
		Okehampton:	north
		Piacenza:	south
		Porto:	south
		Sevilla:	south
		Thiva:	south

Table B.8.6-24: Characteristics of the nine weather- and soil scenarios created by FOCUS

Location	Abbreviation	Soil type	OM [%]	Annual average Air temperature [°C]	Precipitation [mm]
Châteaudun	C	silty clay loam	2.4	11.3	643 + I*
Hamburg	H	sandy loam	2.6	9.0	786
Jokioinen	J	loamy sand	7.0	4.1	638
Kremsmünster	K	loam/silt loam	3.6	8.6	900
Okehampton	N	Loam	3.8	10.2	1038
Piacenza	P	Loam	1.7	13.2	857 + I*
Porto	O	Loam	6.6	14.8	1150
Sevilla	S	silt loam	1.6	17.9	493 + I*
Thiva	T	Loam	1.3	16.2	500 + I*

*irrigation

Calculation procedure of PEC_{gw}

The PEC_{gw}-values were calculated with the model FOCUS-PELMO 3.3.2 to cover the relevant use areas in the EU of chloridazon in beta beets. The input parameters are summarised in Table B.8.6-25.

The PEC_{gw}, the 80th percentile of the average flux concentration leaching below one meter soil depth in the 20 considered application intervals (= cropping periods) was calculated for each scenario.

Metabolism scheme:

The degradation of chloridazon leads to the formation of metabolite B which is further transformed to metabolite B-1 by a reversible methylation. The only degradation pathway for metabolite B-1 is via metabolite B, whereas metabolite B degrades to bound residues and CO_2. For the FOCUS-PELMO calculation the reversible methylation of metabolite B-1 to metabolite B was not taken into account, such as in the recalculations of the DT_{50} values by Dressel (2003) (BASF RegDoc# 2003/1001026) used for the presented PEC_{gw} assessment.

The transformation scheme and the respective formation half-lives are shown in Table B.8.6-23. The percent values for the formation of the metabolite B from the active substance were taken from the laboratory studies of Wood (1989, 1991) (DOC#1989/5165; 191/11618) and for metabolite B-1 and metabolite B were taken from the study of Bayer (2003 c,e) (DOC#202/1004262; Doc#2003/1005450).

Figure B.8.6-1: Metabolism scheme as used in the simulation model FOCUS-Pelmo.

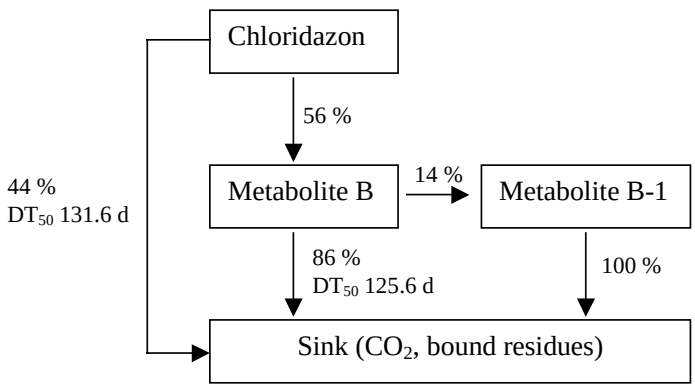


Table B.8.6-25: Summary of FOCUS-PELMO 3.3.2 input parameters for chloridazon and its metabolites B and B-1

Input parameter	Unit	Chloridazon	Metabolite B	Metabolite B-1
PHYSICO-CHEMICAL PARAMETERS				
Molecular weight	g/mol	221.65	145.55	159.6
Saturated vapour pressure (20 °C)	Pa	1e-9	(1e-9)*	(1e-9)*
Molar enthalpy of vaporisation	kJ/mol	(95)**	(95)**	(95)**
Water solubility (20 °C)	mg/L	422	(422)*	(422)*
Molar enthalpy of dissolution	kJ/mol	(27)**	(27)**	(27)**
Formation half-lives in soil	d	- - -	103.4	771.4
Laboratory half-lives DT_{50} soil standardised (20 °C, pF2)	d	57.3 [1]	108 [2]	144.6 [3]
Molar activation energy (Arrhenius)	kJ/mol	0	54	54
exponent of moisture correction function	-	0	0.7	0.7
$K_{f,oc}$-value	L/kg	199 [4]	50 [5]	27 [7]
$K_{f,om}$-value	L/kg	122	29	19.1
Freundlich exponent 1/n	-	0.845 [4]	0.83 [5]	0.9 [6]
Soil adsorption option	-	K_{om}, pH independent		
CROP RELATED PARAMETERS				
Application rate	g as/ha	2600		
treatment pre emergence	d	7		
Interception		no		
TSCF (crop uptake)	-	(0.5)**	(0.5)**	(0.5)**

()* no measured value available, therefore value of parent substance used. No effect on simulation results to be expected.
()** no measured value available, therefore the default value of the model Pearl was used.
1 arithmetic mean from 6 standardised values: 8.6; 9; 40.6; 75.1; 157.1; 173.9 days (IIA7.1.1.2.1/2, DOC#2003/1001026; IIA 7.1.1.2.1/4, DOC#2000/1017056)
2 geometric mean from 4 standardised values: 92.9; 97.3; 116.9; 128.7 days (IIA7.1.1.2.1/2, DOC#2003/1001026; IIA 7.1.1.2.1/4, DOC#2000/1017056)
3 geometric mean from 4 standardised values: 139.5; 131; 135.4; 176.8 days (IIA7.1.1.2.1/2, DOC#2003/1001026; IIA 7.1.1.2.1/4, DOC#2000/1017056)
4 arithmetic mean from Table B.8.3-4
5 arithmetic mean from Table B.8.3-5
6 default value
7 lowest value from Seher 1999 (IIA7.1.2/4, DOC#1999/11086)

Results

The resulting PEC_{gw} for chloridazon and its metabolites B and B-1 and each scenario are listed in Table B.8.6-26 for the annual application and in Table B.8.6-27 for the application every third year of chloridazon. In accordance with the FOCUS groundwater report, the 80th percentile annual leachate concentrations at 1 m depth out of a 20 year simulation period were reported as the relevant values.

