ANNEX B

ENDOSULFAN

B - 8 : ENVIRONMENTAL FATE AND BEHAVIOUR

B. 8 Environmental fate and behaviour

Endosulfan (6,7,8,9,10,10-hexachloro- 1,5,5a,6,9,9a-hexahydro- 6,9-methano- 2,4,3-benzo-dioxathiepin- 3-oxide) consists of two isomers, alpha endosulfan and beta endosulfan, which differ in the configuration of the isomer SO_3 group and the respective ring. Technical endosulfan consists of the two configurational isomers in the ratio of alpha:beta of approximately 6:3.

The investigations on fate and behaviour of endosulfan in the environment have been carried out predominantly with the active substance. In particular, studies on field dissipation and volatilisation were conducted with formulated material, Thiodan 35 EC.

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

B.8.1.1 Aerobic and anaerobic studies

All studies were carried out with the active substance endosulfan (α and β form in a ratio of ± 70:30). Most of them were performed following EPA or BBA guidelines. DT_{50} and DT_{90} values have been calculated for α endosulfan, β endosulfan and for the parent compound.

B.8.1.1.1 Aerobic studies

Stumpf *et al*., 1995 (A53618)

A laboratory study on aerobic degradation of endosulfan substance and of the two isomers in five different soils was performed under BBA guideline (part IV, 4-1, 1986) and GLP. The radiolabelled test compound:

- 15.44 mg of labelled α endosulfan plus 11.68 mg of non-labelled α endosulfan resulting in a specific activity of 44.3 mCi/g and a radiochemical purity of 97.4%, and,

- 10.33 mg of labelled β endosulfan plus 7.41 mg of non-labelled β endosulfan resulting in a specific activity of 45.7 mCi/g and a radiochemical purity of 98%,

was applied at a rate of 1.3 mg/kg soil (1.0 kg/ha) on sandy loam (SLV), loamy sand (LS2.2), silt loam (SL2), sandy loam (F821) and sandy loam Georgia (SLG). These soils were taken from the upper 10-15 cm layer of agricultural fields or from soil plots covered with grass. The soil properties were as follows (table 8.1.1.1-1).

Table 8.1.1.1-1: Soil properties

¡Error! Marcador no definido.**SOIL**	**SANDY LOAM (SLV)**	**LOAMY SAND (LS 2.2)**	**SILT LOAM (SL2)**	**SANDY LOAM (F821)**	**SANDY LOAM (SL G)**
% Sand	52.7-58.6	84.6-85.4	10-15.3	56.8-61	79.6
% Silt	37.8-31.9	9.7-8.9	71.9-66.6	30.8-26.6	10.4
% Clay	9.5	5.7	18.1	12.4	10
pH	5.5	5.0	5.6	7.1	5.8
Maximum water holding capacity (g/100g)	41	41	48.8	44.4	36
% Organic matter	1.63	5.01	1.23	3.92	4.16
% Organic carbon	0.95	2.91	0.72	2.28	2.42

The treated soil samples, two replicates for each sampling date, were incubated for 365 days at 21±2ºC in the dark. Two incubation flask of each soil had appropriate traps in a closed aeration system for collection of volatile radiocarbon.

Soil was sampled at days 0, 2-3, 7, 14, 30, 59-60, 91, 120, 150-153, 182, 240, 272 and 365 days after application. Soil residues were extracted by solid phase extraction on C8 cartridges and identified and quantified by radio-HPLC (reversed phase C18). Non-extractable residues were measured by combustion of the extracted soil. Half-lives of α endosulfan, β endosulfan and total residue (which includes the metabolite endosulfan-sulphate) were calculated by following a first order kinetics (table 8.1.1.1-2).

The obtained measured values of mineralization (%CO_2) in this study are not realible since the tramp employed to trap it may also trap other volatil organic compounds.

Table 8.1.1.1-2: Results from the aerobic laboratory study. DT_{50} and DT_{90} values are expressed in days. Endosulfan sulphate, non-extractable residues and mineralisation are expressed as % of applied radioactivity.

¡Error! Marcador no definido.	**α endosulfan**		**β endosulfan**		**Parent endosulfan**		**Total endosulfan**		**Endosulfan sulphate**	**Non-extractable residues**	
¡Error! Marcador no definido.**SOIL**	DT_{50}	DT_{90}	DT_{50}	DT_{90}	DT_{50}	DT_{90}	DT_{50}	DT_{90}	At 365 days	100 d	365 d
Sandy loam**¡Error! Marcador no definido.**	12	39	158	523	98	326	61	2038	64.5	<8.3	18.8
	R^2=0.89; n=6		R^2=0.92; n=11		R^2=0.77; n=12		R^2=0.65; n=12				
¡Error!	39	128	264	877	128	426	224	7443	77	<4.9	9.5

Marcador no definido. Loamy sand**¡Error! Marcador no definido.**	R^2=0.96; n=8		R^2=0.92; n=13		R^2=0.90; n=13		R^2=0.83; n=13				
¡Error!	19	62.6	132	440	90	299	45	1510	51.4	<21.3	34.2
Marcador no definido. Silt loam**¡Error! Marcador no definido.**	R^2=0.89; n=8		R^2=0.91; n=13		R^2=0.90; n=13		R^2=0.61; n=13				
¡Error!	<10	<30	108	357	92	305	28	958	34.3	<18.3	29.4
Marcador no definido. Sandy loam**¡Error! Marcador no definido.**	r = -		R^2=0.84; n=8		R^2=0.71; n=8		R^2=0.93; n=8				
¡Error!	14	46	115	383	80	265	33	1126	46.1	<19.5	28.2
Marcador no definido. Sandy loam**¡Error! Marcador no definido.**	R^2=0.93; n=6		R^2=0.92; n=11		R^2=0.84; n=11		R^2=0.98; n=11				

Final recoveries were higher than 99% of the applied radioactivity

The aerobic degradation of α endosulfan was more rapid than the isomer β endosulfan and the mixture showed a moderate half-life. The aerobic degradation occurred via oxidation. The main soil metabolite formed was endosulfan-sulphate (6,7,8,9,10,10- hexachloro -1,5,5a,6,9,9 a-hexa-hexahydro- 6,9-methano -2,4,3- benzodioxathiepin- 3,3-dioxide). This compound was slowly further degraded to the more polar metabolites endosulfan-diol and endosulfan-lacton (less than 10% and less than 5% at 365 days, respectively) and unknown polar compounds which appeared in the break-through during cartridge extraction. The latter portion was normally less than 10% of applied radioactivity. Althoug the total amount of CO_2 could not be measured in this study the total mineralisation of endosulfan was expected to be very low in the five soils. Non-extractable residues were lower than 70% in each soil after 365 days.

It can be stated that α endosulfan is degraded rapidly under aerobic conditions in soil. But β endosulphan is more persistent and comparable in half live with the metabolite endosulfan-sulfate which is the main and more relevant metabolite by this degradation route.

Gildemeister and Jordan, 1984 (A29680)

This study was performed following the EPA guideline 162-1. Radiolabelled endosulfan (5a, 9a-^{14}C) (97% radiochemical purity; ratio α : β = 73:27) was added on silty loam and loamy sand soils at a medium rate of 3.51 mg/kg (2.6325 kg/ha). Soil properties were as follow (Table 8.1.1.1-3).

Table 8.1.1.1-3: Soil properties

¡Error! Marcador no definido.**SOIL**	**SILTY LOAM**	**LOAMY SAND**
pH	6.4	4.7
Cation exchange capacity (meq/100g soil)	21.3	2.9
% Sand	7.2	63
% Silt	70.4	31.6
% Clay	22.4	5.4
Water holding capacity (g/100g soil)	45.8	28.3

Soil samples were incubated in darkness (22±2ºC) for 60 days. Samples were collected at 0, 1, 2, 4, 8, 16, 30 and 60 days, and rate, type and main metabolites of degradation were determined. Volatile degradation products were determined by adsorption units containing a mixture of ethanol-amine and methanol, and absorption vessels containing sulphuric acid and ethylene glicol. Measurements were carried out by liquid scintillation counter.

Soil residues were extracted and examined by HPLC to determine the pattern of degradation products. Results from the study are summarised in table 8.1.1.1-4.

Table 8.1.1.1-4: % of applied radioactivity at 60 days after treatment

¡Error! Marcador no	**SILTY LOAM**	**LOAMY SAND**
α endosulfan	3.2	3.6
β endosulfan	12.6	25.7
Endosulfan sulphate	18.6	38.6
Other metabolites	4.8	2.1
Non-extractable residues	45.2	26.3
Mineralisation	1.8	2.8
Total radioactivity	86.2	99.1

The determination of the DT_{50} carried out in the study was not correct due to the Log_{10} was used for it instead the Ln. The correct determination of the DT_{50} was carried out by the Raporteur based on the results of the study, listed in table 8.1.1.1-5.

Table 8.1.1.1-5:% of applied radioactivity

Time	**Silt loam**		**Loamy sand**	
	α Endosulfan	**β Endosulfan**	**α Endosulfan**	**β Endosulfan**

0	56.2	27.5	62.2	32.5
1	54.0	20.2	63.8	21.9
2	60.2	21.8	42.8	20.2
4	57.5	22.6	36.5	19.8
8	44.5	19.4	26.9	19.4
16	49.5	20.1	17.1	21.0
30	19.8	20.4	8.3	16.8
60	3.2	12.6	3.6	25.7

Half-lives of parent endosulfan were determined by first order kinetics.Table 8.1.1.1-6.

Table 8.1.1.1-6: α+β Endosulfan Half lives (days)

Soil	DT_{50}	DT_{90}	R^2	n
Silt loam	25.6	85	0.96	8
Loamy sand	37.5	124.7	0.57	8

Results revealed a rather rapid breakdown of the active ingredient under aerobic conditions. During the incubation period (60 days) the formation of a main metabolite (endosulfan sulphate at more than 10% of the applied radioactivity) was observed in both soils. Non-extractable compounds were lower than 50% in both cases. Mineralisation was rather small in both, silty loam and loamy sand soils. Volatile degradation products were 1.8 and 1.2 % of applied radioactivity in silty loam and loamy sand soils at the end of the study.

Although degradation pathway has not been studied for more than 60 days, endosulfan sulphate has been identified as the main degradation product during the assayed time. So, additional metabolites and CO_2 production were only observed at low rates.

This study was performed with radiolabelled endosulfan in only two positions. The only major metabolite observed in this study is endosulfan sulfate, but endosulfan is slowly degraded and appeared as a residue at >10% . CO_2 production was observed at low rates (1.8 and 2.8% at the end of the study). None of the chlorinated carbons were labeled therefore the mineralization of the chlorinated fraction of the molecule may not be demonstrated in this study.

Stumpf, 1988 (A39429)

This study was performed under EPA guideline (N, 162-1) and GLP. Radiolabelled endosulfan (6,7,8,9,10-^{14}C; 99.2% of radiochemical purity; specific radioactivity 13.6 mCi/g; 66α:33β) was applied to a sandy loam soil with a high content of organic carbon (Table 8.1.1.1-7).

Table 8.1.1.1-7: Soil properties

% SAND	70.0
% SILT	24.0
% CLAY	6.0
pH	7.1
MAXIMUM WATER HOLDING CAPACITY (g/100g)	44.4
CATION EXCHANGE CAPACITY (meq/100g soil)	9.5
% ORGANIC MATTER	5.1

The laboratory application rate was 3.5 mg/kg, equivalent to 2.6 kg as./ha. The treated soil with a moisture content of 40% of the maximum holding capacity, was incubated in open systems under aerobic conditions at 28±2ºC in the dark for 60 days. Volatile degradation products were not estimated because of the expected low mineralization rate..

Soil samples were taken immediately after application and at days 10, 30, 60 after application. The soil was extracted with acetonitrile/toluene for three times. Soil extracts and extracted soils were measured for radioactive levels. The extractable degradation products were identified and quantified by radio-HPLC and GC/MS. Soil bound residues of selected samples were further extracted with hot extraction solvent, with aqueous $Ca(OH)_2$ and with aqueous NaOH. Results are summarised in table 8.1.1.1-8.

Table 8.1.1.1-8: Recovery of applied radioactivity (%).

¡Error! Marcad or no	**α endosulfan**	**β endosulfan**	**Parent endosulfan**	**Endosulfan sulphate**	**Unknown compounds**	**Total endosulfan (α+β+e.sulphate)**	**Non-extractable residues**	**Total recovery of radioactivity**
0	42.0	33.9	75.8	<0.1	<0.1	75.8	8.2	84.0
10	16.9	30.7	47.6	27.7	<0.1	75.2	13.8	89.0
30	7.5	24.3	31.8	34.7	1.3	66.4	23.2	90.9
60	6.2	16.7	22.9	30.0	1.4	52.8	28.7	83.0

DT_{50} and DT_{90} values were calculated by assuming first order kinetics, by linear regression (table 8.1.1.1-9). The DT values for endosulfan sulphate were only estimated due to the slow decline during the period of the study.

Table 8.1.1.1-9: DT_{50} values (days) of endosulfan

¡Error! Marcad	**α endosulfan**	**β endosulfan**	**Parent endosulfan**	**Endosulfan sulphate**	**Total endosulfan (α+β+e.sulphate)**
DT_{50}	23	58	37	100-150	110
DT_{90}	78	194	123	-	366
R^2	0.80	0.99	0.92	-	0.97
n	4	4	4	-	4

During the incubation time (60 days), the breakdown of α-endosulfan was faster than that of the ß-isomer. The main metabolite was endosulfan-sulphate with a maximum of 35 % of applied radioactivity after 30 days. Additionally minor metabolites were detected and were partly identified (i.e. endosulfan ether, endosulfan diol). Non-extractable compounds were lower than 30%.

It can be stated that endosulfan is degraded under aerobic conditions showing:

- DT_{50} values of 37 days (α+β endosulfan) and 110 days (α+β+endosulfan sulphate)

- DT_{90} values of 123 days (α+β endosulfan) and 366 days (α+β+ endosulfan sulphate)

Although degradation pathway has not been studied for more than 60 days, endosulfan sulphate has been identified as the main degradation product during the assay time. Additional metabolites were only observed at low rates. However, non-extractable compounds increased during the study showing values of 28.7% at 60 days.

DT_{50} values were obtained by a linear regresion of only four points.

Timme *et al.*, 1986 (A53503)
Dissipation data for endosulfan were calculated for a number of standard and other field soils using six different kinetic functions. Soil properties, methods used to perform the study and analysed the residues have not been reported. So, this study should not been included in the assessment of endosulfan fate and behaviour in soil.

El Beit *et al*, 1981 (END/L0038)
Results presented in this study were similar to those presented by Stumpf *et al*., 1995 (A53618).

B.8.1.1.2 Anaerobic studies

Gildemeister *et al*., 1988 (A37589)
This study was performed under EPA guideline (N, 162-2) and GLP. Radiolabelled test compound (5a,9a-^{14}C; 66α:33β (28.21 mCi/g specific radioactivity; 97.6% radiochemical purity) + 99% non labelled compound) was applied on sandy loam and silt loam at a rate of 2.6 kg/ha. Soil properties were as follow (Table 8.1.1.2-1).

Table 8.1.1.2-1: Soil properties

¡Error! Marcador no definido.**SOIL**	**SANDY LOAM**	**SILT LOAM**
% ORGANIC MATTER	5.5	1.6
pH	7.2	6.4
CATION EXCHANGE CAPACITY (meq/100g soil)	9.8	21.3
% SAND	59.5	7.2
% SILT	32.7	70.4
% CLAY	7.8	22.4
WATER HOLDING CAPACITY (g/100g soil)	39.2	45.8

The soils were incubated first under aerobic conditions (24 days), converted to anaerobic conditions (5 days) and then incubated under anaerobic conditions (59 days), at 22±2ºC. The whole study was terminated 88 days post treatment.

Soils were taken immediately after application and 24 days after the initiation of the aerobic portion of the study. Subsequent samples were taken immediately after the establishing of anaerobic conditions as well as after 13, 28 and 59 days.

After separation of the water phase, soil residues were extracted with acetonitrile/toluene three times. The extractable degradation products were identified and quantified by radio-HPLC. Volatile degradation products were not trapped. Results are expressed in table 8.1.1.2-2.

Table 8.1.1.2-2: Recovery of applied radioactivity (%) in soils incubated for 88 days (55 days under anaerobic conditions)

¡Error! Marcador no	**DT**	**DC**	**α end.**	**β end.**	**Parent endosulfan**	**E. sulphate**	**Other metabolites**	**Total endosulfan (α+β+e.sulphate)**	**Non-extractable residues**	**Total % of radioactivity**
Sandy loam	24	24 A	17.7	30.6	48.3	32.6	<10	80.9	13	93.9
	29	0 AN	15.1	29.7	44.8	32.7	<10	77.5	6.9	96.5
	42	13 AN	14.2	26.8	41	26.6	<10	67.6	14.2	90.9
	57	28 AN	14.0	24.9	38.9	25.8	<10	64.7	12.7	92
	88	59 AN	10.4	23.0	33.4	22.4	<10	55.8	15	91.1
Silt loam	24	24 A	25.0	32.5	57.5	18.5	<10	76	19.1	95
	29	0 AN	22.0	35.6	57.6	19.5	<10	77.1	9	91.1
	42	13 AN	23.5	33.4	56.9	18.0	<10	74.9	12.7	91.6
	57	28 AN	22.6	30.0	52.6	16.6	<10	69.2	19.7	93.4
	88	59 AN	18.3	26.3	44.6	15.2	<10	59.8	17.5	84.5

DT = Days after treatment
DC = Day condition
A = aerobic
AN = Anaerobic

Anaerobic disappearance times (DT_{50}) were calculated by first order kinetics (Table 8.1.1.2-3).

