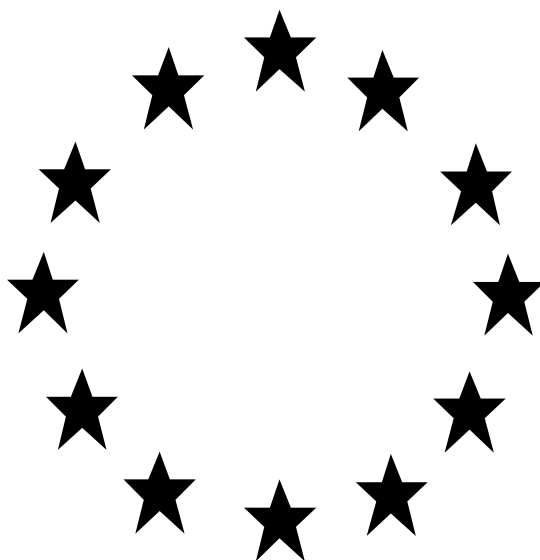




Draft Assessment Report (DAR)

- public version -

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

PYRIDABEN

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

Volume 3, Annex B, part 4, B.8

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B.8 Environmental Fate and Behaviour**B.8.1 Route and rate of degradation in soil (Annex IIA 7.1.1 and Annex IIIA 9.1.1)****B.8.1.1 Laboratory studies****B.8.1.1.1 Aerobic studies****STUDY 1****Characteristics**

reference	:	Crowe A., 2002 (IIA 7.1.1.1.1/01)	incubation time	:	up to 150 d
year of execution	:	2001	nominal concentration	:	0.48-0.50 mg/kg
GLP statement	:	yes	temperature	:	20°C
guideline	:	SETAC 1995)	DT50	:	see results
test substance	:	a) [benzene-U-14C]-pyridaben, lot no. CP-1504. b) [pyridazinone-3,6-14C]-pyridaben, lot no. CP-1505.	metabolites	:	see results
Purity	:	a) chemical purity not reported, radiochemical purity 99.2%. b) chemical purity not reported, radiochemical purity 99.5%.	acceptability	:	acceptable
Soils	:	sandy loam			

Study design

Aliquots of 50 g dry weight portions of a sandy loam soil (sieved over 2 mm, soil properties see Table B.8.1.1.1-01) were adjusted to 40% MWHC and incubated in the dark at 20±2°C for two weeks to stimulate microbial activity. At the end of this period, [Benzene-U-14C]-pyridaben (designated BEN-pyridaben) and [pyridazinone-3,6-14C]-pyridaben (designated PYR-pyridaben) were applied separately in acetonitrile to the surface of the 50 g dry weight soil portions at a rate of 0.48 and 0.50 mg/kg, respectively. Treated soil was incubated under a continuous humid air supply in the dark at 20±2°C for up to 150 days. The soil moisture content was maintained at 40% MWHC. CO₂ was trapped in 2M KOH (2 traps) and 20% ethanolamine (1 trap).

Table B.8.1.1-01 Properties of study soil

Parameter	sandy loam soil
% sand/silt/clay ^(A)	65/24/11
Texture ^(A)	sandy loam
pH	6.2
% organic carbon	2.4
CEC (meq/100 g)	19.1
moisture content	40% MWHC ^(C)
microbial biomass (start) ^(B)	25.6 mgC/100 g (⇔ 1.1% of OC content)
microbial biomass (end) ^(B)	59.6 mgC/100 g (⇔ 2.5% of OC content)

(A) Classification system not reported.

(B) By fumigation/extraction method.

(C) Gravimetric moisture content (% w/w) not reported.

Single soil samples were analysed on days 0, 7, 14, 30, 59, 90, 120 and 150 post-treatment. Trapping solutions were sampled and replaced on days 7, 10, 14, 21, 30, 41, 50, 59, 69, 79, 90, 104, 120 and 150 post-treatment. Soil samples were soxhlet extracted with acetone/water (4/1). Where <90% AR was extracted, this was followed by soxhlet extraction with MeOH/phosphoric acid (4/1). Radioactivity in extracts and liquid traps was determined by LSC. The soil extracts were combined, concentrated, adjusted to pH 2 using HCl, and extracted with ethyl acetate. The recoveries of partition into organo-soluble and aqueous residue were reported. The organo-soluble portion was concentrated, the aqueous residue was analysed without further work-up. The organic phase (after concentration) and aqueous phase were analysed by reversed phase HPLC. Ethanolamine traps were included for volatile organic compounds. Compound identification was by co-chromatography with unlabelled reference standards. Radioactivity in post-extraction solids (PES) was determined by combustion/LSC. Selected samples underwent extraction for fractionation into fulvic acid, humic acid and humin. Radioactivity in selected KOH traps was confirmed to be CO₂ by BaCl₂ precipitation.

Results

Microbial activity of the test soil was confirmed at the start and the end of aerobic incubation by determining the microbial biomass using the fumigation/extraction method (see table B.8.1.1.1-01).

The results for the distribution and identification of radioactivity are given in Table B.8.1.1.1-02 to Table B.8.1.1.1-05. Ranges given here are for both labels unless indicated otherwise. Total recovery of radioactivity ranged from 96 to 108% AR. The amount of extractables decreased from 100-108% AR on day 0 to 70-75% AR on day 150. PES increased from ≤0.6% AR on day 0 to a maximum of 13-18% AR on day 150. Day 120 and 150 PES were shown to consist of humic acids (5.4-7.0% AR), humin (4.9-6.4% AR) and fulvic acids (2.3-5.1% AR). CO₂ was evolved from the soil to a maximum of 21% AR (BEN-label) and 3.4% AR (PYR-label) on day 150.

Pyridaben degraded to 49-52% AR after 150 days. No metabolite accounted for >10% AR at any time. PB-4 was the only metabolite detected at >5% AR during at least two successive samplings (monotonous increase, maximum 7.6% AR after 150 days). All other metabolites were <5% AR and reached their maximum level before study end.

Table B.8.1.1.1-02 Distribution of radioactivity after incubation at 20°C of sandy loam soil treated with [benzene-U-14C] pyridaben at 0.48 mg/kg (% AR)

day	extractable					KOH ^(A)	PES	mass balance
	acetone/ H ₂ O	MeOH/ H ₃ PO ₃	total	organo- soluble	aque- ous			
0	107.6	na	107.6	105.7	nd	na	nd	107.6
7	98.0	na	98.0	96.1	0.9	2.7	3.3	104.0
14	94.8	na	94.8	92.3	1.1	4.8	5.0	104.5
30	78.6	13.1	91.7	85.9	1.8	8.5	5.0	105.3
59	76.5	2.6	79.1	76.3	2.1	13.8	10.5	103.4
90	69.7	2.1	71.8	67.9	1.9	18.2	15.8	105.9
120	65.5	5.1	70.6	65.2	3.5	19.9	17.8	102.3
150	65.1	5.1	70.2	62.0	3.3	21.4	12.9	104.5

na = not applicable; nd = not detected

(A) Including RA in ethanolamine traps (max. 0.8% after 150 days).

Table B.8.1.1.1-03 Distribution of radioactivity after incubation at 20°C of sandy loam soil treated with [pyridazinone-3,6-14C] pyridaben at 0.50 mg/kg (% AR)

day	extractable					KOH ^(A)	PES	mass balance
	acetone/ H ₂ O	MeOH/ H ₃ PO ₃	total	organo- soluble	aque- ous			
0	99.5	na	99.5	93.2	7.4	na	0.6	100.1
7	95.4	na	95.4	89.2	4.9	0.6	3.3	99.3
14	92.6	na	92.6	87.8	7.1	1.4	5.1	99.1
30	82.3	8.7	91.0	82.7	7.7	2.2	8.7	101.9
59	80.3	3.2	83.5	77.4	5.2	2.8	12.1	98.4
90	78.3	3.1	81.4	73.6	5.7	3.0	15.6	100.0
120	72.0	5.8	77.8	73.0	6.1	3.3	15.0	96.0
150	64.4	10.8	75.2	67.6	7.7	3.4	18.0	96.6

na = not applicable; nd = not detected

(A) No RA in ethanolamine traps was detected.

Table B.8.1.1.1-04 Identification of radioactivity after incubation at 20°C of sandy loam soil treated with [benzene-U-14C] pyridaben at 0.48 mg/kg (% AR)

day	pyridaben	PB-4	PB-7	PB-9	PB-22
0	104.6	0.2			
7	93.5	1.0	0.8		
14	87.4	1.9	2.2		
30	78.3	4.0	2.6		0.1
59	67.9	4.3	2.8		0.4
90	58.7	4.1	2.4	0.2	
120	54.5	5.1	2.8		
150	49.4	6.0	2.7		0.6

Note: empty cell means: not detected. Apart from compounds in above table, four unidentified fractions were detected, each ≤0.9% AR at any time point.

Table B.8.1.1.1-05 Identification of radioactivity after incubation at 20°C of sandy loam soil treated with [pyridazinone-3,6-14C] pyridaben at 0.50 mg/kg (% AR)

day	pyridaben	PB-4	PB-7	PB-9	PB-14	PB-22	P-14	P-16
0	98.6							
7	85.8	1.2	0.8	0.3	0.1	1.2	0.3	
14	82.6	1.8	2.1		0.1	0.7	0.8	
30	75.0	3.5	2.5			0.2	2.9	
59	67.9	4.9	2.6		0.3	0.3	0.4	
90	61.8	6.3	2.9		0.2	0.3	0.7	
120	61.2	5.7	2.8		0.5	0.2	0.2	0.3
150	52.4	7.6	3.0		0.3	0.4	0.7	

Note: empty cell means: not detected. Apart from compounds in above table, 16 unidentified fractions were detected, each $\leq 4.9\%$ AR at any time point.

Degradation rates

DT50 values were calculated following the recommendations and procedures of the “Guidance document on estimating persistence and degradation kinetics from Environmental Fate studies on pesticides in EU registration” (SANCO/10058/2005 version 1.0). Calculations were based on the individual measurements and the time zero values for pyridaben were adjusted for % AR in PES. All calculations were performed with ModelMaker v 4.0 software (SFO = single first-order, FOMC = first-order multi-compartment, DFOP = Double-First-Order in Parallel mode).

Pyridaben

Endpoints for persistence

For persistence endpoints, SFO and FOMC were first run by the RMS for the data sets of both labels (M0 free, all data, no weighting). FOMC gave a better visual fit than SFO, and a lower error (1.09% versus 4.39% for Ben-label, 2.27% versus 4.92% for Pyr-label). There were no scientific grounds to justify data elimination, fixing of M0 or weighting. Therefore DFOP was run unmodified, and this model gave the best fit (lowest error, 0.94% for Ben-label, 1.83% for Pyr-label). The persistence endpoints for the best fit model DFOP are presented in Table B.1.1.1-06.

Endpoints for modelling

The first run of the SFO for the data sets of both labels (M0 free, all data, no weighting) gave an acceptable fit, both visually and statistically. The modelling endpoints were therefore obtained from this run and are presented in Table B.1.1.1-06.

Table B.8.1.1.1-06 Half-lives for pyridaben in sandy loam treated with [benzene-U- 14C] pyridaben or [pyridazinone-3,6-14C] pyridaben at 0.48 or 0.50 mg/kg and incubated in the dark at 20°C and 40% MWHC.

label	parameter for	kinetics	quality of fit	χ^2 (err)	r^2	DT50 (20°C)	DT90 (20°C)
BEN	persistence modeling	DFOP	best fit	0.94	1.00	132	597
		SFO	acceptable	4.39	0.95	135	-
PYR	persistence modeling	DFOP	best fit	1.83	0.99	181	778
		SFO	acceptable	4.92	0.90	181	-

PB-4

PB-4 is a minor metabolite. The FOCUS guidance document states that deriving reliable kinetics endpoints may still be possible for minor metabolites, especially if there is a clear formation and decline pattern. This is not the case for PB-4. The levels observed for this metabolite are low, with associated high relative experimental error, and there is a monotonous increase of its levels during the study, with no decline apparent. The lack of accuracy was demonstrated by attempting a fitting procedure. For parent, the best fit model was DFOP for both labels. A run with parent DFOP and PB-4 SFO gave for both labels an acceptable visual fit for the metabolite, but the error (17%) exceeded 15%, and the rate constants were negative (-0.0018 day^{-1} for both labels). The fitting therefore would suggest that no degradation occurs. However, the error term for the rate constant was 0.0099 day^{-1} and 0.0034 day^{-1} for BEN- and PYR-label, respectively, hence a factor of 6 and 2 larger than the estimated value. The large error term indicates that the estimates are not reliable.

Conclusions

In soil treated with BEN- and PYR-labelled pyridaben, non-extractable residues increased from $\leq 0.6\%$ AR on day 0 to a maximum of 13-18% AR on day 150. CO_2 was evolved from the soil to a maximum of 21% AR (BEN-label) and 3.4% AR (PYR-label) on day 150. Pyridaben degraded to 49-52% AR after 150 days (DT50 values 132-181 days). No metabolite accounted for $>10\%$ AR at any time. PB-4 was the only metabolite detected at $>5\%$ AR during at least two successive samplings (monotonous increase, maximum 7.6% AR after 150 days). All other metabolites were $<5\%$ AR and reached their maximum level before study end.

Guidelines & Limitations

1. The dose (0.48-0.50 mg/kg) was 3.5-3.6 times the maximum calculated PECsoil (0.139 mg/kg), but the NOEC of pyridaben for effects on soil microbial processes was 8.0 mg a.s./kg soil (see B.9.8.2).
2. The following information was not available from the report: a record of measured temperatures; HPLC column recovery.
3. Compound identity was based on a single analytical principle (RP HPLC, one solvent system). The notifier has stated that the study was conducted according to the SETAC Guidelines (1995). Confirmation of identity of the test substance by a second analytical method is not specifically required by this guideline. The reversed phase HPLC gradient method gave reproducible results and a good separation of pyridaben and its metabolites. The reversed phase gradient HPLC method used in this study was the same as that used in the sediment/water study, where the identity of pyridaben was confirmed by LC-MS in selected samples. This explanation is considered acceptable by RMS.
4. Acceptability: the study is acceptable.

STUDY 2**Characteristics**

reference	: Crowe A., 2001 (IIA 7.1.1.1/01)	incubation time	: up to 151 d
year of execution	: 2000	nominal concentration	: 0.51 mg/kg
GLP statement	: yes	temperature	: 20°C
guideline	: SETAC 1995)	DT50	: see results
test substance	: [pyridazinone-3,6-14C]-pyridaben, lot no. CP-1505.	metabolites	: see results
Purity	: chemical purity not reported, radiochemical purity 99.0%	acceptability	: acceptable
Soils	: sandy loam (2X), silt loam, clay loam		

Study design

Aliquots of 50 g dry weight portions of three soils (sieved over 2 mm, soil properties see Table B.8.1.1.1-07) were adjusted to 40% MWHC and incubated in the dark at $20 \pm 2^\circ\text{C}$ for 15 days to stimulate microbial activity. At the end of this period, [pyridazinone-3,6-14C]-pyridaben was applied in acetonitrile to the surface of the 50 g dry weight soil portions at a rate of 0.51 mg/kg. Treated soil was incubated under a continuous humid air supply in the dark at $20 \pm 2^\circ\text{C}$ for up to 151 days. The sandy loam soil was also incubated under the same conditions at 10°C . The soil moisture content was maintained at 40% MWHC. CO_2 was trapped in 2M KOH (2 traps) and 20% ethanolamine (1 trap).

Table B.8.1.1.1-07 Properties of study soils

Parameter	clay loam soil	silt loam soil	sandy loam soil (20°C)	sandy loam soil (10°C)
% sand/silt/clay ^(A)	27/39/35	7/85/8	63/30/7	63/30/7
Texture ^(A)	clay loam	silt loam	sandy loam	sandy loam
pH	7.6	6.7	6.0	6.0
% organic carbon	3.8	1.9	0.8	0.8
CEC (meq/100 g)	43.8	21.8	8.6	8.6
moisture content	40% MWHC ^(C)	40% MWHC ^(C)	40% MWHC ^(C)	40% MWHC ^(C)
microbial biomass (start) ^(B)	78.4 mgC/100 g ($\Rightarrow$ 2.1% of OC)	17.0 mgC/100 g ($\Rightarrow$ 0.9% of OC)	15.6 mgC/100 g ($\Rightarrow$ 2.0% of OC)	15.6 mgC/100 g ($\Rightarrow$ 2.0% of OC)
microbial biomass (end) ^(B)	621.4 mgC/100 g ($\Rightarrow$ 16.4% of OC)	87.7 mgC/100 g ($\Rightarrow$ 4.6% of OC)	55.7 mgC/100 g ($\Rightarrow$ 7.0% of OC)	71.0 mgC/100 g ($\Rightarrow$ 8.9% of OC)

(A) Classification system not reported.

(B) By fumigation/extraction method.

(C) Moisture content during incubation; actual gravimetric (w/w) or volumetric content (v/v) not reported.

Single soil samples were analysed on days 0, 7, 14, 29, 60, 90, 120 and 151 post treatment. Trapping solutions were sampled and replaced on days 7, 14, 21, 29, 42, 60, 75, 90, 104, 120, 133 and 151 post-treatment. Soil samples were soxhlet extracted with acetone/water (4/1). Where <90% AR was extracted, this was followed by soxhlet extraction with MeOH/phosphoric acid (4/1). Radioactivity in extracts and liquid traps was determined by LSC. The soil extracts were combined, concentrated, adjusted to pH 2 using HCl, and extracted with dichloromethane and/or ethyl acetate. The recoveries of partition into organo-soluble and aqueous residue were reported. The organo-soluble portion was concentrated, the aqueous residue was analysed without further work-up. The organic phase (after concentration) and aqueous phase were analysed by reversed phase HPLC. Ethanolamine traps were included for volatile organic compounds. Compound identification was by co-chromatography with unlabelled reference standards. Radioactivity in post-extraction solids (PES) was determined by combustion/LSC.

Results

Microbial activity of the test soil was confirmed at the start and the end of aerobic incubation by determining the microbial biomass using the fumigation/extraction method (see table B.8.1.1.1-07).

The results for the distribution and identification of radioactivity are given in Table B.8.1.1.1-08 to Table B.8.1.1.1-15. Total recovery of radioactivity ranged from 91 to 104% AR. In the three soils incubated at 20°C, the amount of extractable radioactivity decreased from 93-100% AR on day 0 to 40-76% AR on day 151, and PES increased from 0.5-3.5% AR on day 0 to a maximum of 23-37% AR on day 120-151. CO₂ was evolved from the soil to a maximum of 0.2-15% AR on day 151. In the sandy loam soil incubated at 10°C, the amount of extractable radioactivity decreased from 99% AR on day 0 to 81% AR on day 151, PES increased from 0.5% AR on day 0 to a maximum of 16% AR on day 151, and CO₂ was evolved from the soil to a maximum of 1.0% AR on day 151.

After 151 days, pyridaben had degraded to 17-59% AR in the three soils incubated at 20°C, and to 68% AR in the sandy loam soil incubated at 10°C. No metabolite accounted for >10% AR at any time. PB-7 was the only metabolite detected at >5% AR during at least two successive samplings, namely in the clay loam soil (plateau from day 29 onwards, maximum 8.5% AR). On a single occasion PB-4 reached a maximum level of >5% AR (5.1-5.5% AR) in the silt loam and the sand loam soil, and the sum of PB-22 and PB-14 (not separable by HPLC) in the clay loam soil (6.2% AR). These two metabolites in the remaining soils, and all other metabolites in all soils, were always <5% AR.

Table B.8.1.1.1-08 Distribution of radioactivity after incubation at 20°C of clay loam soil treated with [pyridazinone-3,6-14C] pyridaben at 0.51 mg/kg (% AR)

day	extractable					KOH ^(A)	PES	mass balance
	acetone/ H ₂ O	MeOH/ H ₃ PO ₃	total	organo- soluble	aque- ous			
0	99.9	na	99.9	97.1	2.8	na	0.5	100.4
7	91.8	na	91.8	86.8	3.3	1.5	6.1	99.3
14	87.3	0.9	88.2	80.2	4.0	3.6	9.0	100.7
29	79.8	1.5	81.3	70.0	6.2	5.5	10.7	97.6
60	70.0	3.1	73.1	63.3	8.3	6.1	17.4	96.5
90	56.1	2.2	58.3	44.2	9.0	10.3	25.7	94.1
120	38.8	8.7	47.5	43.4	5.7	12.8	31.0	91.3
151	38.5	1.8	40.3	33.6	6.6	14.9	37.1	92.4

na = not applicable

(A) Including RA in ethanolamine traps (max. 1.7% after 151 days).

Table B.8.1.1.1-09 Distribution of radioactivity after incubation at 20°C of silt loam soil treated with [pyridazinone-3,6-14C] pyridaben at 0.51 mg/kg (% AR)

day	extractable					KOH ^(A)	PES	mass balance
	acetone/ H ₂ O	MeOH/ H ₃ PO ₃	total	organo- soluble	aque- ous			
0	93.4	na	93.4	92.2	0.5	na	3.5	96.9
7	100.1	na	100.1	99.4	1.1	0.0	1.7	101.8
14	100.0	na	100.0	94.6	2.4	0.0	3.2	103.1
29	94.7	na	94.7	89.1	3.5	0.0	6.8	101.5
60	85.4	1.2	86.6	80.1	5.4	0.1	12.6	99.3
90	78.6	2.6	81.2	76.0	4.2	0.1	17.9	99.2
120	74.4	0.9	75.3	75.0	6.4	0.2	23.4	98.9
151	74.7	1.6	76.3	70.0	7.0	0.2	22.1	98.5

na = not applicable

(A) Including RA in ethanolamine traps (max. 0.1% after 151 days).

Table B.8.1.1.1-10 Distribution of radioactivity after incubation at 20°C of sandy loam soil treated with [pyridazinone-3,6-14C] pyridaben at 0.51 mg/kg (% AR)

day	extractable					KOH ^(A)	PES	mass balance
	acetone/ H ₂ O	MeOH/ H ₃ PO ₃	total	organo- soluble	aque- ous			
0	99.8	na	99.8	97.9	0.4	na	0.6	100.4
7	96.8	na	96.8	94.5	1.8	nd	3.1	99.8
14	94.3	na	94.3	88.9	3.6	0.2	6.4	100.9
29	84.3	2.2	86.5	80.0	6.1	0.5	11.3	98.4
60	76.4	4.9	81.3	70.4	5.4	1.5	18.0	100.7
90	66.6	2.0	68.6	58.7	4.5	1.7	28.2	98.5
120	65.1	1.0	66.1	53.8	7.6	1.9	29.0	97.0
151	60.4	2.1	62.5	53.0	9.9	2.0	30.4	94.9

na = not applicable; nd = not detected

(A) Including RA in ethanolamine traps (max. 0.1% after 151 days).

Table B.8.1.1.1-11 Distribution of radioactivity after incubation at 10°C of sandy loam soil treated with [pyridazinone-3,6-14C] pyridaben at 0.51 mg/kg (% AR)

day	extractable					KOH ^(A)	PES	mass balance
	acetone/ H ₂ O	MeOH/ H ₃ PO ₃	total	organo- soluble	aque- ous			
0	99.2	na	99.2	96.2	0.7	na	0.5	99.8
7	101.6	na	101.6	94.0	1.7	0.0	2.5	104.1
14	96.0	na	96.0	92.8	2.5	0.0	3.9	99.9
29	95.8	na	95.8	89.8	3.7	0.1	5.1	101.0
60	91.3	na	91.3	87.1	4.2	0.4	9.1	100.9
90	85.0	1.4	86.4	82.3	7.9	0.5	12.4	99.3
120	83.6	1.1	84.7	68.5	5.3	0.8	15.0	100.4
151	79.8	1.5	81.3	74.3	6.4	1.0	16.1	98.4

na = not applicable

(A) Including RA in ethanolamine traps (max. 0.3% after 151 days).

Table B.8.1.1.1-12 Identification of radioactivity after incubation at 20°C of clay loam soil treated with [pyridazinone-3,6-¹⁴C] pyridaben at 0.51 mg/kg (% AR)

day	pyridaben	PB-4	PB-7	PB-22/PB-14	P-16	P-14
0	96.6					
7	78.8	1.8	3.8			
14	69.5	0.9	5.8			
29	55.7	1.3	6.7	2.1	0.2	1.9
60	48.2	1.2	8.5	4.4	0.2	1.4
90	32.4	1.0	6.5	4.9	0.3	1.4
120	30.1	1.3	6.9	4.0	0.4	0.3
151	17.3	0.8	7.5	6.2	0.4	2.2

Empty cell means: not detected. Apart from compounds in above table, 9 unidentified fractions were detected, each $\leq 4.5\%$ AR at any time point. PB22 and PB-14 were not separated by HPLC.

Table B.8.1.1.1-13 Identification of radioactivity after incubation at 20°C of silt loam soil treated with [pyridazinone-3,6-¹⁴C] pyridaben at 0.51 mg/kg (% AR)

day	pyridaben	PB-4	PB-7	PB-22/PB-14	P-16	P-14
0	91.6					
7	96.1	1.2				
14	90.6	0.9	1.4			
29	83.6	1.4	2.3	0.6		
60	70.8	1.5	3.7	1.0		
90	65.4	2.4	4.0	1.6		
120	53.3	5.5	5.2	4.3	0.7	0.2
151	59	2.9	4.1	2.9		1.5

Empty cell means: not detected. Apart from compounds in above table, 5 unidentified fractions were detected, each $\leq 4.6\%$ AR at any time point. PB22 and PB-14 were not separated by HPLC.

Table B.8.1.1.1-14 Identification of radioactivity after incubation at 20°C of sandy loam soil treated with [pyridazinone-3,6-¹⁴C] pyridaben at 0.51 mg/kg (% AR)

day	pyridaben	PB-4	PB-7	PB-22/PB-14	P-16	P-14
0	97.1					
7	91.2	1.7	0.9			
14	84.6	1.2	2.1	0.1		
29	70.8	2.0	3.0	1.4		
60	57.1	3.2	4.2	1.7		
90	45.6	3.6	4.2	2.6	0.4	
120	40.4	3.9	4.3	2.1	0.5	1.2
151	36.7	5.1	2.9	4.1	0.4	1.8

Empty cell means: not detected. Apart from compounds in above table, 9 unidentified fractions were detected, each $\leq 5.1\%$ AR at any time point. PB22 and PB-14 were not separated by HPLC.

Table B.8.1.1.1-15 Identification of radioactivity after incubation at 10°C of sandy loam soil treated with [pyridazinone-3,6-14C] pyridaben at 0.51 mg/kg (% AR)

day	pyridaben	PB-4	PB-7	PB-22/PB-14	P-16	P-14
0	95.2	1.4				
7	92.2	1.3				
14	91.6	0.7	0.5			
29	86.9	0.5	1.1			
60	83.4	1.1	1.6			
90	78.2	1.2	1.7	0.3		
120	64.1	1.4	1.6	0.4	0.4	
151	68.2	1.7	2.2	1.1	0.3	

Empty cell means: not detected. Apart from compounds in above table, one unidentified fraction was detected, $\leq 0.2\%$ AR at any time point. PB22 and PB-14 were not separated by HPLC.

