ANNEX B

Ziram

B.7 Environmental fate and behaviour

B.7.1 Route and rate of degradation in soil (Annex IIA 7.1.1; Annex IIIA 9.1.1)

B.7.1.1 Route of degradation (Annex IIA 7.1.1.1)

B.7.1.1.1 Aerobic degradation in soil (Annex IIA 7.1.1.1.1)

Two studies were provided. The second study is not acceptable and was not taken into account in the evaluation of the a.s.

Aerobic soil metabolism of ^{14}C Ziram (Heasook K., 1996)
Guidelines :
40 CFR 158 Environmental Fate, USEPA Pesticide Assessment Guidelines Subdivision N; Series 162-1.
GLP :
Yes
Material and Methods :
Test substance : ziram labeled with ^{14}C at both thiocarbonyl positions of the molecules, Radiochemical purity: >96.54 %. Specific radioactivity: 53.96 mCi/mMol
Soil :
Table B.7.1.1.1-1 : Characteristics of the soil used in the aerobic degradation study

Soil type	Origin	pH	CEC (meq/100g)	OC content (%)	field capacity (1/3 bar moisture %)	Clay content (%)	Silt content (%)	Sand content (%)
sandy loam	Almond Grove	5.4	9.0	1.8	15.4	7	32	61

Test conditions :
Aerobic incubation at 25 ± 1°C in the dark and application rate was 3.05 mg a.s./kg soil. Experiment was performed in duplicate.
Analytical methods :
Soil was extracted with a basic solution of phosphate buffer/acetonitrile. Analyses of a.s; and metabolites was performed by reversed phase HPLC in conjuction with LSC. Major metabolite was identified by LC/MS.
Volatiles (including $^{14}CO_2$ and $^{14}CS_2$) were trapped by KOH and Viles' reagent (triethanolamine and copper acetate in ethanol)
Findings :
Table B.7.1.1.1-2 : Balance and recovery of radioactivity - aerobic degradation at 25°C in the lab (% of applied radioactivity)

	Sampling time											
	0 h	1 h	6 h	12 h	18 h	24 h	2 d	3 d	7 d	14 d	30 d	60 d
Volatiles (KOH and Vile's reagent)	-	1.44	2.57	4.52	5.92	6.29	12.51	17.70	26.80	35.26	42.02	48.35
Extractable (phosphate buffer pH 9/ acetonitrile)	85.46	76.53	67.47	66.49	57.16	54.94	49.45	46.30	20.24	14.74	13.03	8.17
ziram	85.14	74.34	66.54	63.77	54.74	46.27	45.48	44.02	1.55	0.45	0.30	-
metabolite 8 (1,1-dimethylurea)	-	-	-	-	-	-	-	-	8.65	8.67	10.48	5.25
Bound residue	12.52	20.26	24.93	31.66	40.09	38.25	37.06	35.58	48.16	41.30	40.93	41.99
Total recovery	97.98	98.23	94.97	102.6	103.1	99.48	99.02	99.57	95.19	91.30	95.97	98.51

				6	7							

- : not detected

9 other metabolites were detected but none exceeded an average of 8.67% of the applied radioactivity. They were generally in the range 'not detected' to '< 1% of applied radioactivity'.

Conclusions :

A metabolic pathway for ziram was proposed. After cleavage of the molecule to dimethyldithiocarbamic ions, 1,1-dimethylurea is formed. Final metabolites of ziram are CS_2 + CO_2 (48.35% after 60 d) and bound residue (max 48.16 % after 7 d, 42% after 60 d).

DT_{50} of 41.9 hours (1.7 days) was calculated for ziram.

Aerobic Soil Metabolism Study with ^{14}C-Ziram (Cranor W., 1987)

Guidelines :

40 CFR 158 Environmental Fate, USEPA Pesticide Assessment Guidelines Subdivision N; Series 162-1.

GLP :

Yes

Material and Methods :

Test substance :

[^{14}C]Ziram (label position not specified). Radiochemical purity: 99%. Specific radioactivity: 1.19 x 10^5 dpm/µg

Soil :

Loamy sand soil from an almond grove located in Waterford

Test conditions :

Aerobic incubation in the laboratory at 24.8 ± 0.8°C and 83.9 ± 41.9% of field capacity in the dark. Application rate was 10 mg a.s./kg soil

Analytical methods :

Extraction and analytical procedures are unclear.

Extraction was realized by several extracting solvents (hexane, acetone, methanol, methanol/HCl; acetonitrile, ethyl acetate, 1-propanol, toluene, KOH/methanol). The results from these different extractions procedures are not reported in the study.

Lack of specific non-destructive extraction procedure for a.s. and its metabolites prohibited metabolite identification and specific analysis of the a.s.

Findings and conclusion :

Problems of extractability were observed (During the days 0-14, extractable radioactivity never exceeded 27 % of applied radioactivity ; 71-87 % of radioactivity as unextractable).

The study does not provide information on the metabolism (metabolic pathways of the a.s., metabolites) and the degradation rate (DT_{50} of the a.s.).The study is not acceptable.

B.7.1.1.2 Anaerobic degradation in soil (Annex IIA 7.1.1.1.2)

Anaerobic Soil Metabolism of ^{14}C-Ziram (Reynolds J. et al., 1997)

Guidelines :

40 CFR 158 Environmental Fate, USEPA Pesticide Assessment Guidelines Subdivision N; Series 162-1.

GLP :

Yes

Material and Methods :

Test substance : [^{14}C]Ziram (labeled at both thiocarbonyl positions). Radiochemical purity: ³ 97%. Specific radioactivity: 53.96 mCi/mmole

Soil :

Table B.7.1.1.3-1 : Characteristics of the soil

Soil type	**Origin**	**pH**	**CEC (meq/100g)**	**OC content (%)**	**Moisture (1/3 bar) (%)**	**Clay content (%)**	**Silt content (%)**	**Sand content (%)**

Sandy loam	Almond grove	5.4	9.0	1.8	15.4	7	32	61

Test conditions :
Following 2 days of aerobic incubation, the treated soil was flooded with water and the atmosphere replaced with nitrogen to establish anaerobic conditions. This procedure is not in accordance with the SETAC guidelines which recommend to maintain the soil for 30 days under anaerobic conditions prior to application of the a.s. No indication is given about the determination of the redox potential of the sacrificed samples.
Anaerobic incubation in the laboratory at 25 ± 1 °C in the dark; Application rate was 2.99 mg a.s./kg soil
Analytical methods :
The samples were extracted by buffer/acetonitrile. The levels of radioactivity were determined by LSC. Identification of the metabolites was done by HPLC. When ^{14}C levels were too low 'reconstructed chromatograms were produced with the aid of Excel software.'
Findings and conclusions :
'The objectives of the study were to assess the rates, nature and extent of degradation of products formed from ziram in soil incubated under anaerobic conditions after being aged aerobically for approximately one half-life' The caculated half-life under aerobic conditions was 1.6 days. The half-life under anaerobic conditions was 14.12 days. The study is not in accordance with the SETAC recommendations. This study confirms the results of the aerobic metabolism study. The main metabolite dimethyldithiocarbamic acid was detected at level of ~ 4.5% RR during the whole study.