Table 8.1.1.2-3: DT_{50} values (days) of endosulfan

¡Error! Marcado		**α endosulfan**	**β endosulfan**	**Parent endosulfan**	**Endosulfan sulphate**	**Total endosulfan (α+β+e.sulphate)**
Sandy loam	DT_{50}*	110	167	143.4	120	133
	DT_{90}*	366	557	476.6	401	442
	R^2	0.87	0.89	0.98	0.80	0.93
Silt loam	DT_{50}*	124**	136	154	165	158
	DT_{90}*	408	443	504	557	516
	R^2	0.93	0.98	0.95	0.94	0.98

* = Values estimated from n = 4.
** = without day 0 value.

The breakdown of α-endosulfan was faster compared with the isomer β-endosulfan. During the aerobic incubation the main metabolite endosulfan sulphate was formed and accounted for 15-33% of the applied radioactivity. During the anaerobic part of the study, 2-6% of the applied dosage were measured in the water layer. The extractability of the soil was in the range of 63-86% of applied. This was accompanied by the formation of non-extractable residues of 7-20% of applied. The anaerobic incubation continued to find endosulfan sulphate along with other metabolites as endosulfan diol and endosulfan lactone. The anaerobic DT_{50} of parent endosulfan showed values of 144-154 days.

It can be stated that anaerobic soil degradation of endosulfan proceeded slower and with no significant difference between the isomers than during the aerobic degradation. In consequence to this slow degradation, endosulfan sulphate was the main degradation product formed, and non-extractable residues were very low.

DT_{50} values were obtained with only four points and the DT values for endosulfan sulphate are considered irrelevant since the processes of formation and degradation was not considered together in the calculation. The breakdown of α endosulfan was faster in aerobic conditions. In anaerobic conditions the molar ratios of α and β isomers did not changed significantly during the anaerobic incubation.

Martens, 1977 (A12501)

This study was not conducted under any guideline or in compliance with GLP. Radiolabelled endosulfan (8,9-^{14}C; specific activity 8.3-15.2 µCi/mg) was applied at a rate of 10 ppm on seven different soils. They were incubated under three conditions: aerobic, anaerobic and flooded.

However, incubation conditions were not conducted under typical conditions proposed by SETAC guidelines and so, it should not be considered for the endosulfan fate and behaviour assessment.

B.8.1.2 Photolysis

Gildemeist and Jordan, 1983 (A25805)

The study was performed prior to the implementation of GLP but it was carried out under EPA guidelines. Radiolabelled endosulfan (12.1 mCi/g specific activity; purity 98%) was added to sand soil

(2.7 % organic carbon, 4.7 pH). A thin-layer slide was covered with soil and exposed to simulated sun light in a SUNTEST apparatus used as a photoreactor. The radiation intensity was 820 W/m^2 in the wavelength range between 300 and 830 nm. The light intensity amounts to approx. 15 klux. The radiation was cut off at 290 nm in the ultraviolet range. Samples were exposed for 4, 8, 16, 32 and 45 hours in the photoreactor. This compares to a solar exposure of 2, 7 to 30 days on the outside.

Soil samples were extracted 3 times with acetonitrile/toluene (80/20 v/v) after which the non-extractable radioactivity was determined by burning an aliquot of the soil. Radioactivity was measured by liquid scintillation and determinations were performed by TLC. Results are expressed in table 8.1.2-1.

Table 8.1.2-1: Recovery of applied radioactivity (%)

¡Error! Marcador no definido.**Time of sampling**	**Parent endosulfan (alpha + beta)**	**Metabolites**	**Non-extractable compounds**	**Total radioactivity**
4 h	90.8	2.6	2.5	95.9
8 h	90.5	4.5	1.6	96.6
16 h	87.7	4.2	2.7	94.6
32 h	84.6	6.2	4.5	95.3
45 h	84.5	5.9	3.5	93.9
Dark control	88.9	5.4	3.3	97.6

A rather slow photolytic degradation of endosulfan applied on soil could be observed. Therefore, a calculation of the half-life time is not reasonable. It has been suggested as >200 days. Therefore, metabolites and non-extractable residues were not found. However, this study does not provide enough information to evaluate the photolytic degradation of endosulfan. The assay time and the soil used in the laboratory study, can not be considered as the adequate conditions.

Ruzo *et al*., 1988 (A41608)

The study was carried out following the EPA guideline and GLP. The photoreaction kinetics of radiolabelled endosulfan (6,7,8,9,10-^{14}C; 99-99.5% of purity; 66α (32.2 mCi/mmol):33β (32.6 mCi/mmol)) was studied on a silty loam soil at a rate equivalent to 1.12 kg/ha. Samples were exposed to natural sunlight up to 30 days under controlled conditions. Another set of samples was incubated as dark control. The average temperatures during the course of the study were 25.0±1.1ºC for light exposed samples and 23.0±0.6ºC for dark control samples.

Soil samples were extracted 3 times with acetonitrile/toluene (80/20 v/v) after which the non-extractable radioactivity was determined by burning an aliquot of the soil. Radioactivity was measured by liquid scintillation and determinations were performed by TLC. Results are expressed in table 8.1.2-2.

Table 8.1.2-2: Recovery of applied radioactivity (%)

¡Error! Marcador no definido.	Time of sampling	Parent endosulfan	Metabolites	Mineralisation	Non-extractable compounds	Unknown compounds	Total radioactivity
Irradiated samples	0 days	102.7	0	0	0.35	0	103.05
	30 days	92.15	3.8	1.3	1.25	0.01	98.51
Dark samples	0 days	102.6	0	0	0.4	0.2	103.2
	30 days	95.6	4.85	0.02	0.5	0.01	100.95

The photodegradation rate and half-life of parent endosulfan were calculated assuming pseudo-first order kinetics. but was considered irrelevant since the coeficient R^2 was 0.4.

As can be observed, endosulfan was not substantially degraded over the period of the experiment. The endosulfan diol and carbon dioxide were the only products observed in amounts <<10%. Unknown compounds and non-extractable compounds were not observed. The dark control showed a similar degradation behaviour. Therefore, a calculation of the half-life time is not reasonable although it has been suggested as >200 days.

B.8.1.3 Field studies

Field studies were conducted in Northern Europe, Southern Europe and in the United States (in climates comparable to Southern Europe) in order to broaden the basis of evaluation and to confirm the degradation in soil. Three types of studies have been presented:

- Soil dissipation studies.
- Soil residues studies.
- Soil accumulation studies.

All of them have been carried out with the formulated substance Thiodan.

B.8.1.3.1 Soil dissipation studies

Studies were conducted in regions with climates comparable to Northern European conditions (Germany) and Southern European conditions (United States).

Baedelt *et al*., 1992a (A53554)

The study was performed under GLP and the BBA guideline IV, 4-1, stage 2. However the GLP statement was nos signed. A GLP certificate has not been provided for the residue analysis. The quality assurance statement was not signed.

Two different sites in Germany (silty loam and sandy silty loam) were treated with endosulfan during two consecutive years at a rate of 1.056 kg/ha. Soil properties were as follow (Table 8.1.3.1-1).

¡Error! Marcador no definido.**Table 8.1.3.1-1:** Soil properties

	Silty Loam		Sandy silty loam	
	0-20 cm	**20-40 cm**	**0-20 cm**	**20-40 cm**
PH	7.1	6.9	5.2	5.3
% Organic carbon	1.48	1.52	1.0	0.93
% Clay	17.8	19	13.4	15.8
% Silt (<0.02mm-0.02mm)	16.4-17.2	16.3-18.8	19-27.2	19.6-26.3
% Sand (<0.2mm-0.2mm)	30-18.6	30.9-15	29.5-10.9	27.4-10.9

Soil samples were taken from a depth of 0-20 cm and 20-40 cm immediately before and after application of the test substance, as well as at 9 other dates. The determination of the residues of endosulfan was performed by CG-ECD using method AL 60/86. The samples were analysed for residues of α endosulfan, β endosulfan and endosulfan sulphate. The limit of quantification was 0.01 mg/kg. The results of the residues are summarised in tables 8.1.3.1-2 and 8.1.3.1-3.

Table 8.1.3.1-2: Results of endosulfan residues (mg/kg) in the silty loam soil

¡Error! Marcador no		**DEPTH OF SOIL**	**α ENDOSULFAN**	**βENDOSULFAN**	**ENDOSULFAN SULPHATE**
Before application		0-20 cm	<0.01	<0.01	<0.01
¡Error! Marcador no definido. After	0	0-20 cm	0.20	0.09	<0.01
	7	0-20 cm	0.13	0.09	<0.01
	14	0-20 cm	0.08	0.07	0.02
	31	0-20 cm	0.06	0.08	0.05
	62	0-20 cm	0.02	0.06	0.07
	91	0-20 cm	0.01	0.07	0.11
	151	0-20 cm	<0.01	0.06	0.10
	286	0-20 cm	<0.01	0.01	0.05
	353	0-20 cm	<0.01	0.02	0.09
	437	0-20 cm	<0.01	0.01	0.02
¡Error! Marcador no definido. Before application		20-40 cm	-	-	-
¡Error! Marcador no definido. After	0	20-40 cm	-	-	-
	7	20-40 cm	0.02	0.02	<0.01
	14	20-40 cm	<0.01	<0.01	<0.01
	31	20-40 cm	0.01	0.02	0.02
	62	20-40 cm	<0.01	<0.01	<0.01
	91	20-40 cm	<0.01	<0.01	<0.01
	151	20-40 cm	<0.01	<0.01	<0.01
	286	20-40 cm	<0.01	<0.01	<0.01
	353	20-40 cm	<0.01	<0.01	<0.01
	437	20-40 cm	<0.01	<0.01	<0.01

Table 8.1.3.1-3: Results of endosulfan residues (mg/kg) in the sandy silty loam soil

¡Error! Marcador no		**DEPTH OF SOIL**	**α ENDOSULFAN**	**βENDOSULFAN**	**ENDOSULFAN SULPHATE**
Before application		0-20 cm	-	-	-
¡Error! Marcador no definido. After	0	0-20 cm	0.07	0.03	<0.01
	7	0-20 cm	0.10	0.05	<0.01
	14	0-20 cm	0.23	0.15	0.01
	31	0-20 cm	0.09	0.07	0.02
	61	0-20 cm	0.04	0.06	0.06
	91	0-20 cm	<0.01	0.02	0.03
	152	0-20 cm	<0.01	0.02	0.03
	307	0-20 cm	<0.01	0.03	0.04
	363	0-20 cm	<0.01	0.03	0.04
	447	0-20 cm	<0.01	0.03	0.06
¡Error! Marcador no definido. Before application		20-40 cm	-	-	-
¡Error! Marcador no definido. After	0	20-40 cm	-	-	-
	7	20-40 cm	<0.01	<0.01	<0.01
	14	20-40 cm	<0.01	<0.01	<0.01
	31	20-40 cm	<0.01	<0.01	<0.01
	61	20-40 cm	<0.01	<0.01	<0.01
	91	20-40 cm	<0.01	<0.01	<0.01
	152	20-40 cm	<0.01	<0.01	<0.01
	307	20-40 cm	<0.01	<0.01	<0.01
	363	20-40 cm	<0.01	<0.01	<0.01
	447	20-40 cm	<0.01	<0.01	<0.01

The total residues at the end of the study were between 0.01 and 0.2 mg/kg. In both trials, degradation of α endosulfan was considerably more rapid than degradation of β endosulfan. They decreased progressively along the study up to <10% of the initial soil concentration (0.35 mg/kg in the top 0-20 cm assuming a soil density of 1.5 kg/dm^3).

The maximum residue of the metabolite endosulfan sulphate was reached in the silty loam soil after 91 days (0.11 mg/kg in the 0-20 cm soil layer). One year after soil endosulfan application was >10% of the applied radioactivity, but it decreased to 5.7% at the end of the study (437 days).

In the sandy silty loam soil, endosulfan sulphate reached concentrations up to 0.06 mg/kg (17% of the applied radioactivity) which was found at 61 and 447 days after endosulfan application.

Degradation kinetics for endosulfan were determined by the method of Time et al 1986. The regresion calculation started in each case with the significant maximum resiude. In silty loam soil trial the maximum residue of the metabolite endosulfan sulfate was found on day 91. Since concentration values varied too much in sandy silty loam soil, they showed no constant deccrease and the results of regression calculation were thus irrelevant. The calculation of the DT_{50} carried out in the study are considered not relevant.

The optimisation criteria was the minimum of the sum of the square of distances of the measuring points from the calculated kinetic function after reconversion to the original co-ordinates and the maximum coefficient of correlation (r). The coeficient R^2 and the distribution of the residues were not considered in the evaluation of fit. The study established the more appropiate kinetics of degradation of α+β endosulfan for silty loam soil as root 1st order with a R^2 = 0.93 and a DT_{50}=16.5 days and aDT_{90} = 182.6 days, however a good fit was obtained with the 1st order regresion (R^2 = 0.90; DT_{50} = 91.6 days; DT_{90}= 304.2 days) that it was considerd mre relevant. In the sandy silty loam soil the best fit was the root 1st order regresion (R^2=0.64), the fit with 1st order kinetics was not good (R^2=0.41).

DT_{50} and DT_{90} values for the active substance (αendosulfan + βendosulfan) were calculated using the degradation formulas of Timme, 1986 (A53503). These results are shown in table 8.1.3.1-4.

Table 8.1.3.1-4: Dissipation values (days) from field studies

¡Error! Marcador no definido.**SOIL TYPE ¡Error! Marcador no definido.**	**APPLICATION RATE**	**TEST PERIOD**	**α+β ENDOSULFAN**	
			DT_{50}	**DT_{90}**
Silty loam **¡Error! Marcador no definido.**	1.056 kg/ha	437 Days	91.6	304.2
			1st order R^2=0.90; n=10	
¡Error! Marcador no definido. Sandy silty loam **¡Error! Marcador no definido.**	1.056 kg/ha	447 Days	35.9	395.9
			Root 1st order R^2=0.64; n=8	

Baedelt *et al.*, 1992b (A54025)

The study was performed under GLP and the BBA guideline IV, 4-1, stage 2. However the GLP statement was not signed and the quality assurance statement is not signed.

Two different sites in Germany (loamy sand and sandy loam) were treated with endosulfan during two consecutive years at a rate of 1.056 kg/ha. Soil properties were as follow (Table 8.1.3.1-5).

Table 8.1.3.1-5: Soil properties

¡Error! Marcador no definido.	**LOAMY SAND**		**SANDY LOAM**	
¡Error! Marcador no definido.	**0-20 cm**	**20-40 cm**	**0-20 cm**	**20-40 cm**
PH	5.7	4.3	5.65	5.75
% Organic carbon	2.02	1.68	1.27	0.77
% Clay (<0.02mm-0.02 mm)	7.04-3.65	7.80-4.4	18.66-20.51	21.89-21.37
% Silt (<0.063mm-0.063 mm)	5.73-36.04	5.96-36.30	18.55-20.83	16.6-20.17
% Sand	47.53	45.53	21.45	19.97

Soil samples were taken from a depth of 0-20 cm and 20-40 cm immediately before and after application of the test substance, as well as at 9 other dates. The determination of the residues of endosulfan was performed by CG-ECD using method AL 60/86. The samples were analysed for residues of α endosulfan, β endosulfan and endosulfan sulphate. The limit of quantification was 0.01 mg/kg. The results of the residues are summarised in tables 8.1.3.1-6 and 8.1.3.1-7.