Degradation rates

DT50 values were calculated following the recommendations and procedures of the “Guidance document on estimating persistence and degradation kinetics from Environmental Fate studies on pesticides in EU registration” (SANCO/10058/2005 version 1.0). Calculations were based on the individual measurements and the time zero values for pyridaben were adjusted for % AR in PES. All calculations were performed with ModelMaker v 4.0 software (SFO = single first-order, FOMC = first-order multi-compartment, DFOP = Double-First-Order in Parallel mode).

Pyridaben

Endpoints for persistence

For persistence endpoints, SFO and FOMC were first run by the RMS for the data sets of all soils (M0 free, all data, no weighting). FOMC gave a better visual fit than SFO, and a lower error, except for the sandy loam incubated at 10°C, where SFO gave the better fit. There were no scientific grounds to justify data elimination, fixing of M0 or weighting. Therefore DFOP was run unmodified for the three soils incubated at 20°C, and this model gave the best fit for the clay loam and the sandy loam, but no adequate fit could be modelled for the silt loam. The persistence endpoints for the best fit model are presented in Table B.1.1.1-16.

Endpoints for modelling

The first run of the SFO for the data sets of both labels (M0 free, all data, no weighting) gave an acceptable fit, both visually and statistically. For the sandy loam soil incubated at 20°C, visual inspection of the graph and the residual plot indicated that degradation might be biphasic in this soil. Since 90% degradation was not reached within the study duration, DFOP was run for the sandy loam soil incubated at 20°C, and the fit was acceptable. Therefore in first instance the endpoint for modelling for this soil were taken from the slow phase of DFOP yielding a DT50 of 1104 days. However, after correspondence with the notifier, RMS reconsidered this fit and accepted the SFO fit yielding a DT50 of 95 days. The modelling endpoints are presented in Table B.1.1.1-16.

Table B.8.1.1.1-16 Half-lives for pyridaben in soil treated with [pyridazinone-3,6-14C] pyridaben at 0.51 mg/kg and incubated in the dark at 10°C or 20°C and 40% MWHC.

soil	parameter for	kinetics	quality of fit	χ^2 (err)	r^2	DT50	DT90
clay loam	persistence modeling	DFOP	Best fit	4.15	0.99	50	241
		SFO	Acceptable	8.19	0.95	65	-
silt loam	persistence modeling	FOMC	Best fit	3.32	0.96	199	4522
		SFO	Acceptable	3.87	0.94	171	-
sandy loam (20°C)	persistence modeling	DFOP	Best fit	1.13	1.00	80	2057
		SFO	Acceptable	4.19	0.98	95	-
sandy loam (10°C)	persistence modeling	SFO	Best fit	2.66	0.93	279	926
		SFO	Acceptable	2.66	0.93	279	-

PB-4

PB-4 is a minor metabolite. The FOCUS guidance document states that deriving reliable kinetics endpoints may still be possible for minor metabolites, especially if there is a clear formation and decline pattern. This is not the case for PB-4. The levels observed for this metabolite are low ($\leq 5.5\%$ AR), with associated high relative experimental error. The data set for the silt loam soil was considered to be not acceptable for fitting since there is doubt about the validity of the high value for PB-4 after 120 days (possible artefact), when the value for parent pyridaben is also be of doubtful quality (possible outlier).

The only other data set with a measured concentration of this metabolite exceeding 5% AR was the sandy loam soil incubated at 20°C, but in this soil there was a monotonous increase of the metabolite levels during the study, with no decline apparent. The lack of accuracy was moreover demonstrated by attempting a fitting procedure for this data set. For parent, the best fit model was DFOP for both labels. A run with parent DFOP and PB-4 SFO gave for both labels an acceptable visual fit for the metabolite, but the error (23%) exceeded 15%, and the rate constant was negative ($-0.00027 \text{ day}^{-1}$). The error term for the rate constant was 0.0035 day^{-1} , hence a factor of 13 larger than the estimated value. The large error term indicates that the estimates are not reliable.

PB-7

PB-7 is also a minor metabolite. The data set for the silt loam soil was considered to be not acceptable for fitting since there is doubt about the validity of the high value for PB-7 after 120 days (possible artefact), when the value for parent pyridaben is also be of doubtful quality (possible outlier). Only in the clay loam soil, levels of PB-7 were also $>5\%$ AR, but in this soil there was a monotonous increase of the metabolite levels during the study, with no decline apparent. In addition, there are too many uncertainties to construct a suitable simple (e.g. not over-parameterised) model for fitting PB-7. PB-7 is a secondary metabolite, which is likely to be formed by oxidation of the primary metabolite PB-9 (see study 1). PB-9 was also included in the set of reference compounds for the present study, but was not detected at any time point. This may be due to the fact that the rate of degradation of PB-9 is much higher than its rate of formation from parent pyridaben. This might suggest that a simple model may be constructed, which assumes that PB-7 is formed

in a single step from parent pyridaben. This simple model however would ignore the possibility that the intermediate and fast disappearing PB-9 is not only converted into PB-7, but also into other material, e.g. bound residues. Ignoring the latter step would lead to overestimation of the rate of degradation of PB-7 by the model, which is not acceptable. Inclusion of PB-9 would lead to an over-parameterised model. Therefore no fitting was undertaken.

Conclusions

In three soils treated with PYR-labelled pyridaben and incubated at 20°C, PES increased to a maximum of 23-37% AR on day 120-151 and CO₂ was evolved from the soil to a maximum of 0.2-15% AR on day 151. In a sandy loam soil incubated at 10°C, PES increased from 0.5% AR on day 0 to a maximum of 16% AR on day 151, and CO₂ was evolved from the soil to a maximum of 1.0% AR on day 151. Pyridaben degraded with DT50 values (persistence) of 50-199 days (3 soils at 20°C) and 279 days (1 soil, 10°C) and with DT50 values (modelling) of 65-1104 days (3 soils at 20°C) and 279 days (1 soil, 10°C). No metabolite accounted for >10% AR at any time. PB-7 was the only metabolite detected at >5% AR during at least two successive samplings, namely in the clay loam soil (plateau from day 29 onwards, maximum 8.5% AR). PB-4 was detected at low levels (≤5.5% AR). DT50 values for PB-4 and PB-7 could not be estimated.

Guidelines & Limitations

1. The dose (0.51 mg/kg) was 3.7 times the maximum calculated PEC_{soil} (0.139 mg/kg), but the NOEC of pyridaben for effects on soil microbial processes was 8.0 mg a.s./kg soil (see B.9.8.2).
2. The following information was not available from the report: a record of measured temperatures; HPLC column recovery.
3. 3. Compound identity was based on a single analytical principle (RP HPLC, one solvent system). The notifier has stated that the study was conducted according to the SETAC Guidelines (1995). Confirmation of identity of the test substance by a second analytical method is not specifically required by this guideline. The reversed phase HPLC gradient method gave reproducible results and a good separation of pyridaben and its metabolites. The reversed phase gradient HPLC method used in this study was the same as that used in the sediment/water study, where the identity of pyridaben was confirmed by LC-MS in selected samples. This is considered acceptable by RMS.
4. Acceptability: the study is acceptable.

B.8.1.1.2 Anaerobic studies**STUDY 1****Characteristics**

reference	: O'Connor J., 1994 (IIA 7.1.1.1.2/01)	incubation time	: 30 d (aerobic) & 12 months (anaerobic)
year of execution	: 1991-1992	nominal concentration	: 1 mg/kg
GLP statement	: yes	temperature	: 25°C
guideline	: EPA 162-2	DT50	: see results
test substance	: a) [benzene-U-14C]-pyridaben, lot no. CP-1007. b) [pyridazinone-3,6-14C]-pyridaben, lot no. CP-1008.	metabolites	: see results
purity	: a) chemical purity not reported, radiochemical purity 98.25%. b) chemical purity not reported, radiochemical purity 97.51%.	acceptability	: not acceptable
soils	: sandy loam, sand		

Study design

Aliquots of 50 g dry weight portions of a California sandy loam or a Florida sand soil (2 mm sieved, soil properties see Table B.8.1.1.2-01) were adjusted to 75% FC and incubated in the dark at 25±2°C for up to 49 days to stimulate microbial activity. At the end of this period, [Benzene-U-14C]-pyridaben and [pyridazinone-3,6-14C]-pyridaben were applied separately in acetone to the surface of the 50 g dry weight soil portions at a rate of 1 mg/kg. Treated soil was incubated under a continuous humid air supply in the dark for 30 days.

Soils were then incubated under a continuous humid nitrogen supply for 6 months followed by periodic nitrogen purging for the next 6 months. It is stated in the report that the temperature was maintained at 25±2°C throughout the experiment. The soil moisture content was maintained at 75% of 0.33 bar throughout the study. CO₂ was trapped in 0.1M KOH (2 traps) and volatile organic compounds in 2-ethoxyethanol (1 trap).

In addition, 50 g samples of both soils, which had been pre-incubated at 25±2°C, were sterilised by autoclaving at 121°C, treated with BEN- or PYR-pyridaben at 1 mg/kg, and incubated as for the non-sterilised samples.

Table B.8.1.1.2-01 Properties of study soil

Parameter	California sandy loam	Florida sand
% sand/silt/clay ^(A)	73/20/7	89/7/4
Texture ^(A)	sandy loam	sand
pH (H ₂ O)	7.3	5.5
% organic carbon	0.31	0.69
CEC (meq/100 g)	8.2	3.0
% moisture (0.33 bar)	8.8	8.2
microbial biomass (start) ^(B)	45.8 mg C/100 g (⇔ 15% of OC content)	23.6 mg C/100 g (⇔ 3.4% of OC content)

(A) USDA classification system.

(B) By fumigation/extraction method.

Duplicate (non-sterilised soil) or single (sterilised soil) samples were analysed on days 0 and 30 of aerobic incubation and after 1, 6, 9 and 12 months of anaerobic incubation. Trapping solutions were also sampled and replaced on these days, and in addition on intermediate time points. Soil samples were soxhlet extracted with acetone/water (4/1), followed by soxhlet extraction with MeOH/phosphoric acid (4/1). Radioactivity in extracts and liquid traps was determined by LSC. The soil extracts were combined, concentrated to aqueous and analysed by LSC. Following addition of water, the residues were partitioned into dichloromethane.

The soils were extracted and the radiolabelled material quantified within 1 month after sampling. Generally, the chromatographic analysis of radiolabelled components in the organo-soluble extracts had started within 1 month. The organic phase (after concentration) and aqueous phase were analysed by LSC and the organic phase also by normal phase TLC. Compound identification was by co-chromatography with unlabelled reference standards. Radioactivity in PES was determined by combustion/LSC. Samples of PES from the 6 months anaerobic sampling underwent extraction for fractionation into fulvic acid, humic acid and humin.

Results

The results for the distribution of radioactivity are given in Table B.8.1.1.2-02&-04&-06&-08 (non-sterile soil) and Table B.8.1.1.2-03&-05&-07&-09 (sterile soil). The % recovery of RA was calculated by RMS from the sum of KOH, PES and soil extracts, since the concentrated aqueous extract concentrations are not reliable as they far exceed the water solubility of pyridaben (up to 1221 ng/ml). The mass balance was <90% in 4 out of 8 experiments on day 0 of aerobic incubation, and in all experiments on day 30. On day 30, the mass balance ranged between 48 and 81% AR, with 6 out of 8 values <80% AR. Extractability on day 0 was <90% AR in 6 out of 8 experiments (versus 100-108% AR in the previous two studies).

Table B.8.1.1.2-10 presents a summary of the average recovery of concentration (calculated by the RMS) for the combined aqueous soil extracts and the water-dichloromethane partitioning step of the soil extracts after concentration. Recovery values outside the 90-110% range are highlighted in bold print. In the majority of cases, recovery was <90% or >100%, and in many cases the deviations from the acceptable 90-110% range were high. Table B.8.1.1.2-10 also presents an overview of the variation between the amount of radioactivity determined in the extracts of duplicate incubates of non-sterile soil. The variation was high, with CV values >20% in the majority of cases. This variation is probably caused by the aqueous sample extracts, due to the low water solubility of pyridaben. This suggests that the observed inhomogeneity is due to the fact that part of the pyridaben is not in solution. In case the recovery is based on the initial soil extracts, variable recoveries during sample processing occur to a lesser extent than when the concentrated aqueous extracts are used.

The results for the identification of radioactivity are given in Table B.8.1.1.2-11&-13&-15&-17 (non-sterile soil) and Table B.8.1.1.2-12&-14&-16&-18 (sterile soil). The results in Table B.8.1.1.2-11 to Table B.8.1.1.2-

18 were the average of all TLC measurements (two systems, for each system data for linear analysis and autoradiography), calculated by the RMS from the reported raw data (the report presented no tables with overall mean results for compound identification).

The results of this study are considered to be insufficiently reliable (low day 0 extractability, low mass balances during the aerobic incubation, recovery for concentration of soil extracts and for partitioning steps outside the 90-110% range, high variation between duplicate samples).

Table B.8.1.1.2-02 Distribution of radioactivity (% AR, duplicate means) after incubation at 25°C of non-sterilised California sandy loam soil treated with [pyridazinone-3,6-14C] pyridaben at 1 mg/kg (aerobic for 30 days, anaerobic for 12 months)

	aerobic		anaerobic			
	day 0	day 30	1 month	6 months	9 months	12 months
KOH		0.5	0.7	0.8	0.8	0.8
ethoxyethanol						
soil extracts	88.9	54.7	88.0	67.6	66.2	65.6
organo-soluble	79.1	68.7	74.3	51.7	47.5	57.4
water soluble	0.8	5.7	9.0	4.3	4.0	3.0
PES	1.9	15.0	17.9	29.4	26.7	29.3
mass balance	90.8	70.2 ^(A)	107	97.8	93.7	95.7

(A) Sum of RA in KOH, PES and soil extracts, calculated by RMS; the reported value of 89.9% was based on the sum of RA in KOH, PES and organo-soluble and water soluble radioactivity.

Table B.8.1.1.2-03 Distribution of radioactivity (% AR) after incubation at 25°C of sterilised California sandy loam soil treated with [pyridazinone-3,6-14C] pyridaben at 1 mg/kg (aerobic for 30 days, anaerobic for 12 months)

	aerobic		Anaerobic			
	day 0	day 30	1 month	6 months	9 months	12 months
KOH			0.1	0.1	0.1	0.1
ethoxyethanol						
soil extracts	86.8	44.9	92.5	87.5	88.6	81.7
organo-soluble	79.3	75.8	90.0	65.1	81.0	40.4
water soluble	3.8	0.6	0.9	0.9	0.9	0.8
PES	1.1	2.7	6.4	11.1	8.5	9.7
mass balance	87.9	47.6 ^(A)	99	98.7	97.2	91.5

(A) Sum of RA in KOH, PES and soil extracts, calculated by RMS; the reported value of 79.1% was based on the sum of RA in KOH, PES and organo-soluble and water soluble radioactivity.

Table B.8.1.1.2-04 Distribution of radioactivity (% AR, duplicate means) after incubation at 25°C of non-sterilised California sandy loam soil treated with [Benzene-U-14C] pyridaben at 1 mg/kg (aerobic for 30 days, anaerobic for 12 months)

	aerobic		Anaerobic			
	day 0	day 30	1 month	6 months	9 months	12 months
KOH		7.4	9.4	9.8	9.8	9.8
ethoxyethanol		0.1	0.1	0.1	0.1	0.1
soil extracts	86.6	60.7	71.4	58.0	58.9	49.2
organo-soluble	82.9	65.1	68.0	34.3	48.8	52.5
water soluble	3.2	2.8	0.5	1.3	0.8	0.6
PES	1.0	11.2	14.8	21.9	21.2	17.8

mass balance	87.6	79.3 ^(A)	95.7	89.8	90	76.9
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(A) Sum of RA in KOH, PES and soil extracts, calculated by RMS; the reported value of 86.6% was based on the sum of RA in KOH, PES and organo-soluble and water-soluble radioactivity.

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Table B.8.1.1.2-05 Distribution of radioactivity (% AR) after incubation at 25°C of sterilised California sandy loam soil treated with [Benzene-U-14C] pyridaben at 1 mg/kg (aerobic for 30 days, anaerobic for 12 months)

	aerobic		anaerobic			
	day 0	day 30	1 month	6 months	9 months	12 months
KOH						
ethoxyethanol						
soil extracts	89.4	73.8	99.2	92.3	89.3	90.5
organo-soluble	82.5	86.4	93.6	63.2	75.9	70.7
water soluble	0.7	2.0	0.2	1.6	0.1	
PES	1.0	1.5	1.5	7.9	6.1	6.3
mass balance	90.4	75.3 ^(A)	101	100	95.4	96.8

(A) Sum of RA in KOH, PES and soil extracts, calculated by RMS; the reported value of 89.9% was based on the sum of RA in KOH, PES and organo-soluble and water soluble radioactivity.

Table B.8.1.1.2-06 Distribution of radioactivity (% AR, duplicate means) after incubation at 25°C of non-sterilised Florida sand soil treated with [pyridazinone-3,6-14C] pyridaben at 1 mg/kg (aerobic for 30 days, anaerobic for 12 months)

	aerobic		anaerobic			
	day 0	day 30	1 month	6 months	9 months	12 months
KOH						
ethoxyethanol						
soil extracts	91.8	58.0	97.6	85.2	92.6	92.7
organo-soluble	82.3	79.3	96.1	82.1	88.7	99.4
water soluble	0.6	0.6	2.6	2.3	0.7	0.7
PES	1.0	5.3	2.8	4.4	5.2	5.2
mass balance	92.8	63.3 ^(A)	100	89.6	97.8	97.9

(A) Sum of RA in KOH, PES and soil extracts, calculated by RMS; the reported value of 85.2% was based on the sum of RA in KOH, PES and organo-soluble and water soluble radioactivity.

Table B.8.1.1.2-07 Distribution of radioactivity (% AR) after incubation at 25°C of sterilised Florida sand soil treated with [pyridazinone-3,6-14C] pyridaben at 1 mg/kg (aerobic for 30 days, anaerobic for 12 months)

	aerobic		anaerobic			
	day 0	day 30	1 month	6 months	9 months	12 months
KOH						
ethoxyethanol						
soil extracts	93.7	79.1	100.0	90.7	94.7	93.2
organo-soluble	73.7	85.5	96.2	91.3	90.2	78.3
water soluble	4.6	2.2	3.6	3.1	0.2	0.2
PES	0.6	2.2	0.9	2.8	3.9	4.2
mass balance	94.3	81.3 ^(A)	101	93.5	98.6	97.4

(A) Sum of RA in KOH, PES and soil extracts, calculated by RMS; the reported value of 89.9% was based on the sum of RA in KOH, PES and organo-soluble and water soluble radioactivity.

Table B.8.1.1.2-08 Distribution of radioactivity (% AR, duplicate means) after incubation at 25°C of non-sterilised Florida sand soil treated with [Benzene-U-14C] pyridaben at 1 mg/kg (aerobic for 30 days, anaerobic for 12 months)

	aerobic		Anaerobic			
	day 0	day 30	1 month	6 months	9 months	12 months
KOH		1.4	1.5	1.6	1.6	1.7
ethoxyethanol						
soil extracts	88.9	71.0	93.3	80.1	86.5	88.0
organo-soluble	74.0	78.3	96.4	85.6	79.6	84.5
water soluble	6.0	2.6	0.2	0.2	0.1	0.2
PES		2.5	2.9	3.8	6.8	3.9
mass balance	88.9	74.9 ^(A)	97.7	85.5	94.9	93.6

(A) Sum of RA in KOH, PES and soil extracts, calculated by RMS; the reported value of 84.8% was based on the sum of RA in KOH, PES and organo-soluble and water soluble radioactivity.

Table B.8.1.1.2-09 Distribution of radioactivity (% AR) after incubation at 25°C of sterilised Florida sand soil treated with [Benzene-U-14C] pyridaben at 1 mg/kg (aerobic for 30 days, anaerobic for 12 months)

	aerobic		anaerobic			
	day 0	day 30	1 month	6 months	9 months	12 months
KOH						
ethoxyethanol						
soil extracts	68.4	74.7	101.0	96.2	92.3	91.7
organo-soluble	79.4	79.1	98.3	85.2	87.4	135.0
water soluble	1.8	5.7	0.1	7.7	0.2	0.3
PES		0.7	2.0	0.7	2.7	1.9
mass balance	81.2	75.4 ^(A)	103.0	96.9	95.0	93.6

(A) Sum of RA in KOH, PES and soil extracts, calculated by RMS; the reported value of 85.5% was based on the sum of RA in KOH, PES and organo-soluble and water-soluble radioactivity.

Table B.8.1.1.2-10 Variation between replicates, and average recovery of radioactivity (%) after concentration of soil extracts and after partitioning of concentrated soil extracts

soil	sterility	label	parameter	aerobic, day:		anaerobic, month:			
				0	30	1	6	9	12
California	non-sterile	PYR	recovery concentr. extracts	128	63	89	85	85	41
			CV replicates ^(A)	21	12	22	25	80	107
			recovery partition ^(B)	90	136	95	83	78	92
			recovery partition ^(C)	80	234	123	115	143	397
	sterile	PYR	recovery concentr. extracts	285	223	100	76	18	34
			recovery partition ^(B)	96	170	98	75	92	50
			recovery partition ^(C)	34	76	98	100	512	147
	non-sterile	BEN	recovery concentr. extracts	81	96	61	64	54	32
			CV replicates ^(A)	45	4	29	4	177	239
			recovery partition ^(B)	99	112	96	61	84	108
			recovery partition ^(C)	162	120	135	98	351	917
	sterile	BEN	recovery concentr. extracts	77	42	96	71	24	10
			recovery partition ^(B)	93	120	95	70	85	78
			recovery partition ^(C)	121	286	99	98	350	789
Florida	non-sterile	PYR	recovery concentr. extracts	138	146	77	102	23	47
			CV replicates ^(A)	1	5	9	6	41	32
			recovery partition ^(B)	90	138	101	99	97	108
			recovery partition ^(C)	65	97	140	101	340	282
	sterile	PYR	recovery concentr. extracts	178	42	50	106	29	47
			recovery partition ^(B)	84	111	100	104	95	84
			recovery partition ^(C)	47	263	200	98	327	179
	non-sterile	BEN	recovery concentr. extracts	115	61	74	108	16	49
			CV replicates ^(A)	14	50	104	6	47	21
			recovery partition ^(B)	90	114	104	107	92	96
			recovery partition ^(C)	86	254	243	95	746	173
	sterile	BEN	recovery concentr. extracts	113	109	28	92	40	49
			recovery partition ^(B)	119	114	97	97	95	148
			recovery partition ^(C)	105	104	353	105	235	300

(A) Calculated as $100 \cdot SD/X$, where SD = standard deviation of replicate % AR found in concentrated soil extracts, and X is the minimum replicate value.

(B) Calculated as $100 \cdot (A+B)/C$, where A is the % AR in concentrated dichloromethane extract, B is the % AR in the aqueous phase, and C is % AR in the soil extract prior to concentration.

(C) Calculated as $100 \cdot (A+B)/C$, where A is the % AR in concentrated dichloromethane extract, B is the % AR in the aqueous phase, and C is % AR in the soil extract after concentration.

Table B.8.1.1.2-11 Identification of radioactivity (% AR) after incubation at 25°C of non-sterilised California sandy loam soil treated with [pyridazinone-3,6-14C] pyridaben at 1 mg/kg (aerobic for 30 days, anaerobic for 12 months)

compound	aerobic		anaerobic			
	day 0	day 30	1 month	6 months	9 months	12 months
PB-14		1.4	2.1			
PB-7		2.2	2.2		1.5	0.7
PB-5		1.0				0.8
PB-4	1.5	4.0	3.3	1.5	1.3	1.5
Pyridaben	76.0	61.9	64.7	46.9	41.6	50.5
polar					1.7	2.3
PB-11/PB-7				1.1		
PB-11/PB-5		1.3				
PB-7/PB-4		6.7				

Empty cell: not detected. Compounds separated by / could not be separated in one TLC system.

Table B.8.1.1.2-12 Identification of radioactivity (% AR) after incubation at 25°C of sterilised California sandy loam soil treated with [pyridazinone-3,6-14C] pyridaben at 1 mg/kg (aerobic for 30 days, anaerobic for 12 months)

compound	aerobic		anaerobic			
	day 0	day 30	1 month	6 months	9 months	12 months
PB-9						6.9
PB-4	1.1	1.4	1.5	1.3	1.5	
Pyridaben	76.7	77.8	86.7	58.9	77.7	30.0
polar						0.6
PB-12/PB-9		1.3	1.3			
PB-11/PB-9		1.4	1.4	2.9		7.6
PB-11/PB-3	1.3					
PH-4/PB-2		2.5		1.7		

Empty cell: not detected. Compounds separated by / could not be separated in one TLC system.

Table B.8.1.1.2-13 Identification of radioactivity (% AR) after incubation at 25°C of non-sterilised California sandy loam soil treated with [Benzene-U-14C] pyridaben at 1 mg/kg (aerobic for 30 days, anaerobic for 12 months)

compound	aerobic		anaerobic			
	day 0	day 30	1 month	6 months	9 months	12 months
PB-14		1.4	1.4			
PB-7	1.3					
PB-5						1.4
PB-4	1.5	1.9				
B-1					1.5	
Pyridaben	79.4	58.1	59.1	31.3	44.0	47.4
polar		0.6	0.6			
PB-12/PB-7/B-7/B-3		4.8				
PB-12/PB-7/B-7				0.6		
PB-12/B-7		2.4	2.4			
PB-11/B-7						1.3
PB-7/B-7					0.9	
PB-7/B-11						1.2
PB-7/PB-4		3.8	3.8			
PB-4/B-3		3.3	3.2	0.9		
PB-4/B-1					1.6	0.6

Empty cell: not detected. Compounds separated by / could not be separated in one TLC system.

Table B.8.1.1.2-14 Identification of radioactivity (% AR) after incubation at 25°C of sterilised California sandy loam soil treated with [Benzene-U-14C] pyridaben at 1 mg/kg (aerobic for 30 days, anaerobic for 12 months)

compound	aerobic		anaerobic			
	day 0	day 30	1 month	6 months	9 months	12 months
PB-11				0.6	1.5	
PB-5				0.6		1.4
PB-4	1.2	1.1	1.1			
B-1		0.7	0.7			
Pyridaben	80.2	86.9	90.5	59.8	70.9	67.6
PB-11/PB-9/PB-5					1.4	
PB-7/PB-4/B-7		1.0				
PB-4/PB-3/B-1					0.8	
PB-4/B-3				1.0		
PB-4/B-1						

Empty cell: not detected. Compounds separated by / could not be separated in one TLC system.