Table B.8.6-26: PEC_{gw} of chloridazon and its metabolites after annual application

Annual application	Chloridazon	Metabolite B	Metabolite B-1
	[µg/L]		
Châteaudun	0.007	45.223	16.168
Hamburg	0.008	57.025	19.867
Jokioinen	< 0.001	34.288	21.603
Kremsmünster	0.002	41.729	17.245
Okehampton	0.005	44.934	15.158
Piacenza	**0.728**	49.045	11.235
Porto	< 0.001	3.751	7.785
Sevilla	< 0.001	2.497	8.476
Thiva	< 0.001	20.710	14.489

Table B.8.6-27: PEC_{gw} of chloridazon and its metabolites after application every third year (realistic scenario according to good agricultuaral practice)

Annual application	Chloridazon	Metabolite B	Metabolite B-1
	[µg/L]		
Châteaudun	0.001	13.576	5.274
Hamburg	0.001	15.975	6.453
Jokioinen	< 0.001	7.281	6.762
Kremsmünster	< 0.001	10.546	5.783
Okehampton	< 0.001	12.963	4.776
Piacenza	**0.144**	15.456	3.463
Porto	< 0.001	0.599	2.357
Sevilla	< 0.001	0.338	2.435
Thiva	< 0.001	4.332	4.421

The PEC_{gw} values of the parent active substance chloridazon were below the maximum permissible concentration of 0.1 µg/L according to Annex VI of Directive 91/414/EEC at 8 out of 9 FOCUS locations. At the location Piacenza there is leaching of unacceptable amounts of chloridazon after application to sugar beets according to good laboratory practice.

Conclusion

PEC_{gw} values of the parent active substance chloridazon did not exceed the maximum permissible concentration of 0.1 µg/L in the FOCUS scenarios except for the location Piacenza, where the simulations indicate unacceptable leaching of chloridazon to groundwater.

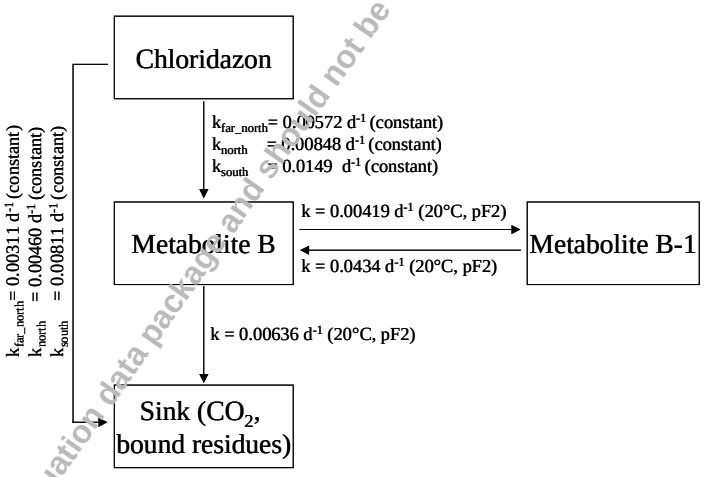
The PEC_{gw} of the metabolites B and B-1 exceeded 0.1 µg/L in all scenarios. These concentrations are expected to be of no ecological concern, since the compounds are of no ecotoxicological relevance: Metabolite B and metabolite B-1 revealed no herbicidal activity higher than the parent compound in the bioassays with algae and with terrestrial plants (seedlings emergence test). No adverse acute effects on fish and daphnia could be observed after exposure to the metabolites. Therefore, the metabolites are considered to be of no ecotoxicological relevance.

Comment of the RMS:
The notifier provided PEC_{gw} calculations using different field DT_{50} values of chloridazon for the different european regions (30.1; 53 and 78.5 see introduction). Furthermore, the notifier calculated the PEC_{gw} based on maize scenarios (see table "Crop or scenario related data"). Therefore, the above presented PEC_{gw} were calculated by the RMS.

Differences in input parameters used by the notifier and the RMS:
- The arithmetic mean of the DT_{50} value of 57.3 taken from 6 laboratory studies and used by the RMS is in good agreement with the field DT_{50} selected by the notifier as representative for the north scenario.
- DT_{50} value of 16 for metabolite B-1 was used by the notifer. The RMS preferred the geometric mean of 4 laboratory studies.
- DT_{50} of metabolite B: RMS used the geometric mean of 4 values, the notifier used the arithmetic mean.
- Percent formation of the metabolites was taken from the laboratory studies Wood (1989, 1991) (DOC#1989/5165; 191/11618) and Bayer (2003 c,e) (DOC#202/1004262; Doc#2003/1005450)

The metabolism scheme, the input parameters and the results as provided by the notifier are shown in the following:

Figure B.8.6-2: Metabolism scheme as used in the simulation model Pearl by the notifier



The arithmetic mean $K_{f,oc}$ / $K_{f,om}$ and *1/n* values obtained from 5 soils (chloridazon), 4 soils (metabolite B) and 3 soils (metabolite B-1) are given in Table B.8.6-28.