Table 8.1.3.1-6: Results of endosulfan residues (mg/kg) in the loamy sand

¡Error! Marcador no		**DEPTH OF SOIL**	**α ENDOSULFAN**	**βENDOSULFAN**	**ENDOSULFAN SULPHATE**
Before application		0-20 cm	<0.01	<0.01	0.021
¡Error! Marcador no definido. After	0	0-20 cm	0.168	0.144	0.083
	7	0-20 cm	0.144	0.125	0.137
	14	0-20 cm	1.131	0.139	0.145
	28	0-20 cm	0.08	0.123	0.175
	56	0-20 cm	0.073	0.141	0.159
	84	0-20 cm	0.027	0.046	0.054
	148	0-20 cm	0.028	0.055	0.088
	273	0-20 cm	0.013	0.023	0.044
	336	0-20 cm	0.019	0.039	0.052
	424	0-20 cm	<0.01	0.036	0.047
¡Error! Marcador no definido. Before application		20-40 cm	<0.01	<0.01	<0.01
¡Error! Marcador no definido. After	0	20-40 cm	<0.01	<0.01	0.045
	7	20-40 cm	<0.01	<0.01	0.014
	14	20-40 cm	<0.01	<0.01	0.013
	28	20-40 cm	<0.01	<0.01	0.018
	56	20-40 cm	<0.01	<0.01	<0.01
	84	20-40 cm	<0.01	<0.01	0.016
	148	20-40 cm	<0.01	<0.01	<0.01
	273	20-40 cm	<0.01	<0.01	<0.01
	336	20-40 cm	<0.01	<0.01	<0.01
	424	20-40 cm	<0.01	<0.01	<0.01

Table 8.1.3.1-7: Results of endosulfan residues (mg/kg) in the sandy loam

¡Error! Marcador no		**DEPTH OF SOIL**	**α ENDOSULFAN**	**βENDOSULFAN**	**ENDOSULFAN SULPHATE**
Before application		0-20 cm	<0.01	<0.01	<0.01
¡Error! Marcador no definido. After	0	0-20 cm	0.544	0.309	0.309
	7	0-20 cm	0.076	0.075	0.082
	14	0-20 cm	0.123	0.162	0.164
	28	0-20 cm	0.063	0.156	0.180
	59	0-20 cm	0.016	0.039	0.070
	86	0-20 cm	<0.01	0.019	0.032
	154	0-20 cm	<0.01	0.017	0.034
	323	0-20 cm	<0.01	0.019	0.047
	363	0-20 cm	<0.01	0.035	0.235
	457	0-20 cm	<0.01	0.010	0.038
Before application		20-40 cm	<0.01	<0.01	<0.01
¡Error! Marcador no	0	20-40 cm	<0.01	<0.01	<0.01
	7	20-40 cm	<0.01	<0.01	<0.01
	14	20-40 cm	<0.01	<0.01	<0.01
	28	20-40 cm	<0.01	<0.01	<0.01

	59	20-40 cm	<0.01	<0.01	<0.01
	86	20-40 cm	<0.01	<0.01	<0.01
	154	20-40 cm	<0.01	<0.01	<0.01
	323	20-40 cm	<0.01	<0.01	<0.01
	363	20-40 cm	<0.01	<0.01	<0.01
	457	20-40 cm	<0.01	<0.01	<0.01

The total residues at the end of the study were between 0.03 and 0.5 mg/kg. α endosulfan and β endosulfan decreased progressively along the study up to <10% of the theoretical initial soil concentration (0.35 mg/kg in the top 0-20 cm assuming a soil density of 1.5 kg/dm^3). The concentration values of the metabolite endosulfan sulphate varied too greatly due to the continuous degradation of the parent compound. **Therefore the calculation of the DT_{50} for the endosulfan sulfate carried out in the stduy is considered not relevant.**

The optimisation criteria was the minimum of the sum of the square of distances of the measuring points from the calculated kinetic function after reconversion to the original co-ordinates and the maximum coefficient of correlation (r). The coeficient R^2 and the distribution of the residues were not considered in the evaluation of fit.

DT_{50} and DT_{90} values for the active substance (αendosulfan + βendosulfan) were calculated using the degradation formulas of Timme, 1986 (A53503). These results are shown in table 8.1.3.1-8.

Table 8.1.3.1-8: Dissipation values from field studies

¡Error! Marcador no definido.SOIL TYPE ¡Error! Marcador no definido.	**APPLICATIO N RATE**	**TEST PERIOD**	**α+β ENDOSULFAN**	
			DT_{50}	**DT_{90}**
Loamy sand **¡Error! Marcador no definido.**	1.056 kg/ha	424 Days	38.5	424.6
			Root 1st order R^2=0.94; n=10	
¡Error! Marcador no definido. Sandy loam **¡Error! Marcador no definido.**	1.056 kg/ha	457 Days	16.5	181.8
			Root 1st order R^2=0.76; n=10	

Stewart and Cairns, 1974 (END/L0009)

Results presented in this study were similar to those presented by Stumpf *et al.*, 1995 (A53618).

Hacker, 1989 (A42193)

The study was performed under EPA No.164-1 guideline and GLP. Technical endosulfan (Thiodan 3 EC) was applied on bareground and cropped (tomatoes) sandy loam soil (sand 68.2%; silt 16%; clay 15.8%;

organic matter 1.8%; pH 5.4), slope 1%, in Georgia to determine its dissipation in soil after 539 days. Five applications at 1.09 kg a.s./ha each 28 days were used.

The soil was sampled to a depth of 36 cm during the early intervals and then depth of samples increased to 66 cm. Subsequent sampling occurred immediately after each application. Following the fifth application, sampling (n=17) was performed until 540 days after the last application. The soil samples were analysed for parent endosulfan (α + β), endosulfan diol and endosulfan sulphate. Results from the most representative samplings are summarised in table 8.1.3.1-9.

Table 8.1.3.1-9: Residues of endosulfan in the 0-5 cm soil layer on cropped and bareground plots.

¡Error! Marcador no definido.**CROP PLOT**						**BAREGROUND PLOT**					
¡Error! Marcador no definido.**Days after fifth treatment**¡Error! Marcador no definido.	**Endosulfan residues (mg/kg)**					**Days after treatment**	**Endosulfan residues (mg/kg)**				
	α	β	α+β	**sulphate**	**diol**		α	β	α+β	**sulphate**	**diol**
-35	<0.005	<0.005	<0.005	<0.005	<0.01	-35	<0.005	<0.005	<0.005	<0.005	<0.01
-28 (AP1)	1.508	1.016	2.524	0.066	0.038	-28 (AP1)	0.742	0.456	1.198	0.036	<0.01
-21(AP2)	0.566	0.482	1.048	0.026	0.076	-21(AP2)	0.712	0.566	1.278	0.026	<0.01
-12 (AP3)	0.622	0.848	1.470	0.274	0.056	-12 (AP3)	0.588	1.126	1.714	0.342	<0.01
-6 (AP4)	0.478	0.642	1.120	0.286	0.024	-6 (AP4)	0.640	0.912	1.552	0.378	<0.01
0 (AP5)	0.718	0.754	1.472	0.150	0.094	0 (AP5)	1.092	0.836	1.928	0.098	<0.01
1	0.140	0.272	0.412	0.086	0.044	1	0.206	0.300	0.506	0.054	<0.01
5	0.438	0.726	1.164	0.202	0.302	5	0.603	0.937	1.540	0.197	0.310
9	0.912	1.860	2.772	0.538	0.418	9	1.040	2.132	3.172	0.580	0.286
14	0.734	1.840	2.574	0.994	0.162	14	0.688	1.132	1.820	1.138	0.294
29	0.312	1.146	1.458	0.652	0.136	29	0.502	1.640	2.142	0.914	<0.01
33	0.514	1.660	2.174	0.940	0.114	33	0.380	1.314	1.694	0.538	0.158
35	0.350	1.496	1.846	0.806	0.120	35	0.384	1.592	1.976	0.866	0.082
36	0.189	0.888	1.077	0.514	0.134	36	0.438	1.158	1.596	0.674	0.084
42	0.194	0.954	1.148	0.884	0.038	42	0.252	1.166	1.418	1.014	0.046
60	0.133	0.930	1.063	0.700	0.052	60	0.284	1.560	1.844	1.028	0.044
96	0.082	0.718	0.800	0.862	0.028	96	0.138	1.252	1.390	1.296	<0.01
120	0.052	0.724	0.776	0.982	0.014	120	0.072	0.762	0.834	0.818	0.028
180	0.062	0.808	0.870	1.146	<0.01	180	0.074	0.962	1.036	1.220	0.014
272	0.007	0.095	0.102	0.237	<0.01	272	0.011	0.180	0.191	0.476	<0.01
370	<0.005	0.032	0.032	0.280	<0.01	370	<0.005	0.082	0.082	0.510	<0.01
452	<0.005	0.032	0.032	0.3287	<0.01	452	<0.005	0.033	0.033	0.296	<0.01
539	<0.005	0.015	0.015	0.220	<0.01	539	0.008	0.047	0.055	0.286	<0.01

Lower values were obtained in deeper layers. The half live of both endosulfan isomers were calculated using first order kinetics. An average value for the replicates at each interval was used for the calculation. Results are shown in table 8.1.3.1-10.

Table 8.1.3.1-10: Dissipation values (in the 0-5 cm soil layer) from US field studies (Georgia)

	CROP PLOT			**BAREGROUND PLOT**		
	α ENDO	**β ENDO**	**α+β ENDO**	**α ENDO**	**β ENDO**	**α+β ENDO**
DT_{50} (days)	46.0	83.1	75.86	47.2	100	89.6
DT_{90} (days)	151.4	276.0	252.02	156.7	332.5	297.7
R^2	0.80	0.84	0.88	0.86	0.80	0.86
n	15	18	18	15	18	18

Linear equations could not be fit to the data from the endosulfan diol and endosulfan sulphate for half live calculation. However, endosulfan sulphate residues decreased by a factor of 4 during the period from their peak of concentration although they yet were higher than 10% of the initial concentration at the end of the study, more than 1 year after the last treatment. Endosulfan diol residues became non-detectable approximately 180 days after their concentration had peaked (<10% of the initial soil concentration). The values obtained in the tomato study were similar to data from the bareground experiment. These results cleraly show that although a persistance of the parent compound (α+β endosulfan) is not expectec the metabolite endosulfan sulphate can persist from one year to the following at levels above 20% of the iniyttial residue.

The leaching data for parent compound and its metabolites at soil depths below 5 cm were generally bellow the minimum quantification level of 0.005 mg/kg which indicated that very little endosulfan or the metabolites leach to lower soil depths under these experiment conditions: sub-tropical climate.

Mester, 1990 (A42997)

The study was performed following the EPA guidelines No. 164-1 and GLP. Technical endosulfan (Thiodan 3 EC) was applied on bareground and cropped (cotton) clay loam soil (pH 6.71; sand 41.2%; silt 29.8%; clay 29%; organic matter 0.7%) in California to quantify the endosulfan resdiues in runoff water, soil and harvest trash. Two aerial applications at 1.68 kg a.s./ha each 30 days were made in Tulare County, California to cotton and bareground plots. The expiremental field had an slope of approximately 1% to the southwest and was graded with an approximate 1% slope to the west for east to west furrow irrigation, it was approximately 10ha. Along the entire southern edge of the field, approximately 3.2 ha received the two aerial treatments applied with a helicopter. The experimental plots were 15.2 by 19.3 m and contained 100 subplots 1.52 by 1.93 m.

During the evaluation period, several types of samples were collected which included drift cards, soil cores, sediment samples from the irrigation tailwater ditch cards, irrigation head water, and run off water from individual furrows within the treated area and from the tailwater ditch.

The results of the drift cards were considered not relevant for the EU monograph since the aerial application is not a GAP in Southern EU.

Results from the soil sampling are summarised in table 8.1.3.1-11.

Table 8.1.3.1-11: Residues of endosulfan (mg/kg) in the 0-5 cm soil layer on cropped and bareground plots

¡Error! Marcador no definido.**CROP PLOT**						**BAREGROUND PLOT**					
¡Error! Marcador no definido.**Days after last treatment ¡Error! Marcador no definido.**	**Endosulfan residues (mg/kg)**					**Days after treatment**	**Endosulfan residues (mg/kg)**				
	α	β	α+β	**sulphate**	**diol**		α	β	α+β	**sulphate**	**diol**
-31	0.007	<0.005	0.007	<0.005	<0.005	-31	0.007	<0.005	0.007	<0.005	<0.005
-29	0.580	0.307	0.887	<0.005	0.067	-29	1.157	0.593	1.750	0.013	0.140
-1	0.033	0.097	0.130	0.103	0.018	-1	0.050	0.127	0.177	0.127	0.023
0	0.713	0.477	1.190	0.120	0.133	0	0.613	0.533	1.177	0.160	0.103
1	0.377	0.283	0.660	0.143	0.067	1	0.747	0.573	1.320	0.157	0.093
7	0.037	0.200	0.237	0.340	<0.005	7	0.060	0.283	0.343	0.427	0.006
14	0.153	0.293	0.447	0.320	0.047	14	0.237	0.377	0.613	0.337	0.060
28	0.057	0.193	0.400	0.200	0.057	28	0.140	0.260	0.400	0.217	0.117
63	0.053	0.247	0.300	0.477	0.009	63	0.027	0.137	0.163	0.180	0.023
93	0.013	0.153	0.167	0.277	0.015	93	0.013	0.087	0.072	0.130	0.005
124	0.013	0.097	0.110	0.253	0.006	124	0.020	0.213	0.233	0.377	0.005
180	0.008	0.053	0.061	0.177	<0.005	180	0.009	0.083	0.093	0.157	<0.005
282	0.008	0.060	0.068	0.145	<0.005	282	0.006	0.045	0.051	0.165	0.013
359	0.008	0.040	0.048	**0.167**	<0.005	359	0.023	0.020	0.025	**0.113**	<0.005
449	<0.005	0.013	0.013	0.057	<0.005	449	<0.005	0.037	0.037	0.150	<0.005
539	<0.005	0.008	0.010	0.053	<0.005	539	<0.005	0.007	0.007	0.053	<0.005

The maximum average detected endosulfan soil residues in the treated cotton plot (0-5 cm) were 0.713 (0 days after the last treatment (DALT), 0.477 (0 DALT), 0.477 (63 DALT), and 0.133 (0 DALT) mg/kg for α endosulfan, β endosulfan , endosulfan sulfate and endosulfan diol, respectively. Since endosulfan was applied twice, there were several periods of residue disipation. The half life estimates were calculated from the second application until the concentrations were stable or until last sampling date, 539 DALT. Half lives were not calculated for endosulfan-sulfate or endosulfan-diol individually since the processes of formation and disssipation of the metabolites could not be differentiated.DT_{50} values in 0-5 cm soil layer were estimated by first linear regression. Results are shown in table 8.1.3.1-12.

The maximum average detected endosulfan soil residues in the treated bareground (0-5 cm) were 1.157 (0 days after the first treatment (DAFT), 0.573 (1 DALT), 0.427 (7DALT) and 0.140 (0 DALT) mg/kg for α endosulfan, β endosulfan , endosulfan sulfate and endosulfan diol, respectively. Since endosulfan was applied twice, there were several periods of residue disipation. The half life estimates were calculated from the second application until the concentrations were stable or until last sampling date, 539 DALT. Half lives were not calculated for endosulfan-sulfate or endosulfan-diol individually since the processes of formation and disssipation of the metabolites could not be differentiated.DT_{50} values in 0-5 cm soil layer were estimated by first linear regression. Results are shown in table 8.1.3.1-12.

Table 8.1.3.1-12: Dissipation values (in the 0-5 cm soil layer) from US field studies (California)

	CROP PLOT			BAREGROUND PLOT		
	α ENDO	**β ENDO**	**α+β ENDO**	**α ENDO**	**β ENDO**	**α+β ENDO**
DT_{50} (days)	68.5	105.9	92.9	70.9	101.3	89.5
DT_{90} (days)	227.6	351.8	308.8	235.7	336.5	297.5
R^2	0.55	0.93	0.89	0.45	0.87	0.82
n	11	13	13	11	13	13

Linear equations could not be fit to the data from the endosulfan diol and endosulfan sulphate for half live calculation.

The irrigation water suplied from the deep well did not contain endosulfan residue and the irrigation water suplied by the Sausalito Irrigation District sporadicaly tested positive for endosulfan residues, but these residues were at or very close to the level of quantification and did not contribute to the residue detected in the treated area.

Total endosulfan residues discharged in the irrigation tailwater was comprised of the α endosulfan, β endosulfan and the endosulfan sulphate. During the irrigation runoff events immediately after each application, α endosulfan and β endosulfan were the primary endosulfan residue components. Endosulfan sulphate became the primary component during the fifth and almost exclusively during the sixth runoff events. The sixth runoff event was approximately one half-life after the last endosulfan application. A period of several half-lives may be necessary to eliminate all endosulfan residues from irrigation tailwater. The maximum observed total endosulfan residue concentration was 16.30 mg/l (4 days after the second application). The total quantity of endosulfan discharged during the first four runoff events was 2166.8 mg which represented 0.20% of the applied endosulfan (0.14% of endosulfan sulphate). There was a strong positive relationship between α and β endosulfan concentration in soil and in the irrigation tailwater, however endosulfan sulfate concentration decreased in the irrigation tailwater between the second and sixth events while the soil concentration increased. This inverse relationship was statisticaly significant.

Table 8.1.3.1-13: Endosulfan residues in irrigation tailwater (mg/trt ha)

Irrigation event	α-Endosulfan	β-Endosulfan	α+β Endosulfan	Endosulfan sulphate
1	10.39	3.15	12.39	49.25
2	88.05	46.43	130.90	95.50
3	25.90	24.90	51.90	156.30
4	11.88	12.80	24.70	157.50
Total	136.26	87.86	219.07	458.07

Czarnecki *et al.*, 1992. (A51819)

A terrestrial field dissipation study was conducted in California under full compliance with USEPA guidelines and GLP. Technical endosulfan (Thiodan 36 EC) was applied on bareground and cropped (cotton) loamy sand soil to determine its dissipation in soil after 1,5 years. Soil properties were as follows (Table 8.1.3.1-14).

Table 8.1.3.1-14: Soil properties

¡Error! Marcador no	
% Organic matter	1.11
pH	6.8
% Sand	76.4
% Silt	17.6
% Clay	6.0
Cation exchange capacity (meq/100g)	7.34

Two applications at 1.68 kg a.s./ha each 39 days were used. Precipitation was supplemented with overhead irrigation to assure >120% of the ten-year average for a given month of the study.