Table B.8.1.1.2-15 Identification of radioactivity (% AR) after incubation at 25°C of non-sterilised Florida sand soil treated with [pyridazinone-3,6-14C] pyridaben at 1 mg/kg (aerobic for 30 days, anaerobic for 12 months)

compound	aerobic		anaerobic			
	day 0	day 30	1 month	6 months	9 months	12 months
PB-4	1.7	3.0	3.1	2.8	2.4	3.2
PB-3						0.8
P-2						0.5
D-2	0.6					
Pyridaben	78.7	80.5	91.4	76.9	84.3	92.2
polar				0.5	0.5	
PB-7/PB-4		3.9				
PB-4/P-2				3.8		
PB-3/P-2						1.8

Empty cell: not detected. Compounds separated by / could not be separated in one TLC system.

Table B.8.1.1.2-16 Identification of radioactivity (% AR) after incubation at 25°C of sterilised Florida sand soil treated with [pyridazinone-3,6-14C] pyridaben at 1 mg/kg (aerobic for 30 days, anaerobic for 12 months)

compound	aerobic		anaerobic			
	day 0	day 30	1 month	6 months	9 months	12 months
PB-14		0.8				
PB-9						0.6
PB-4	1.1	1.2	0.6	0.5	0.5	1.8
P-3	0.7					
D-2	0.6					
Pyridaben	70.7	82.5	94.4	84.8	87.5	74.1
polar		1.1		0.6		
PB-12/PB-11/PB-9		3.8				
PB-12/PB-9/P-3				2.0		
PB-11/PB-9		3.0		2.4		
PB-7/PB-5		1.1				
PB-4/P-2		1.1	1.1	0.7	0.9	
PB-3/P-2						0.7

Empty cell: not detected. Compounds separated by / could not be separated in one TLC system.

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Table B.8.1.1.2-17 Identification of radioactivity (% AR) after incubation at 25°C of non-sterilised Florida sand soil treated with [Benzene-U-14C] pyridaben at 1 mg/kg (aerobic for 30 days, anaerobic for 12 months)

compound	aerobic		anaerobic			
	day 0	day 30	1 month	6 months	9 months	12 months
PB-11						1.1
PB-7	1.2					
PB-5				0.7		
PB-4	1.1	2.8			1.8	
D-2						2.3
Pyridaben	71.0	79.8	90.6	81.0	75.3	78.2
PB-12/PB-7		0.6	0.6			
PB-11/PB-7						0.7
PB-4/B-3		3.7	3.1	2.6		
PB-4/B-1					2.4	0.8

Empty cell: not detected. Compounds separated by / could not be separated in one TLC system.

Table B.8.1.1.2-18 Identification of radioactivity (% AR) after incubation at 25°C of sterilised Florida sand soil treated with [Benzene-U-14C] pyridaben at 1 mg/kg (aerobic for 30 days, anaerobic for 12 months)

compound	aerobic		anaerobic			
	day 0	day 30	1 month	6 months	9 months	12 months
PB-11					0.7	3.8
PB-7	0.6					
PB-4	0.6	1.2	1.8			
B-11				1.1		
B-3						1.0
D-2						1.9
Pyridaben	76.7	82.0	91.9	82.2	83.5	82.5
PB-12/PB-11/PB-9/PB-5					0.6	
PB-12/B-3		1.0				
PB-11/PB-9		2.4	3.6			
PB-7/B-11						3.9
PB-4/B-3				1.0		
PB-4/B-1					0.8	0.5

Empty cell: not detected. Compounds separated by / could not be separated in one TLC system.

Conclusions

No conclusions may be drawn. The results are considered to be insufficiently reliable (low day 0 extractability, low mass balances during the aerobic incubation, recovery for concentration of soil extracts and for partitioning steps outside the 90-110% range, high variation between duplicate samples).

Guidelines & Limitations

1. The dose (1 mg/kg) was 7.2 times the maximum calculated PEC_{soil} (0.139 mg/kg). This might have caused an effect on the soil microflora, but since the NOEC of pyridaben for effects on soil microbial processes was 8.0 mg a.s./kg soil (see B.9.8.2), it can be assumed that soil processes are not inhibited.

2. Following storage of the field collected soil at 4°C for 2-3 months, soil samples (50 g) were pre-incubated under aerobic conditions for up to 49 days. This period of 49 days is considered to be unnecessarily long, and may have lead to less than optimal soil microbial activity at the start of incubation. The notifier states that soil microbial biomasses at the time of dosing were 45.8 and 23.6 mg C/100 g for the California sandy loam and Florida sand respectively. This corresponds to a microbial biomass as a % of OC content of 14.8 and 3.4 % respectively. As this is above the OECD 307 trigger of at least 1% of the total organic carbon, the soil can be considered viable at the start of the test. This is considered acceptable by RMS.
3. Metabolite percentage values were normalised to 100%, based on the % of total area (linear analyser) or the % of total % AR in all spot scrapings (autoradiography). The total recovery from the TLC plates was however not reported. The notifier provided an example calculation showing that the integration of the peak area for the major peak (pyridaben; PB-1) represented 85.92% of the total radioactivity on the TLC plate for that sample, and that value was used to calculate the level (%) of pyridaben remaining in the soil. The linear analysis and autoradiography/LSC analysis provided good comparison for the determination of the level of pyridaben in this sample. This demonstrates the effectiveness of the TLC plate scraping process in removing the radiolabelled material that was applied and chromatographed for this sample – the “normalisation” process thus provides an accurate quantification of pyridaben and its metabolites. This explanation is considered acceptable by RMS.
4. No evidence was provided that for the autoclaved soil sterile conditions were maintained during the study. It was not reported that the addition of water to maintain soil humidity was performed under sterile conditions, and that the air and the nitrogen passed through the incubates were sterile.
5. Compound identity was based on a single analytical principle (normal phase TLC).
6. Acceptability: the study is not acceptable (low day 0 extractability, low mass balances during the aerobic incubation, recovery for concentration of soil extracts during both the aerobic as well as the anaerobic phase and for the partitioning steps outside the 90-110% range, high variation between duplicate samples).

B.8.1.1.3 Soil Photolysis

STUDY 1

Characteristics

reference	:	O'Connor J., 1995 (IIA 7.1.1.1.2/02)	incubation time	:	30 d, 12 hr dark-light cycle
year of execution	:	1993	nominal concentration	:	1 mg/kg
GLP statement	:	yes	temperature	:	25°C
guideline	:	EPA 161-3	light intensity	:	425 W/m ² (290-800 nm)
test substance	:	a) [benzene-U-14C]-pyridaben, lot no. CP-1007; b) [pyridazinone-3,6-14C]-pyridaben, lot no. CP-1008.	DT50	:	14 d (summer, 40°N)
purity	:	a) chemical purity not reported, radiochemical purity 98.65%; b) chemical purity not reported, radiochemical purity 97.37%.	metabolites	:	PB-22
soil	:	sandy loam	acceptability	:	Acceptable

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Study design

Aliquots of 5 g dry weight portions of a California sandy loam soil (2 mm sieved, soil properties see Table B.8.1.1.3-01) were dispensed into glass dishes to a depth of about 10 mm and adjusted to 75% FC. [Benzene-U-14C]-pyridaben and [pyridazinone-3,6-14C]-pyridaben were applied separately in acetone to the surface of the 5 g dry weight soil portions at a rate of 1 mg/kg. Treated soil was incubated at 25±1°C for up to 30 days, either in the dark, or in a Heraeus Suntest unit under irradiation by a Xenon light source (equipped with filter with cut-off at 290 nm) in a 12 hour dark/light cycle. The light intensity was adjusted to 425 W/m² at the start of irradiation. Humid air was supplied to irradiated samples on one occasion each day for between 5 and 50 minutes. The dark samples were incubated under a continuous humid air supply. It was reported that the soil moisture content was maintained at 75% FC throughout the study. CO₂ was trapped in 1M KOH (1 trap) and volatile organic compounds in 20% ethanolamine (1 trap).

Table B.8.1.1.3-01 Properties of study soil

Parameter	California sandy loam
% sand/silt/clay ^(A)	67/25/8
Texture ^(A)	sandy loam
pH (H ₂ O)	8.2
% organic carbon	0.58
CEC (meq/100 g)	5.3
% moisture (0.33 bar)	15.06

(A) USDA classification system.

Duplicate samples were analysed on day 0 and on day 5, 12, 20 and 30 (irradiated samples) and on day 12 and 30 (dark samples). Trapping solutions were also sampled and replaced on these days, and in addition on intermediate time points. Soil samples were soxhlet extracted with acetone/water (4/1), followed by soxhlet extraction with MeOH/phosphoric acid (4/1). Radioactivity in extracts and liquid traps was determined by LSC. The soil extracts were combined, concentrated to aqueous and analysed by LSC. Following addition of water, the residues were partitioned into dichloromethane. The organic phase (after concentration) and aqueous phase were analysed by LSC. Radioactivity in PES was determined by combustion/LSC. Samples of PES from the irradiated samples (day 12 and 30) and from dark samples (day 30) from both labels underwent extraction for fractionation into fulvic acid, humic acid and humin. After concentration, residues in the organic and aqueous phases were quantified by normal phase TLC, with confirmation of identity by reversed phase HPLC. Compound identification was by co-chromatography with unlabelled reference standards.

Results

The results for the distribution of radioactivity are given in Table B.8.1.1.3-02&03. Ranges given here are for both radiolabels unless indicated otherwise. The mass balances were acceptable ((90-99% AR). Extractability decreased from 98-99% AR on day 0 to 50-57% AR on day 30 in irradiated samples, but to only 77-84% AR in dark samples. Formation of PES was higher in irradiated than in dark samples (after 30 days 28-31% and 9.7% AR, respectively). PES of day 12 and 30 irradiated samples and day 30 dark samples consisted of 8-13% humic acid, 5-9% fulvic acid and 52-68% humin (range for both labels). Volatile

radioactivity (probably CO₂) was higher in irradiated than in dark samples (after 30 days 4.6 and 1.2% AR, respectively, for PYR-label and 11.5 and 6.2% AR, respectively, for BEN-label).

The results for the identification of radioactivity (Table B.8.1.1.3-04&05) were the average of all TLC measurements (two systems, for each system data for linear analysis and autoradiography), calculated by the RMS from the reported raw data (the report presented no tables with overall mean results for compound identification). The identity of pyridaben in all samples and of several metabolites (D-1, PB-22 and PB-14 in irradiated samples, PB-4 in irradiated and dark samples) was confirmed by HPLC. Degradation of pyridaben was enhanced by irradiation: levels of pyridaben decreased from 90-92% AR on day 0 to 22-26% AR in irradiated samples, but to only 58-62% AR in dark samples. The main photoproduct was PB-22, which was formed at much higher levels in irradiated samples (9.8-13.0% AR between day 12 and 30) than in dark samples ($\leq 1.1\%$ AR). A multitude of other tentatively identified degradation products was detected in irradiated samples, which were not found in dark samples, but their levels never exceeded 4.1% AR (PYR-label) or 3.6% AR (BEN-label). Unidentified fractions of polar origin material in irradiated samples never exceeded 1.7% AR (PYR-label) or 5.1% AR (BEN-label).

Metabolites that may require further consideration.

Under laboratory conditions (12 hours illumination per day at an intensity approximately equal to that of average midsummer sunlight), the first order photolytic DT50 (25°C) of pyridaben was 16 days, and the environmental DT50 (25°C) for photolysis (midsummer, 40°N) was 14 days (see below). The photolytic rate of degradation of pyridaben hence significantly exceeds that of aerobic microbial and chemical degradation determined in study 1 and 2 of section B.8.1.1.1 (DT50 persistence (SFO, 20°C) 132/181 days in one soil (study 1), and 50, 199 and 80 days (study 2)). In the above study, the metabolite PB-22 was detected at levels up to 13.0% AR in irradiated samples, but only at low levels in dark samples ($\leq 1.1\%$ AR). In study 1 of section B.8.1.1.1, PB-22 was also detected, but never exceeded 1.2% AR. In study 2, PB-22 and PB-14 were analysed together (not separable on TLC), but the sum of the two never exceeded 6.2% AR, and their maximum formation occurred late during incubation (levels of PB-14/PB-22 up to day 30 were $\leq 2.1\%$ AR). It is likely therefore that PB-22 may be formed in soil due to photolysis under practical use conditions at levels $>10\%$ AR. It is proposed that PB-22 is a metabolite that may require further consideration.

Table B.8.1.1.3-02 Distribution of radioactivity (% AR, duplicate means) after incubation at 25°C of California sandy loam soil treated with [pyridazinone-3,6-14C] pyridaben at 1 mg/kg under irradiated and dark conditions

fraction	dark & irr. day 0	irradiated, day				dark, day	
		5	12	20	30	12	30
KOH ^(A)		0.6	1.7	2.8	4.6	0.4	1.2
soil extracts	98.7	85.1	71.4	61.4	57.3	93.3	84.3
organosoluble	93.1	81.3	67.6	54.0	55.4	86.6	72.7
water soluble	0.4	2.9	4.8	4.7	5.7	4.4	7.9
PES	0.1	10.3	21.1	29.5	30.6	3.8	9.7
mass balance	98.8	96.0	94.2	93.7	92.5	97.5	95.2

(A) Including RA in ethanolamine traps, max. 0.1% AR and 0% AR on day 30 in irradiated and dark samples, respectively.

Table B.8.1.1.3-03 Distribution of radioactivity (% AR, duplicate means) after incubation at 25°C of California sandy loam soil treated with [benzene-U-14C] pyridaben at 1 mg/kg under irradiated and dark conditions

fraction	dark & irr. day 0	irradiated, day				dark, day	
		5	12	20	30	12	30
KOH ^(A)		2.5	5.2	7.6	11.5	2.3	6.2
soil extracts	98.0	77.6	65.1	55.3	50.2	90.1	77.2
organosoluble	93.5	77.3	60.8	52.6	44.0	83.6	74.7
water soluble		0.6	0.8	1.1	0.9	0.2	0.8
PES	0.1	12.1	21.2	27.2	27.9	4.4	9.7
mass balance	98.1	92.2	91.5	90.1	89.6	96.8	93.1

(A) Including RA in ethanolamine traps, max. 1.6% AR and 1.1% AR on day 30 in irradiated and dark samples, respectively.

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Table B.8.1.1.3-04 Identification of radioactivity (% AR, duplicate means) after incubation at 25°C of California sandy loam soil treated with [pyridazinone-3,6-14C] pyridaben at 1 mg/kg under irradiated and dark conditions

fraction	dark & irr. day	irradiated, day				dark, day	
	0	5	12	20	30	12	30
pyridaben	90.4	62.4	40.6	24.4	25.8	77.9	58.0
PB-3		0.8	0.6		0.7		0.5
PB-4	1.2	2.2	2.4	1.2	1.8	3.1	5.0
PB-5					0.5	1.2	
PB-11				3.1	1.1		
PB-12				0.6	0.7		
PB-22		6.8	13.0	9.8	11.0		1.0
P-16							3.0
P-2		1.8	1.4	1.3	1.5		1.3
P-1			4.1	0.7	0.7		
D-1		0.6	0.5				
polar	1.2	1.0	1.3	1.6	1.7	2.0	1.5
PB-22/PB-14/P-14				8.1^(A)	7.0		
PB-21-PB-19		1.4	1.0		0.9		
PB-21/PB-19/D-3/D-2		1.0			0.7		
PB-21/D-3/D-2			1.4	0.5			
PB-21/D-2					0.6		
PB-18/PB-15/PB-3			1.5				
PB-15/P-5			0.7				
PB-14/P-14		1.1	0.9^(A)				
PB-12/PB-11				1.7			
PB-12/PB-11/PB-9		3.0					
PB-12/P-1				0.6	0.8		
PB-11/PB-9		0.6					
PB-11/PB-7				2.0	6.1		
PB-7/PB-5				0.9	1.6		
PB-5/P-2			0.8				
PB-5/PB-3				0.9	1.0		
PB-5/PB-4							5.7
PB-4/P-2			1.8	2.2	2.1		1.3
PB-3/P-2		1.4	2.2				
unidentified			0.5			1.1	

Empty cell: not detected. Compounds separated by / could not be separated in one TLC system. Bold print: identity confirmed by HPLC.

(A) Identity confirmed by HPLC for PB-14.

Table B.8.1.1.3-05 Identification of radioactivity (% AR, duplicate means) after incubation at 25°C of California sandy loam soil treated with [benzene-U-14C] pyridaben at 1 mg/kg under irradiated and dark conditions

fraction	dark & irr., day	irradiated, day				dark, day	
	0	5	12	20	30	12	30
pyridaben	91.9	62.9	38.9	28.4	22.2	76.7	62.1
PB-3			2.3		1.4		
PB-4		2.0	3.6				
PB-5							
PB-7			0.9	0.9		0.6	2.1
PB-11		0.5					
PB-12			0.6				
PB-14							1.4
PB-15	0.6	0.7	1.3				
B-3			0.5				
polar		2.2	0.7				
PB-22/PB-14/P-14						0.6	1.1
PB-22/PB-14		2.7	8.2^(B)	13.6	9.8^(B)		
PB-21-PB-19/B-5/D-2		1.0	1.3				
PB-21/B-5/D-2		2.0					
PB-19/B-5/D-2					1.0		
PB-19/D-1		1.5^(A)					
PB-18/PB-3/B-1			0.5				
PB-15/B-3	1.0						
PB-15/PB-11/PB-9/B-1		0.5	0.5	1.1			
PB-15/PB-3/B-3		0.1	1.8		0.5		
PB-15/PB-3/B-1				0.8	0.9		
PB-12/PB-9				0.7			2.9
PB-12/PB-11/PB-9		0.9	1.3				
PB-12/PB-11/PB-9/PB-7				1.2			
PB-12/PB-11/PB-9/PB-7/PB-5					2.2		
PB-11/PB-9			0.5				
PB-11/PB-9/PB-7						3.9	
PB-11/PB-7				0.8			
PB-7/PB-5					1.0		
PB-7/PB-5/PB-4/B-3							6.6
PB-4/B-3		1.5	2.4	2.3	2.2	2.7^(C)	5.8^(C)
PB-3/B-1		0.5					
unidentified		0.6	1.3	0.5	5.1		

Empty cell: not detected. Compounds separated by / could not be separated in one TLC system. Bold print: identity confirmed by HPLC.

(A) Identity confirmed by HPLC for D-1.

(B) Identity confirmed by HPLC for PB-22.

(C) Identity confirmed by HPLC for PB-4.

Degradation rates

Rate constants and DT50 values of pyridaben were calculated by SFO (single first-order) following the recommendations and procedures of the "Guidance document on estimating persistence and degradation kinetics from Environmental Fate studies on pesticides in EU registration" (SANCO/10058/2005 version 1.0). Calculations were based on the mean values for replicates (individual values were not readily available from

the report) and the time zero values for pyridaben were adjusted for % AR in PES. All calculations were performed with ModelMaker v 4.0 software.

The fit for the dark samples was excellent. No good fit was estimated for the day 0-30 data sets of the irradiated samples for both labels: the day 30 data point in particular deviated from the fitted curve. The author of the report argued that the two phase degradation was due to incorporation of pyridaben into the soil, and its varying degrees of irradiance at different positions within the soil matrix. This explanation is not acceptable for the soil treated with PYR-label, since no decline at all was observed, whereas degradation in the dark samples did occur during the last 10 study days. In addition, no explanation was provided in the report concerning the cause of incorporation of pyridaben (e.g., watering, watering followed by mixing etc.). A clearly better fit was obtained when the day 0-20 data instead of the day 0-30 data of irradiated samples were modelled (PYR-label: R^2 0.998 versus 0.953, err (χ^2) 1.62 versus 10.14; BEN-label: R^2 0.988 versus 0.971, err (χ^2) 3.94 versus 7.12). The rate constants for the irradiated samples in the table below are therefore based on the day 0-20 data. This table also presents the rate constants and DT50 values for photolysis under study conditions and in the environment (midsummer, 40°N). All rate constants and DT50 values were calculated by the RMS.

Table B.8.1.1.3-06 Rate constants and half-lives for pyridaben in Florida sandy loam treated with [benzene-U- ¹⁴C] pyridaben or [pyridazinone-3,6-¹⁴C] pyridaben at 1 mg/kg and incubated in the dark or under Xenon light (12 h dark/12 h light) at 25°C and 75% FC.

label	parameter	value	χ^2 (err)	r^2	DT50 (25°C)
PYR	$k_{\text{irradiated}}$ (day ⁻¹)	0.0666085	1.62	0.998	10.4
	k_{dark} (day ⁻¹)	0.0146477	2.29	0.994	47.3
	$k_{\text{photolysis}}$ (day ⁻¹) ^(A)	0.0519608			13.3
	$k_{\text{environment}}$ (day ⁻¹) ^(B)	0.0496440			14.0
BEN	$k_{\text{irradiated}}$ (day ⁻¹)	0.0651327	3.94	0.988	10.6
	k_{dark} (day ⁻¹)	0.0131893	1.02	0.995	52.6
	$k_{\text{photolysis}}$ (day ⁻¹) ^(A)	0.0519434			13.3
	$k_{\text{environment}}$ (day ⁻¹) ^(B)	0.049627335			14.0

(A) $k_{\text{photolysis}} = k_{\text{irradiated}} - k_{\text{dark}}$.

(B) $k_{\text{environment}} = k_{\text{photolysis}} * A / B * 0.75$, where A is the midday light intensity (297.5-800 nm) in summer at 40°N (541.40 W/m², calculated by RMS from data in OPPTS 835.2210), B is the measured light intensity (290-800 nm) in the test (425 W/m²), and 0.75 is a factor accounting for the diurnal variation of natural sunlight (calculation according to point 17 of draft OECD guideline for phototransformation of chemicals on the soil surface of January 2002).

Conclusions

DT50 photolysis (environment, 20°C) 14 days. Metabolite that requires further consideration: PB-22.

Guidelines & Limitations

1. Metabolite percentage values were normalised to 100%, based on the % of total area (linear analyser) or the % of total % AR in all spot scrapings (autoradiography). The total recovery from the TLC plates was however not reported. HPLC analysis gave lower values than TLC analysis. The recovery from the HPLC column however was also not reported.

2. The following information was not available from the report: frequency and method of moisture maintenance of dark and irradiated samples during the test; the exact place where the light intensity was measured (should be at the level of the sample, at representative places); the light intensity at the end of irradiation (only a measurement at the start was given).
3. Soil samples not analysed immediately after collection were kept at -20°C for an unspecified period. The duration of storage and data on storage stability of the main components of the soil residue was not available.
4. Dark and irradiated samples were not incubated under exactly identical conditions, apart from the light regime. Humid air was supplied to irradiated samples on one occasion each day for between 5 and 50 minutes, but the dark samples were incubated under a continuous humid air supply. This may have affected moisture maintenance, but evaluation was hampered by the lack of information on methods to maintain moisture (see comment 2).
5. Acceptability: the study is acceptable.

B.8.1.2 Field studies (Annex IIA 7.1.1.2.2; Annex IIIA 9.1.1.2)

B.8.1.2.1 Terrestrial field dissipation studies

STUDY 1

Characteristics

reference	:	Wilson A., 2003 (IIA 7.1.1.2.2/01)	location	:	Denmark (2X), Spain (2X)
year of execution	:	2001-2002	dose	:	250-300 g a.s./ha (1X)
GLP statement	:	yes	residues	:	pyridaben, P-14, P-16
guideline	:	SETAC (1995), BBA IV, 4-1	DT50	:	pyridaben: 31 & 36 days (Denmark), 5.0 & 128 days (Spain)
test substance	:	Pyridaben 750 g as/kg WP, lot no. OAJ 030.	metabolites	:	<0.01 mg/kg
purity	:	76.5% pyridaben	acceptability	:	Acceptable for pyridaben, not acceptable for P-14 and P-16
soils	:	sand, sandy loam (2X), clay loam,			

Study design

A terrestrial field soil dissipation study was conducted to determine the residues of pyridaben and the metabolites P-14 and P-16 following spraying of Pyridaben 750 g as/kg WP on bare soil at two locations in Denmark (trial 1 & 2) and two in Spain (trial 3 & 4), with a single spring application for trials 1-3 (nominal dose 250 g a.s./ha) or a single autumn application (nominal dose 300 g a.s./ha) for trial 4. Each trial site had one non-treated control plot and two replicated treated plots (120-138 m² each). The properties of the 0-20 cm segment and the application details are shown in Table B.8.1.2-01 below. The applied rate was verified by analysis of pyridaben deposited on five spray deposition cards placed across each plot just prior to application. No irrigation was applied during the trial, and plots were kept clear of vegetation by treatment with glyphosate. Meteorological conditions during the trial (max. and min. air temperature, humidity, daily

rainfall and average wind speed) were recorded at the trial site or from the nearest national weather station (see "Guidelines and Limitations", point 1).

Table B.8.1.2-01 Properties of study soils and application details

Trial number	1	2	3	4
Country	Denmark	Denmark	Spain	Spain
Location	Skarrild	Middelfart	Leon	Benimamet
Soil characteristics				
pH (KCl)	5.7	6.1	7.2	8.2
Organic carbon (%)	2.6	1.5	2.4	1.6
MWHC (%)	35.3	49.3	53.7	41.8
Sand 63 µm-2 mm (%)	93.94	49.51	30.76	33.48
Silt 2-63 µm (%)	4.12	26.92	36.92	42.61
Clay < 2 µm (%)	1.94	23.57	32.32	23.91
Classification (BBA)	Sand	Sandy loam	Clay loam	Sandy loam
Microbial biomass -1DAT	8.88 mg C/100 g (⇔ 0.3% OC)	44.72 mg C/100 g (⇔ 3.0% OC)	4.40 mg C/100 g (⇔ 0.2% OC)	49.04 mg C/100 g (⇔ 3.1% OC)
120 DAT	1.24 mg C/100 g (⇔ 0.05% OC)	1.64 mg C/100 g (⇔ 0.11% OC)	14.56 mg C/100 g (⇔ 0.6% OC)	61.96 mg C/100 g (⇔ 3.9% OC)
Application details				
Application date	9 April 2001	27 April 2001	26 April 2001	16 Oct 2001
Spray volume (L/ha)	400 & 393	401 & 393	403 & 405	391 & 401
Applied dose (g a.s./ha)	255.1 & 250.3	255.5 & 250.8	256.8 & 258.5	299.4 & 306.4

Twenty soil cores (0-30 cm depth) were removed from each plot pre first treatment (-0DAT), post first treatment (+0DAT) and at 8-10 time points up to 180-361 days. The cores were cut into 0-10, 10-20 and 20-30 cm segments and stored frozen (up to 4 months) until extraction and analysis. Pyridaben, P-14 and P-16 were analysed by the method evaluated in study 1 of section B.5.3. Pyridaben and the metabolites P-14 and P-16 were extracted from soil with water/acetone (1:4) followed by methanol/1N phosphoric acid (4:1). An aliquot of the combined extract was centrifuged and filtered prior to LC-MS analysis for P-14 and P-16 on a Phenomenex SAX column using matrix standards. Another aliquot of the initial extract was cleaned up on a C18 mini column followed by ENVI-Carb SPE clean-up, and analysed for pyridaben by LC-MS/MS. The validation provided in study 1 of section B.5.3 was sufficient to support and LOQ in soil of 0.01 mg/kg for all three analytes. In the present study, concurrent validation was provided for each analyte by analysis of untreated soil samples fortified at 0.02, 0.05 and 0.10 mg/kg, which was acceptable (all recoveries within 70-110% range). The LOD (as peak signal $\geq 3X$ baseline noise) was 0.001 mg/kg for pyridaben and 0.0025 mg/kg for P-14 and P-16.