Calculation procedure of PEC_{gw}
The PEC_{gw}-values were calculated with the model FOCUS Pearl, version 1.1.1 to cover the relevant use areas in the EU of chloridazon in beta beets. The input parameters are summarised in Table B.8.6-28.
The PEC_{gw}, the 80^{th} percentile of the average flux concentration leaching below one meter soil depth in the 20 considered application intervals (= cropping periods) of
1 year (annual application, total simulated time: 26 years)
2 years (biannual application, total simulated time: 46 years)
3 years (triannual application, total simulated time: 66 years)
was calculated for each scenario.

Table B.8.6-28: Summary of FOCUS input parameters for chloridazon and its metabolites B and B-1 used by the notifier

Input parameter	Unit	Chloridazon	Metabolite B	Metabolite B-1
PHYSICO-CHEMICAL PARAMETERS				
Molecular weight	g/mol	221.65	145.55	159.6
Saturated vapour pressure (20 °C)	Pa	1e-9	(1e-9)*	(1e-9)*
Molar enthalpy of vaporisation	kJ/mol	(95)**	(95)**	(95)**
Water solubility (20 °C)	mg/L	422	(422)*	(422)*
Molar enthalpy of dissolution	kJ/mol	(27)**	(27)**	(27)**
Formation fraction	-	-	0.648 (from chloridazon) 1.0 (from metabolite B-1)	0.397 (from metabolite B)
Field half lives	d	78.5 (far north) 53 (north) 30.1 (south)	-	-
Half-life at reference conditions (20 °C; matric potential -10 kPa)	d	-	109.0	16.0
Molar activation energy (Arrhenius)	kJ/mol	0	54	54
Exponent of moisture correction function	-	0	0.7	0.7
$K_{f,oc}$-value	L/kg	210	50	33
$K_{f,om}$-value	L/kg	122	29	19.1
Freundlich exponent 1/n	-	0.845	0.834	0.873
Soil adsorption option	-	K_{om}, pH independent		
CROP RELATED PARAMETERS				
TSCF (crop uptake)	-	(0.5)**	(0.5)**	(0.5)**

()* No measured value available, therefore value of parent substance used. No effect on simulation results to be expected.

()** No measured value available, therefore, the default value of the model Pearl was used.

Results

The resulting PEC_{gw}, the 80th percentile average leachate concentration over a period of one or two years, for chloridazon and its metabolites B and B-1 and each scenario are listed in

- Table B.8.6-29 for the annual application of chloridazon (period = 1 year)
- Table B.8.6-30 for the application of chloridazon every other year (period = 2 years)
- Table B.8.6-31 for the application of chloridazon every third year (period = 3 years)

Table B.8.6-29: PEC_{gw} (and the years of simulation it was observed in) of chloridazon and its metabolites after annual application, calculated by notifier

Annual application	Chloridazon	Metabolite B	Metabolite B-1
	[µg/L] (years)		
Châteaudun	< 0.001 (n.a.)	61.662 (19)	8.869 (19)
Hamburg	< 0.001 (n.a.)	66.832 (19)	9.994 (19)
Jokioinen	< 0.001 (n.a.)	54.663 (12)	8.431 (12)
Kremsmünster	< 0.001 (n.a.)	51.641 (26)	7.333 (26)
Okehampton	< 0.001 (n.a.)	53.898 (12)	7.769 (20)
Piacenza	< 0.001 (n.a.)	53.083 (19)	7.405 (19)
Porto	< 0.001 (n.a.)	8.847 (17)	1.628 (11)
Sevilla	< 0.001 (n.a.)	29.930 (12)	4.403 (12)
Thiva	< 0.001 (n.a.)	46.468 (15)	6.569 (23)

n.a. not applicable

Table B.8.6-30: PEC_{gw} (and the years of simulation it was observed in) of chloridazon and its metabolites after application every other year, calculated by notifier

Application every other year	Chloridazon	Metabolite B	Metabolite B-1
	[µg/L] (years)		
Châteaudun	< 0.001 (n.a.)	29.667 (35-36)	4.389 (35-36)
Hamburg	< 0.001 (n.a.)	32.378 (19-20)	4.974 (19-20)
Jokioinen	< 0.001 (n.a.)	24.138 (33-34)	3.887 (33-34)
Kremsmünster	< 0.001 (n.a.)	23.516 (25-26)	3.483 (25-26)
Okehampton	< 0.001 (n.a.)	26.474 (19-20)	3.941 (19-20)
Piacenza	< 0.001 (n.a.)	25.471 (39-40)	3.555 (39-40)
Porto	< 0.001 (n.a.)	3.714 (31-32)	0.699 (31-32)
Sevilla	< 0.001 (n.a.)	15.457 (31-32)	2.341 (31-32)
Thiva	< 0.001 (n.a.)	23.795 (11-12)	3.442 (11-12)

n.a. not applicable

Table B.8.6-31: PEC_{gw} (and the years of simulation it was observed in) of chloridazon and its metabolites after application every third year, calculated by notifier