Soil samples were taken to a depth of four feet immediately pre and post each application as well as 7 and 14 days post application one, and 1, 3, 7, 10, 14, 29, 119, 152, 182, 212, 272, 330, 391, 449 and 540 days post application two. All samples were analysed with a gas chromatographic method which utilised an electron capture detector and a capillary column. Soil samples were extracted with acetone and application card samples were extracted with hexane. Recoveries ≥70% and 120% were considered acceptable. Residue data were not corrected for % of recovery. Results are expressed in table 8.1.3.1-15.

Table 8.1.3.1-15: Residue values (mg/kg) on cropped and bareground crops in the upper layer

¡Error! Marcador no definido.α **ENDOSULFAN**			**β ENDOSULFAN**		
¡Error! Marcador no definido.**Days post 1st application**	**Cropped plot (mg/kg)**	**Bareground plot (mg/kg)**	**Days post 1st application**	**Cropped plot (mg/kg)**	**Bareground plot (mg/kg)**
0	0.271	0.230	0	0.166	0.140
7	0.082	0.155	7	0.115	0.162
14	0.022	0.041	14	0.082	0.076
28	0.017	0.011	28	0.058	0.069
Days post 2nd application			**Days post 2nd application**		
0	0.274	0.398	-	-	-
1	0.270	0.369	10	-	0.301
3	0.124	0.131	14	0.228	0.127
7	0.099	0.137	30	0.082	0.129
10	0.075	0.159	60	0.060	0.073
14	0.058	0.045	90	0.069	0.043
30	0.007	0.014	120	0.041	0.024
60	-	0.007	150	0.034	

Mean residue data from the upper horizon were used to estimate the half lives. Results are given in table 8.1.3.1-16.

Table 8.1.3.1-16: Dissipation values from US field study (California)

¡Error! Marcador no definido. ¡Error! Marcador no definido. ¡Error! Marcador no definido.	α ENDOSULFAN						β ENDOSULFAN					
	Cropped plot			Bareground plot			Cropped plot			Bareground plot		
	DT_{50} (Days)	R^2	n	DT_{50} (Days)	R^2	n	DT_{50} (Days)	R^2	n	DT_{50} (Days)	R^2	n
1st application	7	0.73	4	6	0.95	4	19	0.94	4	23	0.56	4
2nd application	6	0.97	7	11	0.83	8	63	0.58	6	36	0.93	6

Residues of the metabolite endosulfan sulphate steadily increased to initial maximum between 0.20 to 0.25 mg/kg, within two weeks after the second application in both the cropped and bareground plots. In the cropped plot, the residues then declined from the initial maximum to between 0.10 to 0.15 by 150 days (5 months) post the 2nd application before rising to a secondary maximum between 0.20 to 0.25 mg/kg 180 days (6 months) post the second application. In the bareground plot, the endosulfan sulphate declined from the initial maximum to between 0.05 to 0.10 mg/kg by 120 days post the 2nd application and then rose to a secondary maximum between 0.20 to 0.25 mg/kg 150 days post the second application. The endosulfan sulphate residues in both plots then declined from their respective secondary maximum to levels slightly above the limit of quantification (0.01 mg/kg) by 540 days (18 months) post the second application. The pattern of formation and decline of endosulfan sulphate was similar in both treated plots in terms of the magnitude of the residues and in terms of when the maximum and minimum levels were detected.

B.8.1.3.2 Soil residue studies

One study about soil residues has been presented. Data are available for Northern European conditions and Mediterranean climates (e.g. Italy) in ten different soils.

Tiirmaa and Dorn, 1988 (A40218)

This studied was conducted according to prevailing standards (prior GLP regulations) and was accepted for international registration. The dissipation of endosulfan in soil was studied under various climates at locations with a known history of intensive endosulfan use over several years:

Australia	Cotton (2 locations)
Ethiopia	Cotton
Brazil	Soybeans / Coffee (2 locations)
Italy	Hazel nuts (2 locations)
West-Germany	Plums
South Africa	Cotton
Netherlands	Pears

Location and soil characteristics are summarised in tables 8.1.3.2-1 and 8.1.3.2-2:

Table 8.1.3.2-1: Description of soil employed in the study

¡Error! Marcador	COUNTRY	CROP	PRODUCT USED (Thiodan)	YEARS OF USE	MAXIMUM DOSAGE PER YEAR (kg as/ha)	TOTAL DOSAGE (kg as/ha)	MONTHS AFTER LAST APPLICATION
1	AUS85I100	Cotton	35 EC	6	2.92	12.5	6
2	AUS85I200	Cotton	35 EC	7	2.16	9.4	6
3	BRA85I300	Coffee	35 EC	6	1.575	5.3	7
4	ZAF85I100	Cotton	35 MO	5	7.25	7.5	1
5	ITA85I100	Hazel	35 EC	5	3.2	5.5	7
6	ITA85I200	Hazel	35 EC	6	3.2	6.6	7
7	DEU86I100	Plums	35 EC	3	0.5	6.3	7
8	NLD86I100	Pears	50 WP	6	1.8	8.8	9
9	ETH85I001	Cotton		20		24-35	6
10	BRA85I200	Soybeans	35 EC	6	1.05	2.2	6

Table 8.1.3.2-2: Characteristics of soil (0-10 cm depth) employed in the study

¡Error! Marca	COUNTRY	CLAY %	SILT %	SAND %	pH	ORGANIC MATTER %
1	AUS85I100	48.6	36.7	14.7	7.2	1.12
2	AUS85I200	64.8	31.8	3.4	6.9	1.34
3	BRA85I300	3.8	20.4	75.8	4.5	1.33
4	ZAF85I100	25.2	12.9	61.9	5.9	1.14
5	ITA85I100	23.4	49.6	27.0	3.7	1.71
6	ITA85I200	8.5	28.7	62.8	6.8	1.41
7	DEU86I100	11.8	30.6	87.4	6.4	2.86
8	NLD86I100	22.8	45.2	32.0	5.0	1.48
9	ETH85I001	67.8	25.3	6.9	6.9	1.22
10	BRA85I200	38.4	30.0	31.6	4.65	2.71

Samples from all monitoring sites were taken. Depending on the physical feasibility in the different countries the sampling depth varied from 30 cm to 60 cm. Each sample was extracted and analysed for alpha, beta and endosulfan sulphate by gas chromatography. Results are expressed in table 81.3.2-3.

¡Error! Marcador no definido.**Table 8.1.3.2-3:** Summary of Endosulfan Residues of all Monitoring Sites

¡Error! Marcador no definido.**REF** ¡Error! Marcador no definido.	**RESIDUES IN mg/kg IN THE 0 - 10 cm SOIL LAYER***					
	α endosulfan	**ß endosulfan**	**Endosulfan sulphate**	**Endosulfan lactone**	**Endosulfan diol**	**n**
1	<0.02	<0.02	0.03	<0.02	<0.02	2
2	<0.02	0.03	0.08	<0.02	<0.02	2
3	<0.02	<0.02	<0.02	<0.02	<0.02	5
4	<0.02	<0.02	0.03	-	-	1
5	<0.02	0.04	0.40	-	-	1

6	<0.02	<0.02	0.05	-	-	1
7	<0.02	0.02	0.27	<0.02	<0.02	1
8	<0.02	0.06	0.22	-	<0.02	5
9	<0.02	<0.02	0.10	-	-	1
10	<0.02	<0.02	<0.02	<0.02	<0.02	5

* = All deeper layers analysed showed no residues or lower values.
n = number of sampling

Results showed that at some locations (ITA85I100; DEU86I100; NLD86I100) an accumulation of endosulfan residues (10% of the initial rate) took place after use of endosulfan over several years. None of the sites showed any alpha endosulfan in the first 10 cm soil layer. Beta endosulfan was found in trace levels (0.06 mg/kg). Endosulfan sulphate was the only metabolite found up to 0.4 mg/kg (>10% of applied concentration) under Northern and Southern European conditions, where higher degradation rates should be expected. However, it tended to remain in the first soil layers.

It can be stated thateven in areas where endosulfan is used intensively over several years, there are no persistence of endosulfan (active ingredient) and no evidence for leaching. However, residues of endosulfan sulphate could be expected almost 7-9 months after last application. In temperate regions, a total residue plateau of 0.02-0.5 mg/kg must be reckoned with in the top 10 cm of the soil. The crop or growing conditions do not seem to influence dissipation of endosulfan.

B.8.1.3.3 Soil accumulation studies

Only one study about soil accumulation, which covers consecutive endosulfan applications in a soil, is available. Endosulfan accumulation was studied before and after the last application.

Tiirmaa *et al*., 1993 (A53771)

Degradation of endosulfan in soil was studied after application of Thiodan 50 WP over several seasons in an apple orchard in The Netherlands. The study was not conducted under any guidelines. Eighth year old apple trees were treated in a loamy clay (1-2% organic matter; 6.6-6.8 pH) with 12 applications at 1.5 kg a.s./ha each in 4 consecutive years. Soil samples were taken before and after each application; also about 7, 14, 30 and 60 days and 4, 6 and 8 months after the third application. After the last application in 1989 soil samples were taken up to 1 year after the last application. These samples were analysed by method AL 60/86 for residues of α endosulfan, β endosulfan, endosulfan sulphate and endosulfan diol. The limit of quantification for each of these compounds was 0.01 mg/kg. The residue values were corrected with the recovery values (≥ 80% for all cases). Results showed that from the first year of the endosulfan applications (1986) up to the 3rd year, α endosulfan was rapidly degraded and the proportion of the oxidation product endosulfan sulphate increased. β endosulfan was degraded more slowly than α endosulfan although most of it was also degraded to endosulfan sulphate. Both, β endosulfan and endosulfan sulphate were found at > 1.5 mg/kg (>10% of initial rate) in the 0-5 cm soil layer from second year (third application) to 4-5 months before the end of the study (240 days after the last application). These concentrations were always observed up a maximum of 200 days, but they decreased bellow 10% of the initial concentration before the first application of the consecutive year.

The plateau concentration (1 mg/kg) was reached 191 days after the last application. Endosulfan diol occurred at levels around the limit of quantification.

At the end of the study, one year after the last application, total residue (α endosulfan, β endosulfan, endosulfan sulphate and endosulfan diol) was lower than 0.08 mg/kg (<10% of initial rate) in the 0-5 cm soil layer and lower than 0.04 mg/kg in other layers.

B.8.1.4 Summary

¡Error! Marcador no definido.Endosulfan is a labile bicyclic sulphite diester with an additional moiety containing a hexachloronorborene ring. It consists of two isomers (α endosulfan and β endosulfan) which differ in the configuration of the isomer SO_3 group and the respective ring.

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- ¡Error! Marcador no definido.**Aerobic degradation**

Endosulfan aerobic degradation route and rate has been studied by Stumpf *et al*, 1995 (A53618); Gildemeister and Jordan, 1984 (A29680) and Stumpf, 1988 (A39424) in a variety of different soils (predominantly sandy loam and loamy sand soils) at different temperatures (21, 22 and 28ºC) and application rates ≥ than those recommended by GAP.

Results showed that aerobic degradation occurred via oxidation. In all studies**,** α endosulfan degraded quickly than the isomer β endosulfan. The main metabolite formed was endosulfan sulphate at a rate higher than 10% of applied radioactivity (18-40% at 60 days (Gildemeister and Jordan, 1984 (A29680)) and 46.1% at 365 days (Stumpf et al, 1995 (A53618)). This compound was slowly degraded to the more polar metabolites endosulfan diol, endosulfan lacton, endosulfan ether and other unknown compounds which appeared at <10% of applied radioactivity in all studies. Non-extractable residues were lower than 50% of applied radioactivity during the assay time 60 days (Gildemeister and Jordan, 1984 (A29680)) and lower than 25% of applied radioactivity at 100 days (Stumpf *et al*, 1995 (A53618))).

The CO_2 production was not properly measured in any of the studies, in some studies all the volatiles were measured and with this results the mineralization of endosulfan is expected to be low (<5%).

The degradation rate of endosulfan in soil laboratory studies can be summarised as follows (table 8.1.4-1).

Table 8.1.4-1: Summary of DT_{50} values (days) in soil from laboratory studies

¡Error! Marcador	**TEMPERATURE**	**DT_{50}**	**DT_{90}**	**R^2**	**n**
α endosulfan	21-22ºC	12	39	0.89	6
		39	128	0.96	8
		19	63	0.89	8
		14	46	0.93	6
	28	23	78	0.80	4
β endosulfan	21-22ºC	158	523	0.92	11
		264	877	0.92	13
		132	440	0.91	13
		108	357	0.84	8
		115	383	0.92	11
	28	58	194	0.99	4
Parent compound	21-22ºC	98	326	0.77	12
		128	426	0.90	13
		90	299	0.90	13
		92	305	0.71	8
		80	265	0.84	11
		27	85	0.96	8
		37.5	124.7	0.57	8
	28	37	123	0.92	4

The lowest DT_{50} and DT_{90} values were observed at the highest temperatures (28±2ºC) showing a direct relationship. **DT_{50} and DT_{90} values for endosulfan sulphate has not been established in any study due to linear equations could not be fit from the laboratory data at the assay time (365 days for the longest study). The DT_{50} and DT_{90} values of endosulfan sulphate are required since it is a relevant metabolite in soil.**

- **Anaerobic degradation**

Anaerobic degradation was studied by Gildemeister *et al*, 1988 (A37589). Results showed that it proceed slower and with no significant differences between the isomers than during the aerobic degradation. In consequence, endosulfan sulphate was the main degradation product formed (15-33% of the applied radioactivity at 53 anaerobic condition days). It was accompanied by the formation of other metabolites (endosulfan diol and endosulfan lactone at <10% of the applied radioactivity) and low rates of non-extractable residues (15-33% of the applied radioactivity at 53 anaerobic condition days).

- **Photolysis**

Under photolytic conditions, endosulfan has not shown to be substantially degraded, showing similar results than dark controls. Although its half live time could not be estimated, it was suggested as >200 days. Endosulfan diol was the only metabolite observed in amounts lower than 10% of the applied radioactivity. Unknown compounds and non-extractable residues were not observed.

- **Field studies**

Field degradation studies were conducted in Northern Europe, Southern Europe and in the United States (in climates comparable to Southern Europe). Three type of studies have been presented:

Soil dissipation studies

Soil residue studies

Soil accumulation studies

All of them have been carried out with the formulate substance Thiodan 35 EC.

- **Field dissipation studies.**

Different studies under Northern conditions have been carried out by Baetel *et al*, (A53554 and A54025) on silty loam, sandy silty loam, loamy sand and sandy loam soils at single application rates higher than those recommended by GAP, and for more than one year. DT_{50} and DT_{90} values from these studies (table 8.1.4-2).

Total endosulfan residues were found in the upper soil layer (0-20 cm). A relevant metabolite (endosulfan sulphate) was identified in all soil tested. It was accounted for >10% of applied concentration one year after application in three of these studies.

Under Southern conditions, three field dissipation studies have been presented (Hacker, 1989 (A42193); Mester, 1990 (A42997) and Czarnecki *et al*., 1992 (A51819)). These studies were performed on different soil types at application rates higher than those established by GAP and covering multiple endosulfan applications (2 or 5 per year). DT_{50} values presented by Hacker (A42193) and Mester (A42997) were estimated from endosulfan concentrations before the last application, it is considered that these studies represented worst field conditions, regarding application rate and number of applications. In all the studies it can be observed that the concentration of α+β Endosulfan in soil before the last application was <0.05 mg/kg, therefore all the studies are considered valid . **The calculation of the DT_{50} of endosulfan sulphate was considered irrelevant in all the studies since both processes (formation and disapearence) were not considered together in the calculation.** DT_{50} (α+β Endosulfan) values were estimated after each application in cropped and bareground loamy sand soil (table 8.1.4-2).

Table 8.1.4-2: DT_{50} (α+β Endosulfan) values (days) in soils under Southern conditions from field studies

DT_{50} (days)	DT_{90} (days)	R^2	n	Kinetic	pH	Reference
91.6	304.2	0.90	10	1st order	7.1	A53554 Silty loam soil
35.9	395.9	0.64	8	Root 1st order	5.2	A53554 Sandy silty soil
167.1	555.2	0.41	8	1st order		
38.5	424.6	0.9	10	Root 1st order	5.7	A54025 Loamy sand soil
123.7	410.9	0.57	10	1st order		
16.5	181.8	0.76	10	Root 1st order	5.6	A54025 Sandy loam soil
130.6	433.8	0.45	10	1st order		
75.86	252.02	0.88	18	1st order		A42193 Sandy loam (Crop)
89.6	297.7	0.86	18	1st order		A42193 Sandy loam (Bareground)
92.9	308.8	0.89	13	1st order	6.7	A42997 Clay loam (Crop)
89.5	297.5	0.82	13	1st order		A42997 Clay loam (Bareground)
61.10	202.9	0.61	11	1st order	6.8	A51819 Loamy sand (crop)
46.2	153.5	0.72	11	1st order		A51819 Loamy sand (Bareground)

The correct calculation, with the data of the field studies, of the DT_{50} of endosulfan sulfate considering the formation and degradation process is required.