Results

The mean measured residues on spray deposit cards represented 54-95% (mean 77%) of the nominal rates. This agrees reasonably well with the maximum measured concentration of pyridaben in soil, expressed as percentage of the nominal expected concentration (61-94%, mean 75%).

Residues of all analytes in all segments from the control plots during the entire study, from the treated plots prior to treatment, and from the 10-20 cm and 20-30 cm segments of the treated plots after application were below the quantifiable limit (<0.01 mg/kg). Residues of P-14 and P-16 were also below the quantifiable limit (<0.01 mg/kg) in the 0-10 cm segments of the treated plots at all samplings and locations, although these compounds were detected occasionally at levels <0.01 mg/kg. The reported results for detections of P-14 and P-16 were insufficiently detailed to correlate a particular detection with a certain sampling time and trial. Based on the maximum occurrence of the metabolite at all locations (8.1 and 3.3 µg/kg for P-14 and P-16 respectively), and the maximum measured concentration of parent pyridaben in each treated plot, the maximum occurrence of P-14 and P-16 would represent 7-10% and 3-4% of the applied amount of pyridaben (including corrections for differences in molecular mass between parent and metabolites). The accuracy of measurements below the LOQ however is uncertain, and the detections were not confirmed by a second analytical method.

Residues of pyridaben in the 0-10 cm segment of the treated plots are shown in Table B.8.1.2-02&03. Residues of pyridaben were 99-157 µg/kg on the day of treatment, respectively, and were detected up to 119-302 days after treatment.

Table B.8.1.2-02 Residues of Pyridaben (µg/kg) in bare field soil (0-10 cm) treated with Pyridaben 750 g a.s./kg WP at 0.25 kg a.s./ha (Denmark, spring application)

Denmark, trial 1, application on 9 April 2001				Denmark, trial 2, application on 27 April 2001			
DAT	Plot 2	Plot 3	Mean	DAT	Plot 2	Plot 3	Mean
0	110.3	124.4	117.4	0	136.1	157.4	146.8
3	101.7	101.9	101.8	3	78.5	103.1	90.8
8	128.8	91.3	110.1	6	75.6	65.3	70.5
15	93.7	97.5	95.6	13	62	51.7	56.9
28	51.3	55	53.2	26	52.3	65	58.7
60	22.8	36	29.4	60	47.5	43.8	45.7
88	29.9	26.2	28.1	90	29.5	38.1	33.8
121	20.7	20.6	20.7	119	19.8	14	16.9
183	15	15	15	181	<LOQ	<LOQ	<LOQ
301	13	12.4	12.7				
361	<LOQ	<LOQ	<LOQ				

<LOQ: <0.01 mg/kg

Table B.8.1.2-03 Residues of Pyridaben ($\mu\text{g/kg}$) in bare field soil (0-10 cm) treated with Pyridaben 750 g a.s./kg WP at 0.25-0.30 kg a.s./ha (Spain, spring & autumn application)

Spain, trial 1, application on 26 April 2001				Spain, trial 2, application on 16 Oct 2001			
DAT	Plot 2	Plot 3	Mean	DAT	Plot 2	Plot 3	Mean
0	106.9	148.1	127.5	0	99.4	124.1	111.8
4	78.2	76.7	77.5	3	137.7	98.7	118.2
7	49.1	50.6	49.9	8	85.6	87.8	86.7
14	24.3	20.8	22.6	14	95.8	85.5	90.7
29	21.7	26.6	24.2	28	75.3	98.3	86.8
60	20.3	<LOQ	12.7	62	77.8	93.5	85.7
89	12.9	12.7	12.8	91	86.2	76.4	81.3
119	13.9	12.7	13.3	122	54.3	81.6	68
180	<LOQ	11	<LOQ	182	22.6	31.3	27
				302	<LOQ	10.3	<LOQ

<LOQ: <0.01 mg/kg.

Degradation rates

DT50 values were calculated following the recommendations and procedures of the "Guidance document on estimating persistence and degradation kinetics from Environmental Fate studies on pesticides in EU registration" (SANCO/10058/2005 version 1.0). Calculations were based on the individual measurements. For values <LOQ it was not reported if these values were between LOQ and LOD. Therefore values <LOQ were set at $0.5 \times \text{LOQ}$ ($5 \mu\text{g/kg}$). All calculations were performed with ModelMaker v 4.0 software (SFO = single first-order, FOMC = first-order multi-compartment, DFOP = Double-First-Order in Parallel mode).

Endpoints for persistence

For persistence endpoints, SFO and FOMC were first run by the RMS (M0 free, all data, no weighting). FOMC gave a better fit than SFO in all cases, except for trial 4, where SFO and FOMC gave identical endpoints. There were no scientific grounds to justify data elimination, fixing of M0 or weighting. Therefore DFOP was run unmodified for the data sets of trials 1-3, and this model gave a better fit than FOMC for trials 2 and 3. The persistence endpoints are presented in Table B.1.2-04. For spring applications, DT50 and DT90 values were 5-36 and 98-186 days, respectively, and for the autumn application 128 and 424 days, respectively.

Endpoints for modelling

Endpoints for modelling may be calculated if the degradation rate does not include photolysis (see SANCO/10058/2005 version 1.0, point 9.1). Pyridaben however undergoes photolytic degradation on soil, at a rate which exceeds that for chemical and biological degradation (see section B.8.1.1.3). Therefore no attempt to derive modelling endpoints was undertaken.

Table B.8.1.2-04 Half-lives for pyridaben in field soils treated with Pyridaben 750 g a.s./kg WP at 0.25-0/30 kg a.s./ha

trial no.	parameter for	kinetics	quality of fit	χ^2 (err)	r^2	DT50	DT90
1	persistence	FOMC	best fit	9.28	0.94	31	186
2	persistence	DFOP	best fit	7.09	0.96	36	160
3	persistence	DFOP	best fit	7.58	0.96	5.0	98
4	persistence	SFO	acceptable	11.21	0.80	128	424

Conclusions

Following single treatment of bare soil at two locations in Denmark (trial 1 & 2) and two in Spain (trial 3 & 4), with a spring application for trials 1-3 (nominal dose 250 g a.s./ha) or an autumn application (nominal dose 300 g a.s./ha) for trial 4, residues of pyridaben, which were confined to the 0-10 cm segment, dissipated with DT50 and DT90 values of 5-36 and 98-186 days, respectively, for the spring applications, and 128 and 424 days, respectively, for the autumn application. Residues of P-14 and P-16 were always below the quantifiable limit (<0.01 mg/kg).

Guidelines & Limitations

1. The reporting of meteorological measurements was confined to graphs presenting the time course of the parameters that were monitored. Tabulated numerical results were not available. The origin of the meteorological data was not clarified in detail (not specified whether measured on site or obtained from a nearby weather station).
2. Soil samples were stored frozen for up to 4 months prior to extraction and analysis. Storage stability of pyridaben, P-14 and P-16 were not available in the report. It has been demonstrated however that pyridaben was stable in frozen field fortified soil dust for at least 7 months (study B.6.14.3-04), and in frozen sediment for 12 months (study B.9.2.2.14-01). This storage stability data is considered to be sufficient to accept the study results for pyridaben. Storage stability data are required however for P-14 and P-16 to accept the results for these compounds.
3. Acceptability: the study is acceptable for pyridaben, the study is not acceptable for P-14 and P-16 until the storage stability of P-14 and P-16 is addressed.

B.8.1.2.2 Soil residue studies

No studies were submitted. Planting of succeeding crops after treatment of citrus is not relevant, but succeeding crops may be planted in greenhouse or tunnel soil after treatment of tomato with pyridaben. In a study on uptake of succeeding crops, summarised in section B.7.9, however, the total extractable residue in succeeding crops, back-planted 30 and 240 days after 2 treatments of the soil with pyridaben at 0.75 kg a.s./ha, were always <0.05 mg eq./kg. The total dose in this study of 1.5 kg a.s./ha was applied to bare soil and is a factor of 6 higher than the dose in tomato (0.25 kg a.s./ha), which is applied to the plant canopy. Residues in succeeding crops planted after treatment of tomato in greenhouses are therefore anticipated to be negligible, and soil residue studies are hence not needed.

B.8.1.2.3 Soil accumulation studies

No studies were submitted. This data is not required since model calculations were performed in section B.8.3 to estimate the plateau concentrations in soil using the highest value of four available DT₅₀ (field) values.

B.8.1.3 Summary route and rate of degradation in soil**Aerobic degradation**

In laboratory studies on aerobic incubation of pyridaben at 20°C in four soils (pH 6.0-7.6, 0.8-3.8% oc), pyridaben degraded with DT₅₀ values of 50-199 days (persistence) and 65-1104 days (non normalised - modelling). DT₉₀ (persistence) values were 241-4522 days. During aerobic incubation of pyridaben at 10°C in one soil (pH 6.0, 0.8% oc), pyridaben degraded with a DT₅₀ value of 279 days (persistence & modelling) and a DT₉₀ (persistence) value of 926 days.

No metabolite accounted for >10% AR at any time. Metabolites exceeding 5% AR at 2 consecutive time points were PB-4 (maximum 7.6% AR) and PB-7 (maximum 8.5% AR). DT₅₀ values for PB-4 and PB-7 could not be estimated.

Table B.8.1.3-01 presents a summary of the available DT₅₀ (persistence) and DT₉₀ (persistence) values of pyridaben. Modelling DT₅₀ values are given in Table B.8.1.3-02. This table also presents moisture corrected DT₅₀ (modelling) values. Details on the methods to calculate moisture corrected DT₅₀ (modelling) values are presented in section B.8.6.3 (PEC_{GW} estimations), in particular Table B.8.6.3-02.

Table B.8.1.3-01 Laboratory DT₅₀ (persistence) and DT₉₀ (persistence) values for the aerobic degradation of pyridaben in soil, at 20°C

substance	soil	pH	% oc	moisture	dose (mg/kg)	temp. (°C)	DT ₅₀ (d)	DT ₉₀ (d)	kine-tics	DT ₅₀ (20°C, d)	DT ₉₀ (20°C, d)
Pyridaben	sandy loam ¹	6.2	2.4	40% mwhc	0.48	20	132	597	DFOP	132	597
	sandy loam ²	6.2	2.4	40% mwhc	0.50	20	181	778	DFOP	181	778
	mean									157	688
	clay loam	7.6	3.8	40% mwhc	0.51	20	50	241	DFOP	50	241
	silt loam	6.7	1.9	40% mwhc	0.51	20	199	4522	FOMC	199	4522
	sandy loam	6.0	0.8	40% mwhc	0.51	20	80	2057	DFOP	80	2057
	overall mean									121	1877

FOMC = First Order Multi-Compartment model

DFOP = Double-First-Order in Parallel model

¹ Treatment with benzene-labeled 14C-pyridaben

² Treatment with pyridazinone-labeled 14C-pyridaben

Table B.8.1.3-02 Laboratory DT₅₀ (modelling) values for the aerobic degradation of pyridaben in soil, at 20°C

substance	soil	pH	% oc	moisture	dose (mg/kg)	temp. (°C)	DT ₅₀ (d)	kine-tics	DT ₅₀ (20°C, d)	DT ₅₀ (20°C, d) pF 2/10 kPa ³
Pyridaben	sandy loam ¹	6.2	2.4	40% mwhc	0.48	20	135	SFO	135	
	sandy loam ²	6.2	2.4	40% mwhc	0.50	20	181	SFO	181	
	mean								158	106.4
	clay loam	7.6	3.8	40% mwhc	0.51	20	65	SFO	65	37.6
	silt loam	6.7	1.9	40% mwhc	0.51	20	171	SFO	171	104.1
	sandy loam	6.0	0.8	40% mwhc	0.51	20	95.0	SFO	95.0	63.9
	overall geometric mean									71.8

SFO = Single First-Order model

DFOP = Double-First-Order in Parallel model

¹ Treatment with benzene-labeled 14C-pyridaben² Treatment with pyridazinone-labeled 14C-pyridaben³ Details on the methods to calculate moisture corrected DT50 (modelling) values are presented in section B.8.6.3 (PEC_{GW} estimations), in particular Table B.8.6.3-2.

Mineralisation of pyridaben (Ben-label) in one soil at 20°C represented 18% AR on day 90 (21% AR on day 150). Mineralisation of pyridaben (Pyr-label) at 20°C amounted to 10% AR on day 90 (15% AR on day 151) in one soil, but in three other soils only 0.1-3.3% AR on day 90-120 (0.2-3.4% AR on day 150-151). Non-extractable residues however at 20°C never exceeded 70% AR: for pyridaben Ben-label (one soil) and Pyr-label (4 soils) 12-31% AR after 90-120 days, 13-37% AR after 150-151 days, max. 16-37% AR.

Aerobic metabolism of pyridaben proceeds due to microbial processes involving oxidation giving PB-4, PB-7 and PB-9. The sulphide and sulphoxide bridges are hydrolysed producing metabolites with either the benzene or the pyridazinone ring. PB-14 and PB-22 are formed by rearrangement. The ultimate breakdown products are CO₂ and non-extractable residues. Figure B.8.1.3-01 shows the proposed metabolic pathway with the main degradation products.

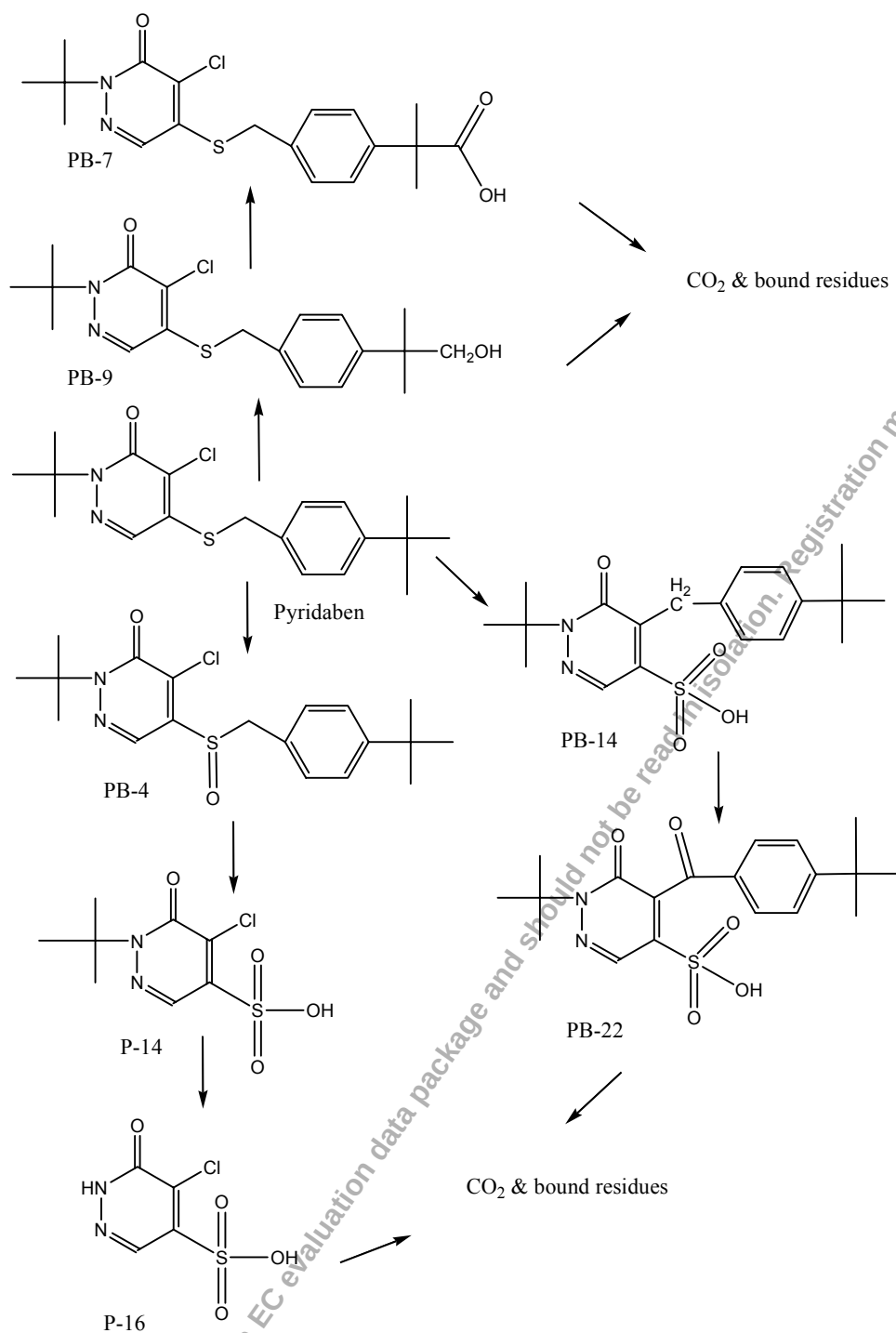


Figure B.8.1.3-01 Aerobic metabolic pathway of pyridaben in soil

Anaerobic degradation

No acceptable data on anaerobic degradation of pyridaben in soil were submitted. This information is not required because anaerobic conditions in soil treated with pyridaben are not anticipated, considering the proposed use pattern (greenhouse application and treatment of citrus).

Soil photolysis

Degradation of pyridaben in irradiated soil (≥ 290 nm & 425 W/m^2 , 12 hour dark-light cycles: DT₅₀ 11 days) was faster than in dark soil (DT₅₀ 50 days). The metabolite PB-22 was not detected in dark soil, but found at levels up to 13% AR in irradiated samples, and requires therefore further consideration.

Field dissipation trials

Following single treatment of bare soil at two locations in Denmark (trial 1 & 2) and two in Spain (trial 3 & 4), with a spring application for trials 1-3 (nominal dose 250 g a.s./ha) or an autumn application (nominal dose 300 g a.s./ha) for trial 4, residues of pyridaben were confined to the 0-10 cm segment and dissipated in trials 1, 2, 3 and 4, respectively, with DT₅₀ values of 31, 36, 5.0 and 128 days and DT₉₀ values of 186, 160, 98 and 424 days.

Data requirements

DT₅₀ values in three soils are required for the metabolite PB-7 and the photodegradate PB-22. For PB-4, an assumed worst-case DT₅₀ of 1000 days was used for the groundwater exposure assessment. The resulting PEC_{gw} values based on this unrealistic worst-case DT₅₀ value were below the trigger value of 0.1 µg/l for all scenarios. Therefore, no soil degradation study for PB-4 is necessary at this stage.

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

B.8.2.1 Batch sorption

B.8.2.1.1 Active substance

STUDY 1

Characteristics

reference	:	O'Connor J., 1992 (IIA 7.1.2/01)	soils	:	sand, sandy loam, silt loam (2X), clay loam
year of execution	:	1991-1992	concentrations	:	0.6, 2.0, 4.0 & 6.0 µg/L
GLP statement	:	yes	temperature	:	25°C
guideline	:	EPA N:163-1	K _{oc}	:	34858-87918 L/kg (4 soils)
test substance	:	[3,6-pyridazinone - ¹⁴ C] pyridaben; batch CP-1008	1/n	:	0.90-1.03 (4 soils)
purity	:	radiochemical purity 99.23%	acceptability	:	acceptable

Study design

A batch equilibrium adsorption/desorption study with five soils was conducted on pyridaben.

Aliquots (20 mL) of 0.01 N calcium chloride were added to centrifuge tubes containing samples (0.1 g dw for both California soils and Mississippi silt loam, 0.05 g for remaining two soils) of 2-mm sieved soils and re-equilibrated for 2 hours. Duplicate samples of each soil were then fortified with 10, 33, 66 or 100 µL of a solution of [3,6-pyridazinone-¹⁴C] pyridaben in acetone, to give concentrations of 0.60, 2.0, 4.0 and 6.0 µg/L. Treated slurries were shaken in capped glass centrifuge tubes at 25±1°C in the dark for 24-72 hours, depending on the soil type (required time to reach equilibrium was determined in a pre-test). At each concentration, four tubes without soil were included to check adsorption of pyridaben on glass walls. After equilibration, the supernatants were removed by centrifugation and analysed by LSC. Desorption was performed by adding the same volume of fresh 0.01 N calcium chloride solution to each tube and shaking the slurries for 24 hours in the dark at 25±1°C, after which the supernatant was removed by centrifugation and analysed by LSC. Stability of pyridaben was verified by TLC (2 solvent systems) of concentrated dichloromethane extracts of adsorption and desorption supernatants of the highest concentration samples. Desorbed soil from the two highest concentrations was extracted with acetone/water (4/1) and MeOH/1N phosphoric acid (4/1). After radioactivity measurements, the soil extracts were combined, concentrated and extracted with dichloromethane. The organic phase (after concentration) was analysed by TLC (2 solvent systems). Radioactivity in all residual soils was determined by combustion/LSC and mass balances were determined.

The amount of test substance adsorbed to glass was considerable (e.g., at 6 µg/L the average decline of the concentration in the liquid phase of 4 tubes without soil was 36%). In the report, the amount of test material adsorbed to soil was calculated as the difference between the amount of test substance present in equilibrium adsorption supernatants of tubes without soil and tubes with soil. This method of correction for the amount of test substance adsorbed to glass is not accurate, since the adsorption to glass in tubes with soil is presumably less than in tubes without soil. Since however this calculation method leads to underestimation of the amount of test substance adsorbed to soil (hence worst case), and taking into consideration the order magnitude of the calculated Koc values (>34000 L/kg), it is deemed acceptable. Freundlich adsorption isotherms were calculated by linear first order regression analysis.

Results

Mass balances ranged from 78-111% AR. The author of the report stated that the lower recoveries in certain tubes may be related to the very low amount of soil (50-100 mg) used for each tube, which leads to high variability during combustion analysis. This explanation is acceptable.

Pyridaben remained stable throughout the adsorption study. Only pyridaben was identified in organo-soluble extracts of adsorption supernatants and desorbed soils, whilst the extracted aqueous phases contained insignificant radioactivity, if any.

Desorption parameters were reported but not included in this summary. The Freundlich adsorption parameters were taken from the report and the results are given in Table B.8.2.1-01. Adsorption K_f values were 108-445 L/kg (1/n values 0.90-1.03 L/kg) in 4 of 5 tested soils, and corresponding adsorption K_{oc} values 34858-87918 L/kg. Sorption in these four soils showed a relationship to organic carbon content (linear regression analysis of the K_f values of these 4 soil versus % OC gave $r^2 = 0.76$), where no relationship was observed with clay or smectite content (r^2 0.08 and 0.04, respectively). The K_f value for the fifth tested soil, a Mississippi clay loam, was 6659 L/kg (1/n = 1.28), and sorption was much higher than expected on the basis of its organic carbon content. The author of the report argued that the high sorption may be explained by the high smectite content. This is supported by the high coefficient of correlation obtained for linear regression analysis of the K_f values of all 5 soil versus % smectite ($r^2 = 0.99$), where no correlation was observed between K_f values of all 5 soils and % oc ($r^2 = 0.06$), and a weaker correlation between K_f values of all 5 soils and % clay ($r^2 = 0.87$). For the Mississippi clay loam, therefore, no K_{oc} was calculated.

Table B.8.2.1-01 Adsorption and desorption coefficients for pyridaben

origin of soil	California	California	Mississippi	Mississippi	Florida
Texture ^(A)	sandy loam	silt loam	clay loam	silt loam	sand
%sand/silt/clay ^(A)	73/20/7	35/52/13	23/40/37	19/66/15	89/7/4
% smectite ^(B)	0.21	1.04	28.86	3.45	1.72
pH (H ₂ O)	7.3	7.0	6.2	5.2	5.5
% organic carbon ^(A)	0.31	0.42	0.31	0.25	0.69
CEC [meq/100 g]	8.2	23.2	26.6	4.1	3.2
Adsorption K _f [L/kg]	108	330	6659	220	445
Adsorption K _{oc} [L/kg]	34858	78683	— ^(C)	87918	64551
1/n	0.92	1.03	1.28	0.96	0.90
r ²	0.99	1.00	0.98	0.99	0.96

(A) According to USDA classification system.

(B) As % of total minerals.

(C) No K_{oc} calculated, sorption in this soil not related to oc content (see text for further detail).

Conclusions

Adsorption K_f values were 108-445 L/kg (1/n 0.90-1.03 L/kg) in 4 soils, and corresponding adsorption K_{oc} values 34858-87918 L/kg. Sorption in these four soils showed a relationship to organic carbon content, but not with clay or smectite content. The K_f value for the fifth tested soil, a clay loam, was 6659 L/kg respectively (1/n = 1.28), and sorption was much higher than expected on the basis of its organic carbon content. The high sorption in the latter soil may be explained by the high clay and in particular smectite content, and therefore no K_{oc} was calculated.

Guidelines & Limitations

No further comments.

B.8.2.1.2 Metabolites

No experimentally determined Koc values are available for metabolites of pyridaben. The notifier submitted Koc values of 71490 and 19330 L/kg for PB-4 and PB-7, respectively, which were estimated by the computer programme Syracuse (EPIWIN). These estimates are based on the non-dissociated state of the molecule. PB-4 will not undergo a charge transition in the environmentally relevant pH range (pH 4-9), and this compound will occur in the non-dissociated state in the environment. Comparison of the molecular structure of PB-4 and parent pyridaben suggests that the Koc values will be of comparable magnitude. For this reason, and because of the order of magnitude of the measured Koc values of pyridaben (mean 66503 L/kg, see section B.8.2.3) and PB-4 (71490 L/kg), the estimate for PB-4 is acceptable. PB-7 however has an acidic group and the pKa of this group (estimated by RMS using Pallas version 3.0) was 4.29. This indicates that in the environment (soil pH 4 or higher) PB-7 will occur partly or entirely in the dissociated state. The estimate of the Koc of PB-7 by EPIWIN, which is based on the non-ionised state of the molecule, is therefore not accepted.

B.8.2.2 Column leaching studies, leaching of aged residues and field leaching studies (Annex IIA 7.1.3.1, 7.1.3.2, 7.1.3.3; Annex IIIA 9.1.2.1, 9.1.2.2)

B.8.2.2.1 Column leaching

No studies were submitted. These studies are not required since adsorption constants are available for pyridaben and PB-4, and are requested for the soil metabolite PB-7 and the soil photodegrade PB-22.