Application every third year	Chloridazon	Metabolite B	Metabolite B-1
	[µg/L] (years)		
Châteaudun	< 0.001 (n.a.)	20.397 (43 - 45)	3.301 (43 - 45)
Hamburg	< 0.001 (n.a.)	20.511 (37 - 39)	3.166 (37 - 39)
Jokioinen	< 0.001 (n.a.)	13.787 (64 - 66)	2.213 (13 - 15)
Kremsmünster	< 0.001 (n.a.)	17.139 (28 - 30)	2.522 (28 - 30)
Okehampton	< 0.001 (n.a.)	16.779 (16 - 18)	2.561 (19 - 21))
Piacenza	< 0.001 (n.a.)	16.042 (58 - 60)	2.242 (40 - 42)
Porto	< 0.001 (n.a.)	2.162 (37 - 39)	0.419 (28 - 30)
Sevilla	< 0.001 (n.a.)	8.361 (28 - 30)	1.352 (58 - 60)
Thiva	< 0.001 (n.a.)	15.398 (19 - 21)	2.237 (19 - 21)

n.a. not applicable

B.8.6.3 Monitoring data

Surface water

Reference number: II A 7.4/1

Report: Steen R.J.C.A et al., 2000; BOD 2003-318
A study on the behaviour of pesticides and their transformation products in the Scheldt estuary using liquid chromatography-electrospary tandem mass spectrometry
Free University of Amsterdam, Amsterdam, Netherlands
J. Environ. Monit., 2000, 2, 507-602. BASF RegDoc# 2000/1020998

Guidelines: Not relevant

GLP: No

Test system
A concentration gradient of several active substances including chloridazon in the Scheldt estuary (surface water, Netherlands) from the river end to the North sea was determined at the end of July 1998. Before this, the flush time of the estuary was determined to be 45 d. Therefore, the concentrations at the river end had been monitored by three samplings over 45 d prior to the sampling for the concentration gradient. The sampling was performed with a pumping unit equipped with sensors for salinity, temperature, oxygen content, turbidity, pH and natural fluorescence from an oceano-graphic vessel. The analysis comprised filtration, off-line solid phase extraction of 1 L of sample, deep freezing of the extraction cartidges (onboard the vessel) and elution (methanol), addition of internal standard, evaporation to 200 µL and injection of 20 µL into an HPLC-ESI-MS-MS separation and detection system (in the laboratory). Identification of chloridazon was performed by retention time and mass spectra for the product ions. The detection limit was 7 ng/L for real samples.

Findings
At the river end chloridazon showed a concentration time course starting at 0.09 µg/L (June 11, 1998) to a maximum concentration of 0.15 µg/L (June 26, 1998) and a decrease to 0.08 µg/L (July 27, 1998). The gradient of chloridazon concentrations from the river end to the sea showed a linear decrease of concentrations when plotted against the salinity of the water from 0.12 µg/L to 0.01 µg/L, thus indicating dilution with seawater.

Chloridazon was detected at very low concentrations in a large surface waterbody integrating the water and substance export of a large catchment area. A risk to the aquatic environment can be negated.

Comment of the RMS:
In the publication no information is given concerning the agricultural area in use treated with chloridazon in the catchment area of the investigated waterbody. Therefore, the monitoring study can not be used as positive proof for negligible entry of chloridazon into the aquatic environment. However, the data can be used as complementary information.

Reference number: II A 7.4/2

Report: Laporte S., 2001; BOD 2003-319
Main findings and conclusions of the implementation of directive 76/464/EEC concerning the monitoring of organic pollutants in surface waters (Portugal, April 1999-May 2000)
Department of Environmental Chemistry, Barcelona, Spain
J. Environ. Monit., 2001, 3, 475-482. BASF RegDoc# 2001/1020985

Guidelines: Not relevant

GLP: No

Test system
A large scale, systematic surface water monitoring program of organic pollutants in Portuguese rivers was carried out over 14 months with monthly sampling of 46 sampling points throughout the country. Samples were taken from the middle river bed and stored in amber glass bottles at 4 °C until extraction which always was performed within 15 d after

sampling. The samples were filtered, fortified with an internal standard and solid phase extracted. The cartridges were stored at –20 °C until elution. The stability of the compounds on the cartridges was assured. After elution the samples were analysed using GC-MS.

Findings
Chloridazon (= pyrazon) was never detected in any single surface water sample. A risk to the aquatic environment in Portugal can therefore be strongly negated.

Comment of the RMS:
In the publications no information concerning the agricultural area in use treated with chloridazon or the amounts normally used in the catchment area of the investigated waterbody is given. Therefore, the monitoring study can not be used as positive proof for negligible entry of chloridazon into the aquatic environment.
However, the data can be used as complementary information, provided that chloridazon is regularly used in the respective areas.

Conclusion
In both studies the chloridazon surface water concentrations were in a range where no concern for the aquatic environment is expected, provided that chloridazon is regularly used in the respective areas. No information concerning the agricultural area in use treated with chloridazon were given. Though the studies provided a full areal coverage of one EU member state over one year and a large surface water catchment in the expected time of ocurrence in surface waters, the findings are not a positive proof for negligible entry of chloridazon into the aquatic environment.
However, the studies give hints that no surface water concentrations of concern may be expected, since a common use of chloridazon in the investigated catchment area can be assumed.

Groundwater
A compilation of ground water monitoring data from water companies, private wells and offcial federal monitoring programmes is available in the UBA (German Federal Environmental Agency). These data are also regularly published by LAWA (Federal Working Group - Water).