B.7.1.1.3 Soil photolysis (Annex IIA 7.1.1.1.2)

Photolysis of ^{14}C-Ziram on soil (Reynolds, 1997)
Guidelines :
40 CFR 158 Environmental Fate, USEPA Pesticide Assessment Guidelines Subdivision N; Series 161-3.
GLP :
Yes
Material and Methods :
Test substance : thiocarbamate-labeled [^{14}C]Ziram. Radiochemical purity: >97%. Specific radioactivity: 48 mCi/mMol
Soil :
Table B.7.1.1.3-1 : Characteristics of the soil

Soil type	**Origin**	**pH**	**CEC (meq/100g)**	**OC content (%)**	**Moisture (1/3 bar) (%)**	**Clay content (%)**	**Silt content (%)**	**Sand content (%)**
Sandy loam	Almond grove	5.4	9.0	1.8	15.4	7	32	61

Test conditions :
2 g soil spiked with 15 and 3 mg/kg [^{14}C]ziram was subjected to photolysis with a Heraeus Suntest CPS xenon arc lamp equipped with a UV filter (< 290 nm).
Discontinuous illumination (12 h light/12 h dark) at a temperature of 25 °C during 24 hours
Analytical methods :
The soil was extracted by buffer/acetonitrile. Radioactivity was determined by LSC.
Degradates were identified by HPLC.
When ^{14}C levels were too low 'reconstructed chromatograms were produced with the aid of Excel software.'
Findings :

Table B.7.1.1.3-2 : Balance and recovery of radioactivity in soil photolysis study (100 % Radioactivity = 15 ppm)

	Extractable residue	**Bound residue**	**Volatiles (KOH Vile's reagent and H2SO4)**	**Balance**	**Parent compound and degradates found in extractable residue**		
					Ziram	**Thiram**	**Thiram oxide**
Irradiated samples							
0	93.44	2.30	-	95.73	68.43	25.01	-
2 h	77.92	13.12	4.79	95.82	43.89	14.82	12.92
4 h	77.01	15.63	5.37	98.00	44.00	0.77	20.44
8 h	68.37	19.82	8.25	96.44	28.71	1.42	20.68
16 h	51.60	23.57	10.97	86.14	16.98	-	24.69
24 h	49.89	28.97	15.70	94.55	9.40	-	27.32
Dark samples							
2 h	90.76	9.65	1.07	101.47	49.75	26.67	9.37
4 h	86.48	13.54	1.62	101.63	51.32	19.54	12.83
8 h	83.72	15.77	2.58	102.06	49.33	6.00	17.85
16 h	77.36	17.37	4.26	98.99	33.48	4.19	36.75
24 h	72.06	20.40	7.01	99.47	21.43	0.31	47.03

The results of the 3 ppm experiment are not reported here because they were similar to the results of the 15 ppm experiment.

In addition to ziram, 10 other degradates were detected at various time points : Major compounds >10 % RR are in the table. Other compounds accounting for less than 10% RR were dithiocarbamic acid, N,N-dimethylformamide. Three unique metabolites never found in other soil studies were detected at low level (<3.1 % RR) and therefore were not identified.
Thiram oxide which appeared in both irradiated and dark samples was considered as an artifact because its 'levels depend upon the volume of solvent used to dose the soil with ziram'.

Conclusions :
DT_{50} of 8-8.9 hours and 20-16.2 hours were calculated respectively for irradiated and dark samples. Nevertheless the results of the study are impaired by shortcomings (no explanation of the degradation of ziram to thiram, presence of thiram oxide considered as an artifact but present in the degradation pathway of the a.s.)

Determination of Photodegradation of Ziram on the Surface of Soil (Carpenter M., 1985)
Guidelines :
40 CFR 158 Environmental Fate, USEPA Pesticide Assessment Guidelines Subdivision N; Series 161-3.
GLP :
Yes
Material and Methods :

Test substance : thiocarbamate-labeled [^{14}C]Ziram. Radiochemical purity: > 90%. Specific radioactivity: 16.4 mCi/mMol
Soil :
Table B.7.1.1.3-1 : Characteristics of the soil

Soil type	Origin	pH	CEC (meq/100g)	OC content (%)	Field capacity (1/3 bar) (%)	Clay content (%)	Silt content (%)	Sand content (%)
Loamy sand	-	6.4	3.4	0.63	4.53	4	16	80

Test conditions :
1 g soil spiked with 10.7 µg [^{14}C]ziram was subjected to photolysis with a 275-watt sunlamp (General Electric Type RS lamp). Borosilicate glass was used to exclude wavelengths <290 nm.
Continuous illumination at a temperature of 25 °C during 30 days
Analytical methods :
Extraction of residue by methanol.
Ziram was identified by one-dimensional Thin Layer Chromatography (TLC) on silica gel plates using methanol:butanol = 95:5 (v/v).
Radioactivity was determined by LSC
Findings :
Table B.7.1.1.3-2 : Balance and recovery of radioactivity in soil photolysis study (100 % Radioactivity = 10.7 µg a.s.) - irradiated samples

	Extractable residue	Bound residue	Volatiles (KOH and urethane foam traps	Balance	Ziram (from extractable residue)
0	71.4	34.0	9.3	114.8	18.5
1	36.6	49.2	2.9	88.7	4.6
2	21.9	54.2	3.0	79.1	0.8
3	18.3	64.2	3.4	86.0	2.9
4	21.3	51.2	18.7	91.2	3.3
7	13.6	52.0	4.8	70.4	4.7
15	9.8	41.4	9.7	60.9	1.9
30	7.00	36.8	11.7	55.5	3.9

Conclusions :
The total radioactivity recovered after 30 days is 55.5% (very low value indicating that substances were not recovered completely from the system). The % extractable radioactivity seems relatively low in comparison with the % recovered in the aerobic metabolism study (Heasook, 1996)
No identification of metabolites was realized.
Observed DT_{50} < 1 day (with light)
The value of the study is questionable.