B.8.2.2.2 Aged residue column leaching

No studies were submitted. These studies are not required since available and requested data on adsorption of pyridaben and metabolites of pyridaben are sufficient to address the risk for contamination of ground water.

B.8.2.2.3 Field leaching studies

No studies were submitted. These studies are not required.

B.8.2.3 Summary adsorption, desorption and mobility in soil

Batch sorption

Table B.8.2.3-01 presents a summary of the adsorption coefficients of pyridaben determined in batch sorption studies with 4 soils (pH 5.2-7.3, 0.25-0.69% organic carbon) at 25°C and a soil:water ratio of 1:20 or 1:40.

Table B.8.2.3-01 Adsorption coefficients of pyridaben from batch sorption studies

substance	Soil	pH	% oc	CEC (meq/100 g)	% clay	% smectite	K _F (L/kg)	1/n	K _{Foc} (L/kg)
Pyridaben	sandy loam	7.3	0.31	8.2	7	0.21	108	0.92	34858
	silt loam	7.0	0.42	23.2	13	1.04	330	1.03	78683
	silt loam	5.2	0.25	4.1	15	3.45	220	0.96	87918
	sand	5.5	0.69	3.2	4	1.72	445	0.90	64551
	mean							0.953	66503

The K_F value for the fifth tested soil, a clay loam, was 6659 L/kg (1/n = 1.28), and sorption was much higher than expected on the basis of its organic carbon content (0.31%). The high sorption in the clay loam soil may be explained by the high clay and in particular smectite content, and therefore no K_{oc} was calculated. No pH dependency of adsorption was observed.

Estimation methods

For the soil metabolite PB-4 a K_{oc} value of 71490 L/kg is available, which was estimated by the computer programme Syracuse (EPIWIN).

Non-aged column leaching

Data were not submitted and are not required.

Aged column leaching

Data were not submitted and are not required.

PEC_{gw} estimations

PEC_{gw} were estimated using FOCUS-PEARL version 2.2.2. PEC_{gw} were estimated for pyridaben and for PB-4. PEC_{gw} calculations could not be performed for the soil metabolite PB-7 (exceeding 2 x 5% at two consecutive time points in laboratory soil degradation studies) and the soil photodegradate PB-22. Since for these two compounds no reliable K_{oc} values were available, worst case modelling might be performed using K_{oc} = 0 L/kg. Since however no DT₅₀ values were available for PB-7 and PB-22, PEC_{gw} calculations were not made for these compounds.

In all FOCUS citrus scenarios and in the Dutch standard spring application scenario (representative for greenhouse application of tomato), estimated 80th percentile concentrations in groundwater were <0.001 µg/L for pyridaben and PB-4, and the groundwater trigger of 0.1 µg/L was not exceeded.

Data requirements

Koc values in three soils are required for the soil metabolite PB-7 and for the soil photodegradate PB-22.

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

Authorisation is requested for treatment of tomato (under glass) involving one application at 0.25 kg a.s./ha (Northern and Southern Europe, cGAP). Calculations were performed according to the methods outlined in 7617/VI/96 "Soil persistence models and EU registration" and Sanco/10058/2005 vs. 1 March 2005 "FOCUS degradation kinetics". Initial PEC_S values were calculated under the following assumptions: 80% crop interception (i.e. application at BBCH 40-89 in tomato); homogeneous distribution in the top 5 cm layer and a soil bulk density of 1.5 g/cm³. The requested application on citrus (Southern Europe only) involves a single application of 0.3 kg a.s./ha. For this application, initial PEC_S values were calculated under the following assumptions: 70% crop interception (all growth stages); homogeneous distribution in the top 5 cm layer and a soil bulk density of 1.5 g/cm³.

In the soil metabolism studies no metabolites >10% AP were observed.

Time weighted average (TWA) PECs values for pyridaben were based on the worst case DT₅₀ (field) value. The worst-case DT₅₀ (field) value was 36 days for Europe-N (obtained by DFOP; g = 0.515924, k₁ = 0.435319, k₂ = 0.00985516) and 128 days for Europe-S (obtained by SFO; k_p = 0.00543386).

For Europe-N, soil concentrations (at time t) were calculated as $PEC_t = PIEC \times (g \exp(-k_1 t) + (1-g) \exp(-k_2 t))$

TWA PECs values were using the formula below:

$$PEC_{S, twa} = (PEC_{S,0}/t) \{ (g/k_1) [1 - \exp(-k_1 t)] + [(1-g)/k_2] [1 - \exp(-k_2 t)] \}$$

For Europe-S, TWA PECs values for Southern Europe were calculated according to the formula:

$$PEC_{twa} = PEC_i \cdot (1 - e^{-k \cdot t}) / (k \cdot t), \text{ where:}$$

PEC_i is the initial PEC_S value;

$$k = \ln(2)/DT_{50};$$

t is the time period.

Table B.8.3-01 presents the substance parameters used for the calculations.

Table B.8.3-01 Substance parameters used for PECs estimations.

parameter	pyridaben
max. DT ₅₀ field (d)	36 (Europe-N) and 128 (Europe-S)
Kinetic model	DFOP (Europe-N) and SFO (Europe-S)
DFOP Model parameter g	0.515924
DFOP Model parameter k ₁	0.435319
DFOP Model parameter k ₂	0.00985516

Under the above assumptions, application of pyridaben (applied as a 75WP formulation according to the cGAP) will lead to the PECs values in Table B.8.3-02/03 (Tomatoes) and B.8.3-04 (Citrus).

Table B.8.3-02 Actual and TWA PECs (mg/kg) of pyridaben following application in tomato according to the cGAP in Northern Europe (1 x 0.25 kg a.s./ha).

days after treatment	pyridaben	
	actual	TWA
0	0.067	-
1	0.054	0.060
2	0.046	0.055
4	0.037	0.048
7	0.032	0.042
21	0.026	0.033
28	0.024	0.031
50	0.020	0.027
100	0.012	0.021

Table B.8.3-03 Actual and TWA PECs (mg/kg) of pyridaben following application in tomato according to the cGAP in Southern Europe (1 x 0.25 kg a.s./ha).

days after treatment	pyridaben	
	actual	TWA
0	0.067	-
1	0.066	0.066
2	0.066	0.066
4	0.065	0.066
7	0.064	0.065
21	0.060	0.063
28	0.057	0.062
50	0.051	0.058
100	0.039	0.051

Table B.8.3-04 Actual and TWA PECs (mg/kg) of pyridaben following application in citrus according to the cGAP in Southern Europe (1 x 0.3 kg a.s./ha).

days after treatment	pyridaben	
	actual	TWA
0	0.120	-
1	0.119	0.120
2	0.119	0.119
4	0.117	0.119
7	0.116	0.118
21	0.107	0.113
28	0.103	0.111
50	0.092	0.105
100	0.070	0.093

The worst-case $DT_{50\text{lab}}$ (20°C) for pyridaben is 199 days, and exceeds 60 days. The worst-case $DT_{50\text{field}}$ and $DT_{90\text{field}}$ for pyridaben (Southern Europe) were 128 and 424 days (SFO) and exceed 3 months and 1 year, respectively. Therefore, accumulation was calculated for pyridaben using the worst-case $DT_{50\text{field}}$ (128 d) and SFO kinetics. Average and maximum plateau values were calculated for pyridaben after yearly applications in tomato and citrus (according to the methods outlined in 7617/VI/96 "Soil persistence models and EU registration").

The time course of the pyridaben concentrations and plateau maximums in soil following ten yearly applications of pyridaben in tomato and citrus is illustrated in Figures B.8.3-01 and B.8.3-02. The actual, TWA, plateau maximum and plateau average concentrations are given in Table B.8.3-05.

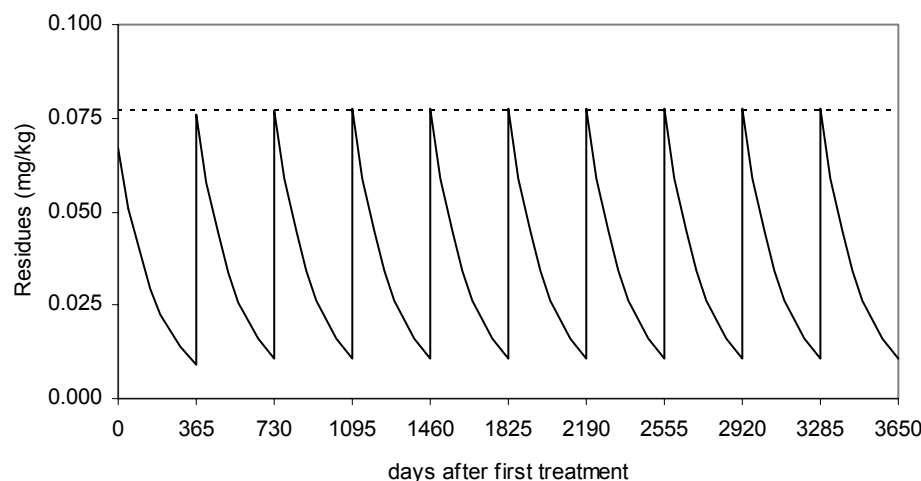


Figure B.8.3-01 Accumulation of pyridaben in soil after yearly applications of pyridaben in tomato.

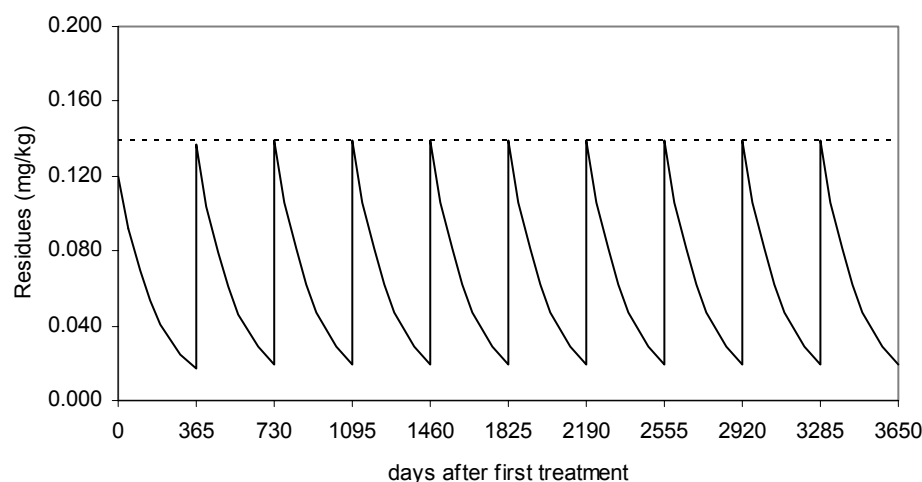


Figure B.8.3-02 Accumulation of pyridaben in soil (Southern Europe) after yearly applications of pyridaben in citrus.

Table B.8.3-05 Actual and TWA PECs (mg/kg) of pyridaben following the plateau maximum reached after 10 yearly pyridaben applications in tomato (Northern and Southern Europe) and citrus (Southern Europe).

Time after last application (days)	Tomato		Citrus	
	actual	TWA	actual	TWA
1	0.077	0.077	0.139	0.139
2	0.077	0.077	0.138	0.139
4	0.076	0.077	0.136	0.138
7	0.075	0.076	0.134	0.137
21	0.069	0.073	0.124	0.132
28	0.067	0.072	0.120	0.129
50	0.059	0.068	0.106	0.122
100	0.045	0.060	0.081	0.108
plateau maximum	0.077		0.139	
average plateau conc.	0.034		0.061	
plateau reached after	2 years (on the day of the 3 rd annual application)		2 years (on the day of the 3 rd annual application)	

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 Hydrolysis (Annex IIA 7.2.1.1)

Hydrolysis data are summarised in Volume 3, B.2. No hydrolytic degradation was observed after 30 days incubation at pH 5.0, pH 7.0 and pH 9.0 and 25°C.

B.8.4.2 Photolytic degradation (Annex IIA 7.2.1.2)**STUDY 1****Characteristics**

reference	: O'Connor J., 1995 (IIA 7.2.1.2/01)	incubation time	: 6 hours (final kinetic study 24 hours)
year of execution	: 1991-1995	nominal concn.	: 5 µg/L
GLP statement	: yes	temperature	: 25°C
guideline	: EPA N:161-2	DT50	: Under test conditions (Xenon light, 425 W/m ²), the DT50 (photolysis, 25°C) for pyridaben is 6.8 minutes.
test substance	: [benzene-U-14C]-pyridaben, lot no. CP-1007 & CP-1504; [pyridazinone-3,6-14C]-pyridaben, lot no. CP-1008 & CP-1505.	metabolites	: Major photodegradates W-1 (max. 16.1% AR, DT50 <1.5 hours) and B-3 (max. 27.2% AR, photolytically stable).
purity	: [benzene-U-14C]-pyridaben: chemical purity not reported, radiochemical purity ≥97.4%; [pyridazinone-3,6-14C]-pyridaben, chemical purity not reported, radiochemical purity ≥96.6%	acceptability	: acceptable
test system	: Aqueous photolysis (Xenon light)		

Study design

The aquatic photolysis of pyridaben was studied in a buffered aqueous solution at pH 7.

The design of the definitive studies was based on the results of a preliminary study conducted in test solution containing 1% of the photosensitiser acetone, where the level of pyridaben decreased from 70% AR at 0 hour to 6.7% AR after 3 hours of irradiation.

Preliminary kinetic study

Test solutions of sterilised 0.007 M aqueous buffer solutions (1% acetonitrile) at pH 7 containing [pyridazinone-3,6-14C]-pyridaben at 5 µg/L were dispensed into silanised and sterilised glassware, sealed and continuously irradiated by a Xenon light source (cut off at 290 nm, 425 W/m²) for up to 120 minutes at 25±1°C. Dark controls were held in a dark room at 25±1°C. Duplicate irradiated samples were taken after 0, 15, 30, 60, 90 and 120 minutes, and duplicate dark samples after 120 minutes. The samples were extracted with ethyl acetate after adjustment of the pH to 2. Radioactivity in the organic phases and the remaining aqueous layer was quantified by LSC. The organic extracts were analysed by TLC using two solvent systems using only pyridaben as reference standard.

Definitive photolysis study

Test solutions of sterilised 0.007 M aqueous buffer solutions (0.8% acetonitrile) at pH 7 containing [pyridazinone-3,6-14C]-pyridaben or [benzene-U-14C]-pyridaben at 5 µg/L were continuously irradiated by a Xenon light source (425 W/m²) for up to 120 minutes at 25±1°C. Dark controls were held in a dark room at 25±1°C. Single irradiated samples were taken after 0, 0.5, 2, 4 and 6 hours, and single dark samples after 6

hours. The samples were extracted with ethyl acetate (no adjustment of the pH). The aqueous phase (incompletely extracted because the pH was not adjusted to 2) underwent SPE extraction using Mega Bond Elut NH₂ cartridges. The non-retained filtrate was adjusted to pH 1 and extracted with ethyl acetate followed by concentration of the organic phase. Retained radioactivity was eluted with methanol/HCl (95/5 v/v) and concentrated. Radioactivity in the organic phases and the remaining aqueous layer was quantified by LSC. All extracts were analysed by reversed phase HPLC with radiodetection and/or fraction collection/LSC. In addition, the extracts were analysed by TLC using two solvent systems and a range of reference standards.

Sterility was not confirmed but this is unnecessary, since sterilised glassware was used, the duration of the experiments was short and the dark control showed insignificant degradation. The pH was measured at each sampling time and did not deviate significantly from the target (pH 7).

Study into identification of major photodegradates

An additional irradiation experiment was performed exposing test solutions of ¹⁴C-pyridaben of both labels in acetonitrile/water (50/50 v/v) at 250 µg/L to generate sufficient amounts of the photodegradates W-1, B-3 and D-1 for isolation and identification by spectroscopic methods (GC/MS or LC-MS).

Final kinetic study

This study was undertaken to accurately determine the photolysis rate of degradation of pyridaben and the photodegradate B-3. Test solutions of sterilised 0.007 M aqueous buffer solutions (0.04% acetone) at pH 7 containing [benzene-U-¹⁴C]-pyridaben at 5 µg/L were irradiated by a Xenon light source (425 W/m²) on a 12 hour light/dark cycle for up to 360 hours at 25±1°C. Dark controls were held in a dark room at 25±1°C. Single irradiated samples were taken after 0, 3, 5, 10, 15 and 60 minutes and after 4, 8 and 24 hours. The samples were extracted with ethyl acetate after adjustment of the pH to 1-2. Radioactivity in the organic phases and the remaining aqueous layer was quantified by LSC. The organic extracts were analysed by HPLC using pyridaben and B-3 as the only reference standard.

Note: It was stated in the report that after 120 hour and 360 hour samples were taken and analysed but results were not reported as the aim was achieved after 24 hours. The results for these samples however were the reason to conduct a supplementary study, which is summarised as study 2 in this section.

Results

Preliminary kinetic study

Recovery of radioactivity ranged between 77% AR and 87% AR. Since recovery in the other experiments was acceptable, and the concentration of pyridaben in the stock solutions used for preparing the test solutions was in agreement with the nominal concentration (98%), this is likely to be the result of a dosing error, and the results for pyridaben may be used for DT50 estimation.

Pyridaben represented 74% AR in the 0-hour sample, and 10%, 5.0%, 6.7%, 3.7% and 3.7% AR in irradiated solutions after 15, 30, 60, 90 and 120 minutes. Degradation in the dark control was insignificant as pyridaben represented 72% AR in the dark control at the end of the test (120 min). The DT50 for photolysis is well below 15 minutes. When assuming a first order degradation process, from the results of the 0-hour and 15-min samples a DT50 (photolysis, 25°C) of 5.2 minutes can be estimated (linear regression analysis of log-transformed concentrations versus time).

Definitive photolysis study

The results for the distribution of radioactivity are given in Tables B.8.4.2-01 (PYR-label) and -02 (BEN-label). The mass balances were 97-108% AR. Losses during work-up of the initial aqueous fraction were <10% AR. A fraction of 11% AR remained in the filtrate of SPE work-up after extraction of the 6-hour sample from PYR-label with ethyl acetate. Further work (identification) on this fraction is considered unnecessary, as the radioactivity level is only slightly higher than 10% AR (hence not "clear above 10% AR", a term used in the Guidance Document on Aquatic Ecotoxicology (SANCO/3268/2001 rev. 4 final of 17 October 2002)). Moreover, this very polar aqueous residue is likely to consist of more than one compound. All other not analysed but characterised fractions were $\leq 6.8\%$ AR.

Pyridaben was degraded into numerous compounds. The results for the identification of the major compounds ($\geq 10\%$ AR) are given in Table B.8.4.2-03 (PYR-label and BEN-label). These are the results obtained by HPLC analysis, which were confirmed by TLC analysis.

Pyridaben represented 95-106% AR in the 0-hour sample and 4.2-9.5% AR in irradiated solutions after 30 minutes. Degradation in the dark control was insignificant as pyridaben represented 87-99% AR in the dark control at the end of the test (6 hours). The DT50 for photolysis is well below 30 minutes. Assuming a first order degradation process, from the results of the 0-hour and 30-min samples a DT50 (photolysis, 25°C) for PYR- and BEN-label of 6.7 and 8.6 minutes, respectively, can be estimated (linear regression analysis of log-transformed concentrations versus time).

The major photodegradates were B-3 (maximum 27.2% AR) and W-1 (maximum 27.9% AR). W-1 was short-lived (DT50 less than 1.5 hours), but B-3 was stable. In addition, the following compounds were identified in test solutions of BEN- or PYR-label: P-14 (max. 3.8% AR); PB-14/PB-22 (not separated; max. 6.6% AR); PB-18/P-16 (not separated; max. 4.6% AR); P-1 (max. 3.1% AR); P-2 (max. 4.1% AR); PB-7 (max. 4.0% AR); PB-5 (max. 2.4% AR); PB-9 (max. 1.6% AR); PB-12 (max. 2.7% AR); PB-11 (max. 1.2% AR); PB-4 (max. 1.8% AR); PB-3 (max. 1.4% AR); D-3 (max. 1.4% AR); PB-19 (max. 0.8% AR); D-6 (max. 2.8% AR); D-1 (max. 4.7% AR). Numerous unidentified fractions were found, mostly at insignificant levels (individual fractions all well below 5% AR for PYR-label, and at the most 7.1% AR for BEN-label).

Study into identification of major photodegradates

The identity of W-1 was confirmed by LC-MS, and that of B-3 and D-1 by GC/MS.

Final kinetic study

Recovery of radioactivity ranged between 92% AR and 109% AR. Pyridaben represented 87% AR in the 0-hour sample, and 66%, 55%, 16%, 17% and 6.6% AR in irradiated solutions after 3, 5, 10, 15 and 60 minutes. The test solutions contained the photosensitiser acetone. However, the presence of 0.04% acetone was very low, and may be regarded as insufficient to act as a photosensitiser. The DT_{50} of pyridaben is 5.3 minutes, which is in the same range as the results from the preliminary kinetic test and the definitive photolysis test described above.

The levels of B-3 increased from 0.8% AR at 0 hour to 9.1% AR after 10 minutes, and they remained around that level (7.2-13% AR) until the end of the study (24 hours). This confirms the photolytic stability of B-3 already observed in the definitive study. The notifier has derived a DT_{50} value of 35 hours for B-3. However, this value is not considered to be adequate by RMS (only 3 points in time). The indicative DT_{50} furthermore confirms photolytic stability as it is longer than 30 hours. Therefore, the photometabolite B-3 will be regarded as photolytically stable. A degradation half-life value is not crucial, since the initial exposure concentration may be used for the aquatic risk assessment.

Overall DT_{50} values

The mean DT_{50} (photolysis, 25°C) for pyridaben from the above studies is $(5.2 + 6.7 + 8.6) / 3$ minutes = 6.8 minutes under test conditions (425 W/m²). The DT_{50} for W-1 is <1.5 hours under test conditions (425 W/m²). B-3 is photolytically stable ($DT_{50} > 30$ hours).

Table B.8.4.2-01 Distribution of radioactivity (% AR) in irradiated and dark control solutions of [pyridazinone-3,6-14C]-pyridaben

regime	hour	Ethyl acetate extractable	aqueous				mass balance ^(D)
			initial ^(A)	organo-soluble ^(E)	polar aqueous ^(C)	retained on SPE ^(B)	
irradiated	0	99.2	nd	na	na	na	99.2
	0.5	78.0	19.2	14.7	4.1	1.4	97.2
	2	53.6	41.2	27.9	5.8	3.2	94.8
	4	37.8	54.1	33.9	6.8	3.8	91.9
	6	31.0	56.3	35.9	11.0	3.7	87.3
dark	6	87.6	nd	na	na	na	87.6

na = not analysed

nd = not detected

(A) After ethyl acetate extraction of test solution.

(B) Not eluted by methanol/HCl 95/5; solubilised from SPE material by treatment with Lumagel (not chromatographed).

(C) Remaining in water phase of non-retained filtrate of SPE extraction after acidification and extraction with ethyl acetate (not chromatographed).

(D) Sum of radioactivity in ethyl acetate extract of test solution and extracted water phase.

(E) Sum of radioactivity in organo-soluble fraction resulting from SPE work-up of initial aqueous phase, which were subjected to HPLC analysis.

Table B.8.4.2-02 Distribution of radioactivity (% AR) in irradiated and dark control solutions of [benzene-U-14C]-pyridaben

regime	hour	Ethyl acetate extractable	aqueous				mass balance ^(D)
			initial ^(A)	organo-soluble ^(E)	polar aqueous ^(C)	retained on SPE ^(B)	
irradiated	0	108	nd	na	na	na	108
	0.5	91.8	nd	na	na	na	91.8
	2	80.3	22.6	15.1	4.5	2.4	103
	4	69.8	28.2	17.8	4.1	2.0	98.0
	6	65.7	29.8	17.0	3.6	2.1	95.5
dark	6	99.7	nd	na	na	na	99.7

na = not analysed

nd = not detected

(A) After ethyl acetate extraction of test solution.

(B) Not eluted by methanol/HCl 95/5; solubilised from SPE material by treatment with Lumagel (not chromatographed).

(C) Remaining in water phase of non-retained filtrate of SPE extraction after acidification and extraction with ethyl acetate (not chromatographed).

(D) Sum of radioactivity in ethyl acetate extract of test solution and extracted water phase.

(E) Sum of radioactivity in organo-soluble fraction resulting from SPE work-up of initial aqueous phase, which were subjected to HPLC analysis.

Table B.8.4.2-03 Identification of radioactivity (% AR) in irradiated and dark control solutions of [pyridazinone-3,6-14C]-pyridaben and [benzene-U-14C]-pyridaben

regime	hour	PYR-label		BEN-label		
		pyridaben	W-1	pyridaben	W-1	B-3
irradiated	0	95.3		105.8		
	0.5	4.2	16.1	9.5	27.9	20.3
	2	1.3	4.7		9.0	21.1
	4	0.7	0.3			24.3
	6	0.7	0.2			27.2
dark	6	87.1		99.1		

Conclusions

Under test conditions (Xenon light, 425 W/m²), the DT50 (photolysis, 25°C) for pyridaben is 6.8 minutes. Major photodegradates were W-1 (max. 27.9% AR, DT50 <1.5 hours) and B-3 (max. 27.2% AR, photolytically stable).

Guidelines & Limitations

Comments on the study were incorporated in the above summary. The study is acceptable.

STUDY 2

Characteristics

reference	: O'Connor J., 1997 (IIA 7.2.1.2/02)	incubation time	: 360 hours
year of execution	: 1995-1996	nominal concn.	: 5 µg/L
GLP statement	: yes	temperature	: 25°C
guideline	: EPA N:161-2	DT50	: not applicable
test substance	: [benzene-U-14C]-pyridaben, lot no. CP-1007; [pyridazinone-3,6-14C]-pyridaben, lot no. CP-1505.	metabolites	: not applicable
purity	: [benzene-U-14C]-pyridaben: chemical purity not reported, radiochemical purity ≥99.28%; [pyridazinone-3,6-14C]-pyridaben, chemical purity not reported, radiochemical purity ≥98.57%	conclusion	: After 360 hours, CO ₂ major photodegrade (10.6% AR); radioactivity adsorbed to photolysis cells 5.4-6.2% AR.
test system	: Aqueous photolysis (Xenon light)	acceptability	: acceptable

Study design

In the final kinetic study of the previous study (Study 1 of this section, O'Connor, 1995) with 14C-pyridaben (Ben-label), the mass balances obtained after 120 and 360 hours were only 86% AR and 74% AR. The present aquatic photolysis study on pyridaben was undertaken to investigate the cause for these low mass balances. Underlined parts in the description below indicate essential differences in design between test 1 and 2.