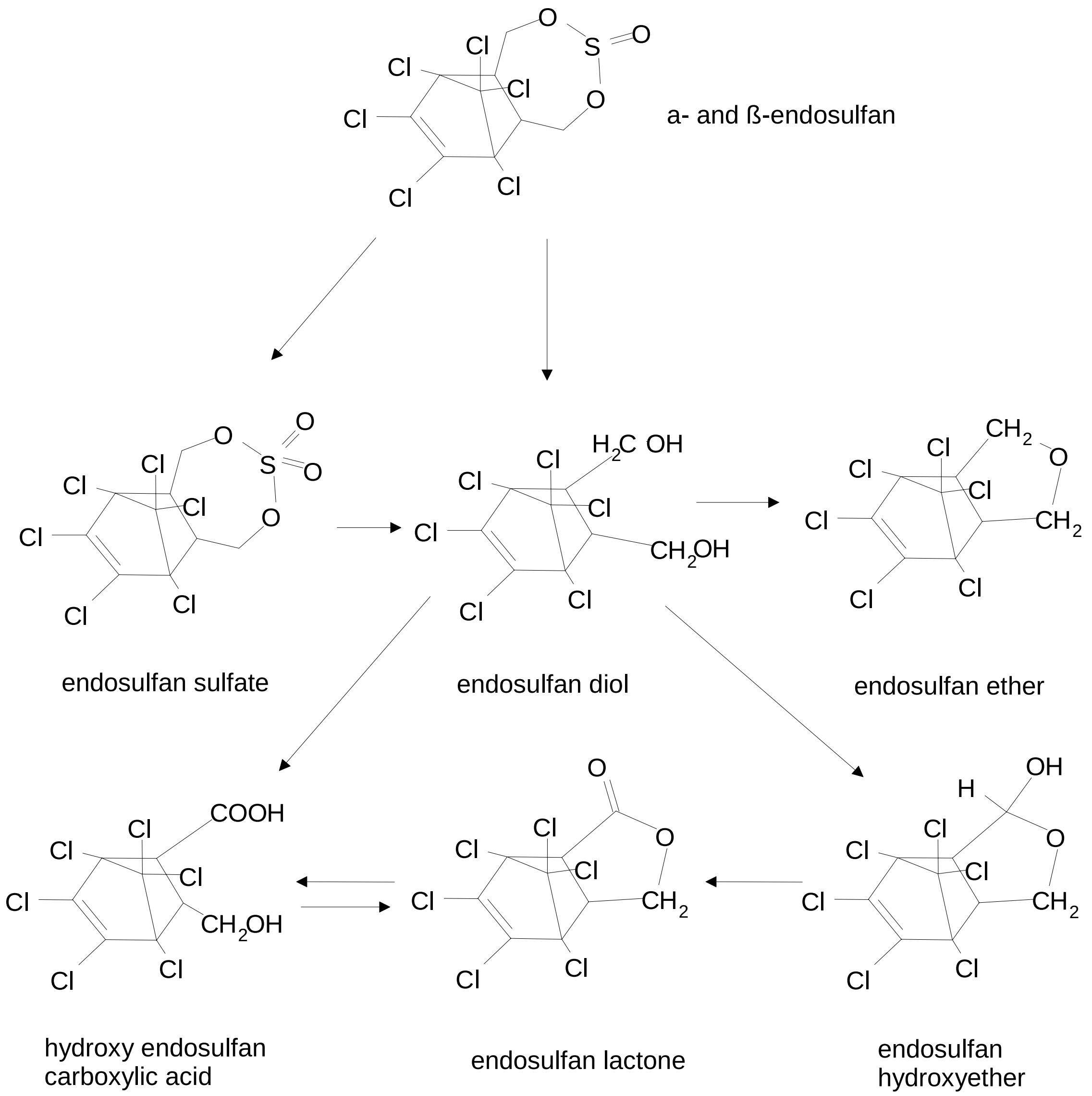
Soil residues were studied by Tiirma and Dorn, 1988 (A40218) in ten different soils after more than 3 years of use of formulated endosulfan. The maximum dosages per year were always higher than those proposed by GAP, from 0.5 to 3.2 kg as/ha. Monitoring was done 6 or 7 months after the last application. In all cases, even in areas where endosulfan was used intensively over several years, residues of parent endosulfan were lower than 10% of the applied concentration and there was no evidence of leaching. The crop conditions do not seem to influence dissipation of endosulfan. However, **residues of endosulfan sulphate (>10% of the initial concentration) were observed in some cases.**

Soil accumulation was studied by Tiirmaa et al, 1993 (A53771). Eighth year old apple trees were treated in a loamy clay soil with 12 applications at 1.5 kg as/ha each in 4 consecutive years. Total residue (parent compound plus endosulfan sulphate) was always lower than 10% of the applied concentration at the end of each year of use. So, accumulation from one year to another should not be expected. Even though, should be taken into account, that the main metabolite endosulfan sulphate was observed at more than 10% of the initial concentrations up to 200 days after the 3rd application. Its plateau concentration rose 20-50 % of the initial concentration 5 months before the end of the study.

In summarising the results from all relevant degradation studies in soil, the following degradation scheme is proposed.

The degradation of endosulfan in soil did not show any alteration of the hexaclor norborene bicycle and showed a very low mineralization (<5%). These two facts suggest a high persistence of a soil residue constituted by a number of chlorinated metabolites, which may not account

individually for more than 10% of applied dose but that all together may represent high amount of it. Based on their chemical structure it may be expected that their physico chemical properties of these compound will be similar and generally persistent and bioaccumulable. Therefore, a wider investigation of the degradation routes of this compound must be done.



NO FURTHER DEGRADATION HAS BEEN DEMONSTRATED

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

Goerlitz and Eyrich, 1988a (A37591)

The adsorption/desorption of α endosulfan and β endosulfan were studied under EPA guideline 163-1 and GLP on four soils at four test concentrations: 0.02-0.13 mg/L and 0.02-0.16 mg/L. Soil properties were as follows (table 8.2-1).

Table 8.2-1: Soil properties

¡Error! Marcador no definido.	**Silt loam**	**Sandy loam**	**Sandy loam**	**Loamy sand**
pH	5.4	5.9	5.8	5.8
Cation exchange capacity (meq/100g)	16.11	6.3	6.74	10.59
Organic matter (%)	1.06	2.17	4.16	4.53
Sand (%)	16.1	58.8	79.6	79.7
Silt (%)	65.6	31.6	10.4	18.2
Clay (%)	18.3	9.6	10.0	9.1
Maximum water holding capacity (g/100g)	39.0	36.2	36.0	33.0

In the adsorption kinetic, time to reach equilibrium in the soil/water system was determined to be 8 hours for α endosulfan and 16 hours for β endosulfan. Each experiment was carried out twice and each solution was analysed by LSC. Results are shown in table 8.2-2.

Table 8.2-2: Adsorption Coefficient and Koc values from the Freundlich-Isotherm for α-endosulfan and β-endosulfan.

¡Error! Marcador no definido.**Soil** ¡Error! Marcador no definido.	**α-endosulfan**			**β-endosulfan**		
	Ka	**Koc**	**r**	**Ka**	**Koc**	**r**
silt loam	63	10 161	0.998	74	11 935	0.997
sandy loam	102	7 969	0.995	178	13 906	0.997
sandy loam	523	21 347	0.997	211	8 612	0.999
loamy sand	364	13 684	0.971	324	12 180	0.993

The α- endosulfan and β-endosulfan isomers showed strong adsorption on soils related to organic carbon content.

Following to the adsorption experiment, desorption experiments were carried out. Results are summarised in table 8.2-3.

Table 8.2-3: Adsorption and desorption Coefficient for α-endosulfan and β-endosulfan

¡Error!	**α-endosulfan**	**β-endosulfan**

Marcador no definido.**Soil** ¡Error! Marcador no definido.	**Ka**	**Kd**	**Ka**	**Kd**
silt loam	65	81-87	78	89-97
sandy loam	154	164-424	197	218-244
sandy loam	211	237-252	243	276-285
loamy sand	323	334-1022	412	473-416

For both substances adsorption was found to be almost completely reversible, adsorption constants determined by desorption only marginally higher than those determined by adsorption. No systematic difference between the adsorption/desorption behaviour of α and β endosulfan was observed.

Goerlitz and Eyrich, 1988b (A39353)

The determination of the adsorption/desorption properties of endosulfan metabolites on four different soils were performed following the EPA guideline No.163-1 and GLP. Concentrations ranged from approx. 0.2 mg/L to 2.5 mg/L for the test substances, respectively. Soil properties were as follows (Table 8.2-4).

Table 8.2-4: Soil properties

¡Error! Marcador no definido.	**Silt loam**	**Sandy loam**	**Sandy loam**	**Loamy sand**
pH	5.4	5.9	5.8	5.8
Cation exchange capacity (meq/100g)	16.11	6.3	6.74	10.59
Organic matter (%)	1.06	2.17	4.16	4.53
Sand (%)	16.1	58.8	79.6	79.7
Silt (%)	65.6	31.6	10.4	18.2
Clay (%)	18.3	9.6	10.0	9.1
Maximum water holding capacity (g/100g)	39.0	36.2	36.0	33.0

In the adsorption kinetic, time to reach equilibrium in the soil/water system was determined to be 16 hours. Results are shown in table 8.2-5.

Table 8.2-5: Adsorption Coefficient and Koc values from the Freundlich-Isotherm for endosulfan sulphate and endosulfan diol

¡Error! Marcador no definido.**Soil** ¡Error! Marcador no definido.	**Endosulfan sulphate**		**Endosulfan diol**	
	Ka	**Koc**	**Ka**	**Koc**
silt loam	45	7311	6.2	994
sandy loam	119	9300	14.4	1122
sandy loam	139	5667	17.7	724
loamy sand	304	11445	32.3	1216

The results indicated that endosulfan metabolites are strongly adsorbed to soil. Following to the adsorption experiment, desorption experiments were carried out. Results are summarised in table 8.2-6.

Table 8.2-6: Adsorption and desorption Coefficient for endosulfan metabolites

¡Error! Marcador no definido.**Soil** ¡Error! Marcador no definido.	**Endosulfan sulphate**		**Endosulfan diol**	
	Ka	**Kd**	**Ka**	**Kd**
silt loam	43.5	53.5-56.7	6.2	8.7-11.3
sandy loam	119	147.4-145.5	14.4	15.7-18.3
sandy loam	138.8	152-174.7	17.7	19.9-22.5
loamy sand	304.4	303.1-358	32.3	37.2-37.4

For both substances, adsorption was found to be almost reversible, adsorption constants determined by desorption being consistently but not with a large margin higher those determined by adsorption.

¡Error! Marcador no definido.B.8.2.2 Leaching studies

Leaching studies were carried out with the formulated (Thiodan 35%) and the active substance under laboratory conditions.

B.8.2.2.1 Laboratory studies

- **Active substance**

Studies on active substance were performed on aged residues.

Gildemeister and Grundschoettel, 1985 (A31700)

Leaching behaviour of endosulfan was examined by soil thin layer chromatography following the EPA guideline No.163-1 and GLP. The mobility of ^{14}C endosulfan (5a, 9b) 0.017 mg blended with 0.334 mg non-labelled material (0.351 mg resulting in a specific radioactivity of 1.37 mCi/g) was studied on four soil types. Soil properties were as follows (Table 8.2.2.1-1).

Table 8.2.2.1-1: Soil properties

¡Error! Marcador no definido.**Soil type**	**Silt loam**	**Loamy sand**	**Sand**	**Sandy loam**
pH	6.4	4.1	6.9	7.5
Exchange capacity (meq/100 g soil)	21.3	2.9	2.7	9.7
Organic matter (%)	1.6	1.8	0.7	1.3
Sand (%)	7.2	77.5	91.8	70.8
Silt (%)	70.4	19.9	6.3	25.2
Clay (%)	22.4	2.6	1.9	3.7
Moisture capacity (g/100g soil)	45.8	31.5	30	29.6

After soil activation, a sample of soil corresponding to 100 g dry weight was weighted into a 500 mL Erlenmeyer flask. Radioactive substance was added at a rate of 35 mg/L. The incubation period was about 28 days at 22±2ºC in darkness. During the incubation, distilled water was added at 2-3 days intervals to restore the initial moisture. At day 28 after application the soil was extracted with a total of 400 mL acetonitrile/toluene and examined for radioactivity with the liquid scintillation counters. The radioactivity which persisted in the soil was determined by combustion. The pattern of degradation in the soil extract was determined by HPLC.

The leaching behaviour of the pure test substance endosulfan and that of the aged residues from a soil extract were very similar. In all tested soils, 90-93% of the applied radioactivity could be classified as immobile. The Rf values were 0.00-0.09, which remaining at the starting zone. Another 5-9% of applied radiolabel compound showed low mobility with Rf values of 0.10-0.34. According to the results of this study, endosulfan should be considered as being low mobility or completely immobile.

Gildemeister and Jordan, 1982 (A49273)

The study was carried out under BBA guidelines and prior to GLP. Leaching behaviour of the active substance (14C endosulfan 5a, 9a (specific activity 1 mCi/g)) after ageing period of one half-life (29, 12 and 16 days) in three standard soils was investigated using soil leaching columns with application rates equivalent to 2.156 kg as/ha. Soil properties were as follows (Table 8.2.2.1-2).

¡Error! Marcador no definido.**Table 8.2.2.1-2:** Soil properties

¡Error! Marcador	**Organic carbon (%)**	**Clay and silt (%)**	**pH**
Sand	0.8	4.2	7.0
Sand	2.6	10.1	6.8
Sandy loam	1.0	19.5	5.2

After daily irrigation during 16 days with 200 mm water, less than 0.2% of the applied amount of radioactivity were found in the leachate. Due to the very small amounts the residues could not be identified in the leachates by TLC. Examinations of the columns showed that after the irrigation period almost all radioactivity was still in the top layer of the soil (≈45%).

Gildemeister and Remmert, 1983 (A27287)

Leaching behaviour study of endosulfan and its metabolites was carried out following the EPA and BBA guidelines. The active substance (97.1% purity) was applied to three soil which properties were as follows (Table 8.2.2.1-3).

Table 8.2.2.1-3: Soil properties

¡Error! Marcador	**ORGANIC MATTER (%)**	**PARTICLES <20 µm (%)**	**pH**
Sand	0.8	4.2	7.0
Loamy sand	2.6	10.1	6.8
Sandy loam	1.0	19.5	5.2

For the experiments the soils (air dried) were passed through a one mm sieve. Then they were filled up to 28 cm into glass-columns and saturated with distilled water. After addition of test substance (873 µg in 0.5 mL CH_2Cl_2) on the soil the flask were sealed with cotton-wool pliugs and incubated for 30 days in the dark at 22±2ºC for ageing of residues. During the incubation, distilled water was added at 4 day intervals to restore the initial moisture.

The incubated soils were added to different soil columns. Each column was eluted with 200 mm water in 2 days. Eluates were examined for radioactivity by LSC and TLC. Additionally, soil residues were extracted by acetonitrie/toluene (8/2 v/v) and determined in 5 cm segments of the columns by LSC and TLC. Aliquots of the extracted soil segments were combusted in a Packard Sample Oxidiser to determine the amount of bound residues. Results are summarised in table 8.2.2.1-4.

Table 8.2.2.1-4: Results from leaching laboratory study

¡Error! Marcador no definido.**Soil** ¡Error! Marcador no definido.	% Of Applied Radioactivity			
	In The Eluate	**In The Extracts Of The Soil Segments**	**In The Soil Segments**	**Total**
Sand	0.2	100.4	1.6	102.2
Loamy sand	0.2	107.2	2.0	109.4
Sandy loam	<0.1	97.5	1.3	98.8

Only traces of the active ingredient and of the main metabolite were leached. Most of the two compounds could be extracted from the column segments; especially in the two upper segments.

- **Plant Protection Product**

Thier, 1975 (A49270)

Leaching behaviour of endosulfan was studied under the BBA guideline No.37. Formulated endosulfan (Thiodan 35) was applied to the top of a soil column containing sandy soil (0.8% organic carbon; 4.2% particles removable by elutriation; pH 7.0) at a rate corresponding to 3 kg/ha (1.6 kg a.s./ha). After irrigation with 200 mm water within 2 days, less than 0.17% of the applied amount of radioactivity were found in the leachate.

B.8.2.2.2 Semi-field studies

No information about semi-field studies have been submitted.

B.8.2.3 Summary

- ¡Error! Marcador no definido.**Adsorption/desorption**

A range of different soils were used to determine Kd and Koc values (Goerlitz and Eyrich, 1988 (A37591 and A39353). α endosulfan, β endosulfan, endosulfan sulphate and endosulfan diol showed to be immobile in soil. All substances showed strong adsorption on soils related to organic carbon content, although this process was found to be almost completely reversible.

- ¡Error! Marcador no definido.**Leaching**

Laboratory leaching studies were performed with the active substance (Gildemeister and Grundschoettel, 1985 (A31700); Gildemeister and Jordan, 1982 (A49273) and Gildemeister and Remmert, 1983 (A27287)) and the formulated product (Thier, 1975 (A49270) in different soil types.