B.7.1.2 Rate of degradation (Annex IIA 7.1.1.2.1; Annex IIIA 9.1.1.1.1)

B.7.1.2.1 Aerobic degradation

One value of DT_{50} lab of 1.7 days was calculated in the aerobic metabolism study (B.7.1.1.1)
Supplementary data about the rate of degradation of ziram in 3 other soils are necessary.

The degradation rate of the a.s. at 10°C in one soil should be determined.

B.7.1.2.2 Anaerobic degradation

See point B.7.1.1.2.

B.7.1.3 Field studies (Annex IIA 7.1.1.2.2; Annex IIIA 9.1.1.2)

B.7.1.3.1 Soil dissipation testing

Two studies are ongoing in California and North Carolina. The dissipation rate is measured for 9 applications in the growing season. Preliminary information indicates that the DT_{50} is 5-6 days.

Ziram soil dissipation study (Selman F.; 1987a and 1987b)
Two dissipation study in almond orchard were performed. The results are not acceptable.
Conclusions : (from the study)
'Stability study data for 60 days of sample storage show a decrease in levels of ziram to an average of 59% of the initial dose of 0.1 and 1.0 ppm. Based on these data results of analysis of samples taken after the final application would have been greatly affected due to time lags between sampling and analysis. Therefore any calculation of a t½ would be invalid because of sample degradation in storage.'

B.7.1.3.2 Soil residue testing - soil accumulation testing

The two studies ongoing in the USA can be considered as soil accumulation testing studies.

B.7.2 Adsorption, desorption and mobility in soil (Annex IIA 7.1.2 and 7.1.3; Annex IIIA 9.1.2)

B.7.2.1 Adsorption and desorption of the active substance and relevant metabolites (Annex IIA 7.1.2)

Determination of Adsorption/Desorption Constants of [^{14}C]Ziram (Warren J., 1985)

Guidelines :

40 CFR 158 Environmental Fate, USEPA Pesticide Assessment Guidelines Subdivision N; Series 163-1.

GLP :

Yes

Material and Methods :

Test substance : **[^{14}C]Ziram (label position not specified). Radiochemical purity: ≥96.4%. Specific radioactivity: 16.4 mCi/mMol**

Soils :

Table B.7.2.1-1 : Characteristics of the soils used in the adsorption-desorption study

Soil type	Origin	pH	CEC (meq/100g)	OC content (%)	Field capacity (1/3 bar) (%)	Clay content (%)	Silt content (%)	Sand content (%)
Loamy sand	Missouri (USA)	8.0	7.7	0.304	5.44	4.0	14.0	82.0
Loamy sand	Hanford (USA)	6.4	3.4	0.478	4.53	4.0	16.0	80.0
Sandy loam	Manteca (USA)	8.2	11.5	1.00	16.71	10.0	36.0	54.0
Sandy loam	Stockton (USA)	7.1	11.6	1.43	16.58	18.0	26.0	56.0

Test conditions :

Soil samples (1 g for the Hanford loamy sand; 2 g soil for the other soils) in suspension with 10 ml [^{14}C]ziram-treated solution (0, 0.472, 0.868, 3.94, and 7.08 µg [^{14}C]ziram/mL 0.01 N calcium sulfate solution) were shaken during 48 hours at 25°C in the dark.

For desorption the suspensions were shaken in the dark at 25°C for 72 hours with 0.01N calcium sulfate solution.

Analytical methods :

Analysis by LSC

Findings :

Table B.7.2.1-2 : Adsorption and desorption constants of ziram (Kd, Koc, n)

	Adsorption			Desorption		
	Kd	**Koc**	**n**	**Kd**	**Koc**	**n**
Loamy sand	13.6	4470	1.57	88.0	28947	0.903
Loamy sand	57.4	12010	1.11	11299	2363808	0.294
Sandy loam	9.87	987	1.68	33.2	3320	1.39
Sandy loam	8.0	559	1.39	22.4	1566	1.02

Conclusions :

The study was realized with only two types of soil (loamy sand and sandy loam).

According to Mc Call (1988) , ziram exhibits low mobility to immobility in the soil. (Koc = 559-12010). The stability of ziram should be determined.

Adsorption/desoption of ^{14}C Ziram (Spare W., 1995)
Guidelines :
40 CFR 158 Environmental Fate, USEPA Pesticide Assessment Guidelines Subdivision N; Series 163-1. The guideline is acceptable.
GLP :
Yes
Material and Methods :
Test substance : **Ziram** labeled with ^{14}C at both thiocarbonyl positions of the molecules**. Radiochemical purity: > 98%. Specific radioactivity: 53.96 mCi/mMol**
Soils :
Table B.7.2.1-3 : Characteristics of the soils used in the adsorption-desorption study

Soil type	Origin	pH	CEC (meq/100g)	OC content (%)	Field capacity (1/3 bar) (%)	Clay content (%)	Silt content (%)	Sand content (%)
Clay	Mississippi	6.6	33.4	1.8	35.9	47	32	21
Sand	Maryland	6.0	3.5	0.2	4.7	3	8	89
Silt loam	Maryland	6.7	14.1	1.0	27.1	15	60	25
Sandy loam	California	5.4	9.0	1.8	15.4	7	32	61

Test conditions :
Soil samples (0.5 g clay; 18 g sand, 8 g silt loam and 8 g sandy loam) were placed in 50 ml tubes. 0.01M Calcium solution was added to the tubes to completely filled them eliminating all headspace. Ziram concentrations were 0.2, 0.6, 1, 2 and 4 µg/mL.
Soil samples were shaken for 4 hours (24 hours for clay) at 25°C in the dark.
Desorption was performed with the same shaking periods (4 hours; 24 hours for clay) after addition of calcium solution to the wet soils.
Analytical methods :
analysis of solutions and soils by LSC. On en replicate of the soils with highest concentrations were analyzed by HPLC
TLC and HPLC check of the test subtance and solutions.
Findings :

Table B.7.2.1-4 : Adsorption and desorption constants of ziram (Kd, Koc, n)

	Adsorption			Desorption		
	Kd	**Koc**	**n**	**Kd**	**Koc**	**n**
Clay	68.1	3732	2.907	450.6	24709	1.386
Sand	2.9	1232	1.054	81.1	34479	0.680
Silt loam	7.6	759	1.537	4092.7	409270	0.480
Sandy loam	5.7	314	1.146	40.2	2207	0.990

Conclusions :
According to Mc Call (1988) , ziram has medium to slight mobility in the soil. (Koc = 314-3732). The stability of ziram should be determined. The role of organic matter in adsorption and hence use of Koc is questionable when considering the Koc range obtained.