Test 1

Test solutions of sterilised 0.007 M aqueous buffer solutions (0.1% acetonitrile) at pH 7 containing [pyridazinone-3,6-14C]-pyridaben or [benzene-U-14C]-pyridaben at 5 µg/L were dispensed into silanised and sterilised glassware, sealed and irradiated by a Xenon light source (cut off at 290 nm, 425 W/m²) on a 12 hour light/dark cycle for up to 360 hours at 25±1°C. Dark controls were held in a dark room at 25±1°C. Duplicate photolysis cells were connected to a 2-ethoxyethanol trap followed by a 0.1M KOH trap and the headspace was purged for 30 minutes per day. Duplicate irradiated samples were taken after 0, 24, 120 and 360 hours, and duplicate dark samples after 360 hours. The trapping solutions were analysed by LSC. Each light exposed sample was adjusted to pH 2, connected to a 0.1M KOH trap and the headspace was purged for 5 minutes. The 0.1M KOH trap was then analysed by LSC. One of the duplicate light exposed samples was then extracted using method A and the other sample using method B:

- Extraction with ethyl acetate and quantification of radioactivity in organic and aqueous phases by LSC.
- The test solution was transferred to a measuring cylinder, the photolysis cells were rinsed with acetone, the rinses were combined with the sample in the measuring cylinder and the radioactivity of the resulting solution was quantified by LSC.

The 360 hours dark samples were connected to a 2-ethoxyethanol trap followed by a 0.1M KOH trap and the headspace was purged for 5 minutes. The traps was analysed by LSC. Each sample was adjusted then to pH 2, connected to a 0.1M KOH trap and the headspace was purged for 5 minutes. The 0.1M KOH trap was

then analysed by LSC. One sample was then extracted using method A and the other sample using method B as described above.

In order to account for the relatively low mass balances, the 360 hour light exposed photolysis cells from PYR-label were rinsed with a series of solvents (including organic solvents, 1M acid, 10% Decon in hot water) and the radioactivity in the rinses was determined by LSC.

Test 2

Test solutions of sterilised 0.007 M aqueous buffer solutions (0.1% acetonitrile) at pH 7 containing [pyridazinone-3,6-¹⁴C]-pyridaben at 5 µg/L were dispensed into silanised and sterilised glassware, sealed and irradiated by a Xenon light source (cut off at 290 nm, 425 W/m²) on a 12 hour light/dark cycle for up to 360 hours at 25±1°C. Duplicate photolysis cells were connected to a 2-ethoxyethanol trap followed by a 0.1M KOH trap and the headspace was continuously purged throughout the test. Duplicate irradiated samples were taken after 0 and 360 hours. The trapping solutions were analysed by LSC. One of the duplicate samples was treated using method A and the other sample using method B:

- A) The sample was adjusted to pH 2, placed on a magnetic stirrer, connected to a 0.1M KOH trap and the headspace was purged for 24 hours. The 0.1M KOH trap was then analysed by LSC. The sample was then extracted with ethyl acetate and radioactivity in organic and aqueous phases was quantified by LSC.
- B) The test solution was transferred to a measuring cylinder, the photolysis cells were rinsed with acetone, the rinses were combined with the sample in the measuring cylinder and the radioactivity of the resulting solution was quantified by LSC.

The 360 hour light exposed photolysis cells were rinsed with a series of solvents (including organic solvents, 1M acid, 10% Decon in hot water) and the radioactivity in the rinses was determined by LSC.

Results

The results for the distribution of radioactivity are given in Table B.8.4.2-04 and Table B.8.4.2-05 (test 1) and Table B.8.4.2-06 (test 2).

Test 1 (purging headspace for 30 minutes per day, PYR- and BEN-label)

Organic volatiles (not measured in previous study) were not detected. In irradiated samples, CO₂ (not measured in previous study) increased to up to 2.5% AR (PYR-label) or 0.8% AR (BEN-label) after 360 hours. Solvent rinses (measured for PYR-label only) were 6% after 360 hours. The mass balances at 120 and 360 hours were ≥89% AR except for BEN-label, 360 hours, test A (85% AR), but the photolysis cell of this sample was not rinsed.

Test 2 (purging headspace continuously, PYR-label)

Organic volatiles (not measured in previous study) were not detected. In irradiated samples, CO₂ (not measured in previous study) increased to up to 11% AR (PYR-label) after 360 hours (as opposed to 2.5% AR in test 1). This suggests that there were leaks in the photolysis cells, necessitating continuous purging to trap CO₂ quantitatively. Solvent rinses were on average 6% after 360 hours. The mass balances at 360 hours were ≥93% AR.

Table B.8.4.2-04 Distribution of radioactivity (% AR) in irradiated and dark control solutions of [pyridazinone-3,6-14C]-pyridaben (test 1, headspace purged for 30 min per day)

fraction	0 hour		24 hours		120 hours		360 hours		360 hours	
	test A	test B	test A	test B	test A	test B	test A	test B	dark control	dark control
organic volatiles	na	na	nd	nd	nd	nd	nd	nd	nd	nd
CO ₂	na	na	nd	nd	0.2	0.2	2.5	2.5	nd	nd
CO ₂ (pH 2)	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
organosoluble	100	-	70	-	60.9	-	47	-	99.9	-
aqueous	nd	-	21.9	-	29.3	-	32.9	-	nd	-
sample + acetone	-	101	-	97.6	-	92.1	-	80.5	-	103
cell rinses	-	-	-	-	-	-	6.2	5.8	-	-
mass balance	100	101	91.9	97.6	90.4	92.3	88.6	88.8	99.9	103

na = not applicable

nd = not detectable

Table B.8.4.2-05 Distribution of radioactivity (% AR) in irradiated and dark control solutions of [benzene-U-14C]-pyridaben (test 1, headspace purged for 30 min per day)

fraction	0 hour		24 hours		120 hours		360 hours		360 hours	
	test A	test B	test A	test B	test A	test B	test A	test B	dark control	dark control
organic volatiles	na	na	nd	nd	nd	nd	nd	nd	nd	nd
CO ₂	na	na	nd	nd	0.6	0.6	0.8	0.8	nd	nd
CO ₂ (pH 2)	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
organosoluble	97.5	-	85.9	-	77.0	-	67.5	-	104	-
aqueous	nd	-	8.4	-	15.3	-	16.5	-	nd	-
sample + acetone	-	91.0	-	99.1	-	98.5	-	89.8	-	96.6
mass balance	97.5	91.0	94.3	99.1	92.9	99.1	84.8	90.6	104	96.6

na = not applicable

nd = not detectable

Table B.8.4.2-06 Distribution of radioactivity (% AR) in irradiated solutions of [pyridazinone-3,6-14C]-pyridaben (test 2, headspace continuously purged)

fraction	0 hour		360 hours	
	test A	test B	test A	test B
organic volatiles	na	na	nd	nd
CO ₂	na	na	10.6	10.6
CO ₂ (pH 2)	nd	na	1.3	na
organo-soluble	95.0	-	38.3	-
aqueous	nd	-	37.1	-
sample + acetone	-	93.2	-	78.6
cell rinses	-	-	5.4	5.8
mass balance	95.0	93.2	92.7	95.0

na = not applicable

nd = not detectable

Conclusions

After 360 hours: CO₂ was a major photodegradate (10.6% AR); radioactivity adsorbed to photolysis cells represented 5.4-6.2% AR.

Guidelines & Limitations

The study is acceptable.

STUDY 3

Characteristics

reference	: Crowe A., 2002 (IIA 7.2.1.2/03)	incubation time	: 60 minutes
year of execution	: 2000-2001	nominal concn.	: 5 µg/L
GLP statement	: yes	temperature	: 20°C
guideline	: SETAC (1995)	DT50	: 11.8 minutes
test substance	: [benzene-U-14C]-pyridaben, lot no. CP-1504	metabolites	: B-3 (max. 29.2%); PB-4 (max. 18.7%); W-1 (max. 24.4%).
purity	: chemical purity not reported, radiochemical purity 99.2%	conclusion	: quantum yield of pyridaben 0.0304 mole/Einstein
test system	: Aqueous photolysis (Xenon light)	acceptability	: acceptable

Study design

The quantum yield of pyridaben in 0.01M aqueous buffer of pH 7 was determined at 20°C.

Test solutions of sterilised 0.01M aqueous buffer solutions (0.5% acetonitrile) at pH 7 containing [benzene-U-14C]-pyridaben at 5 µg/L, and of p-nitroaniline (actinometer, 0.01M pyridine) were dispensed into silanised and sterilised glassware, sealed and irradiated by a Xenon light source (cut off at 290 nm, 425 W/m²) for up to 60 minutes at 20±2°C. Dark controls were held in a dark room at 20±2°C. Duplicate samples of the test and actinometer solutions were taken at T0 and after 1, 3, 5, 10, 15 and 60 minutes of irradiation, and duplicate dark samples after 60 minutes. The test samples were extracted with ethyl acetate after adjustment of the pH to 2. Radioactivity in the organic phases and the remaining aqueous layer was quantified by LSC. The organic extracts were analysed by reversed phase radio-HPLC using a range of reference standards for comparison. The actinometer solutions were analysed by HPLC/UV.

Results

The organosoluble extracts of test solutions contained 96-101% AR, the aqueous phases ≤4.9% AR, and the total recovered amount of radioactivity was 96-105% AR. The results for the identification of radioactivity in the organic phases are given in Table B.8.4.2-07. Pyridaben degraded with a first order ($r^2 = 0.85$) $k_{\text{photolysis}}$ of 0.05887 min⁻¹ (DT50_{photolysis} 11.8 min). Photodegradates >10% AR were B-3 (max. 29.2% AR), PB-4 (max. 18.7% AR) and W-1 (max. 24.4% AR). Also identified were PB-7 (max. 0.5% AR) and D-1 (max. 9.1% AR). Eight unidentified fractions accounted for each ≤8.7% AR.

The actinometer degraded with a first order ($r^2 = 0.99$) $k_{\text{photolysis}}$ of 0.011080 min⁻¹ (DT50_{photolysis} 62.6 min). The quantum yield for pyridaben was calculated from the above rate constants, the molar extinction

coefficients at 290-800 nm (determined from measurements of the UV spectrum of each compound), irradiance value and the known quantum yield of the actinometer (0.00456 mole/Einstein). The calculation method followed the procedures described under point 118 in the draft (2000) OECD guideline for phototransformation in water. The quantum yield of pyridaben was 0.0304 mole/Einstein.

The report also presented a calculation for the equivalent minutes (M) of natural summer sunlight at 40°N of the test duration of 60 minutes of irradiation by the artificial Xenon light. The formula used was:

$M = h \times r \times c / 0.75 \times 12$, where

h = duration of irradiation in test in hours;

r = ratio of test irradiance to sunlight (0.99 in present test);

c = correction factor for latitude and date (factor used was 0.84¹; the natural sunlight measurement was performed on 7 August 1998);

0.75 = correction factor for diurnal variation of sunlight;

12 is conversion of hours to days.

According to this formula, 60 minutes of irradiation by the artificial Xenon light was equivalent to 130 minutes of natural summer sunlight at 40°N. The magnitude of the correction factor of 0.84 (stated to be a published factor) was not justified in the report.

¹ Mill et al., (1982), Laboratory Protocols for Evaluating the Fate of Organic Chemicals in Air and Water, United States Environmental Protection Agency (EPA-600/3-82-022)

Table B.8.4.2-07 Identification of radioactivity (% AR, duplicate means) in irradiated and dark control solutions of [benzene-U-14C]-pyridaben

exposure type sampling time (min)	irradiated							dark
	0	1	3	5	10	15	60 ^(A)	60
pyridaben	95.4	73.1	68.9	50.4	54.5	32.9	9.3	94.3
polar material	nd	nd	nd	0.4	0.2	1.0	2.6	nd
B-3	nd	0.7	4.9	7.6	7.9	15.4	29.2	nd
unknown	nd	nd	nd	nd	nd	2.2	nd	nd
PB-7	nd	nd	nd	nd	nd	0.5	nd	nd
unknown	nd	nd	nd	nd	nd	0.9	nd	nd
unknown	nd	nd	nd	nd	nd	1.3	nd	nd
unknown	nd	3.1	3.0	8.5	3.9	6.9	8.7	nd
unknown	nd	0.5	nd	nd	nd	nd	nd	nd
PB-4	3.8	18.7	7.7	10.9	4.6	5.2	4.3	1.2
unknown	nd	nd	nd	nd	0.6	1.0	2.1	nd
W-1	nd	3.4	14.8	14.8	20.5	24.4	19.5	nd
D-1	nd	nd	nd	2.0	0.7	3.8	9.1	nd
unknown	nd	nd	nd	nd	0.4	nd	nd	nd
unknown	nd	nd	nd	nd	nd	0.4	nd	nd
TOTAL	99.3	99.5	99.2	94.6	93.3	95.9	84.8	95.5

nd = not detectable

(A) Result for single sample; values for other replicate sample were stated to be anomalous and therefore not reported (see "Guidelines and Limitations").

Conclusions

The quantum yield of pyridaben was 0.0304 mole/Einstein.

Guidelines & Limitations

Results of compound identification for the 60 minutes irradiated sample were those for a single sample. It was reported that the values for the other replicate sample were stated to be anomalous and therefore not reported. However, accountability of the replicate that was reported also deviated from that of all other samples, in that the organosoluble fraction contained 97.4% AR, whilst the total radioactivity identified represented only 84.8% AR, hence 12.6% AR was not accounted for. This unaccounted fraction may represent a photodegrade >10% AR. The HPLC chromatogram shows a relatively large amount of low level radioactivity that has not been integrated, compared to the earlier samples. There is no need to ask further questions since the primary aim of the present study was to determine the quantum yield. The metabolism of pyridaben as a result of aqueous photolysis was already sufficiently established in study 1 of this section.

B.8.4.3 Biological degradation

B.8.4.3.1 Ready biodegradability (Annex IIA 7.2.1.3.1)

STUDY 1

Characteristics

reference	:	Barnes S.P., 2001 (IIA 7.2.1.3.1/01)	incubation time	:	28 d
year of execution	:	2001	nominal concentration	:	10 mg C/L
GLP statement	:	yes	temperature	:	21-23°C
guideline	:	EEC C.4-C, OECD 301B	result	:	not readily biodegradable
test substance	:	Pyridaben technical, lot no. 129T950808	acceptability	:	acceptable
purity	:	99.2% pure			
test system	:	activated sludge, modified Sturm test			

The ready biodegradability of pyridaben was studied in a modified Sturm test according to OECD 301B.

Test solutions (3000 mL, duplicate) containing pyridaben (10 mg C/L) and activated sludge inoculum (30 mg solids/L) were incubated in siliconised flasks (to reduce adsorption to glass) in the dark for 28 days at a measured temperature of 20.8-22.9°C under continuous magnetic stirring with a supply of CO₂ free air. Outgoing air was passed through three adsorption bottles containing 0.025 N Ba(OH)₂ solution. Duplicate flasks for inoculum blank controls (inoculum, no test substance) and single flasks for the reference substance (sodium benzoate, 10 mg C/L) and the inhibition control (pyridaben and sodium benzoate, both 10 mg C/L) were included. On day 28, concentrated HCl (1 mL) added to each flask to drive off dissolved CO₂ and the contents of the vessels were aerated overnight. CO₂ evolution from each flask was determined by titration of residual Ba(OH)₂ on day 2, 3, 5, 7, 9, 13, 20, 28 and 29.

Results

Table B.8.4.3.1-01 summarises the results. CO₂ evolution in the controls (83-84 mg after 29 days) satisfied the validity criterion of OECD 301B (≤120 mg). The pass level for the reference substance (60% degradation) was reached within 7 days. Pyridaben did not show inhibitory effects on the inoculum. Pyridaben was not readily biodegradable in this test (≤3% biodegradation after 29 days).

Table B.8.4.3.1-01 Biodegradation of Pyridaben (% degradation as % of ThCO₂, corrected for degradation in the inoculum blank).

day	reference substance	toxic control	pyridaben
2	22	24	1
3	40	41	2
5	55	55	3
7	65	63	3
9	72	-	3
13	79	-	3
20	85	-	3
28	90	-	3
29	93	-	3

Conclusions

Pyridaben was not readily biodegradable in the modified Sturm test.

Guidelines & Limitations

The study was performed in accordance with OECD 301B and is acceptable.

B.8.4.3.2 Water-sediment studies (Annex IIA 7.2.1.3.2)**STUDY 1****Characteristics**

reference	:	Crowe A., 2002 (IIA 7.2.1.3.2/01)	incubation time	:	120 days
year of execution	:	2000-2001	nominal concentration	:	12 µg/L
GLP statement	:	yes	temperature	:	20°C
guideline	:	SETAC, 1995, BBA IV, 5-1	DT50	:	see results
test substance	:	a) [benzene-U-14C]-pyridaben, lot no. CP-1504; b) [pyridazinone-3,6-14C]-pyridaben, lot no. CP-1505.	metabolites	:	see results
purity	:	a) radiochemical purity 99.8%; b) chemical purity not reported, radiochemical purity 99.5%.	acceptability	:	acceptable
test system	:	silty clay & sandy silt loam sediment			

Study design

The behaviour of [benzene-U-14C]-pyridaben and [pyridazinone-3,6-14C]-pyridaben was studied in two water/sediment systems.

Sediment and associated water were sampled from two locations A and B and sieved through a 2 mm (sediment) and 0.2 mm (water) sieve. The water/sediment properties are listed in Table B.8.4.3.2-01. Sediment (187/100 g dw for A/B) and water (650/500 g for A/B) were dispensed into 1 L flasks (8.5 cm inner diameter, 15 cm high), which were pre-incubated at 20°C in the dark for 20 days prior to treatment. Aliquots (227-228 µL) of [Benzene-U-14C]-pyridaben (designated BEN-pyridaben) and [pyridazinone-3,6-14C]-pyridaben (designated PYR-pyridaben) in acetonitrile were added to the water layer at a concentration of 12 µg/L (equal to the water solubility of the test compound). The water/sediment systems were incubated at

20±2°C in the dark under a continuous humidified CO₂-free air supply. Volatiles and CO₂ were trapped in ethyl digol (1 trap; from day 38), 2M KOH (2 traps) and 20% ethanolamine (1 trap). Redox potential (sediment and water), pH (water) and dissolved oxygen (water) were measured at various time points in the equilibration and incubation phase of the study. Systems had reached equilibrium at the time of treatment. During the 120-day test period, the sediment redox potential was -259 to -462 mV, the mean oxygen saturation in the water was 77-82%, and the mean pH of A/B was 7.8/6.3.

Table B.8.4.3.2-01 Physico-chemical characterisation of water and sediment determined at the time of sampling

parameter	A: silty clay		B: sandy silt loam	
	water	sediment	water	sediment
textural class ^(A)	na	silty clay	na	sandy silt loam
% sand/silt/clay ^(A)	na	5/46/49	na	37/47/16
CEC [meq/100 g]	na	21.4	na	38.2
% organic carbon	na	2.2	na	8.1
TOC (mg/kg)	4.6	na	2.8	na
pH	8.1	6.0	7.2	5.6
microbial biomass [g C/100 g] (start)	na	5.30 ^(B)	na	7.62 ^(B)

na = not applicable

(A) Classification system not reported.

(B) Determined by fumigation/extraction method.

Single flasks and traps were analysed at 0, 1, 2, 7, 14, 30, 59, 90 and 120 days after treatment. The water and sediment layer were separated by decantation. Radioactivity in liquid traps was quantified by LSC.

The water layer was acidified to pH 2 (HCl) and extracted with ethyl acetate. Radioactivity in the water layer, ethyl acetate extract and remaining aqueous phase was determined by LSC. Organo-soluble and aqueous extracts containing >5% AR were concentrated prior to analysis by reversed phase HPLC.

Sediment samples were soxhlet extracted with acetone/water (4/1) or (from day 30 onwards) with acetone. This was followed by soxhlet extraction with MeOH/1N phosphoric acid (4/1). Radioactivity in extracts was determined by LSC. The sediment extracts were combined, concentrated and extracted with ethyl acetate. Both phases were analysed by LSC. After concentration the organic phase was analysed by reversed phase HPLC. Compound identification was by co-chromatography with unlabelled reference standards. The identity of pyridaben and PB-7 in selected samples was confirmed by LC-MS. Radioactivity in PES was determined by combustion/LSC. Sediment samples from day 90 and 120 underwent extraction for fractionation into fulvic acid, humic acid and humin.

Where recoveries were <90%, flasks were rinsed with ethyl acetate, 1M HCl and detergent. The rinses were filtered and radioactivity in filtrates was quantified by LSC, and in filter papers by combustion/LSC. Flask washes (rinsates) containing >5% AR were additionally analysed by HPLC.

Results

The distribution of radioactivity is shown in Tables B.8.4.3.2-02 to -05.

Mass balances were 92-104% AR in system A (PYR-label), but lower (78-96% AR) in system A (BEN-label) and in system B (both labels). The author of the report stated that the low recoveries might be due to the low amount of radioactivity used for treating the systems (22-26 kBq), but this explanation is not satisfactory. Another cause may lie in the strong adsorption of pyridaben to other materials, e.g. glass (confirmed in study 1 of section B.8.1.2), not only of test containers but also of containers used for sample work-up. However, the notifier stated that vessels used for incubation of the samples were extensively washed, where recoveries were low. Pyridaben is soluble in organic solvents, so it is unlikely to adsorb to sample containers for extracts.

The radioactivity level in water decreased from 60-73% AR on day 0 to 14-17% AR (systems A) and 1% AR (systems B) on day 120. The amount of radioactivity partitioning into the sediment increased from 20-36% AR on day 0 to 76-88% AR on day 120. In systems A, the non-extractable fraction in sediment increased from 3.0-4.0% AR on day 0 to 38-47% AR on day 120. In systems B, the non-extractable fraction in sediment increased from 2.2-8.6% AR on day 0 to 39-40% AR on day 59 and 34-39% AR on day 120. Radioactivity in traps (mainly in KOH traps, presumably CO₂) increased to 0.1-6.2% AR on day 120.

The non-extractable sediment radioactivity of day 90 and 120 (both systems, both labels), consisted of 2-13% (mean 8%) fulvic acids, 29-44% (mean 35%) humic acids and 44-68% (mean 56%) humin. The procedural losses during the fractionation were high (2-18% AR, mean 8% AR; mean work up recovery 76%).

Table B.8.4.3.2-02 Distribution of radioactivity (% AR) in silty clay (system A) water and sediment treated with [pyridazinone-3,6-14C] pyridaben at 12 µg/L and incubated at 20°C in the dark

day	water			sediment						traps ^(A)	mass balance ^(B)
	total	org.-soluble	aqueous	total	extractable	org.-soluble	aqueous	PES	flask wash		
0	69.0	69.0	nd	26.1	22.1	21.6	nd	4.0	na	na	95.2
1	56.1	54.9	1.2	41.5	34.3	33.6	0.2	7.2	na	nd	97.5
2	42.7	42.7	nd	52.8	37.0	35.5	0.2	15.8	na	nd	95.5
7	61.6	58.9	2.7	31.6	23.4	23.2	nd	8.2	na	nd	93.2
14	20.0	16.4	3.6	73.6	58.7	55.3	0.6	7.1	7.8	nd	93.6
30	35.3	26.6	8.7	56.5	42.7	39.2	1.3	13.8	na	nd	91.9
59	29.4	22.3	7.1	63.1	33.2	31.9	1.0	29.3	0.6	0.7	93.3
90	19.8	15.6	4.2	81.3	43.8	40.9	0.7	34.3	3.2	0.7	101.8
120	17.0	12.8	4.2	80.4	31.0	28.7	0.4	47.4	2.0	6.2	103.6

na = not applicable; nd = not detected

(A) Mainly in 2M KOH; RA in ethanolamine max. 0.5% AR and in ethyl digol max. 0.1% AR.

(B) Reported values: sum of RA in organo-soluble and aqueous residue from water partition, extractable and non-extractable RA in sediment, flask washes and traps.

Table B.8.4.3.2-03 Distribution of radioactivity (% AR) in silty clay (system A) water and sediment treated with [U-benzene-14C] pyridaben at 12 µg/L and incubated at 20°C in the dark

day	water			sediment						traps ^(A)	mass balance ^(B)
	total	org.-soluble	aqu-eous	total	extrac-table	org.-soluble	aqu-eous	PES	flask wash		
0	68.3	68.3	nd	23.8	20.8	20.5	nd	3.0	na	na	92.1
1	24.9	24.9	nd	65.1	41.1	36.1	nd	24.0	na	nd	90.0
2	25.4	25.4	nd	67.3	59.7	55.6	0.3	7.6	na	nd	92.6
7	20.1	20.1	nd	66.3	52.2	50.8	nd	8.6	5.5	0.0	86.4
14	26.1	25.0	1.2	62.2	49.1	49.0	nd	8.1	5.0	0.4	88.7
30	21.1	21.1	nd	68.3	51.5	47.5	nd	14.0	2.8	0.8	90.2
59	23.2	21.1	2.1	60.3	32.6	27.5	1.0	23.7	4.0	4.8	88.4
90	15.9	13.1	2.8	57.0	33	31.4	0.5	16.8	7.2	5.3	78.1
120	14.2	11.4	2.8	75.5	35.8	28.2	0.7	38.0	1.7	3.7	93.3

na = not applicable; nd = not detected

(A) Mainly in 2M KOH; RA in ethanolamine max. 1.2% AR and in ethyl digol not detectable.

(B) Reported values: sum of RA in organo-soluble and aqueous residue from water partition, extractable and non-extractable RA in sediment, flask washes and traps.

Table B.8.4.3.2-04 Distribution of radioactivity (% AR) in sandy silt loam (system B) water and sediment treated with [pyridazinone-3,6-14C] pyridaben at 12 µg/L and incubated at 20°C in the dark

day	water			sediment						traps ^(A)	mass balance ^(B)
	total	org.-soluble	aqu-eous	total	extrac-table	org.-soluble	aqu-eous	PES	flask wash		
0	59.5	59.5	nd	36.2	27.6	28.2	nd	8.6	na	na	95.6
1	41.0	38.6	2.4	48.2	38.6	28.4	nd	8.6	1.0	nd	89.3
2	29.7	28.3	1.4	60.4	43.7	39.9	0.9	14.4	2.3	nd	90.1
7	8.3	7.2	1.1	85.5	51.0	44.9	1.7	34.5	na	0.0	93.8
14	10.3	8.7	1.6	77.4	46.7	36.3	3.5	20.3	10.4	0.0	87.8
30	10.3	7.9	2.4	79.8	43.0	37.3	0.9	36.8	na	0.0	90.1
59	2.1	1.0	1.1	78.9	37.0	36.6	2.2	40.0	1.9	0.1	81.1
90	4.3	2.7	1.6	86.0	55.8	38.7	1.4	26.7	3.5	0.1	90.5
120	1.0	na	1.0	81.7	37.6	34.6	1.4	39.3	4.8	0.1	82.8

na = not applicable; nd = not detected

(A) Mainly in 2M KOH; RA in ethanolamine max. 0.1% AR and also in ethyl digol max. 0.1% AR.