Results showed that endosulfan had not leaching potential but, on the contrary, to be nearly immobile under laboratory conditions. Even when irrigated with unrealistic high rates of water (200 mm/48 hours) and high application rates (1.4 kg a.s./ha) (Gildemeister and Remmert, 1983 (A27287)) no residues of endosulfan or its metabolites were detected in the leachates. These results showed to be confirmed by soil field studies where endosulfan was only detected in the upper soil layers. Therefore, a ground-water contamination by the parent endosulfan is not expected. **However, as the degradation route in soil is not well defined and complete, it may not be discarded the formation of more polar metabolites able to reach ground water.**

B.8.3 Predicted environmental concentrations is soil (PECs) (IIIA, 9.1.3)

The calculated PEC_s was for $\alpha+\beta$ Endosulfan, the main metabolite endosulfan sulphate was not considered in this calculation since a good determination of its DT_{50} was not carried out. From the soil dissipation studies in field it can be considered that the higher amount of the endosulfan sulphate was 60% of the applied concentration (Initial PEC), multiplied by a factor of 0.9624. This estimation was confirmed by the soil accumulation study in which the plateau concentration of endosulfan sulphate rose 20-50% of the initial concentration 5 months before the end of the study, from this study it can be concluded that accumulation from one year to another would not be expected.

The Table 8.3-1 show the DT_{50} of $\alpha+\beta$ endosulfan calculated from the field studies.

Table 8.3-1: DT_{50} of $\alpha+\beta$ endosulfan (days) in soils from filed studies

DT_{50} (days)	DT_{90} (days)	R^2	n	Kinetic	pH	Reference
91.6	304.2	0.90	10	1st order	7.1	A53554 Silty loam soil
35.9	395.9	0.64	8	Root 1st order	5.2	A53554 Sandy silty soil
167.1	555.2	0.41	8	1st order		
38.5	424.6	0.9	10	Root 1st order	5.7	A54025 Loamy sand soil
123.7	410.9	0.57	10	1st order		
16.5	181.8	0.76	10	Root 1st order	5.6	A54025 Sandy loam soil
130.6	433.8	0.45	10	1st order		
75.86	252.02	0.88	18	1st order	5.4	A42193 Sandy loam (Crop)
89.6	297.7	0.86	18	1st order		A42193 Sandy loam (Bareground)
92.9	308.8	0.89	13	1st order	6.7	A42997 Clay loam (Crop)
89.5	297.5	0.82	13	1st order		A42997 Clay loam (Bareground)
61.10	202.9	0.61	11	1st order	6.8	A51819 Loamy sand (crop)
46.2	153.5	0.72	11	1st order		A51819 Loamy sand (Bareground)

The higher value of the best fitted kinetics (R^2>0.8)was DT_{50} = 93 days, this DT_{50} represents a realistic worst case for all European condition

It was assumed to be 1.5 g/cm^3 dry weight. The depth of the penetrated soil layer was assumed to the immobility of endosulfan. This simulates a worst case scenario, since the active substance is concentrated in the top 5 cm which is considerably less than the plough layer. Adsorption/desorption and leaching studies summarised in point B.8.2.3. Confirm the immobility of endosulfan.

Based on these assumption, predicted environmental concentrations of endosulfan (PEC_{soil}) were calculated from the BBA draft guide based on:

> The highest number of treatments, the shortest interval in between, and the single maximum application rates for each crop. This information was taken from data according to the GAP (July, 1998).

According to this scenario, the initial predicted environmental concentrations, PIEC values, have been calculated considering a crop intercept of 50% and 0%, this initial PEC are summarised in Table 8.3-2 and 8.3-3 repectively.

Table 8.3-2: Calculation of PIEC values for endosulfan assuming a crop intercept of 0%

¡Error! Marcador no definido.**Crops**	**Maximum Single Treatment Rate kg a.s./ha**	**Number of Applications**	**Spraying interval**	**PIEC mg sa/kg single application**	**PIEC mg sa/kg several applications**
Citrus , pome fruit and wine grapes	1.05	2	14	1.40	2.66
Cotton	0.84	3	14	1.12	3.03
Tomatoes	0.53	2	7	0.70	1.37
Potatoes	0.53	2	14	0.70	1.34
Stone fruits	0.8	3	14	1.06	2.89
Cucurbits	0.53	3	7	0.70	2.01
Sugar beet	0.5	2	14	0.66	1.26
Hazel nuts	0.8	2	14	1.06	2.02

Table 8.3-3: Calculation of PIEC values for endosulfan assuming a crop intercept of 50%

¡Error! Marcador no definido.**Crops**	**Maximum Single Treatment Rate kg a.s./ha**	**Number of Applications**	**Spraying interval**	**PIEC mg sa/kg single application**	**PIEC mg sa/kg several applications**
Citrus , pome fruit and wine grapes	1.05	2	14	0.70	1.33
Cotton	0.84	3	14	0.56	1.52
Tomatoes	0.53	2	7	0.35	0.69
Potatoes	0.53	2	14	0.35	0.67
Stone fruits	0.8	3	14	0.53	1.44
Cucurbits	0.53	3	7	0.35	1.00
Sugar beet	0.5	2	14	0.33	0.63
Hazel nuts	0.8	2	14	0.53	1.01

Based on these PIEC, the time weighted average predicted environmental concentration in soil (PEC_{TWA}) have been calculated, three cases have been considered as a worst case: citrus, cotton and cucurbit. They are summarised in tables 8.3-4, 8.3-5 and 8.3-6:

Table 8.3-4: Estimated PECs and TWA-PECs after last application in citrus fruit and assuming a crop intercept of 50%.

Days	PECs	TWA-PECs
0	1.33	1.33
1	1.32	1.32
2	1.31	1.32
4	1.29	1.31
7	1.26	1.29
14	1.18	1.25
21	1.13	1.23
28	1.08	1.20
42	0.97	1.14
86	0.70	0.98
156	0.41	0.78
286	0.16	0.55
351	0.09	0.47

Table 8.3-5: Estimated PECs and TWA-PECs after last application in cotton and assuming a crop intercept of 50%.

Days	PECs	TWA-PECs
0	1.52	1.52
1	1.51	1.51
2	1.49	1.50
4	1.45	1.49
7	1.44	1.48
14	1.36	1.44
21	1.29	1.40
28	1.23	1.37
42	1.11	1.30
72	0.88	1.17
152	0.48	0.90
272	0.20	0.65
337	0.12	0.55

Table 8.3-6: Estimated PECs and TWA-PECs after last application in cucurbit and assuming a crop intercept of 50%.

Days	PECs	TWA-PECs
0	1.00	1.00
1	0.99	1.00
2	0.99	0.99
4	0.97	0.99
7	0.95	0.98
14	0.90	0.95
21	0.86	0.93
28	0.81	0.90
42	0.73	0.86
136	0.36	0.63
286	0.11	0.41
351	0.07	0.35

No accumulation of parent endosulfan (α+β endosulfan) is expected due to continuous use of endosulfan, the highest PECs is 1.52 mg a.s/kg. **However, an accumulation of the endosulfan sulfate can be expected due to a continuous use during several years of endosulfan. Therefore the PEC and the plateau concentration for endosulfan sulphate should be estimated by the applicant, . So, its DT_{50} should be estimated. As a worst case estimation the highest expected concentration of endosulfan sulphate will be 0.88 mg/kg.**

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

The investigations on fate and behaviour of endosulfan in water have been carried out predominantly with the active substance.

B.8.4.1 Hydrolysis

- **Active substance**

Goerlitz and Kloeckner, 1982 (A31069)

This study has not been conducted under GLP or directive. The abiotic hydrolytic of endosulfan isomers (2α:1β at concentrations of 0.151 and 0.187 mg/L respectively) were determined in buffered solutions at different pH values (5,7 and 9) and temperatures of 50ºC for pH=5, 40ºC for pH=7 ansd 9 and 22ºC for pH=9in darkness. Samples were collected at 0, 2, 5, 7, 24, 48, 96 and 120 hours, extracted 3 times with CH_2Cl_2 and analysed by HPLC. Results are given in table 8.4.1-1:

Table 8.4.1-1: Hydrolysis half-lives for α- and β-endosulfan

¡Error! Marcador no	**pH5**	**pH7**	**pH9**
Temperature	**50ºC**	**40ºC**	**22ºC**
α-endosulfan	>1 year	22 days	7.0 hours
β-endosulfan	>1 year	17 days	5.1 hours

Mass balance of parent materials and endosulfan-diol was always >97 %. Therefore, speed of hydrolysis for both isomers of endosulfan strongly increases with alkalinity of systems. Endosulfan diol was the only hydrolytic product of both isomers which appeared at high rates (>50% of the applied radioactivity) at the end of the study.

The study is not acceptable, since the statistical analysis or the degradation curve was not reported, moreover the temperature is diferent at the diferent pH solutions and for pH=5 only two points were considered for the DT values calculation.

Goerlitz and Rutz, 1989 (A40003)

This study was performed under EPA guidelines and GLP. The abiotic hydrolytic of endosulfan isomers (>99% purity) applied at concentrations of 0.16 each of them were determined in buffered solutions at different pH values (5,7 and 9) and 25ºC in darkness. Samples were taken at several times (0, 3, 8, 13, 16, 22, 27 and 30 days) during the trial, extracted by methylene chloride and analysed by HPLC. Results are shown in table 8.4.1-2:

Table 8.4.1-2: Hydrolysis half-lives for α- and β-endosulfan

¡Error! Marcador no definido. ¡Error! Marcador no definido.	**PH5**			**pH7**			**pH9**		
	DT_{50} days	**R^2**	**n**	**DT_{50} days**	**R^2**	**n**	**DT_{50} hours**	**R^2**	**n**
α-endosulfan	> 200	0.4	7	19	0.98	7	6.2	0.99	6
β-endosulfan	> 200	0.09	8	10.7	0.99	6	4.1	0.99	6

Mass balance of parent material was always 94-99%. The rate of hydrolysis of α endosulfan and β endosulfan was extremely dependent of the pH. Under acidic conditions no hydrolysis could be observed, in a neutral medium the rate was moderate and in an alkaline environment, hydrolysis was very rapid. The hydrolysis product was identified as endosulfan diol which appeared at high rates at the end of the study.

B.8.4.2 Photolysis

- **Active substance**

Schumacher *et al*., 1973 (A25698)

The study was conducted according to prevailing standards and prior to GLP. α endosulfan and β endosulfan were tested for photochemical reactions in different media. Slow photodegradation of isomers was observed and small amounts (<10%) of a variety of dechlorination products were detected.

Dujera and Mukerjee, 1982 (A27138)

The photolysis of endosulfan has been examined under different conditions, including environmental conditions. Two new photometabolites, photo-alpha-endosulfan and photo-beta-endosulfan have been isolated from alpha- and beta-isomers of endosulfan respectively. Irradiation in polar solvents gives metabolites similar to those formed under biotic conditions. When exposed to sunlight on plant leaves, alpha-endosulfan not only forms the photometabolite but also undergoes isomerisation to beta-endosulfan which showed to be more stable.

Stumpf and Schink, 1988 (A37588)

The study was conducted under EPA guidelines and GLP. α endosulfan and β endosulfan were irradiated separately with polychromatic light at 25ºC filtered to remove UV below 290 nm. Samples were maintained under sterile conditions in aqueous buffer solution (pH 5) for up to 120 hours (1 hour irradiation = 3.4 hours of natural sunlight). Both endosulfan isomers were photolytically stable. Considerable amounts of endosulfan evaporated. On the basis of the results, half lives of more than one year were estimated.

Stumf, 1988 (A37588)

The aqueous hydrolysis of endosulfan was studied to determine the route of degradation and the nature of photolytic products. The study was conducted under Guideline 161-2. Sterile aqueous solutions of radiolabelled α (11.4 mCi/g) and β (18.2 mCi/g) endosulfan (radiochemical purity >98%; 0.24 mg/L) buffered to pH 5 were placed in a sterile, closed all-glass photoreactor equipped with volatile traps. The solutions were irradiated at 25ºC with a mercury vapour lamp filtered to remove UV below 290 nm for 0, 6, 24, 78 and up to 120 hours of continuous exposed. Dark controls were also carried through the procedures. Radiolabelled endosulfan, after extraction from the buffer with CH_2Cl_2, and reference compounds were measured by reverse phase-C18 radio-HPLC using a gradient solvent system. The material balance based on zero-value recovery ranged from 72.8% to 106.2%.

The photolysis study did not show any breakdown neither of α endosulfan nor of β endosulfan during the whole irradiation period. The dark control did not differ from the irradiated. The total of radioactivity was in the water extracts. Volatile samples showed increasing amounts of α endosulfan up to >10% at 78 and 120 hours. β endosulfan showed a range of volatility 20 orders of magnitude less that of α endosulfan.

Stumpf and Jordan, 1991 (A49585)

The study was performed following the EPA and Japan guidelines and GLP. The study was carried out for the two isomers of endosulfan, α and β, separately in three different media: in sterile acetate buffer solution, in sterile acetate buffer solution with the addition of acetone and in non-sterile surface water from the river Nidda in Frankfurt. Solutions of endosulfan with a concentration of 0.25 mg/L in the respective medium were irradiated at 25±1ºC. The buffer samples were irradiated for 101 to 142 hours and the surface water for 96 hours for up 290 nm. Suitable traps were used to collect 14CO2 and other metabolites. The irradiated solutions were examined by radio-HPLC using a RP 18 system. Dark control samples were handled identically except that were kept in the dark. Half lives in continuous days of irradiation were calculated for the different series.

However the DT values calculated are not valid because of the high absorption in the lubricating grease. The determination of α and β endosulfan in lubricating grease is not completed, this can affect seriously the DT $_{50}$ determination.

It can be stated that the photolysis in water is not an important route for the elimination of endosulfan from the aqueous environment. Endosulfan showed a very low photolytical breakdown although a high amount of α endosulfan and a significant amount of β endosulfan disappeared from the respective vessels of the irradiation and dark control series. These effects were explained by the author of the study by the high volatility of α endosulfan and the tendency of both isomers to dissolve in the lubricating grease.

The addition of acetone did not show any significant effect on the degradation rate. However, this rate was accelerated when used natural water: half lives of 8 hours (α endosulfan) and 5 hours (β endosulfan) were calculated. Therefore, photolysis was not the relevant degradation mechanism, this was a simple hydrolysis, since the pH of the surface was 8.5. Under these conditions, the main degradation product was endosulfan diol.

The study is not acceptable.

B.8.4.3 Biological degradation

None study was submitted concerning the biological degradation of endosulfan. The degradation in natural water (river and sea water) was studied in three trials, it is concluded that the main degradation route of endosulfan in water is the hydrolysis and that it is pH dependent.

- **Active substance**

Eichelberger and Lichtenberg, 1971 (END/L0028)

The study was performed under EPA guidelines without GLP. α endosulfan and β endosulfan were applied on raw water from the Little Miami River, a small stream receiving domestic and industrial wastes and farm runoff. 15 vessels containing endosulfan (10 µg/L, starting from a 0.1% freshly prepared solution) and five blacks were sealed and stored on a laboratory bench under sunlight and artificial fluorescence light. The test vessels were shaken periodically. Samples were taken at 1 hour, 1, 2, 4 and 8 weeks. On each sampling day, three test and one control vessel were sampled. Extractions were performed with 15% ethyl ether in hexane and analysed by GC/ECD. The recovery of the extraction procedure was checked to be between 90 and 100% at the 1 to 10 µg/L level. Results showed that endosulfan concentrations declined relatively fast in time. After 1,2,4 and 8 weeks concentrations of 30%, 5%, 0% and 0% (as sum of α and β endosulfan isomers) relative to the initial concentration were determined, respectively. One new peak appeared in the chromatogram. It was argued by the author, but not confirmed, that endosulfan alcohol could be the decomposition product. The half-life of endosulfan (sum of α and β endosulfan isomers) in river water could be estimated from the findings to be approximately 4 days.

Greve, 1971 (END/L0041)

The study was not carried out under standardised guidelines., there is no data concerning degradation kinetics, only the degradation constant was reported, therefore the study is not acceptable.

Cotham and Bidleman, 1989 (A41218)

The study has not been conducted under any guideline or GLP. Seawater (salinity 34 ppt) obtained from North Inlet estuary was filtered through 0.45 µm cellulose acetate filters and 450 mL was placed in each of 500mL Erlenmeyer flasks. Half of these flasks were autoclaved and cooled to room temperature. Each flask (unesterile and autoclaved) was then fortified with 28 ng of endosulfan. The flasks were incubated under laboratory light at 20ºC. Duplicate flasks from each of the two groups, unesterile and autoclaved, were sampled on days 0, 2, 4, 8, 16, 32 and 40.

Endosulfan was extracted on C8 columns. Before use, C8 cartridges were extracted in a soxhlet apparatus for 3 hours with 1:1 ethyl ether/n-hexane and dried in a heated vacuum desiccator at 40ºC. Half-lives were estimated by first order kinetics (Table 8.4.3-1).

Table 8.4.3-1: DT_{50} values of endosulfan in the seawater

¡Error! Marcador no definido.	**UNESTERILE**	**ESTERILE**
	pH 8.05-8.0	**pH 8.2-8.0**
¡Error! Marcador no definido.**DT_{50} values (days)**		
¡Error! Marcador no definido.α endosulfan	2.0-2.2	1.3-2.0
β endosulfan	4.4-4.9	1.9-3.1
Parent endosulfan	6.2-8.2	2.8-4.4

The results showed in table 8.4.3.1-1 indicate that for endosulfan hydroxide-catalyzed hydrolysis is a major pathway for their degradation in marine systems.