B.7.2.2 Column leaching studies with the active substance and relevant metabolites (Annex IIA 7.1.3.1; Annex IIIA 9.1.2.1)

Leaching Characteristics of Parent Ziram (Warren J., 1985)
Guidelines :
40 CFR 158 Environmental Fate, USEPA Pesticide Assessment Guidelines Subdivision N; Series 163-1.
GLP :
Yes
Material and Methods :
Test substance : **thiocarbamate-labeled [^{14}C]Ziram. Radiochemical purity: 97%. Specific radioactivity 16.4 mCi/mMol**
Soil :
Table B.7.2.2-1 : Characteristics of the soils used in thecolumn leaching study

Soil type	Origin	pH	CEC (meq/100g)	OC content (%)	Field capacity (1/3 bar) (%)	Clay content (%)	Silt content (%)	Sand content (%)
Loamy sand	Missouri (USA)	8.0	7.7	0.304	5.44	4.0	14.0	82.0
Loamy sand	Hanford (USA)	6.4	3.4	0.478	4.53	4.0	16.0	80.0
Sandy loam	Manteca (USA)	8.2	11.5	1.00	16.71	10.0	36.0	54.0
Sandy loam	Stockton (USA)	7.1	11.6	1.43	16.58	18.0	26.0	56.0

Test conditions :
10 g of soil containing respectively 11.6, 9.39, 14.9 and 84.0 mg a.s. /kg was applied onto the top of laboratory soil columns (7.6 cm internal diameter, filled with 30.5 cm soil) filled with 4 different soils (3 replicates/soil)
Elution was made with 50.8 cm deonized water. Leaching time was not recorded.
After leaching the colums were segmented in 2.5 cm slices and analyzed.
Analytical methods :
Analysis by LSC
Findings :
Table B.7.2.2-2 : Distribution of radioactivity in column leaching study with fresh residue

	Loamy sand Missouri	Loamy sand Hanford	Sandy loam Manteca	Sandy loam Stockton
KOH traps	2.2	0.8	0.7	1.3
1' segment (top)	89.0	66.3	74.9	81.2
2' segment	1.0	0.7	0.9	8.1
3' segment	0.5	0.5	0.7	3.0
4' segment	0.3	0.1	0.5	1.7
5' segment	0.3	0.1	0.4	1.3
6' segment	0.2	0.1	0.3	1.2
7' segment	0.2	< 0.1	0.4	1.1

	Loamy sand Missouri	Loamy sand Hanford	Sandy loam Manteca	Sandy loam Stockton
8' segment	0.2	< 0.1	0.3	0.8
9' segment	0.2	< 0.1	0.3	0.8
10' segment	0.1	< 0.1	0.4	0.7
11' segment	0.1	< 0.1	0.2	0.6
12' segment (bottom)	0.1	< 0.1	0.2	0.5
Total segments	92.2	67.8	79.5	101.0
Leachates	6.6	9.6	10.6	14.6
Balance : KOH traps + segments + leachates	101.0	78.2	90.8	116.9

Conclusions :
Ziram had low mobility in 30.5 cm columns of two loamy sand and two sandy loam soils eluted with 50.8 cm of water. 6.6-14.6% radioactivity was recovered in leachates. 66.3-89.0% of applied radioactivity was recovered in the top 1 inch of the soil columns. The quality of the study is questionable : it shoud be necessary to characterize the radioactivity recovered in the leachates.

B.7.2.3 Aged residue column leaching (Annex IIA 7.1.3.2; Annex IIIA 9.1.2.1)

Leaching Characteristics of Aged Ziram (Warren J., 1985)
Guidelines :
40 CFR 158 Environmental Fate, USEPA Pesticide Assessment Guidelines Subdivision N; Series 163-1.
GLP :
Yes
Material and Methods :
Test substance : [^{14}C]Ziram (label position not specified). Radiochemical purity: not specified . Specific radioactivity: 16.4 mCi/mMol
Soil :
Table B.7.2.3-1 : Characteristics of the soil used in the leaching study with aged residue.

Soil type	Origin	pH	CEC (meq/100g)	OC content (%)	Moisture content (%)	Clay content (%)	Silt content (%)	Sand content (%)
Loamy sand	Hanford (USA)	6.4	3.4	0.478	4.53	4.0	16.0	80.0

Test conditions :
10 mg [^{14}C]ziram/kg soil was applied. For the aging period, the treated soil was incubated in darkness at 25 $\pm$ 1 °C and 60% of field moisture capacity for 21 days.
90.6% of the radioactivity in the aged residue was recovered as bound residue, 12.3% as extractable residue, there was no parent compound present in the extractable residue characterized by TLC A 10 g sample of the aged treated soil was used for the leaching phase.
Soil was applied onto the top of laboratory soil columns (7.6 cm internal diameter, filled with 30.5 cm soil) (3 replicates/soil) Elution was made with 50.8 cm deonized water. Leaching time was not recorded. After leaching the colums were segmented in 2.5 cm slices and analyzed.
Analytical methods :
Analysis by LSC. Characterization of the leachate was not performed.

Findings :

Table B.7.2.3-2 : Distribution of radioactivity (% of applied) in column leaching study with aged residue (21 days)

	Loamy sand Hanford
KOH traps	0.5
1' segment (top)	71.4
2' segment	3.6
3' segment	0.5
4' segment	0.2
5' segment	0.2
6' segment	0.2
7' segment	0.1
8' segment	0.1
9' segment	0.1
10' segment	0.1
11' segment	0.1
12' segment (bottom)	0.1
Total segments	76.7
Leachates	9.8
Balance : KOH traps + segments + leachates	87.0