Based on the data from 7 Federal States involving 1446 ground water sampling points, 5 instances of chloridazon residues exceeding 0.1 µg/L in ground water have been detected in 1999. In 2000, 8 Federal States and 1482 ground water sampling points have been involved in the monitoring and in 3 cases exceedings of 0.1 µg/L have been detected in the ground water samples. In 2001, 3 cases out of 1425 sampling points in 9 Federal States exceeded 0.1 µg/L and in 2002, exceedings of 0.1 µg/L have been detected in 4 ground water samples out of 1682 sampling points in 10 Federal States. Details are shown in Table B.8.6-32.

Table B.8.6-32: Ground water monitoring data from Germany (1999-2002)

Year	Federal states number	Sampling points total	Number of sampling points			
			n > LOQ*	<= 0.1 µg/L	> 0.1 - 1.0 µg/L	> 1.0 µg/L
1999	7	1446	1433	8	4	1
2000	8	1482	1470	7	2	1
2001	9	1425	1419	3	2	1
2002	10	1701	1682	14	4	0

*LOQ limit of quantification

Conclusions
In agreement with the PEC groundwater calculations chloridazon can be present in groundwater. Concentrations above 0.1 µg/L were found in a minor fraction of the sampling points between 0.2 and 0.34 %. However, hot spots with more than 1 µg/L chloridazon seems to be possible.

B.8.7 Fate and behaviour in air (Annex IIA 7.2.2; Annex IIIA 9.3)

Reference number: II A 7.2.2/1

Report: Sarafin R., 1992(b); LUF 98-00151
Laboratory study on the volatilisation of chloridazon after application of BAS 119 33 H on soil and plant surfaces
BASF AG, Agrarzentrum Limburgerhof, Limburgerhof, Germany, unpublished, BASF RegDoc# 1992/11838

Guidelines: BBA IV 6-1

GLP: Yes

Test system
The volatilisation study was performed with the WG-formulation BAS 119 33 H (containing nominal 650 g as/kg) based on a field application rate of 3 kg as/ha. The formulation was mixed with 0.7 % [pyridazinone-4,5-^{14}C]-labelled active substance to enable a total balance. The specific radioactivity of the labelled chloridazon was 2.26 MBq/mg, the radiochemical purity was > 99 %. Soil and plant were treated in a special glass container. The formulation was applied via a nozzle (1.2 bar) to a small dish filled with soil (first experiment), and to a dish with a plant (bush bean, soil covered; second experiment). The soil characteristics were: 85 % sand, 12 % silt, 3 % clay, organic C 0.6 %, pH ($CaCl_2$) 5.7, MWC 25 g/100 g dry soil. Application losses were determined by rinsing the glass container and all equipment with methanol. The treated soil/plant was kept in a special volatilisation chamber which allowed an air flow rate to be controlled (200 L/h) and the temperature of the air to be measured (20 - 21 °C). The wind speed was adjusted to 1 m/s. The radioactive volatiles was determined with the help of charcoal traps. The charcoal traps were sampled 1, 3, 6 and 24 h after application. At the end of the study, the remaining radioactivity in soil and plant was determined.

Findings
The total recovery of radioactivity was 97 % for the soil experiment and 99 % for the plant experiment. The volatilisation rates were < 4 % from the soil surface and < 1 % from plant

surface. As these values are within the uncertainty of the experimental method, volatilisation of chloridazon under field conditions is considered to be negligible.

Reference number: II A 7.2.2/2

Report: von Goetz N., 2000(b); LUF 2003-37
Photochemical oxidative degradation of chloridazon (BAS 119 H) (QSAR estimates)
BASF AG, Agrarzentrum Limburgerhof, Limburgerhof, Germany, unpublished, BASF DocID 1999/11873, study no NG-00-01

Guidelines: EEC 94/37

GLP: No, not subject to GLP regulations

Test system
For the degradation rate resulting from OH-attack QSAR estimates according to the Atkinson method were performed. The degradation rate resulting from attack of ozone is calculated according to an OECD method.
Using the computer program AOPWIN Anonymous 1997): which is based on the increment system published by Atkinson (1987), the degradation rate for reactions of chloridazon with hydroxyl radicals was calculated based on the structural formula. Assuming a pseudo-first order reaction, the degradation half-life via this reaction route was calculated by taking into account the diurnally and seasonally averaged concentration of hydroxyl radicals in the troposphere.

The degradation of a compound A by OH-radicals can then be calculated by

$$-d[A]/dt = k' \cdot [A] \qquad \text{with } k' = k \cdot [\text{OH-radicals}] \qquad (1)$$

The half-life of this process can be calculated by equation (2):

$$t_{1/2} = \ln 2/k' = \ln 2 / (k \cdot [\text{OH-radicals}]) \qquad (2)$$

The degradation rate resulting from ozone attack can be determined with an increment method described in [5]. The half-life for this process can then be derived as described in equation 2 by taking into account the concentration of ozone molecules in the air:

$$t_{1/2} = \ln 2/k' = \ln 2/k \cdot [\text{ozone molecules}] \qquad (3)$$

Findings
Degradation resulting from OH-radical attack
The AOPWIN program uses the SMILES notation as basis for the calculation. The SMILES code for chloridazon (BAS 119 H) is: c1ccccc1N2C(=O)C(CL)=C(N)C=N2.
For N-containing molecules data for the Atkinson method are missing. The missing data were approximated.
OH-addition to olefinic bonds: AOP uses a substituent value of 0.6 for C(-N**). As the substituent of the olefinic bond is an amine and amines rather activate than deactivate double bonds, a value of at least 1 (>1) has to be used for this substituent. The resulting k-value is