- **Plant Protection Product**

Stumpf, 1990a (A45100)

The study was carried out following the OECD guidelines (number not submitted), but without GLP, no detaills concerning this study was submitted (material and methods, results, discussion and conclusion), therefore this study is not acceptable .

¡Error! Marcador no definido.**B.8.4.4 Water/sediment**

- **Active substance**

Gildemeister, 1985 (A31182)

The study was performed under EPA guidelines and GLP. Radiolabelled endosulfan (5[a], 9[a]; 97.4% purity; 28.21 mCi/g of specific activity) was exposed to aerobic conditions in two water/sediment systems for up to 55 days at 22ºC. Water/sediment properties were as follows (Table 8.4.4-1).

Table 8.4.4-1: Water /sediment properties

¡Error!	**PARAMETHER**	**RIVER MAIN (system I)**	**GRAVEL PIT (System II)**
Water **¡Error! Marcador no definido. ¡Error! Marcador no definido.**	PH	7.3	7.8
	Number of cells/mL		
	Aerobic bacteria	4.2×10^2	5.4×10^3
	Actinomycetes	Not detected	Not detected
	Fungi	<10	<10
Sediment	pH	7.2	7.9
	Organic carbon (%)	0.36	0.53
	Sand (%)	98.3	98.8
	Silt (%)	1.7	0.8
	Clay (%)	0.0	0.4
	Cation exchange capacity (meq/100g)	1.22	1.10

10g sediment (dry weight) and 190g water were weighted into 500 mL Erlenmeyer flasks resulting in a water depth of 2.5 cm. After application of the test substance (0.229 mg/kg) the flasks were gently agitated to obtain a homogeneous distribution of the test substance. For the total degradation study four flasks (two replicates per water/sediment system), protected against sunlight with aluminium foil, were fixed in the closed aeration system. The content of the flasks was agitated and the whole apparatus aerated daily for eight hours to flush the $^{14}CO_2$ into adsorption units containing ethanolamine and methanol. Other volatile degradation products were absorbed in absorption vessels containing sulphuric acid and ethylene glycol, respectively. The other flasks (two replicates per water/sediment system and per sampling day) were loosely sealed with cotton-wool plugs, protected against sunlight with aluminium foil, and incubated on magnetic stirrers at 22±2ºC. The batches were sampled at days 0, 1, 2, 4, 8, 16, 32 and 51.

Measurements of $^{14}CO_2$ and of volatile degradation products were performed by using methanol and LSC. At each sampling date the sediment was separated from water by centrifugation. The sediment was extracted with acetonitrile and toluene. The extracts and the water were examined by LSC. The radioactivity which persisted in the sediment following solvent extraction was determined by combustion of aliquots of the dried sediment in a sample oxidiser. The results from the study are presented in table 8.4.4-2.

Table 8.4.4-2: Results from the water/sediment study as % of the applied radioactivity

¡Error! Marcador no definido.**System ¡Error! Marcador no definido.** ¡Error! Marcador no definido.	**Time Days**	**% of Applied Radioactivity**									
		Endosulfan		**Endosulfan sulphate**		**Endosulfan hydrocarboxylic acid**		**Total endosulfan**			**Bound residues**
		S	**W**	**S**	**W**	**S**	**W**	**S**	**W**	**S+W**	**S**
River Main	0	21.7	61.4	0.0	0.0	0.0	0.0	21.7	61.4	83.1	0.1
	1	41.4	9.0	1.3	19.5	0.0	0.0	42.7	28.5	71.1	1.8
	2	37.1	9.4	4.4	20.2	0.0	0.4	41.4	29.6	71.0	4.7
	4	37.7	10.8	5.5	18.8	0.0	1.1	43.1	29.6	72.7	0.8
	8	14.2	2.3	16.2	24.1	0.2	7.9	30.4	26.3	56.7	7.9
	16	2.2	1.2	9.0	7.9	1.1	24.7	11.2	9.0	20.3	13.1
	32	2.4	1.7	11.6	9.3	4.0	19.4	14.0	11.0	24.9	18.7
	51	1.1	2.5	10.6	0.8	1.5	6.8	11.7	3.3	15.0	23.2
Gravel pit	0	22.7	4.4	0.0	57.6	0.0	0.0	22.7	62.0	84.7	0.1
	1	30.6	5.7	2.6	37.1	0.0	1.0	33.2	42.8	76.0	3.3
	2	20.9	7.4	4.4	32.9	0.3	0.5	25.3	40.3	65.6	3.5
	4	14.3	5.3	7.0	35.8	0.0	6.5	21.3	41.1	62.3	2.2
	8	7.5	2.3	9.5	16.4	1.7	1.2	17.0	18.6	35.6	7.3
	16	2.1	0.0	2.2	5.8	2.8	21.2	14.3	5.8	20.1	19.8
	32	2.9	0.4	5.7	5.5	3.1	28.4	8.5	5.8	14.3	15.5
	51	0.5	0.0	9.5	2.7	3.1	6.3	10.0	2.7	12.7	20.1

The half live of parent compound in the total system was estimated by first order kinetics (table 8.4.4-3). However the determination of the DT values carried out in the study is not correct due to the Log_{10} was used for that determination intead of Ln. The correct values of DT_{50} for the parent compound are 12 days for river main and 10 days for gravel pit.

The DT values for the parent compound and the metabolites in sediment were not calculated, the residue is strongly absorbed to the sediment and this fact can affect to its bioavailability. Moreover the detected metabolites were the extractable an effort should be done to characterize the bound residues that they were 20% of the applied radioactivity and the plateu were not got.

Table 8.4.4-3: Concentrations of parent endosulfan (α+β) in the total system (mg/kg) and its estimated half live

¡Error! Marcador	**Days**	**Parent Endosulfan (mg/kg)**	**DT_{50} (days)**	**R^2**	**n**
River main	0	0.19	12	0.92	7
	1	0.12			
	2	0.11			
	4	0.11			
	8	0.04			
	16	-			
	32	0.02			
	51	0.07			
Gravel pit	0	0.06	8	0.85	6
	2	0.07			
	4	0.05			
	8	0.02			
	16	0.01			
	32	0.01			
	51	<0.001			

The amount of radioactivity in the total system decreased progressively to the end of the study. Bound residues rose to ≈20% of the initial applied radioactivity. During the incubation period (51 days) the formation of two main metabolites, endosulfan-sulphate and endosulfan hydrocarboxylic acid was observed in both systems and mainly in the water phase, at >10% of the applied radioactivity (up to day 8 and at 16-32 days respectively). At the end of the study, both of them were found at <10% in the water, sediment and bound sediment fractions. Other different metabolites as endosulfan lactone, endosulfan diol, endosulfan ether and an unidentified metabolite were detected in one or both of the systems tested at very low levels (<10% of the applied radioactivity). The $^{14}CO_2$ detected in the traps throughout the study was < 0.1%. Volatile compounds were always lower than 10% of the applied radioactivity (2-4%).

Stumpf, 1990b (A44231)

The author used the data provided by Gildemeister, 1985 (A31182) (as % of the applied radioactivity) to recalculate DT_{50} and DT_{90} values for parent and total endosulfan. Results are shown in table 8.4.4-4.

Table 8.4.4-4: Dissipation of endosulfan from the whole water/sediment systems

¡Error! Marcador	**COMPOUND**	**DT_{50} (Days)**	**DT_{90} (Days)**	**R^2**	**SYSTEM**
Total system	Total endosulfan	21	68	0.82	River main
	Parent endosulfan	12	39	0.70	
Water phase	Total endosulfan	15	-	0.86	
	Parent endosulfan	<1	-	-	
Total system	Total endosulfan	18	59	0.83	Gravel pit
	Parent endosulfan	10	32	0.87	
Water phase	Total endosulfan	12	-	0.85	
	Parent endosulfan	8	-	0.97	

Cotham and Bidleman, 1989 (A41218)

The study has not been conducted under any guideline or GLP. Sediment cores and about 130 mL of overlying seawater (salinity 30 ppt) were obtained from Leadenwah Creek located south of Charleston. The cores, averaging 7 cm in depth, were obtained in 22 cm length, 5 cm i.d. glass tubes. The sediment had a moisture content of 60% and contained 1.22% ± 0.30 total organic carbon on a dry weight basis by oxidative combustion after leaching with 40% phosphoric acid solution to remove carbonate. The pH of the overlying seawater averaged 7.7 and the pH of the interstitial water in the sediment layer at 1.5 cm depth averaged 7.3. Cores were fortified with 849 ng of endosulfan. Cores were incubated at 20ºC under laboratory light for the duration of the experiment. Duplicate cores were sampled on days 1, 2, 2, 4, 9 and 20.

Water and sediment were analysed separately. Endosulfan was extracted on C8 columns. Before use, C8 cartridges were extracted in a soxhlet apparatus for 3 hours with 1:1 ethyl ether/n-hexane and dried in a heated vacuum desiccator at 40ºC. The top 1.5 cm of each sediment core was removed, transferred to soxhlet and extracted by different solvents. Analysis was carried out by gas chromatography. Attempts were made to identify endosulfan metabolites in the water/sediment experiment. Half-lives were estimated by first order kinetics (Table 8.4.4-5).

Table 8.4.4-5: DT_{50} values of endosulfan at pH 7.3-7.7 in a seawater/sediment study

¡Error! Marcador	**DT_{50} (days)**
α endosulfan	8.3
β endosulfan	22
Parent compound	13.6-15.6

Endosulfan diol was the only metabolite identified in the seawater/sediment experiment.

There is not enough data about the degradation kinetics (only DT_{50} and standard deviation). Therefore this study is not acceptable.

- **Field Studies**

Cornaby *et al*., 1989 (A41298)

The study has been carried out with GLP. Thiodan 35 EC (endosulfan 97-99% purity; 33.7 mCi/g as) was applied to tomatoes under worst-case conditions: minimal buffer between tomatoes and pond-edge (5-6 m); the highest application rate (1.12 kg endosulfan /ha) and forced irrigation after the last application. Two watershed/pond systems served as treatment sites, with two additional watershed/pond systems as reference sites. Tomatoes planted in the reference watershed received no endosulfan. Characteristics of soil treated (Table 8.4.4-6), and the water quality characteristics of each pond (Table 8.4.4-7) are summarised in the following tables.

Table 8.4.4-6: Characteristics of treated soil cropped with tomatoes at Georgia sites

¡Error! Marcador no definido.**PARAMETER**	**EXPERIMENTAL PONDS**		**CONTROL PONDS**	
¡Error! Marcador no definido.	**C271**	**M554**	**M558**	**T41**
% Sand	77	82	78	73
% Silt	8	7	9	14
% Clay	15	11	13	13
Cation exchange capacity (meq/100g)	3.7	2.4	2.7	3.6
PH	5.2	5.5	5.5	6.1
% organic matter	1.8	1.3	2.0	1.8

Table 8.4.4-7: Water quality characteristics of experimental and control plots

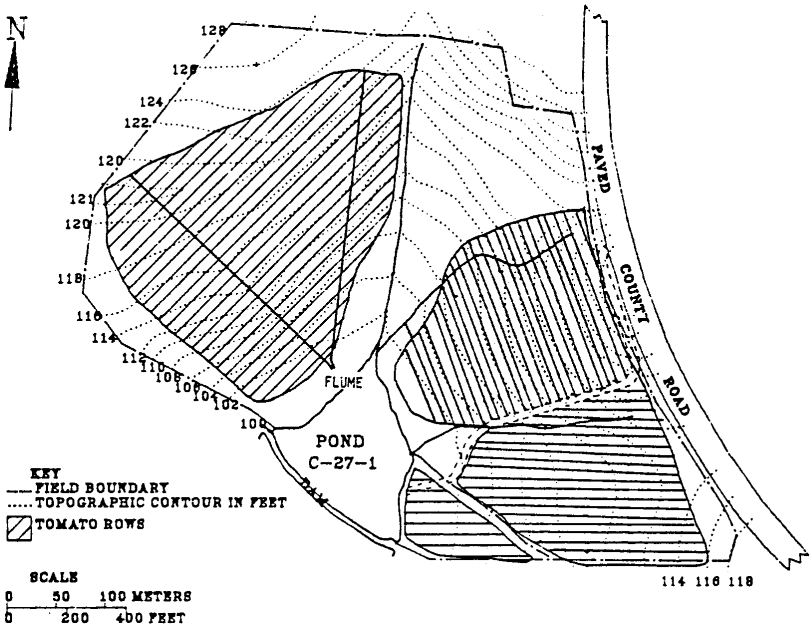
¡Error! Marcador no definido.**PARAMETER** ¡Error! Marcador no definido.	**EXPERIMENTAL PLOTS**		**CONTROL PLOTS**	
	C271	**M558**	**M554**	**T41**
PH	7.2	7.7	7.5	7.4
Temperature (ºC)	24.7	25.7	24.2	26.0
Conductivity (µmhos/cm)	66	88	76	66
Dissolved oxygen (mg/L)	8.0	8.7	8.8	8.1
Alkalinity (mg $CaCO_3$/L)	16	19	16	11
Acidity (mg $CaCO_3$/L)	5	4	5	4
Hardness (mg $CaCO_3$/L)	12	16	15	12
Turbidity (NTU)	63.6	29.3	12.5	21.5
Nitrates (mg/L)	0.34	0.37	0.43	0.28

Climatological data are from the two closest weather stations in Albany and Moultrie, Georgia. At Albany mean monthly temperature is 66.1ºF (19ºC) with a mean daily maximum of 92.2ºF (33.4ºC) in August and a mean daily minimum of 49.2ºF (9.5ºC) in january. Mean precipitation total is 49.48 inches (125.67 cm) with up to 3.98 inches (10.1 cm) per day for greatest daily precipitation. At Moultrie tha pattern is similar. Mean monthly temperature is 66.7ºF (19.2ºC) with mean daily maximum of 91.6ºF (33.1ºC) in August. Precipitation patterns are similar to those for Albany.

Pond descriptions:

Pond C271: It was located in Colquitt County, Georgia. It had 1.4 ha and a surrounding watershed of 20.4 ha. The greatest depth of 1.8 m occurs in the southwest part of the pond near the dam. The pond is roughly triangular, with the two longer sides surronded. Crops in the three years preceding the study included cotton, peanuts, soybeans, black-eye peas, and garden vegetables. The most recently planted crops were peanuts, cotton and vegetables. Endosulfan had not been used for at least 3 years before the application phase of the study. Preliminary analysis of the soil showed that no pesticide residues remained. No efforts to keep a fix buffer zone were made as can be seen in the figure, the distance between the crop and the pond varied from 5 to more than 50 m.

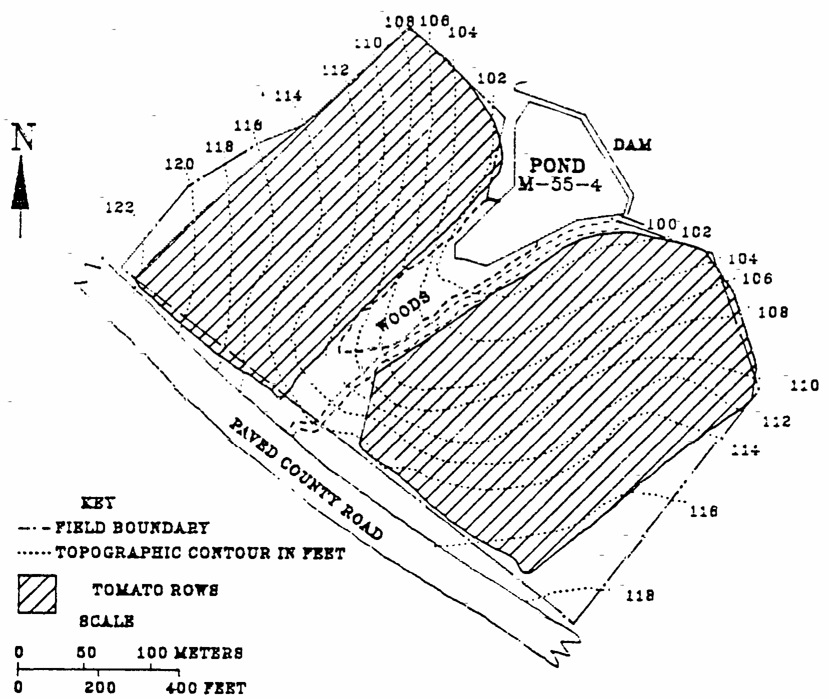
Figure 8.4.4-1: Situation and location of the Pond C-27-1



TOMATO ACREAGE AT C-27-1. 14.2 hectares (35 acres) of tomatoes were planted in the two fields. Location of the flume in this drainage area is also shown.