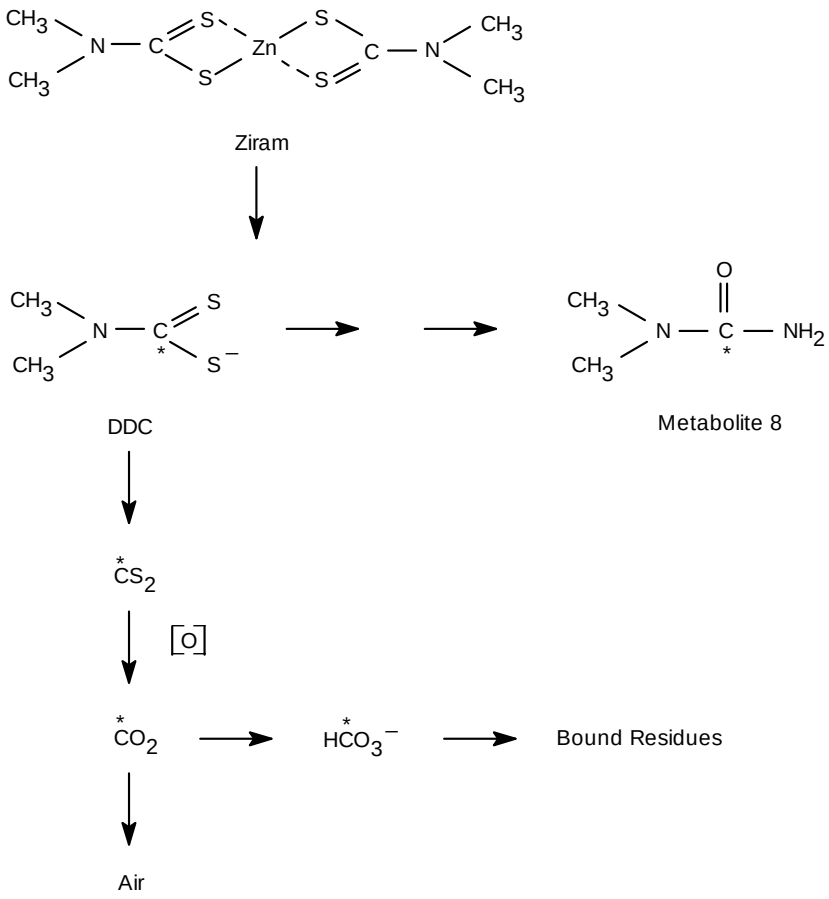
Conclusions :
Aged residue of ziram had low mobility in 30.5 cm columns of loamy sand leached with 50.8 cm of water. 9.8% **radioactivity was recovered in leachates. 76.7% of applied radioactivity was recovered in the top 1 inch of the soil columns. The quality of the study is questionable : it shoud be necessary to characterize the radioactivity recovered in the leachates.**

B.7.2.4 Lysimeter and field leaching studies (Annex IIA 7.1.3.3; Annex IIIA 9.1.2.2)

Not submitted; not necessary

B.7.3 Summary of behaviour in soil and predicted environmental concentration in soil (PECs) Annex IIIA 9.1.3)

Figure B.7.3-1 : Metabolic pathway of ziram in soil



The data concerning the behaviour of ziram in soil are scarce. The studies present several shortcomings.

Degradation rates under different soil and temperatures conditions are absent.
It would be also necessary to have more information about the major metabolite (1,1-dimethylurea) identified in the aerobic degradation study (physico-chemical characteristics, persistence, leaching potential, effects on human and non-target organisms)

Table B.7.3-1 : Summary of behaviour of ziram in soil

Test soil				**Test system**	**Results**	**References**
Soil type	**Soil $pH_{(KCl)}$**	**CEC**	**Organic carbon content (%)**			
Sandy loam	5.4	9.0	1.8	Aerobic degradation at 25°C (lab)	- DT_{50} a.s. = 1.7 days - major metabolite of ziram is 1,1-dimethylurea (max 10.48% after 30 d) - final metabolites of ziram are CS2 + CO2 (48.35% after 60 d) and bound residue (48.16% after 7 d, 42% after 60 d)	Heasook K., 1996
Sandy loam	5.4	9.0	1.8	Photolysis at 25°C	DT_{50} of 8-8.9 h (irradiated samples) DT_{50} of 20-16.2 h (dark samples)	Reynolds J., 1997
2 Loamy sands 2 Sandy loams	6.4-8.2	3.4-11.6	0.3-1.4	Adsorption/ desorption study (lab)	Koc = 559-12010	Warren J., 1985
Clay Sand Silt loam Sandy loam	5.4-6.7	3.5-33.4	0.2-1.8	Adsorption/ desorption study (lab)	Koc = 314-3732	Spare W., 1995
2 Loamy sands 2 Sandy loams	6.4-8.2	3.4-11.6	0.3-1.4	Column leaching with fresh residue (lab)	the a.s. has low mobility. 6.6-14.3% radioactivity in the leachate 66.3-89.0 % radioactivity in the top 1 inch of the soil columns	Warren J., 1985
Loamy sand	6.4	3.4	0.478	Column leaching with aged residue (21 days) (lab)	Low mobility of the a.s. and metabolites (but no characterization of the compounds) 9.8% radioactivity in the leachate 76.7 % radioactivity in the top 1 inch of the soil columns	Warren J., 1985

PEC soil

At this stage, due to the lack of data, it is only possible to calculate an initial PEC soil.

The following assumptions were made to calculate an initial PEC
- application rate of 3.040 kg a.s./ha in orchard
- 50 % of the deposit reaching the soil surface
- dispersion in a 5 cm soil layer
- soil density = 1.5 kg/dm^3

Initial PEC = 2.027 mg a.s./kg soil

The notifier should provide information on the PEC soil short term and long term after repeated applications for the a.s. and the relevant metabolites. The notifier should also provide information on the PEC groundwater.

B.7.4 Fate and behaviour in water (Annex IIA 7.2.1; Annex IIIA 9.2)

B.7.4.1 Hydrolysis rate of relevant metabolites, degradation and reaction products (Annex IIA 7.2.1.1)

One valid study of hydrolysis of the a.s. was provided. Description of the study is given under this point because information about metabolites was reported.

Hydrolysis of [^{14}C]ziram in water at pH 5, 7, 9 (Heasook K., 1995)
Guidelines :
40 CFR 158 Environmental Fate, USEPA Pesticide Assessment Guidelines Subdivision N; Series 161-1.
GLP :
Yes
Material and Methods :
Test substance : ziram labeled with ^{14}C at both thiocarbonyl positions of the molecules, Radiochemical purity: >98 %. Specific radioactivity: 53.96 mCi/mMol
Test conditions :
Buffer solutions at pH 5, 7 and 9, with acetone as cosolvent; sterile conditions at ~25°C in the dark.
Findings :
pH 5 : DT_{50} = 10.4 minutes
pH 7 : DT_{50} = 17.67 hours
pH 9 : DT_{50} = 6.31 days
Under pH 5 and 7 the main metabolite was CS_2 which is volatile.
The major metabolite found at pH 9 was dimethyldithiocarbamic acid (DDC) (~ 75% after 30 days). Carbon oxysulfide, isothiocyanic acid or thiocyanic acid, and N, N-dimethylformamide also were detected at pH 9.
Conclusions :
The a.s. is not persistent at pH 5 to 7. DDC is the major degradation product at pH 9.