$k_{add} > 8.1 \times 10^{-12}$ cm^3 molecule^{-1}s^{-1}

OH-addition to aromatic rings: AOP uses an Es+ of –0.6 for (-N<**). Values determined for similar groups are –0.16 for (-NH_2) and –1.7 for (-$N(CH_3)_2$). As a worst case –0.16 is used and from $\log K_{ar} < -11.71 + (-1.34 \times (-0.16))$ the following k-value results:

$k_{ar} > 3.16 \times 10^{-12}$ cm^3 molecule^{-1}s^{-1}

With the values k_{abst} and k_N (for N-groups) calculated by AOP which amount to

$k_{abst} = 1.94 \times 10^{-12}$ cm^3 molecule^{-1}s^{-1}
$k_N = 21.0 \times 10^{-12}$ cm^3 molecule^{-1}s^{-1}

the total rate constant is $\underline{k > 34.2 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1}\text{s}^{-1}.}$

The weighted global average tropospheric hydroxyl radical concentration is 8×10^5 cm^{-3}. Conclusively, the half-life for the degradation of chloridazon is:

$t_{1/2}$ $< \ln 2 / (34.2 \times 10^{-12}\ 8 \times 10^5)$ s
< 7.0 h
$\underline{< 0.29 \text{ d (24 h day)}}$

Degradation resulting from ozone attack
Chloridazon contains two reactive sites with respect to ozone attack: an unsaturated carbon-carbon bond and the aromatic ring. Therefore, the degradation rate has to be calculated as follows

$k_{O3} = (C_6H_5\text{-N}) + (R_2C{=}CR_2)\ S(Cl)\ S(C(O)R)\ S(\text{-}NH_2)\ S(CH{=}N)$

For the (C_6H_5-N) group as well as for the olefinic bond no increments are available and no reasonable assumptions can be made. Therefore, the degradation of chloridazon by ozone attack cannot be quantified.

Valid: yes

Conclusion
Chloridazon has a very low volatilisation potential and, if reaching the troposphere, is degraded fast by photochemical processes ($DT_{50} < 7.0$ hours).

B.8.8 Predicted environmental concentrations in air (PEC_A) (Annex IIIA 9.3)

The volatilisation behaviour of chloridazon from plant and soil surfaces after application according to good agricultural practice is discussed in detail in Sarafin 1992b (AII 7.2.2/1, DOC#1992/11838). Less than 4 % of chloridazon volatilise within 24 hours after application both from soil and plant surface, which is within the precision range of the experiment. Considering these experimental results and the relatively high water solubility and the

extremely low vapour pressure it can be concluded that the active substance has no tendency to enter the air.
For the degradation rate in the troposphere resulting from OH-attack QSAR estimates according to the Atkinson method yielded a half life < 7.0 h.

Conclusion
Chloridazon has a very low volatilisation potential and, if reaching the troposphere, is degraded fast by photochemical processes ($t_{1/2}$ < 7.0 hours).

B.8.9 Definition of the residue (Annex IIA 7.3)

B.8.9.1 Soil

According to the presented results, the parent compound BAS 119 H (chloridazon) and metabolite B are the only relevant residues for quantitation in soil.
The only metabolite occurring in significant amounts is metabolite B, which was formed in amounts up to 56 % in the aerobic soil metabolism study and was detected in all field soil dissipation studies. Metabolite B-1 did not occur in the soil metabolism study but in a soil degradation study for metabolite B as a transformation product. In all field dissipation studies metabolite B-1 was only detected around the limit of quantification (0.01 mg/kg).

Conclusion
The parent compound chloridazon and the metabolite B are the relevant residues in soil.

B.8.9.2 Water

Surface water
According to the presented results, the parent compound BAS 119 H (chloridazon) is to be defined as a relevant residue for quantitation in water. Metabolite B is the only degradation product that occurred in significant amounts (up to 43 % in water/sediment systems). All photolytical transformation products occurred in amounts < 10 %.

Conclusion
The parent compound chloridazon and the metabolite B are the relevant residues in surface water.

Groundwater
Since metabolites B and B-1 can be expected to leach to groundwater and lead to groundwater concentrations > 0.1 µg/L (lysimeter study and FOCUS groundwater scenario) they are to be defined as a relevant residues for quantitation.

Conclusion
The metabolites B and B-1 are the relevant residues in ground water.

B.8.9.3 Air

Due to the low vapour pressure < 10^{-6} Pa (1×10^{-9} Pa at 20 °C) it is unlikely that chloridazon will ever reach the air, or remain for any length of time in the air, for monitoring purposes. Therefore, no residues in air can be defined.

B.8.9.4 Overall residue definition

- In soil the active substance chloridazon and metabolite B are the relevant residues.
- In surface water the active substance chloridazon and metabolite B are defined as the relevant residues.
- In ground water metabolite B and metabolite B-1 are the relevant residues.
- In air no residues are expected due to the low vapour pressure of chloridazon.