(B) Reported values: sum of RA in organo-soluble and aqueous residue from water partition, extractable and non-extractable RA in sediment, flask washes and traps.

Table B.8.4.3.2-05 Distribution of radioactivity (% AR) in sandy silt loam (system B) water and sediment treated with [U-benzene-14C] pyridaben at 12 µg/L and incubated at 20°C in the dark

day	Water			sediment						traps ^(A)	mass balance ^(B)
	total	org.-soluble	aqu-eous	total	extrac-table	org.-soluble	aqu-eous	PES	flask wash		
0	73.0	73.0	nd	19.7	17.5	16.7	nd	2.2	na	na	92.7
1	28.5	28.5	nd	54.1	43.2	35.9	nd	8.3	2.6	nd	82.5
2	21.1	19.9	1.2	64.9	57.6	50.2	1.3	5.8	1.5	nd	85.9
7	14.7	13.7	1.0	76.7	39.4	32.1	0.8	29.2	8.1	1.1	92.5
14	5.4	4.8	0.6	86.0	65.9	45.5	1.5	15.3	4.8	1.7	93.1
30	15.7	12.0	3.7	67.4	53.3	46.9	1.2	9.0	5.1	0.1	83.3
59	2.2	1.4	0.8	82.3	42.2	40.1	0.6	38.9	1.2	4.4	88.8
90	4.2	3.3	0.9	75.0	50.7	35.6	0.5	23.1	1.2	8.2	87.3
120	0.8	Na	0.8	88.2	53.4	38.1	0.9	34.0	0.8	5.0	94.0

na = not applicable; nd = not detected

(A) Mainly in 2M KOH; RA in ethanolamine max. 1.4% AR and in ethyl digol max. 0.1% AR.

(B) Reported values: sum of RA in organo-soluble and aqueous residue from water partition, extractable and non-extractable RA in sediment, flask washes and traps.

Identified compounds in water or sediment found at $\geq 5\%$ AR in water or sediment are shown in Table B.8.4.3.2-06 to -09. Besides the tabulated compounds, the following metabolites were found at low levels: PB-4 (max. 2.1% AR in whole system), PB-22 (max. 0.4% AR in whole system), PB-14 (max. 0.1% AR in whole system), P-14 (max. 0.6% AR in whole system), B-7 (max. 0.1% AR in whole system), B-11 (<0.1% AR in whole system). PB-9 (>5% AR in system A, PYR-label) was found in system A (Ben-label) and in systems B at low levels (max. 2.7% AR). Unidentified fractions (4-10) were detected at low levels, individual fractions never exceeding 4.1% AR.

The level of parent pyridaben in water fell from 59-72% AR on day 0 to <5% AR by day 30 in systems A and day 7 in systems B. The levels of parent pyridaben reached a maximum in sediment of 41-55% AR on day 2-14, and were 11-26% AR on day 120. The level of parent pyridaben in the whole system fell from 87-90% AR on day 0 to 11-26% AR on day 120. The main metabolite was PB-7, which reached maximum levels in water and sediment of 5.8-17% AR and 11-14% AR respectively. Single occurrences of PB-9 and P-16 at levels >5% AR (but <10% AR) were only found in system A treated with PYR-label.

Table B.8.4.3.2-06 Identification of radioactivity (% AR) in silty clay (system A) water and sediment treated with [pyridazinone-3,6-14C] pyridaben at 12 µg/L and incubated at 20°C in the dark

day	water				sediment			system			
	pyridaben	PB-9	PB-7	P-16	pyridaben	PB-9	PB-7	pyridaben	PB-9	PB-7	P-16
0	68.9				21.4			90.3			
1	30.0	8.5	11.9	0.1	32.7	0.3	0.2	62.7	8.8	12.1	0.1
2	39.1	0.9	1.8		34.6	0.2	0.2	73.7	1.1	2.0	
7	47.2	1.6	7.1		22.7	0.1	0.0	69.9	1.7	7.2	
14	5.7	1.3	6.7		49.8		10.2	55.5	1.3	16.9	
30	0.9	0.4	16.0	5.2	37.0	0.9	0.9	38.0	1.3	17.0	5.2
59	0.4		17.2	3.7	17.8		12.0	18.2		29.3	3.7
90	0.4		12.1		25.6		13.7	26.0		25.8	
120	0.4		7.3	0.0	16.2	0.5	10.1	16.6	0.5	17.5	0.0

na = not applicable; empty cell = not detected

Table B.8.4.3.2-07 Identification of radioactivity (% AR) in silty clay (system A) water and sediment treated with [U-benzene-14C] pyridaben at 12 µg/L and incubated at 20°C in the dark

day	water		sediment		system	
	pyridaben	PB-7	pyridaben	PB-7	pyridaben	PB-7
0	68.2		20.2		88.3	
1	23.7	0.3	35.7		59.5	0.3
2	22.1	1.6	55.1		77.3	1.6
7	12.0	5.0	48.9	0.9	60.9	5.9
14	8.4	12.4	45.7	2.5	54.0	14.9
30	3.4	13.1	42.0	3.4	45.4	16.5
59	2.8	15.3	14.8	10.6	17.6	26.0
90	0.5	8.4	23.8	12.7	24.3	21.1
120	0.1	9.1	10.9	14.1	11.0	23.1

na = not applicable; empty cell = not detected

Table B.8.4.3.2-08 Identification of radioactivity (% AR) in sandy silt loam (system B) water and sediment treated with [pyridazinone-3,6-14C] pyridaben at 12 µg/L and incubated at 20°C in the dark

day	water		sediment		system	
	pyridaben	PB-7	pyridaben	PB-7	pyridaben	PB-7
0	59.2		28.0		87.2	
1	34.8	1.4	27.8	0.1	62.6	1.5
2	20.4	3.8	39.2	0.2	59.6	4.0
7	3.1	3.2	40.9	2.2	44.0	5.4
14	1.5	5.8	38.8	2.7	40.3	8.5
30	0.0	5.3	25.1	7.9	25.2	13.2
59	na	na	21.9	11.8	21.9	11.8
90	na	na	26.6	9.5	26.6	9.5
120	na	na	20.7	9.1	20.7	9.1

na = not applicable; empty cell = not detected

Table B.8.4.3.2-09 Identification of radioactivity (% AR) in sandy silt loam (system B) water and sediment treated with [U-benzene-14C] pyridaben at 12 µg/L and incubated at 20°C in the dark

day	water		sediment		system	
	pyridaben	PB-7	pyridaben	PB-7	pyridaben	PB-7
0	71.7		16.7		88.4	
1	25.2	1.9	35.5	0.1	60.7	2.1
2	12.9	5.4	49.1	0.4	62.0	5.8
7	3.0	9.5	33.4	3.4	36.4	12.9
14	na	na	42.8	1.8	42.8	1.8
30	7.4	2.4	47.8	2.3	55.2	4.7
59	na	na	28.9	10.7	28.9	10.7
90	na	na	20.9	14.0	20.9	14.0
120	na	na	26.4	9.8	26.4	9.8

na = not applicable; empty cell = not detected

DT50 estimations

Level P-I DT₅₀ values of pyridaben were calculated following the recommendations and procedures of the "Guidance document on estimating persistence and degradation kinetics from Environmental Fate studies on pesticides in EU registration" (SANCO/10058/2005). SFO = single first-order, FOMC = first-order multi-compartment, DFOP = double first-order parallel model, HS = hockey stick. All calculations were performed with ModelMaker v 4.0 software. DT50 values for dissipation of parent pyridaben in sediment were calculated using the data from the point of maximum occurrence onwards. No DT50 (modelling) values were calculated for disappearance of parent pyridaben from water and sediment, since these processes involve not only degradation but also mass transfer. No level M-I DT₅₀ values were calculated for PB-7, the only metabolite >10% AR, since the number of data points from the maximum onwards was limited, and the point of 50% disappearance after the maximum had not (or not unequivocally) been reached before study end.

Pyridaben

SFO, FOMC, and where required HS and DFOP models were evaluated by the RMS, and the results for the best fit model are presented in Table B.8.4.3.2-10.

Table B.8.4.3.2-10 Half-lives for pyridaben in various compartments of silty clay and sandy silt loam water/sediment systems treated with [U-benzene-14C] or [pyridazinone-3,6-14C] pyridaben at 12 µg/L and incubated at 20°C in the dark

system	label	compartment	process	endpoint for	best fit kinetics	Chi ² (error)	r ²	DT50 (d)	DT90 (d)
silty clay	PYR	water	degradation & mass transfer	persistence	SFO	40.72	0.80	7.7	25.4
		sediment	degradation & mass transfer	persistence	HS	12.31	0.94	49.4	1245
		system	degradation	persistence	HS	11.81	0.93	28.8	985
			degradation	modelling	HS	11.81	0.93	651	-
	BEN	water	degradation & mass transfer	persistence	DFOP	7.14	1.00	0.39	16.2
		sediment	degradation & mass transfer	persistence	SFO	12.14	0.90	51.7	172
		system	degradation	persistence	FOMC	13.42	0.91	31.1	210
			degradation	modelling	SFO ^(A)	13.55	0.89	38.9	-
sandy silt loam	PYR	water	degradation & mass transfer	persistence	DFOP	1.08	1.00	1.3	4.9
		sediment	degradation & mass transfer	persistence	HS	7.32	0.93	207	2340
		system	degradation	persistence	FOMC	5.83	0.98	7.0	3769
			degradation	modelling	DFOP	9.40	0.96	72	-
	BEN	water	degradation & mass transfer	persistence	FOMC	11.47	0.99	0.49	4.9
		sediment	degradation & mass transfer	persistence	SFO	14.09	0.62	118	392
		system	degradation	persistence	DFOP	13.96	0.87	14.9	278
			degradation	modelling	DFOP	13.96	0.87	113	-

(A) Fit considered to be acceptable, or equally good as fits for other models.

Conclusions

In two water/sediment systems, treated with [benzene-U-14C]-pyridaben or [pyridazinone-3,6-14C]-pyridaben at a concentration of 12 µg/L and incubated at 20°C in the dark for 120 days, pyridaben degraded in the total water/sediment system with half-lives of 7.0-31 days (persistence) and 39-651 days (modelling). The levels of parent pyridaben reached a maximum in sediment of 41-55% AR on day 2-14, and pyridaben dissipated from the sediment with persistence half-lives of 49-207 days, and from the water phase with persistence half-lives of 0.4-7.7 days. The non-extractable fraction in sediment increased to a maximum of 38-47% AR on day 59-120, and CO₂ to 0.1-6.2% AR on day 120. The main metabolite was PB-7, which reached maximum levels in water and sediment of 5.8-17% AR and 11-14% AR respectively. No other metabolites were found at >10% AR in water or sediment.

Guidelines & Limitations

1. The test concentration of 12 µg/L was equal to the water solubility of pyridaben. The water phase was not gently mixed after treatment. The formation of a surface film and/or inhomogeneous distribution of pyridaben in the water phase immediately after treatment may explain the very high levels of radioactivity determined in some day 0 water samples.
2. The following information was not available: recovery of concentration procedures; HPLC column recovery.

B.8.4.4 Summary and assessment

Hydrolysis

No hydrolytic degradation of pyridaben was observed after 30 days incubation at pH 5.0, pH 7.0 and pH 9.0 and 25°C.

Photolysis

The DT₅₀ for aquatic photolysis of pyridaben at 25°C (Xenon light, 425 W/m²) is 6.8 minutes. Major photodegradates were W-1 (max. 27.9% AR, DT₅₀ <1.5 hours) and B-3 (max. 29.2% AR, photolytically stable, a DT₅₀ of 35 hours is available but not considered reliable). The structures of these two compounds are shown in Figure B.8.4.4-01. The quantum yield of pyridaben at 20°C was 0.0304 mole/Einstein.

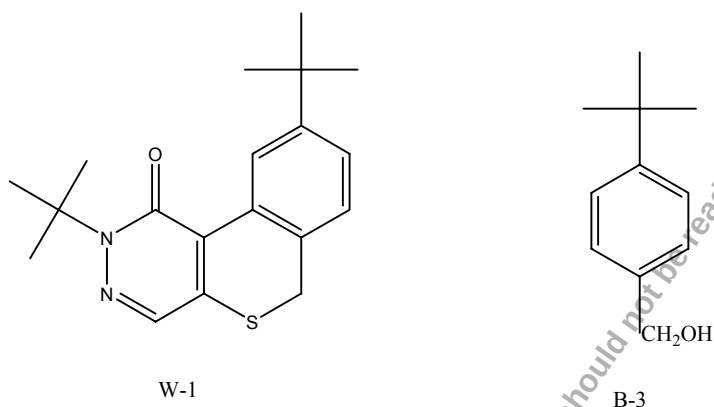


Figure B.8.4.4-01 Aqueous photodegradates of pyridaben detected at >10% AR

Biodegradability

Ready biodegradability

Pyridaben was not readily biodegradable in a modified Sturm test.

Aerobic water/sediment studies

In two water/sediment systems, treated with [benzene-U-14C]-pyridaben or [pyridazinone-3,6-14C]-pyridaben at a concentration of 12 µg/L and incubated at 20°C in the dark for 120 days, pyridaben degraded in the total water/sediment system with half-lives of 7.0-31 days (persistence) and 39-651 days (modelling). The levels of parent pyridaben reached a maximum in sediment of 41-55% AR on day 2-14, and pyridaben dissipated from the sediment with persistence half-lives of 49-207 days, and from the water phase with persistence half-lives of 0.4-7.7 days. The non-extractable fraction in sediment increased to a maximum of 38-47% AR on day 59-120, and CO₂ to 0.1-6.2% AR on day 120. The main metabolite was PB-7, which reached maximum levels in water and sediment of 5.8-17% AR and 11-14% AR respectively. No other metabolites were found at >10% AR in water or sediment.

The (persistence) half-lives of pyridaben are listed in Table B.8.4.4-01. DT₅₀ values for modelling are listed in Table B.8.4.4-02. No DT50 values could be evaluated for the major water/sediment metabolite PB-7.

Table B.8.4.4-01 Persistence DT₅₀ and DT₉₀ values (20°C) of pyridaben in water-sediment systems.

compound	system	14C-label	DT ₅₀			DT ₉₀		
			water ¹	sediment ¹	total ²	water ¹	sediment ¹	total ²
Pyridaben	silty clay	Pyr	7.7 ³	49.4 ⁵	28.8 ⁵	25.4 ³	1245 ⁵	985 ⁵
		Ben	0.39 ⁴	51.7 ³	31.1 ⁶	16.2 ⁴	172 ³	210 ⁶
	sandy silt loam	Pyr	1.3 ⁴	207 ⁵	7.0 ⁶	4.9 ⁴	2340 ⁵	3769 ⁶
		Ben	0.49 ⁶	118 ³	14.9 ⁴	4.9 ⁶	392 ³	278 ⁴
	mean		2.5	107	20.5	12.9	1037	1311

¹ half-lives for dissipation

² half-lives for degradation

³ based on SFO model (Single First-Order)

⁴ based on DFOP model (Dual First-Order-in-Parallel)

⁵ based on HS model (Hockey Stick)

⁶ based on FOMC model (First-Order-Multi-Compartment)

Table B.8.4.4-02 Modelling DT₅₀ and DT₉₀ values (20°C) of pyridaben in water-sediment systems.

compound	system	14C-label	DT50 (system) ¹
Pyridaben	silty clay	Pyr	651 ⁴
		Ben	38.9 ²
	sandy silt loam	Pyr	72.0 ³
		Ben	113 ³
	mean		219

¹ half-lives for degradation

² based on SFO model (Single First-Order)

³ based on DFOP model (Dual First-Order-in-Parallel)

⁴ based on HS model (Hockey Stick)

Anaerobic water/sediment studies

No studies were submitted. These studies are not required.

The main transformations of pyridaben in water-sediment systems are shown in Figure B.8.4.4-02.

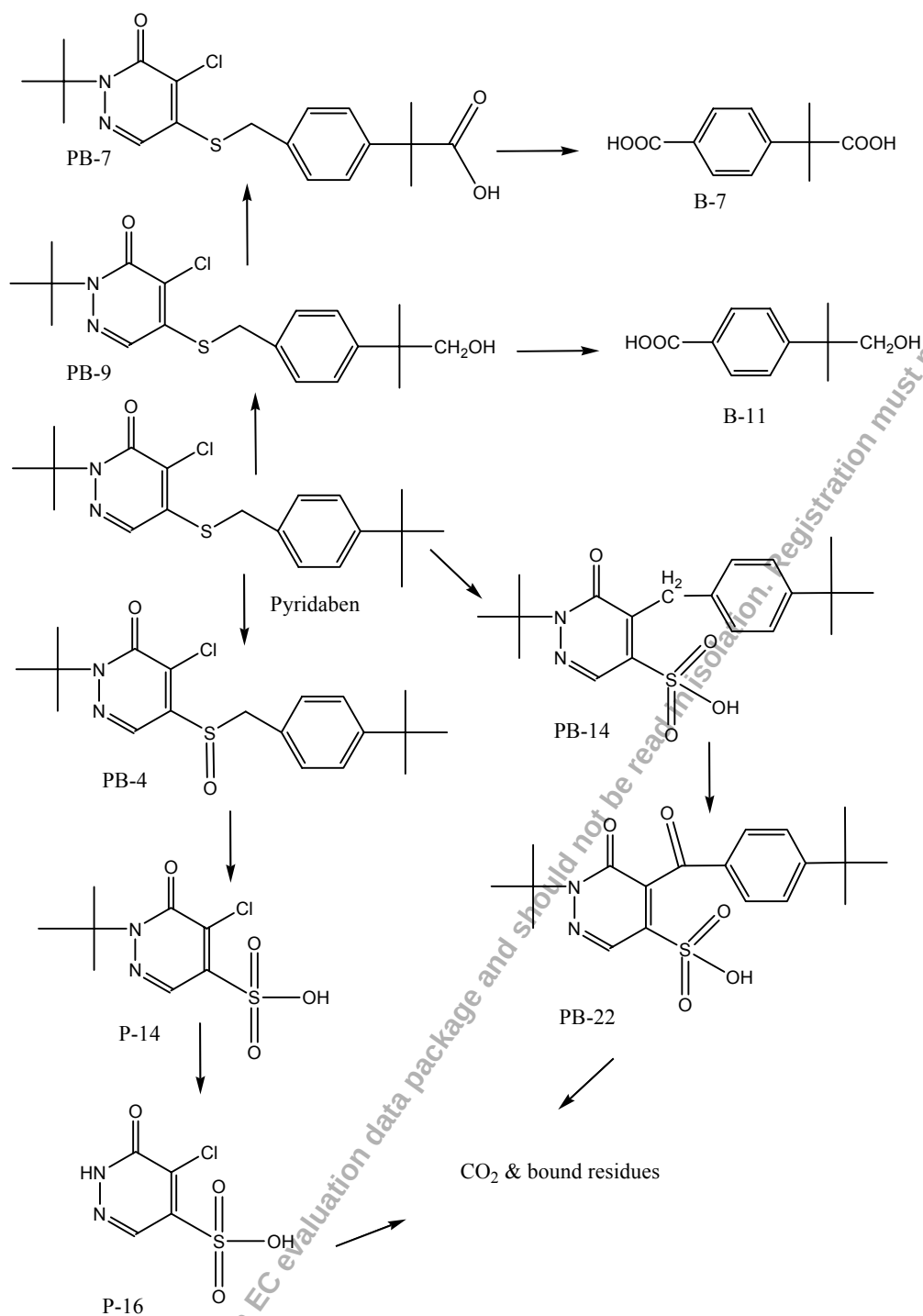


Figure B.8.4.4-02 Main transformations of pyridaben in water-sediment systems

Data requirements

None.

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

Given the nature of the proposed uses (indoor or outdoor spraying of crops), it is unlikely that pyridaben will reach sewage treatment works in significant levels to have an impact on water treatment procedures (taking into consideration also a 3 hour EC50 value for bacterial respiration of >100 mg a.s./L).

B.8.6 Predicted environmental concentrations in surface water, in sediment and in groundwater (PEC_{sw}, PEC_{sed}, PEC_{gw}) (Annex IIIA 9.2.1, 9.2.3)**B.8.6.1 Predicted concentrations in surface water (Annex IIIA 9.2.3)****Application to tomato**

Predicted environmental concentrations in surface water (PEC_{sw}) of pyridaben were calculated according STEP 2 procedures outlined in Sanco/4802/2001 rev.2 final (May 2003) "FOCUS surface water scenarios in the EU evaluation process under 91/414/EEC" using FOCUS 1-2 software, version 1.1 (STEP 1 calculations were not performed because the STEP 1 default scenario is not applicable for greenhouse applications). In order to mimic a greenhouse application, inputs through runoff and drainage were set equal to zero. For soil, the geometric mean soil DT_{50,lab} (modelling endpoint, 20°C, corrected for moisture content) and K_{om} were used in agreement with the guidance (Sanco/10058/2005 vs 1.0 March 2005 and Sanco/4802/2001). For water and sediment, no individual DT₅₀ values are available. Therefore the arithmetic mean of the available DT₅₀ values for the whole water/sediment system was used for both water and sediment in agreement with the guidance (Sanco/4802/2001).

The proposed use on tomato involves a greenhouse application with limited exposure of surface water. A total surface water loading of 0.1% of the dose is assumed (the value of 0.1% emission is used in The Netherlands for greenhouse applications). STEP 2 calculations have a default drift value of 2.759% (single application). Therefore, the STEP 2 results were divided by a factor 27.59 to obtain PEC_{sw} and PEC_{sed} concentrations relevant for a total assumed loading of 0.1% of the dose for greenhouse applications.

In the water/sediment studies, one major metabolite (PB-7) was observed (max 29% AR in total system, max 17% AR in water and max 14% AR in sediment). Because no half-lives for PB-7 could be calculated, no PEC_{sw} calculations according to the above methods were performed. A rough indication of the maximum concentration can be obtained by multiplying the T=0 result for pyridaben with the maximum % of occurrence of PB-7 in water or sediment and by applying a MW correction factor of 1.08 (i.e. 394.9/364.9). In the aqueous photolysis studies, major photodegradates were W-1 (max. 27.9% AR, DT50 <1.5 hours) and B-3 (max. 29.2% AR, photolytically stable).

Similar to PB-7, because no half-lives for W-1 and B-3 are available, no PEC_{sw} calculations according to the above methods were performed. A rough indication of the maximum concentration can be obtained by multiplying the T=0 result for pyridaben with the maximum % of occurrence of W-1 or B-3 in water or sediment and by applying a MW correction factor of 0.90 (i.e. 328.5/364.9) for W-1 and of 0.45 for B-3 (i.e.

164.3/364.9). As worst-case approach, the maximum % of occurrence of W-1 and B-3 in the aqueous photolysis study was either completely attributed to the water or to the sediment phase.

STEP 2:

The following substance specific input data were used to run the model:

Application rate:	250 g ai/ha (cGAP for greenhouse applications)
Application/crop type:	vegetables, fruiting
Application number:	1
Application interval:	not applicable
Water solubility:	Pyridaben: 0.012 mg/L (24°C).
K _{OC} :	Pyridaben: 66503 L/kg.
DT ₅₀ water/sediment:	Pyridaben: 218.7 d (arithmetic mean, modelling endpoint).
DT ₅₀ water:	Values for total system were used.
DT ₅₀ sediment:	Values for total system were used.
DT ₅₀ soil:	Pyridaben: 132.6 d (geometric mean, modelling endpoint).*

* during the evaluation process, one of the soil DT50 values was changed from 1104 days to 95 days, leading to a new geomean DT50 value for modelling of **71.8** days. This will affect the PEC_{sw} and PEC_{sed} values. However, the presented values can be considered as worst-case, so the aquatic risk assessment will not underestimate the risk when the presented values are used.

Besides the data presented above the following additional information is considered in STEP 2:

Region and season of application:	No Runoff/Drainage
Crop interception:	Average crop cover (i.e. 50% interception)

The default model data selection in STEP 2 used for the calculations is:

Distance to water body:	1 m
Spray drift (multiple application):	2.759% (note: STEP 2 results were divided by a factor 27.59 to simulate a loading of 0.1%)
Ratio of field to water body:	10 : 1
Water depth:	30 cm
Sediment depth:	5 cm
Effective sediment for sorption:	1 cm
Sediment organic carbon:	5 %
Sediment bulk density:	0.8 kg/L

Under the above assumptions, application of pyridaben formulated as 75WP on tomato in greenhouses according to cGAP (1 x 0.25 kg a.s./ha; cGAP) will lead to PEC_{SW} values of pyridaben, PB-7, W-1 and B-3 listed in Table B.8.6.1-01 to -04.

Table B.8.6.1-01 Calculated pyridaben concentrations in water and sediment (STEP 2) for application on tomato (1 x 0.25 kg a.s./ha; cGAP)

Time (d)	PEC _{sw} (µg/L)		PEC _{sed} (µg/kg dry sediment)	
	Actual	TWA	Actual	TWA
0	0.0833	-	0.6026	-
1	0.0283	0.0558	0.6023	0.6024
2	0.0102	0.0375	0.6009	0.6020
4	0.0023	0.0214	0.5973	0.6005
7	0.0014	0.0129	0.5917	0.5979
14	0.0013	0.0071	0.5787	0.5916
21	0.0013	0.0052	0.5660	0.5851
28	0.0013	0.0042	0.5536	0.5788
42	0.0012	0.0032	0.5295	0.5664
50	0.0012	0.0029	0.5163	0.5594
100	0.0010	0.0020	0.4406	0.5184

Table B.8.6.1-02 Calculated PB-7 concentrations in water and sediment (STEP 2) for application on tomato (1 x 0.25 kg a.s./ha; cGAP)

Time (d)	PEC _{sw} (µg/L)		PEC _{sed} (µg/kg dry sediment)	
	Actual	TWA	Actual	TWA
0	0.0153	-	0.0913	-

water: calculated as PEC_{sw} pyridaben x 0.17 x 1.08

sediment: calculated as PEC_{sed} pyridaben x 0.14 x 1.08

Table B.8.6.1-03 Calculated W-1 concentrations in water and sediment (STEP 2) for application on tomato (1 x 0.25 kg a.s./ha; cGAP)

Time (d)	PEC _{sw} (µg/L)		PEC _{sed} (µg/kg dry sediment)	
	Actual	TWA	Actual	TWA
0	0.0209	-	0.1513	-

water: calculated as PEC_{sw} pyridaben x 0.279 x 0.90

sediment: calculated as PEC_{sed} pyridaben x 0.279 x 0.90

Table B.8.6.1-04 Calculated B-3 concentrations in water and sediment (STEP 2) for application on tomato (1 x 0.25 kg a.s./ha; cGAP)

Time (d)	PEC _{sw} (µg/L)		PEC _{sed} (µg/kg dry sediment)	
	Actual	TWA	Actual	TWA
0	0.0109	-	0.0792	-

water: calculated as PEC_{sw} pyridaben x 0.292 x 0.45

sediment: calculated as PEC_{sed} pyridaben x 0.292 x 0.45

Application on citrus

Predicted environmental concentrations in surface water (PEC_{sw}) of pyridaben were calculated according STEP 1 and STEP 2 procedures outlined in Sanco/4802/2001 rev.2 final (May 2003) "FOCUS surface water scenarios in the EU evaluation process under 91/414/EEC" using FOCUS 1-2 software, version 1.1. The appropriate (worst case) standard scenarios were used for the calculations for applications on citrus. For

soil, the geometric mean soil $DT_{50,lab}$ (modelling endpoint, 20°C, corrected for moisture content) and K_{om} was used in agreement with the guidance (Sanco/10058/2005 vs 1.0 March 2005 and Sanco/4802/2001). For water and sediment, no individual DT_{50} values are available. Therefore the arithmetic mean of the available DT_{50} values for the whole water/sediment system was used for both water and sediment in agreement with the guidance (Sanco/4802/2001).