Determination of hydrolysis rate with [^{14}C]ziram (Daly D., 1987)
Conclusions :
The identification of labile metabolites was very difficult at the time of the work. The DT_{50} were in the range 8-191 days. It was estimated that they do not reflect the actual degradation rate of ziram. The results of this study were not taken into account in the final evaluation since a valid study was provided.

B.7.4.2 Direct phototransformation of relevant metabolites, degradation and reactions products in water (Annex IIA 7.2.1.2)

One valid study was provided concerning the phototransformation of ziram. Description of the study is given under this point because some information about photodegradates were reported.
Some more information about the photodegradation of the major metabolites is required.

Aqueous photolysis of [^{14}C]ziram (Heasook K., 1996)
Guidelines :
40 CFR 158 Environmental Fate, USEPA Pesticide Assessment Guidelines Subdivision N; Series 161-2.
GLP :
Yes
Material and Methods :
Test substance : ziram labeled with ^{14}C at both thiocarbonyl positions of the molecules, Radiochemical purity: >96.54 %. Specific radioactivity: 53.96 mCi/mMol
Test conditions :
Suntest xenon lamp with UV was filter was used; test in phosphate buffer pH 9 at 25°C during 24 hours.
Findings :
Ziram is rapidly photodegraded in water (DT_{50} = 8.66 hours) .

A metabolic pathway of ziram in water was established. 15 major transformation products were observed in the 24 hour-duration of the study.
The two major degradates (Degradates A and E), which amounted to an average of 26.83 % and 20.59 % of the total radioactivity, were identified as sole N,N-dimethylformamide (!). Another major degradate (Degradate F) observed at an average level of 15.28 % was identified as N,N-dimethylthioformamide.
Degradate B, which amounted to an average of 20.98 % at the 24-hour sampling interval, was composed of six degradates identified as N,N-dimethylthioformamide (Degradate B-1), N,N-dimethyl-N-formyl sulfinic acid (Degradate B-2), N,N-dimethyl-N-thioformyl sulfinic acid (Degradate B-3), N,N-dimethyl-N-thioformyl sulfonic acid (Degradate B-4), N,N-dimethyl-N-thioformyl-O-sulfonic acid (Degradate B-5), dimethyldithiocarbamic acid (Degradate B-7), and one unknown (Degradate B-6).
Conclusions :
This study performed on the a.s. revealed the presence of several transformation products. It would be necessary to have more information about the fate and the effects of these metabolites in water (physico-chemical characteristics, persistence, effects on human and non-target organisms)

Determination of photodegradation of ziram in aqueous solution (Cranor W., 1985)
Conclusions :
The quality of this study is questionable : the range of recovery balance is very large. The regression coefficients of the dissipation curve are low (-0.02969 and -0.5051 for the exposed samples. The study was not taken into account in the final evaluation.
Without photosensitizer, DT_{50} (light) = 7.84 days; DT_{50} (dark) = 6.04 days
With photosensitizer, DT_{50} (light) = 139 days; DT_{50} (dark) = 4 days

B.7.4.3 Ready biodegradability of the active substance (Annex IIA 7.2.1.3.1)

Not submitted. The study is required to decide whether the R53 phrase is applicable.

B.7.4.4 Water/sediment study (Annex IIA 7.2.1.3.2)

Not submitted. The study is required.

B.7.4.5 Degradation in the saturated zone of active substance, metabolites, degradation and reaction products (Annex IIA 7.2.1.4)

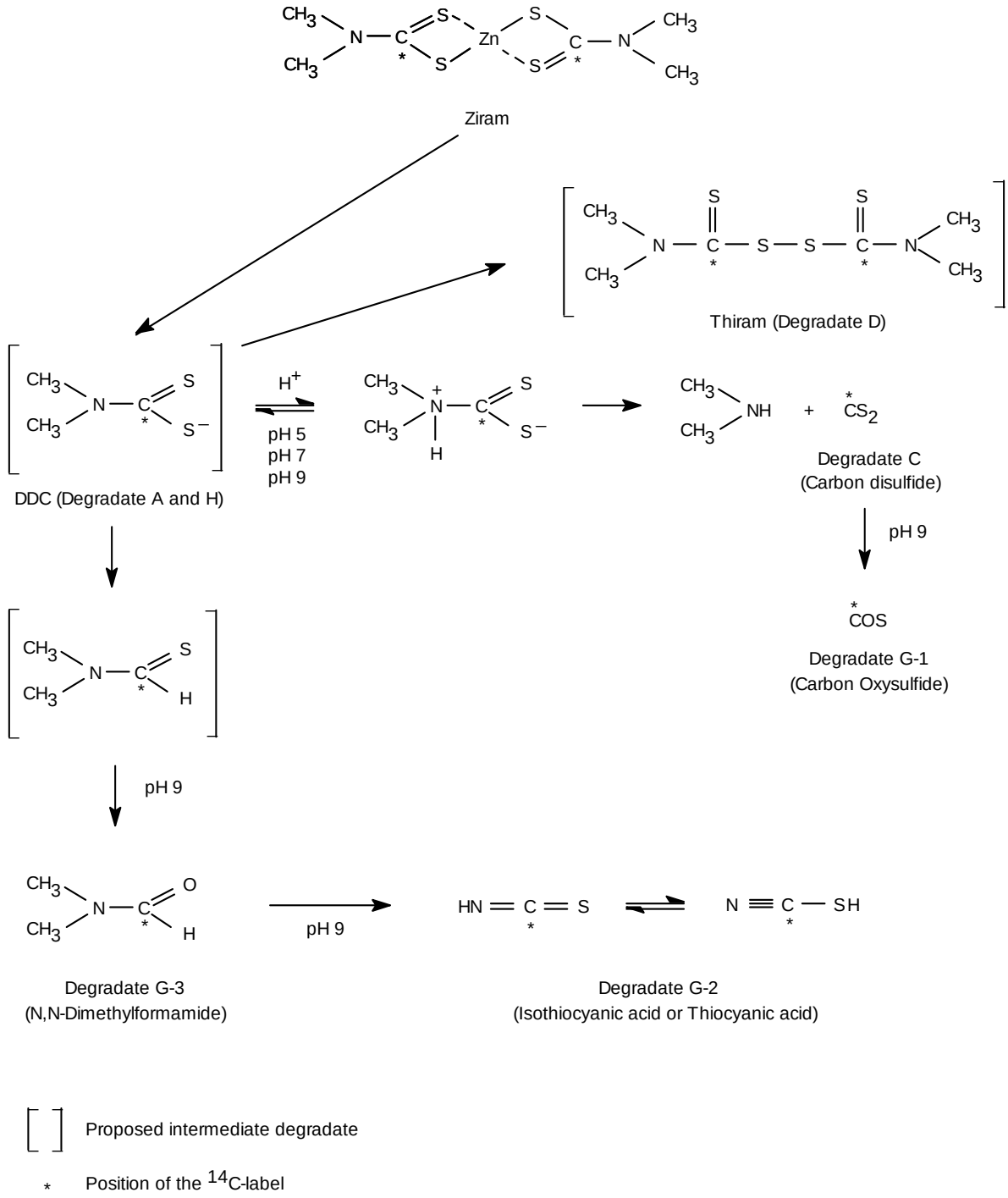
Not submitted - The study is not required. It is not expected that the substance would reach the saturated zone under the proposed conditions of use.