B.8.10 References relied on

Annex point/ reference number	Author(s)	Year	Title source (where different from company) report no. GLP or GEP status (where relevant), published or not BBA registration number	Data protection claimed Y/N	Owner[1]
AIIA-7.1.1.1.1	Bayer, H.	2003	Report amendment No. 1 to final report: Aerobic degradation of metabolite B (metabolite of BAS 119 H, chloridazon) in 4 soils (DT_{50}/DT_{90}). 2003/1005450 GLP, unpublished BOD2003-276	Y	BAS
AIIA-7.1.1.1.1; AIIA-7.1.1.2.1	Bayer, H.	2003	Aerobic degradation of metabolite B (metabolite of BAS 119 H, chloridazon) in 4 soils (DT_{50}/DT_{90}). 2002/1004262 GLP, unpublished BOD2003-307	Y	BAS
AIIA-7.1.1.1.1; AIIA-7.1.1.2.1	Bayer, H. and Erzberger, B.	2003	Aerobic degradation of metabolite B-1 (metabolite of BAS 119 H, chloridazon) in 4 soils (DT_{50}/DT_{90}). 2002/1004263 GLP, unpublished BOD2003-308	Y	BAS
AIIA-7.1.1.1.1; AIIA-7.1.1.2.1	Dams, W.	1989	Degradation behaviour of chloridazon in soil. BASF 1989/10209 GLP, unpublished BOD2000-839	N	BAS

[1] Only notifier listed

Annex point/ reference number	Author(s)	Year	Title source (where different from company) report no. GLP or GEP status (where relevant), published or not BBA registration number	Data protection claimed Y/N	Owner[1]
AIIA-7.1.1.1.1	Wood, N.F.	1991	Metabolic fate of the phenyl moiety in the aerobic soil metabolism of pyrazon. Addendum to BASF Rep.No. M8910. BASF 91/11618 not GLP, unpublished BOD2001-593	N	BAS
AIIA-7.1.1.1.1; AIIA-7.1.1.2.1	Wood, N.F.	1989	Aerobic soil metabolism of pyrazon, 5-amino-4-chloro-2-phenyl-3(2H)-pyridazinone. BASF 1989/5165 not GLP, unpublished BOD2000-841	N	BAS
AIIA-7.1.1.1.2	Singh, M. and Tanaka, F.	1993	Photolysis of ^{14}C-chloridazon (BAS 119 H) on soil. BASF 93/5008 GLP, unpublished BOD2001-596	Y	BAS
AIIA-7.1.1.1.2; AIIA-7.1.1.2.1	Wood, N.F.	1990	Anaerobic soil metabolism of pyrazon. BASF 89/5166 not GLP, unpublished BOD2001-594	N	BAS
AIIA-7.1.1.2.1; AIIIA-9.1.3	Dressel, J.	2003	Compilation of parameters characterising the environmental fate of BAS 119 H (chloridazon) and its metabolites. 2003/1001026 not GLP, unpublished BOD2003-309	Y	BAS
AIIA-7.1.1.2.1	Platz, K.	2001	Estimation of half-lives of chloridazon in 4 soils from a laboratory degradation study. 2000/1017056 not GLP, unpublished BOD2003-310	Y	BAS
AIIA-7.1.1.2.2	Domenichini, P.	2003	Terrestrial field degradation of chloridazon applied to bare soil in Southern Europe (Italy and Spain in the year 2000). 2003/1001025 GLP, unpublished BOD2003-313	Y	BAS
AIIA-7.1.1.2.2	Eubanks, M.W. and Clark, J.R.	1989	Pyramin herbicide (chloridazon) field soil dissipation studies for fall and spring use: Summary report. BASF 89/5154 GLP, unpublished BOD2001-602	N	BAS

Annex point/ reference number	Author(s)	Year	Title source (where different from company) report no. GLP or GEP status (where relevant), published or not BBA registration number	Data protection claimed Y/N	Owner[1]
AIIA-7.1.1.2.2	Hesse, B. and Sasturain, J.	1993	Investigation into the dissipation behaviour of chloridazon in the soil under field conditions. 1993/11484 GLP, unpublished BOD2003-400	Y	BAS
AIIA-7.1.1.2.2	Kellner, O. et al	2003	Field soil dissipation of BAS 119 H (formulation BAS 119 33 H) on bare soil in Sweden 2000-2001. 2003/1001009 GLP, unpublished BOD2003-312	Y	BAS
AIIA-7.1.1.2.2	Sasturain, J. and Kellner, O.	1998	Study of the dissipation of chloridazon in the soil under field conditions. BASF 98/1000787 GLP, unpublished BOD2001-603	Y	BAS
AIIA-7.1.2	Daum, A.	1998	Determination of the pKa of Reg. No. 14 456 (BH 119 Metabolite B) in water at 20 °C. 1998/11081 GLP, unpublished BOD2003-316	Y	BAS
AIIA-7.1.2	Ellenson, J.L.	1987	Soil adsorption/desorption of pyrazon. 1987/5074 not GLP, unpublished BOD2000-845	N	BAS
AIIA-7.1.2	Keller, W.	1980	Adsorption behaviour of crop protection products in the system soil/water. 1980/1000066 not GLP, unpublished BOD2003-315	N	BAS
AIIA-7.1.2	Seher, A.	1999	Soil adsorption/desorption study of 035 375 (BH 119-B-Me) on soils. 1999/11086 GLP, unpublished BOD2003-358	Y	BAS
AIIA-7.1.3.1	Keller, W.	1985	Leaching behaviour of pesticides - BAS 119 33 H. BASF 85/10062 not GLP, unpublished BOD2001-605	N	BAS
AIIA-7.1.3.2	Keller, E.	1988	The leaching ^{14}C-chloridazon after aerobic aging. BASF 88/10126 GLP, unpublished BOD2001-606	N	BAS