STEP 1:

The following substance specific input data were used to run the first tier of the model:

Application rate:	300 g ai/ha
Application type:	citrus
Application number:	1
Water solubility:	See above (tomato)
K_{OC} :	See above (tomato)
DT_{50} water/sediment:	See above (tomato)

The default model data selection in STEP 1 used for the calculations is:

Distance to water body:	1 m
Spray drift	15.725%
Runoff + drainage:	10% (of applied amount)
Ratio of field to water body:	10 : 1
Water depth:	30 cm
Sediment depth:	5 cm
Effective sediment for sorption:	1 cm
Sediment organic carbon:	5 %
Sediment bulk density:	0.8 kg/L

STEP 2:

Besides the data presented above the following additional information is considered in STEP 2:

Region and season of application:	Southern Europe, June-Sep, Mar-May and Oct-Feb (according to cGAP)
Crop interception:	Average canopy (i.e. 70% interception)
DT_{50} water:	Values for total system were used (see tomato)
DT_{50} sediment:	Values for total system were used (see tomato)
DT_{50} soil:	See above (tomato)

The model data selection on STEP 2 differs then as compared to STEP 1 as follows:

Runoff + drainage: 3% (June-Sep) or 4% (Mar-May and Oct-Feb)

STEP 1 and STEP 2 calculations resulted in PEC_{sw} concentrations of pyridaben (15.7-16.8 µg/L) exceeding the water solubility of 12 µg/L. Therefore STEP 3 calculations were performed for pyridaben.

In the water/sediment studies, one major metabolite (PB-7) was observed (max 29% AR in total system, max 17% AR in water and max 14% AR in sediment). Because no half-lives for PB-7 could be calculated, no PEC_{sw} calculations were performed according to the above methods. A rough indication of the maximum concentration can be obtained by multiplying the T=0 results for pyridaben (STEP 1) with the maximum % of occurrence of PB-7 in water or sediment and by applying a MW correction factor of 1.08 (i.e. 394.9/364.9) (Table B.8.6.1-05). In the aqueous photolysis studies, major photodegradates were W-1 (max. 27.9% AR, DT50 <1.5 hours) and B-3 (max. 29.2% AR, photolytically stable). Similar to PB-7, because no half-lives for W-1 and B-3 are available, no PEC_{sw} calculations according to the above methods were performed. A rough indication of the maximum concentration can be obtained by multiplying the T=0 result for pyridaben with the maximum % of occurrence of W-1 or B-3 in water or sediment and by applying a MW correction factor of 0.90 (i.e. 328.5/364.9) for W-1 and of 0.45 for B-3 (i.e. 164.3/364.9). As worst-case approach, the maximum % of occurrence of W-1 and B-3 in the aqueous photolysis study was either completely attributed to the water or to the sediment phase (Table B.8.6.1-06 and -07).

Table B.8.6.1-05 Calculated PB-7 concentrations in water and sediment (STEP 1) for application on citrus (1 x 0.3 kg a.s./ha; cGAP)

Time (d)	PEC _{sw} (µg/L)		PEC _{sed} (µg/kg dry sediment)	
	Actual	TWA	Actual	TWA
0	3.0982	-	112.3653	-

water: calculated as STEP 1 PEC_{sw} pyridaben (16.8402) x 0.17 x 1.08

sediment: calculated as STEP 1 PEC_{sed} pyridaben (741.6361) x 0.14 x 1.08

Table B.8.6.1-06 Calculated W-1 concentrations in water and sediment (STEP 1) for application on citrus (1 x 0.3 kg a.s./ha; cGAP)

Time (d)	PEC _{sw} (µg/L)		PEC _{sed} (µg/kg dry sediment)	
	Actual	TWA	Actual	TWA
0	4.2286	-	186.2248	-

water: calculated as STEP 1 PEC_{sw} pyridaben (16.8402) x 0.279 x 0.90

sediment: calculated as STEP 1 PEC_{sed} pyridaben (741.6361) x 0.279 x 0.90

Table B.8.6.1-07 Calculated B-3 concentrations in water and sediment (STEP 1) for application on citrus (1 x 0.3 kg a.s./ha; cGAP)

Time (d)	PEC _{sw} (µg/L)		PEC _{sed} (µg/kg dry sediment)	
	Actual	TWA	Actual	TWA
0	2.2128	-	97.4510	-

water: calculated as STEP 1 PEC_{sw} pyridaben (16.8402) x 0.292 x 0.45

sediment: calculated as STEP 1 PEC_{sed} pyridaben (741.6361) x 0.292 x 0.45

STEP 3:

FOCUS STEP 3 calculations were performed by the RMS for pyridaben according to the procedures outlined in Sanco/4802/2001 rev.2 final (May 2003) "FOCUS surface water scenarios in the EU evaluation process under 91/414/EEC" using the SWASH software tool, version 2.1. The FOCUS wizard was used to generate all relevant crop-scenario combinations for citrus (according to FOCUS, only the D6 ditch and R4 stream scenario is applicable to citrus). Because no application dates were specified by the notifier, several application windows were assessed: January, May and October. These windows encompass winter, spring and fall applications and can be considered representative for year-round use. The substance data were the same as used for the STEP 1-2 calculations, with following additions: DT50 sediment 1000 days (default value from FOCUS Kinetics), vapour pressure 1E-5 Pa (40°C) and arithmetic mean Freundlich 1/n value 0.953. The vapour pressure was determined at 52.7°C, however FOCUS does not allow values >40°C, hence 40°C was used as temperature. All other input parameters were set at the default FOCUS values. Pyridaben inputs in surface water via drainage were calculated using MACRO in FOCUS software version 4.3b and via run-off by PRZM in FOCUS version 3.21.b. PEC_{sw} values were obtained using TOXSWA in FOCUS software version 2.1.1.F1.

The STEP 3 pyridaben PEC_{sw} and PEC_{sed} concentrations and the time weighted average PEC_{sw} and PEC_{sed} concentrations after application on citrus according to the cGAP are presented in Table B.8.6.1-08 and B.8.6.1-09.

Table B.8.6.1-08 Calculated pyridaben concentrations in water and sediment (STEP 3, D6 ditch and R4 stream scenario) for application on citrus

Scenario	Time	Jan		May		Oct	
		PECsw (µg/L)	PECsed (µg/kg)	PECsw (µg/L)	PECsed (µg/kg)	PECsw (µg/L)	PECsed (µg/kg)
D6 ditch	0	10.402	58.824	10.402	57.757	10.402	57.910
	1	5.207	58.694	5.187	57.613	5.190	57.771
	2	4.192	58.353	4.162	57.241	4.166	57.405
	4	3.204	57.251	3.163	56.047	3.169	56.227
	7	2.356	55.068	2.307	53.694	2.314	53.900
	14	1.257	49.652	1.213	47.893	1.219	48.153
	21	0.761	44.975	0.725	42.905	0.730	43.209
	28	0.512	35.677	0.483	38.554	0.487	39.372
	42	0.019	27.860	0.255	32.015	0.267	33.713
	50	0.027	25.679	0.191	29.166	0.204	31.244
	100	0.046	18.448	0.054	17.896	0.067	22.199
R4 stream	0	7.820	15.982	7.736	11.320	7.165	14.784
	1	0.018	6.903	0.011	3.091	0.001	14.316
	2	0.006	5.803	0.003	2.233	0.000	14.147
	4	0.002	4.998	0.001	1.603	0.000	13.928
	7	0.001	4.505	0.000	1.221	0.000	13.740
	14	0.000	4.029	0.065	2.525	0.001	13.421
	21	0.000	3.798	0.000	5.564	0.000	13.172
	28	0.000	3.646	0.000	5.285	0.000	12.955
	42	0.000	3.426	0.000	4.873	0.000	12.586
	50	0.000	3.332	0.000	4.689	0.000	12.401
	100	0.000	3.349	0.000	3.735	0.000	11.448

Note: calculated maximum values in bold.

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

Table B.8.6.1-09 Calculated pyridaben TWA concentrations in water and sediment (STEP 3, D6 ditch and R4 stream scenario) for application on citrus

Scenario	Time	Jan		May		Oct	
		TWA PEC _{sw} (µg/L)	TWA PEC _{sed} (µg/kg)	TWA PEC _{sw} (µg/L)	TWA PEC _{sed} (µg/kg)	TWA PEC _{sw} (µg/L)	TWA PEC _{sed} (µg/kg)
D6 ditch	0	-	-	-	-	-	-
	1	6.482	58.812	6.470	57.744	6.472	57.897
	2	5.577	58.777	5.558	57.706	5.561	57.859
	4	4.616	58.637	4.589	57.555	4.593	57.710
	7	3.820	58.269	3.785	57.154	3.790	57.314
	14	2.779	56.829	2.737	55.595	2.743	55.772
	21	2.179	54.929	2.138	53.540	2.144	53.740
	28	1.791	52.894	1.752	51.346	1.757	51.568
	42	1.237	47.590	1.285	47.092	1.292	47.510
	50	1.042	44.676	1.115	44.890	1.122	45.482
	100	0.547	33.822	0.609	34.750	0.619	36.529
R4 stream	0	-	-	-	-	-	-
	1	1.102	9.962	0.883	8.574	0.331	14.506
	2	0.556	8.183	0.445	8.530	0.166	14.376
	4	0.280	6.784	0.223	8.476	0.086	14.211
	7	0.160	6.114	0.128	8.424	0.052	14.052
	14	0.080	6.009	0.069	8.350	0.037	13.817
	21	0.054	5.931	0.052	8.339	0.027	13.645
	28	0.040	5.861	0.039	8.301	0.021	13.502
	42	0.027	5.782	0.026	8.215	0.014	13.259
	50	0.023	5.777	0.022	8.167	0.012	13.138
	100	0.013	5.511	0.011	7.850	0.006	12.528

Note: calculated maximum TWA₂₈ values in bold.

A STEP 3 calculation was also provided by the notifier for PB-7, using default half-life values of 1000 days for soil, water and sediment, a worst-case molar kinetic fraction of 0.25, and a K_{oc} value of 19300 L/kg. However, since this K_{oc} value was not accepted due to the acidic nature of the molecule PB-7, this STEP 3 calculation is not considered.

B.8.6.2 Predicted concentrations in sediment (Annex IIIA 9.2.3)

For calculations of concentrations of pyridaben and metabolites in aqueous sediment after application of pyridaben formulated as 75WP in tomato and citrus, see B.8.6.1.

B.8.6.3 Predicted concentrations in groundwater (Annex IIIA 9.2.1)

PEC_{gw} were estimated using FOCUS-PEARL version 2.2.2. Model input was based on the recommendations in "FOCUS groundwater scenarios in the EU review of active substances" Sanco/321/2000 rev.2 and "Generic guidance for FOCUS groundwater scenarios" version 1.1 of April 2002. For citrus, annual applications were simulated for a period of 20 years with a six year "warm-up period". Simulations were performed for the Piacenza, Porto, Thiva and Sevilla FOCUS scenarios (the only scenarios applicable to citrus).

For tomato, no FOCUS calculations were performed because all uses for which authorisation is requested are in greenhouses (for which no FOCUS scenario is applicable). Instead, for tomato, PECgw values of pyridaben and PB-4 were estimated using the standard Dutch spring scenario as defined in PEARL version 2.2.2 for a dose of 1 kg/ha for each compound.

PECgw were estimated for pyridaben and for PB-4. PECgw calculations could not be performed for the soil metabolite PB-7 (exceeding 2 x 5% at two consecutive time points in laboratory soil degradation studies) and the soil photodegradate PB-22. Since for these two compounds no reliable Koc values were available, worst case modelling might be performed using Koc = 0 L/kg. Since however no DT50 values were available for PB-7 and PB-22, PECgw calculations were not made for these compounds.

Crop parameters and dose

According to cGAP, the maximum dose of pyridaben on citrus is 1 x 0.3 kg/ha (Southern Europe). Pyridaben is applied as a foliar spray (no later than BBCH 83) with a PHI of 14 days. Because no application dates were specified by the notifier, calculations were performed for applications in January, April and October to simulate year-round use. The application dates encompass winter, spring and fall applications and are assumed to encompass worst-case conditions. Further, given the high Koc value, no leaching of pyridaben is expected in other months. According to the FOCUS recommendations, application was set “to the soil surface” and the dose was manually corrected for interception by the crop. The dose for PB-4 was derived from that of pyridaben by correction for the difference in molecular mass (i.e. 380.9/364.9). No correction of the dose was made for the formation fraction of PB-4, which produces worst case values. Crop interception of 70% is assumed at all citrus growth stages (FOCUS default). The used model inputs are summarised in Table B.8.6.3-01.

Table B.8.6.3-01 Proposed model inputs for pyridaben application on citrus in Southern Europe

compound	timing	repeat interval	Interception (%)	corrected dose pyridaben (kg/ha)	corrected dose PB-4 (kg/ha)
pyridaben	January 15	1 year	70	0.09	0.094
	April 10	1 year	70	0.09	0.094
	October 17	1 year	70	0.09	0.094

Substance parameters

The geometric mean DT_{50,lab} and arithmetic mean K_{oc} value were used for modelling. The DT_{50,lab} values of pyridaben were taken from the acceptable soil degradation studies and corrected to a temperature of 20°C where necessary (Table B.8.6.3-02). DT_{50,lab} values of pyridaben were further corrected to the reference moisture value (pF=2). No actual soil moisture contents for the lab studies were reported, hence the actual moisture contents were estimated using standard moisture contents at MWHC given in FOCUS guidance. K_{oc} and 1/n values of pyridaben used for the FOCUS groundwater simulations are presented in Table B.8.6.3-03. No experimental DT50 and Koc values are available for PB-4. The DT50 value of 1000 days was

used for the simulation. The Koc value was estimated by EPIWIN. This value is acceptable. Physico-chemical parameters used for the simulations are shown in Table B.8.3.2-04.

Table B.8.6.3-02 DT₅₀ values of pyridaben and PB-4 used for the FOCUS groundwater simulations

Substance	Soil	DT ₅₀ (lab) (20°C, d)	θ %w/w	θ _{ref} %w/w	f	DT ₅₀ moisture corrected (20°C, d)	Geometric mean DT ₅₀ (d)
Pyridaben	Sandy loam	158	10.8	19	0.673	106.4	71.8
	Clay loam	65	12.8	28	0.578	37.6	
	Silt loam	171	12.8	26	0.609	104.1	
	Sandy loam	95	10.8	19	0.673	63.9	
PB-4							1000^(A)

(A) No experimental DT50 value available, value of 1000 days used for the simulation.

Table B.8.6.3-03 Koc values of pyridaben and PB-4 used for the FOCUS groundwater simulations

Substance	Soil	1/n	Koc (L/kg)	Mean 1/n	Mean Koc (L/kg)
Pyridaben	Sandy loam	0.92	34858	0.953	66503^(A)
	Silt loam	1.03	78683		
	Silt loam	0.96	87918		
	Sand	0.90	64551		
PB-4					71490^(B)

(A) Mean Kom = Koc / 1.724 = 38575 L/kg.

(B) Estimated by Syracuse (EPIWIN), no experimental Koc value available; mean Kom = Koc / 1.724 = 41468 L/kg.

Table B.8.6.3-04 Physico-chemical parameters of pyridaben used for the FOCUS groundwater simulations

Substance	Vapour pressure (Pa)	Water solubility (mg/L)	Molecular mass
Pyridaben	1E-5 (30°C) ^(A)	0.012 (24°C)	364.9
PB-4	1E-5 (30°C) ^(B)	100 ^(C)	380.9

(A) Value determined at 52.7°C. PEARL does not allow values >30°C, hence 30°C was used.

(B) No experimental value available, value for pyridaben was used.

(C) No experimental value available, set at 100 mg/L (i.e. not limiting due to low solubility).

All other substance parameters in FOCUS-PEARL were set at the default values recommended by the FOCUS document. All FOCUS runs were generated using the FOCUS wizard. The results of the FOCUS groundwater simulations are shown in Table B.8.6.3-05 and B.8.6.3-06.

Table B.8.6.3-05 FOCUS-PEARL estimations of pyridaben concentrations in groundwater (80th percentile, µg/L)

FOCUS scenario			80th percentile concentration in groundwater [µg/L]	
Crop	GAP	location	application date	pyridaben
Citrus	cGAP Southern Europe	Piacenza	January 15	<0.001
		Porto	January 15	<0.001
		Sevilla	January 15	<0.001
		Thiva	January 15	<0.001
		Piacenza	April 10	<0.001
		Porto	April 10	<0.001
		Sevilla	April 10	<0.001
		Thiva	April 10	<0.001
		Piacenza	October 17	<0.001
		Porto	October 17	<0.001
		Sevilla	October 17	<0.001
		Thiva	October 17	<0.001

Table B.8.6.3-06 FOCUS-PEARL estimations of PB-4 concentrations in groundwater (80th percentile, µg/L)

FOCUS scenario			80th percentile concentration in groundwater [µg/L]	
Crop	GAP	location	application date	PB-4
Citrus	cGAP Southern Europe	Piacenza	January 15	<0.001
		Porto	January 15	<0.001
		Sevilla	January 15	<0.001
		Thiva	January 15	<0.001
		Piacenza	April 10	<0.001
		Porto	April 10	<0.001
		Sevilla	April 10	<0.001
		Thiva	April 10	<0.001
		Piacenza	October 17	<0.001
		Porto	October 17	<0.001
		Sevilla	October 17	<0.001
		Thiva	October 17	<0.001

In all citrus scenarios, estimated 80th percentile concentrations in groundwater were <0.001 µg/L for pyridaben and PB-4, and the groundwater trigger of 0.1 µg/L was not exceeded.

The maximum average substance concentrations in the upper groundwater, calculated using the standard Dutch spring application scenario (representative for greenhouse application of tomato), were <0.001 µg/L for pyridaben and metabolite PB-4.

B.8.7 Fate and behaviour in air (Annex IIA 7.2.2; Annex IIIA 9.3)**STUDY 1****Characteristics**

reference	:	Comb A.L., 2000 (IIA 7.2.2/01)	purity	:	not relevant (estimation method)
year of execution	:	2000	test system	:	Estimation method (Atkinson)
GLP statement	:	yes	hydroxyl rate constant	:	40.8×10^{-12} cm ³ /molecule-sec
guideline	:	OECD monograph no. 61 (1993)	half-life in air	:	4.8 hours
test substance	:	Pyridaben	acceptability	:	acceptable

Study design

A theoretical calculation of the atmospheric oxidation rate of pyridaben was presented based on the method of Atkinson and using AOP Version 1.88 software.

Results

The hydroxyl rate constant was 40.8×10^{-12} cm³/molecule-sec. The half-life in air based on reaction with hydroxyl radicals (assuming a concentration in the atmosphere of 1.5×10^6 OH radicals/cm³) was 3.1 hours. The employed OH radical concentration of 1.5×10^6 OH radicals/cm³ has been revised in a more recent publication by Atkinson², which states a global, annual, 24 hour average OH radical concentration of 9.7×10^5 molecule/cm³. The half-life, recalculated by the RMS using a OH radical concentration of 9.7×10^5 molecule/cm³, was 4.8 hours.

Conclusions

The calculated half-life in air of pyridaben was 4.8 hours (based on a global, annual, 24 hour average OH radical concentration of 9.7×10^5 molecules/cm³).

Guidelines & Limitations

Comments on the study have been incorporated in the above study summary. The conclusion is acceptable.

² Atkinson (2000) Chapter 14 of Handbook of Property Estimation Methods for Chemicals, Robert S. Boethling and Donald Mackay Eds, Lewis Publishers.

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

Pyridaben

Based on a vapour pressure of 1×10^{-5} Pa at 24°C (Volume 3, section B.2) and a water solubility of 0.012 mg/L at 24°C, the calculated Henry's Law Constant of pyridaben at 24°C was $0.304 \text{ Pa} \cdot \text{m}^3 \cdot \text{mol}^{-1}$ (Volume 3, section B.2). Results for photochemical oxidative degradation of pyridaben (DT_{50} 4.8 hrs) and the Henry's Law constant of $0.304 \text{ Pa} \cdot \text{m}^3 \cdot \text{mol}^{-1}$ suggest that the concentrations of pyridaben in air are likely to be negligible.

Metabolites PB-22, PB-7, B-3

The vapour pressure, water solubility, Henry's law constant and the atmospheric half-life for the three metabolites were calculated by the Notifier using the models EPISUITE programme and AOPWIN:

- Vapour pressure : PB-22: 6.3×10^{-13} Pa; B-3: 0.157 Pa; PB-7: 2.87×10^{-9} Pa
- Water solubility at 25°C : PB-22: 166.8 mg/l; B-3: 97.8 mg/l; PB-7: 1.65 mg/l
- Henry's law constant : PB-22: $1.5 \times 10^{-17} \text{ atm} \cdot \text{m}^3 / \text{mol}$; B-3: $4.3 \times 10^{-7} \text{ atm} \cdot \text{m}^3 / \text{mol}$; PB-7: $6.8 \times 10^{-12} \text{ atm} \cdot \text{m}^3 / \text{mol}$
- Atmospheric oxidation half-life : PB-22: 1.0 days; B-3: 1.1 days; PB-7: 7.0 days

It can be concluded that based on the physical-chemical properties (i.e. very low vapour pressure, relatively high water solubility, and Henry's law constant) of these metabolites an exposure to air is very unlikely to occur.

In addition, the metabolites PB-22 and B-3 would undergo a very fast degradation when entering the atmosphere.

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

Detailed guidance to define the environmental residue is not available. Provisionally therefore, the active substance and major metabolites are listed in the definition. No metabolites were formed at >10% AR under aerobic laboratory conditions in soil treated with pyridaben, but PB-4 and PB-7 exceeded 5% AR at 2 consecutive time points (and are hence relevant for exposure of groundwater). The metabolite PB-22 was found at levels up to 13% AR in irradiated soil samples but not in dark controls, and is hence relevant for exposure of soil. PB-7 reached maximum levels in water and sediment of 17% AR and 14% AR respectively. Major aqueous photodegradates of pyridaben were W-1 (max. 27.9% AR, DT_{50} <1.5 hours, therefore not included in residue definition for air) and B-3 (max. 29.2% AR, photolytically stable).

The components of the environmental residue are therefore as follows:

Soil: pyridaben, PB-22

Surface Water: pyridaben, PB-7, W-1, B-3

Sediment: pyridaben, PB-7

Ground water: pyridaben, PB-4, PB-7, PB-22

Air: pyridaben, PB-22, PB-7, B-3

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B.8.10 References relied on

Annex point reference number	Author(s)	Year	Title, Source, Company, Report No GLP or GEP status (where relevant), Published or not	Data Protection Claimed Y/N	Owner
IIA, 7.1.1.1.1	Crowe, A.	2002	Pyridaben: Aerobic soil metabolism (route of degradation) Huntingdon Life Sciences Ltd. Nissan Chemical Industries, Ltd. Report no. M37 GLP, Unpublished	Y	NCI
IIA, 7.1.1.1.2/02	O'Connor, J.	1995	NC-129: Photodegradation on soil Pharmaco LSR Ltd. Nissan Chemical Industries, Ltd. Report no. M32 GLP, Unpublished	Y	NCI
IIA, 7.1.1.2.1/01	Crowe, A.	2002	Pyridaben: Aerobic soil metabolism (route of degradation) Huntingdon Life Sciences Ltd. Nissan Chemical Industries, Ltd. Report no. M37 GLP, Unpublished	Y	NCI
IIA, 7.1.1.2.1/02	Crowe, A.	2001	Pyridaben: Aerobic soil rate of degradation Huntingdon Life Sciences Ltd. Nissan Chemical Industries, Ltd. Report no. M35 GLP, Unpublished	Y	NCI
IIA, 7.1.1.2.2/01	Wilson, A.	2003	Pyridaben: Terrestrial field dissipation study with Pyridaben 750 g as/kg WP applied to bare soil in Denmark and Spain 2001/2002 Huntingdon Life Sciences Ltd. Nissan Chemical Industries, Ltd. Report no. M39 GLP, Unpublished	Y	NCI
IIA, 7.1.2	O'Connor, J.	1992	NC-129: Determination of soil adsorption/desorption properties Life Science Research Ltd Nissan Chemical Industries, Ltd. Report no. M25 GLP, Unpublished	Y	NCI
7.2.1.2/01	O'Connor, J.	1995	NC-129: Photodegradation in water Pharmaco LSR Ltd. Nissan Chemical Industries, Ltd. Report no. M33 GLP, Unpublished	Y	NCI
7.2.1.2/02	O'Connor, J.	1997	Determination of the photodegradation of NC-129 in water (supplementary study) Huntingdon Life Sciences Ltd. Nissan Chemical Industries, Ltd. Report no. M34 GLP, Unpublished	Y	NCI

Annex point reference number	Author(s) /)	Year	Title, Source, Company, Report No GLP or GEP status (where relevant), Published or not	Data Protection Claimed Y/N	Owner
7.2.1.2/03	Crowe, A.	2002	Pyridaben: Determination of Quantum yield Huntingdon Life Sciences Ltd. Nissan Chemical Industries, Ltd. Report no. P41 GLP, Unpublished	Y	NCI
IIA, 7.2.1.3.1	Barnes, S. P.	2001	Pyridaben: Assessment of ready biodegradability – modified Sturm test Huntingdon Life Sciences Ltd. Nissan Chemical Industries, Ltd. Report no. M36 GLP, Unpublished	Y	NCI
IIA, 7.2.1.3.2	Crowe, A.	2002	Pyridaben: Degradability and fate in the water/sediment system Huntingdon Life Sciences Ltd. Nissan Chemical Industries, Ltd. Report no. M38 GLP, Unpublished	Y	NCI
IIA, 7.2.2-01	Comb, A.L.	2000	Pyridaben photochemical oxidative degradation in air Huntingdon Life Sciences Ltd. Nissan Chemical Industries, Ltd. Report no. P39 GLP, Unpublished	Y	NCI