B.7.5 Impact on water treatment procedures (Annex IIIA 9.2.2)

Not submitted. No guidance is proposed.

B.7.6 Summary of behaviour in water and predicted environmental concentrations in surface water and in ground water (PECsw, PECgw) (Annex IIIA 9.21, 9.2.3)

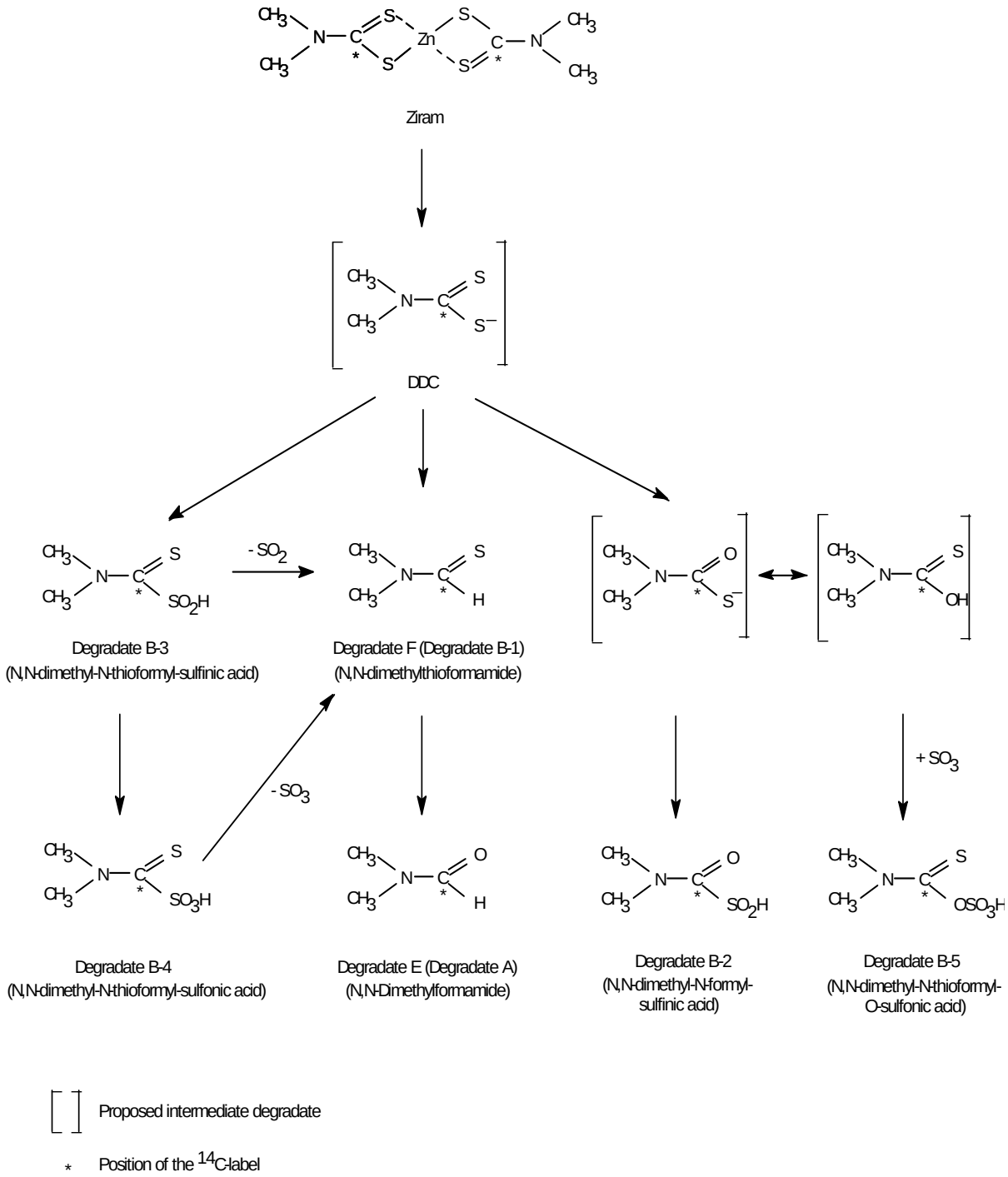
Figure B.7.6-1 : Proposed hydrolytic degradation pathway of ziram



[ ] Proposed intermediate degradate

* Position of the ^{14}C-label

Figure B.7.6.1-2 : Proposed aqueous photolytic degradation pathway of ziram



The data concerning the behaviour of ziram and its metabolites in water are scarce :

Information on the major transformation products is required
Ready biodegradability of the a.s. is required.
Water/sediment study is required.

Table B.7.6-1 : Summary of behaviour of ziram in water

Test medium (soil, sediment, water)				**Test system**	**Results**	**References**
Medium type	**pH**	**CEC**	**Organic carbon content (%)**			
Buffer solution	9	-	-	24 hour photolysis at 25°C (Suntest with Xenon lamp with UV filter)	DT_{50} = 8.7 hours major degradates : *N*,*N*-dimethylformamide *N*,*N*-dimethylthioformamide	Heasook K., 1996
Buffer solutions	5 7 9	-	-	Hydrolysis at 25°C in the dark	DT_{50} = 10.4 minutes DT_{50} = 17.67 hours DT_{50} = 6.31 days major degradate : CS_2; DDC at pH9	Heasook K., 1995

The estimations of the PECsw were calculated assuming that :
- DT_{50} = 18 hours (Hydrolysis rate at pH 7)
- Water layer = 30 cm
- Spray drift scenarios according to Ganzelmeier (1995)
- Degradation rate was calculated according to first order kinetics
- Scenario in orchard with the highest application rate of 3.040 kg a.s./ha

The PECsw seem to be very favourable (0.2-0.3 µg a.s./l after 7 days). Nevertheless, due to the very high aquatic toxicity of the a.s. and the fact that repeated applications are made, it is necessary that the notifier determines accurate short term and long term PEC in surface water in order to evaluate the chronic risk to aquatic organisms.