Annex point/ reference number	Author(s)	Year	Title source (where different from company) report no. GLP or GEP status (where relevant), published or not BBA registration number	Data protection claimed Y/N	Owner[1]
AIIA-7.1.3.3	Gatzweiler, E. et al.	1992	Field lysimeter study with (4,5-^{14}C)-chloridazon. 1992/11927 not GLP, unpublished BOD2003-317	N	BAS
AIIA-7.1.3.3	Mittelstaedt, W. and Führ, F.	1993	Field lysimeter study with ^{14}C-quinmerac. BASF 93/11386 not GLP, unpublished BOD2001-607	Y	BAS
AIIA-7.1.3.3	Nicolaisen, R.K.	1993	Note from the translator on discrepencies between the original German report and the English translation. BASF 93/11384 not GLP, unpublished BOD2001-608	Y	BAS
AIIA-2.9.1; AIIA-7.2.1.1	Ellenson, J.L. and Brem, G.	1988	Hydrolysis of ^{14}C-pyrazon in pH 5, 7 and 9 solutions at 25 degrees Celsius. BASF 88/5518 not GLP, unpublished WAS2001-267	N	BAS
AIIA-2.9.2; AIIA-7.2.1.2	Ellenson, J.L. et al.	1989	Photolysis of BAS 119 H in pH 7 aqueous solution at 25 degrees Celsius. BASF 89/5090 not GLP, unpublished LUF2001-228	N	BAS
AIIA-2.9.3; AIIA-7.2.1.2	Sarafin, R.	1992	Chloridazon - Determination of quantum yield. BASF 1992/10441 GLP, unpublished LUF98-00155	N	BAS
AIIA-7.2.1.2	Sarafin, R.	1991	Chloridazon (BAS 119 H) absorption coefficients at pH 4, pH 7 and pH 9. BASF 1991/10347 GLP, unpublished LUF2003-57	N	BAS
AIIA-7.2.1.2	Scharf, J.	1999	Photolysis of metabolite BH 119-B-Me (BI) of chloridazon in a natural water. BASF 1999/10696 GLP, unpublished LUF2003-40	Y	BAS
AIIA-7.2.1.2	Scharf, J.	1998	Photolysis of chloridazon and its metabolite B in a natural water. BASF 1998/10128 GLP, unpublished LUF2003-39	Y	BAS

Annex point/ reference number	Author(s)	Year	Title source (where different from company) report no. GLP or GEP status (where relevant), published or not BBA registration number	Data protection claimed Y/N	Owner[1]
AIIA-2.9.2; AIIA-7.2.1.2	Scharf, J.	1999	Photolytical halflife of chloridazon in the top layer of aqueous systems. BASF 99/10693 not GLP, unpublished LUF2001-225	Y	BAS
AIIA-2.9.2; AIIA-7.2.1.2	Tanaka, F.S.	1992	Aqueous photolysis of ^{14}C-chloridazon at pH 7. BASF 92/5090 GLP, unpublished LUF2001-229	N	BAS
AIIA-7.2.1.2	von Goetz, N.	2000	Aqueous photolysis of the metabolite B of chloridazon (BAS 119 H). BASF 2000/1000147 GLP, unpublished WAS2004-250	Y	BAS
AIIA-7.2.1.3.1; AIIA-7.2.1.3.2	Bieber, W.-D.	1998	Degradation of [^{14}C]chloridazon in two aerobic water/sediment systems. BASF 98/10916 GLP, unpublished WAS1999-7	Y	BAS
AIIA-7.2.1.3.2; AIIIA-9.2.1	Dressel, J.	2003	Compilation of parameters characterising the environmental fate of BAS 119 H (chloridazon) and its metabolites. 2003/1001026, CALC-415 not GLP, unpublished WAS2003-189	Y	BAS
AIIA-2.10; AIIA-7.2.2	Sarafin, R.	1992	Laboratory study on the volatilisation of chloridazon after application of BAS 119 33 H on soil and plant surface. BASF 92/11838 GLP, unpublished LUF98-00151	N	BAS
AIIA-7.2.2	von Götz, N.	2000	Photochemical oxidative degradation of chloridazon (BAS 119 H) (QSAR estimates). 1999/11873 not GLP, unpublished LUF2003-37	Y	BAS
AIIA-7.4	Lacorte, S. et al.	2001	Main findings and conclusions of the implementation of directive 76/464/CEE concerning the monitoring of organic pollutants in surface waters (Portugal, April 1999-May 2000). J. Environ. Moni., 3, 2001, 475-482 2001/1020985 not GLP, published BOD2003-319	N	-

Annex point/ reference number	Author(s)	Year	Title source (where different from company) report no. GLP or GEP status (where relevant), published or not BBA registration number	Data protection claimed Y/N	Owner[1]
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AIIIA-9.1.3	Hauck, T.	2003	Predicted environmental concentrations of BAS 119 H (chloridazon) and its metabolites in soil (PEC_{soil}) after field application of BAS 119 33 H. 2003/1001029 not GLP, unpublished BOD2003-320	Y	BAS
AIIIA-9.2.1	Dressel, J.	2003	Predicted environmental concentrations of BAS 119 H (chloridazon) and its metabolites in groundwater (PEC_{gw}) after field application of BAS 119 33 H according to FOCUS. 2003/1001028, CALC-417 not GLP, unpublished WAS2003-190	Y	BAS
AIIIA-9.2.1	FOCUS Workgroup	2001	FOCUS groundwater scenarios in the EU, review of active substances. Report of the FOCUS Groundwater Scenarios, 40-42 sanco/321/20000, Rev. 2 not GLP, published BOD2004-557	N	-

Codes of owner

BAS: BASF Aktiengesellschaft