Table B.7.6.-2 : PEC_{sw} (mg a.s./l)

Time after applications (days)	Orchard (early growth stage) 3.040 kg a.s./ha			Orchard (late growth stage) 3.040 kg a.s./ha		
	direct application (drift = 100 %) (*)	application at 5 m of the water surface (drift = 20%)	application at 20 m of the water surface (drift = 4%)	direct application (drift = 100 %) (*)	application at 5 m of the water surface (drift = 10 %)	application at 20 m of the water surface (drift = 1.5%)
0	1.013	0.203	0.040	1.013	0.101	0.015
1	0.402	0.080	0.016	0.402	0.040	0.006
2	0.160	0.032	0.006	0.160	0.016	0.002
4	0.025	0.005	0.001	0.025	0.002	0.0004
7	0.002	0.0003	-	0.002	0.0002	-
14	-	-	-	-	-	-
21	-	-	-	-	-	-
28	-	-	-	-	-	-
42	-	-	-	-	-	-

- : < 0.0001 mg/l
(*) : unrealistic situation; only given to help the reader

B.7.7 Fate and behaviour in air (Annex IIA, 7.2.2; Annex IIIA 9.3)

Not submitted; information is required

B.7.8 Summary of behaviour in air and predicted environmental concentrations in air (PECa) (Annex IIIA 9.3)

No information available

B.7.9 Definition of the residue (Annex IIA 7.3)

Residue in soil : ziram
Residue in water : ziram, dimethyldithiocarbamic acid, dimethyldithioformamide, dimethylformamide

B.7.10 References relied on

Environmental fate and behaviour

Annex point(s) Dir 91/414/EEC	Author(s)	Title Generated by (company or organisation), Submitted by (company(ies) or organisation), Report/file No. of submitting company Date of report for publication: reference	GLP GEP	Published Protected
IIA7.1.1.1.2	Carpenter M.	Determination of Photodegradation of ^{14}C-Ziram on the Surface of Soil. ABC Lab Inc. Report N° 33370; 21 Oct 1985a. Submitted by UCB-Elf Atochem Agri	yes	unpublished protected
IIIA7.2.1.2	Carpenter M.	Determination of Photodegradation of ^{14}C-Ziram in Aqueous Solution. ABC Lab Inc. Report N° 33369; - 3 Oct 1985b. Submitted by UCB-Elf Atochem Agri	yes	unpublished -
IIA7.1.1.1.1	Cranor W.	Aerobic soil metabolism study with ^{14}C-Ziram. ABC Labs, Inc. - Report n° 33366 - 15 Jan 1987. Submitted by UCB-Elf Atochem Agri	yes	unpublished -
IIA7.1.1	Cranor W.	Anaerobic soil metabolism study with ^{14}C-Ziram. ABC Labs, Inc. Report n° 33367 - 15 Jan 1987. Submitted by UCB-Elf Atochem Agri	yes	unpublished -
IIA7.2.1	Daly D. *et al*	Determination of hydrolysis rate with ^{14}C-Ziram. ABC labs Inc. Report N. 33363 - 18 Nov 1987	yes	unpublished -
IIA7.1.1.1.1	Heasook K-K	Aerobic soil metabolism of ^{14}C-Ziram XenoBiotic Labs Inc. N° XLB 94072 17 April 1996 Submitted by UCB-Elf Atochem Agri	yes	unpublished protected
IIIA7.2.1.2	Heasook K-K	Aqueous photolysis of ^{14}C-Ziram XenoBiotic Labs Inc. N° XLB 94073 - 15 August 1995 Submitted by UCB-Elf Atochem Agri	yes	unpublished protected
IIIA7.2.1	Heasook K-K	Hydrolysis of ^{14}C-Ziram in water at pH 5, 7 and 9 XenoBiotic Labs Inc. N° XLB 94071 - 13 November 1995 Submitted by UCB-Elf Atochem Agri	yes	unpublished protected
IIA 7.1.1.2.2	Novak A., Binari L.	Terrestrial field dissipation of ziram 76 DF fungicide in California NPC study F 96-7203 - 29 April 1998 Submitted by UCB-Elf Atochem Agri (not evaluated due to very late submission date)	yes	unpublished protected
IIA7.1.1.1.2	Reynolds J.	Photolysis of ^{14}C-Ziram on soil XenoBiotic Labs Inc. N° XLB 95051 27 February 1997 Submitted by UCB-Elf Atochem Agri	yes	unpublished protected
IIIA7.1.1.1.	Reynolds J.,	Anaerobic soil metabolism of ^{14}C-Ziram		unpublishe

Annex point(s) Dir 91/414/EEC	Author(s)	Title Generated by (company or organisation), Submitted by (company(ies) or organisation), Report/file No. of submitting company Date of report for publication: reference	GLP GEP	Published Protected
2	Smalley J.	XenoBiotic Labs Inc. N° XLB 95052 24 February 1997 Submitted by UCB-Elf Atochem Agri	yes	d protected
IIIA 9.1.1.2	Selman F.	Ziram soil dissipation study (76 WDG) ABC Labs, Inc. - Report n° 35028 - 15 Jan 1987a Submitted by UCB-Elf Atochem Agri	yes	unpublished -
IIIA 9.1.1.2	Selman F.	Ziram soil dissipation study (76 WDG) ABC Labs, Inc. - Report n° 35029 - 14 Jan 1987b Submitted by UCB-Elf Atochem Agri	yes	unpublished protected
IIA7.1.2	Spare W.	Adsorption/desorption of ^{14}C-Ziram Agrisearch Inc. N° 2526 5 December 1995 Submitted by UCB-Elf Atochem Agri	yes	unpublished protected
IIA7.1.3.1	Warren J.	Leaching Characteristics of Parent Ziram techn. ABC Labs, Inc. Report 33365 - 26 Sept 1985b Submitted by UCB-Elf Atochem Agri	yes	unpublished protected
IIA7.1.3.2	Warren J.	Leaching Characteristics of Aged Ziram techn. ABC Labs Inc. Report 33364 - 27 Sept 1985c Submitted by UCB-Elf Atochem Agri	yes	unpublished protected
IIIA7.1.2	Warren J.	Determination of Adsorption / Desorption Constants of ^{14}C-Ziram. ABC Labs Inc. Report 33368 - 24 Sept 1985a Submitted by UCB-Elf Atochem Agri	yes	unpublished protected