Pond M554: It was located in Mitchell County, Georgia. It has 0.8 surface hectareas and an associated watershed of 9.6 ha. The greatest measured depth was about 2.8 m in the eastern part of he pond near the middle of the dam. M554 has farm fields of 3.8 and 5.8 ha, that slope into the pond on each of the longer slides. Crops in the last 3 years preceding this study have been peanuts, corn, tomatos and snap beans. The most recent crops were corn and peanuts. The following pesticides have been used on the fields for normal agronomic operations: atrazine, 2-,4-DB, Balan, Basagran, Bravo, Dinitro, Dyanap, Lannate, Lasso, Maneb, Manzate, Nudrin, parathion, Prowl, Pyridin, pyrethroids, Temik, Thiodan, Treflan, and Vernam. Preliminary analysis of the soil showed no pesticide residues remained. No efforts to keep a fix buffer zone were made as can be seen in the figure, the distance between the crop and the pond varied largely, from 15 to more than 50 m in the right and left sides of the pond.

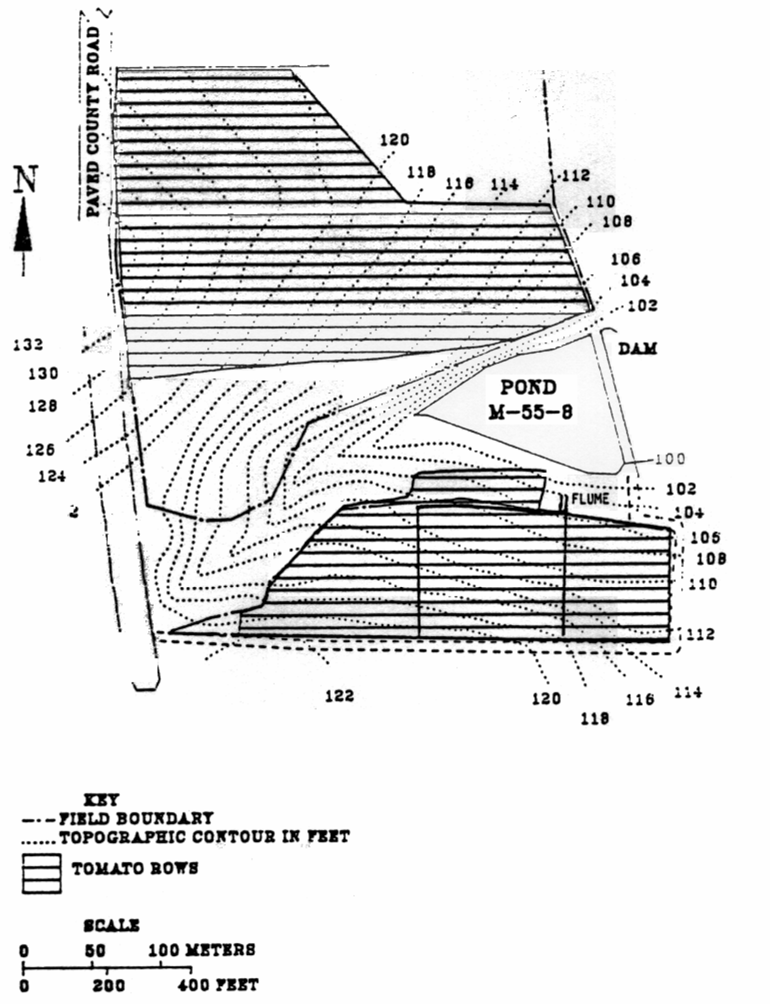
Figure 8.4.4-2: Situation and location of the Pond M-55-4



TOMATOES ACREAGE AT M-55-4. 8.5 hectares (21 acres) of tomatoes were planted in the two fields.

Pond M558: It was located in Mitchell County, Georgia. This pond surface has 0.9 ha and watershed of 9.9 ha. The ratio of water to land es about 1:11. The greatest measured depth was about 1.5 m, near the southern part of the dam. It is triangular in shape, with fields of 3.8 and 5.8 haon each of the longer sides that slope into the pond. The slope is from an arbitrary 30.5 m elevation at the pond’s surface to 40.2 m to the northwest and 34.1 m to the east. Crops in the last three years have limited to corn. The following pesticides have been used during the last three years: atrazine, basagran, dyanap, lannate, manzate, nudrin, parathion, prowl, pydrin, temik and vernam. Endosulfan has not been used for at least 3 years preceding the application phase of the study. Preliminary analysis of the soil showed no pesticide residues remained.

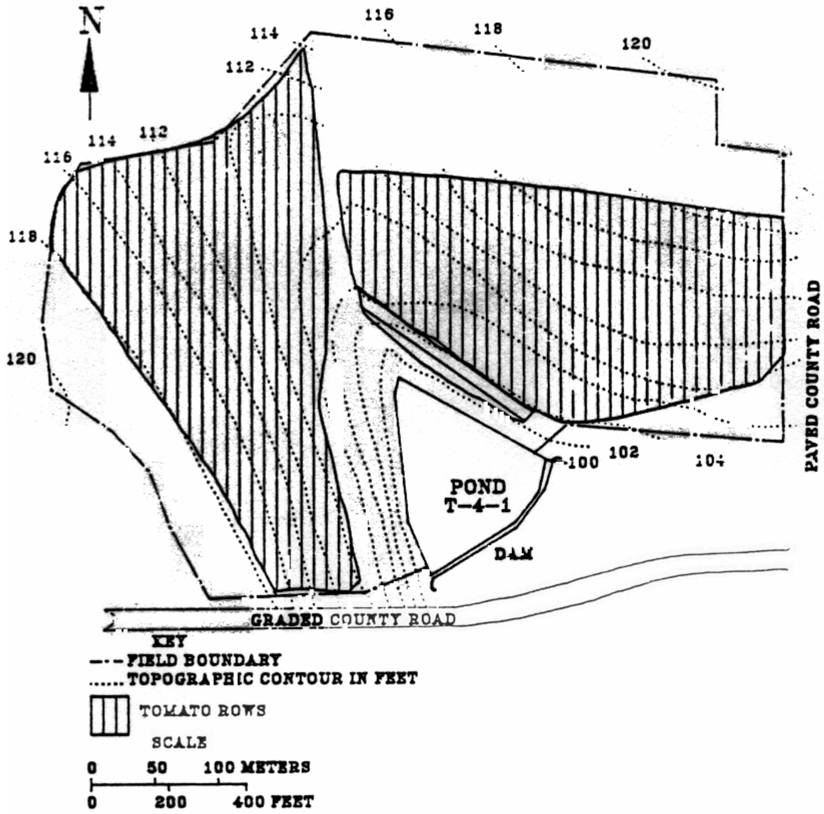
Figure 8.4.4-3: Situation and location of the Pond M-55-8



TOMATOES ACREAGE AT M-55-8. 8.5 hectares (21 acres) were planted in the two fields. Location of the flume in this drainage area is also shown.

Pond T41: It was located in Thomas County, Georgia, immediately southeast of Mitchell County. The pond surface has 1.0 ha, and a watershed of 15.1 ha. The ratio of water to land is about 1:14. The greatest depth is about 1.2 m, in front of the dam. This pond is triangular in shape, with fields that slope into the pond in each side. One field is 6.9 ha and the other is 5.0 ha, with a fence separated it from a third field of 3.3 ha, for a total of 15.2 ha. The slope is from an assumed 30.5 m at the pond surface to 36.6 in the far western and eastern end of the watershed. Crops in the past three years havw been soybeans and corn. The pesticides used were atrazine, balan, bravo, dinitro, gramoxone, lasso, sencor, temik, treflan, and 2,4-DB on these crops. Endosulfan has not been used for atleast three years preceding the application phase of the study. Preliminary soil analyses showed toxaphene present in the northeast portions of the area for study but no other pesticides were found.

Figure 8.4.4-4: Situation and location of the Pond T-4-1



TOMATO ACREAGE AT T-4-1. 10 hectares (25 acres) of tomatoes were planted in the two fields.

During 1988, rainfall was below the annual average of 129 cm, in 1988 approximately 104 cm of rain fell at Moultrie, thus precipitation was below average by 25 cm. Rainfall amounts during 1988 sampling period of March 15 to December 15 were 49.8 cm at C271, 43.9 cm at M554, 52.3 cm at M558 and 47.2 at T41. Rainfall events ocurred infrequently as showed by the plateau during the May-June growing season, which coincided with endosulfan applications. On may 10, prior the first application, an intense storm yielded 9.18 cm of rain at C271, resulting in substantial surface from the adjacent fields into the pond, producing a muddy appearance in the pond that remained for several weeks. Rainfall ocurred more frequently after applications had been completed, and resulted in numerous runoff events.

Thiodan was applied three times to each of two study sites. For the first application, C-27-1 and M-55-8 were both sprayed on May 27, 1988. The second application was conducted on June 10 and 11 for C-27-1 and M-55-8, respectively. The third application was on June 27 at M-55-8 and at C-27-1.

Flumes at the two treatment sites permitted runoff monitoring and sampling runoff for endosulfan. Runoff from 3.6 ha at C-27-1 and from 0.9 ha at M-55-8 were diverted into the flumes . Diversions were achieved by cutting trenches sloping to the flumes. Endosulfan entered the treatment ponds through two pathways: aerial drift and runoff. Runoff provided the primary exposure, and was induced by irrigation and/or natural rainfall following the third application. Precipitation runoff volumes from the flume drainage areas on C271 and M558 were continually monitored with water level recorders installed on the stilling wells of the flumes. The runoff volumes from the control ponds were not monitored.

Monitoring runoff ocurred at the flume drainage areas of C271 and M558. Monitoring at the time of the first endosulfan application (May 27, 1988) and continued until mid-December 1988. Seventeen runoff events were sampled for endosulfan at the two ponds (10 runoffs ocuured at C271 and 7 runoff at M558). The runoff events are summarised in the following tables (Table 8.4.4-9 and 8.4.4-10).

Monitoring of the ten runoff events ocurred at C271 (Table 8.4.4-9), this included an induced runoff event following the third endosulfan application when runoff from the non-flume side of the field was also sampled. Storms resulting in runoff ocurred in June, July, August, September, October and November. The minimum precipitation (measured at the flume) resulting in runoff was 0.99 cm. Lesser amounts resulted in insufficient runoff to activate the water sampler or results in indicernible readings on the water level recorder chart Mechanical failures of the water level recordeder prevented runoff volume calculations for three events. The average precipitation resulting in runoff was 2.8 cm; the average recorded runoff from the drainage area was 7.25 m^3 per event.

Runoff from the C-27-1 fields contained maximum mean total endosulfan of 203000 ng/l endosulfan two days after the final applications. The maximum at M-55-8 was 79600 ng/l at 3 hours after the third spray. Maximum concentrations for C-27-1 were more than twice tha meximum levels detected at M-55-8, due in part to the larger watershed area. Endosulfan continued to be present at the rainfall events for the duration of the study.

Table 8.4.4-9: Runoff events at C271. Precipitation and runoff for each event was mrasured at the flume of the drainage area in the tomato field.

				Average concentration (µg/l)			
Runoff Event	**Day Date Week**	**Precipitation (cm)**	**Drainage Area Volume (m^3)**	α	β	**sulphate**	**Total**

				Average concentration (μg/l)			
Runoff Event	**Day Date Week**	**Precipitation (cm)**	**Drainage Area Volume (m^3)**	α	β	**sulphate**	**Total**
3	32 June 28 78	Induced (2.03-3.05)	--	-	-	-	-
4	33 June 29 78	Induced (2.03-3.05)	8.17	52.3	86	13	151
5	39 July 5 79	1.57	2.73	13	33	9.25	55
6	46 July 12 80	2.16	20.90	1.9	11.4	2.4	15.6
8	74 Aug 9 84	4.32	No Data	0.4	5.7	4.0	9.8
10	75 Aug 10 84	1.52	No Data	0.11	3.7	4.2	7.84
11	81 Aug. 16 85	0.99	9.96	0.11	3.7	4.2	7.84
12	101 Sep. 5 88	4.45	0.30	0.022	1.05	2.25	3.23
14	129 Oct.3 92	4.83	8.46	0.018	1.0	2.5	3.42
16	164 Nov. 7 97	2.29	0.25	0.017	1.5	4.0	5.36

Seven runoff events were monitores at M558 (Table 8.4.4-10); only one ocurred prior to the final endosulfan application and was caused by a natural rainfall event. Storms resulting in runoff ocurred in June, August, September, October, and November. The least amount of precipitation resulting in a runoff event was 1.32 cm. Mechanical failures of the water level recorder prevented runoff calculations for one event. The average precipitation resulting in runoff was 2.75 cm; the runoff from the drainage area averaged 17.18 m^3 per event.

Table 8.4.4-10: Runoff events at M558. Precipitation and runoff for each event was mrasured at the flume of the drainage area in the tomato field.

Runoff Event	Day Date Week	Precipitation (cm)	Drainage Area Volume (m^3)	Average concentration (μg/l)			
				α	β	sulphate	Total
1	14 June10 75	1.93	19.25	9	18	7.2	33.9
2	29 June 25 77	3.18	21.72	33..5	36	8.25	77.4
7	68 Aug.3 83	2.79	25.70	0.83	4.5	3.2	8.46
9	74 Aug. 9 84	1.32	2.20	0.56	5.7	5	10.6
13	124 Sept. 28 91	2.54	2.56	0.11	2.1	6.5	8.45
15	129 Oct. 3 92	6.12	31.65	0.57	1.025	2.5	3.5
17	178 Nov. 21 99	1.35	No data	0.012	0.064	2.6	3.26

Soil samples were collected one to two days before and one to two days follwoing each endosulfan application and approximately 7±1, 14±3, 28±3, 60±3, 90±3 and 180±3 days following the final application. Composite soil samples were analyzed to a detection limit of 10μg/kg. Total endosulfan concentrations were similar in fields adjacent to the two tratment ponds. Soil concentrations of total endosulfan peaked after the third application, but decreased by 86% by December, 180 days after the last application . . The ratio of alpha, beta and sulphate forms of endosulfan were also similar at the two treatment ponds. Initial ratios (after the first application) averaged 63:33:5, but by December had shifted to 5:54:41. Results are sumarised in the following tables (Table 8.4.4-11 and Table 8.4.4-12)

Table 8.4.4-11: C-27-1: Concentrations µg/kg of Endosulfan in top 5 cm soil. (mean of 6 samples)

Day Date Week	α Endosulfan	βEndosulfan	Sulphate Endosulfan	Total
-3 5/24 73	<DL	<DL	<DL	<DL
1 5/28 73	178	132	21.5	331
11 6/7 75	8.6	26.5	11.5	46.2
14 6/10 75	405	400	80.5	882
29 6/25 77	210	803	135	1140
32 6/28 78	870	1260	158	2280
39 7/5 79	410	1050	179	1640
45 7/11/ 80	183	440	114	733
59 7/25 82	198	911	182	1280
86 8/23 88	136	1220	278	1630
123 9/27 91	9.0	381	676	1040
204 12/17 102	1.8	175	151	322

Table 8.4.4-12: M-55-8: Concentrations µg/kg of Endosulfan in top 5 cm soil. (mean of 6 samples)

Day Date Week	**α Endosulfan**	**βEndosulfan**	**Sulphate Endosulfan**	**Total**
-2 5/25 73	<DL	<DL	<DL	<DL
1 5/28 73	295	106	7.2	408
12 6/8 75	62.3	121	46.0	227
15 6/11 75	593	495	96.1	1180
26 6/22 77	293	613	119	1020
27 6/23 77	1120	1230	161	2510
33 6/29 78	408	573	95.8	1070
41 7/7 79	327	515	95.8	1070
55 7/21/81	334	902	235	1460
87 8/22 86	46.8	329	243	609
117 9/21 90	38.8	247	182	461
200 12/13 102	28.7	191	133	347

Endosulfan Spray drift was monitored using absorbent cards at the field edges, pond edges and pond surface. Fifteen stations were located at the outer edge of the fields, 10 stations were located at the pond edges and 10 were located at the pond surfaces. The drift cards from each station were anlyzed together to a detection limit of 0. 1 µg total endosulfan. Results are sumarised in the tables 8.4.4-13 and 8.4.4-14.

At the pond edges, concentrations for the applications 1 and 2 were higher at C-27-1 than at M-55-8 but were similar for application 3. Endosulfan concentrations at the pond surface showed the same pattern as at the pond edge. Based on drift estimates, mean concentrations of endosulfan on the pond surface of C-27-1 were 83 and 99 times greater than the mean concentrations calculated at M-55-8 for applications 1 and 2, but changed at application 3, where they were about 1/3 the concentration of M-55-8. The total input from all three applications of endosulfan measured at the pond surface of C-27-1 was 412 µg/m^2 while at M-55-8 the total was 104 µg/m^2.

Table 8.4.4-13: C-27-1:Average Concentrations (μg/m²) of Endosulfan on pond surface drift cards

Day Date Week	α Endosulfan	βEndosulfan	Sulphate Endosulfan	Total
0 5/27 73	114	51.4	<DL	166
14 6/10 76	169	49.5	<DL	218
31 6/27 78	21.6	6.5	<DL	28.1

Table 8.4.4-14: M-55-8: Average Concentrations (μg/m²) of Endosulfan on pond surface drift cards

Day Date Week	α Endosulfan	βEndosulfan	Sulphate Endosulfan	Total
0 5/27 73	1.3	<DL	<DL	2.0
15 6/11 75	2.2	<DL	<DL	2.2
27 6/23 77	76.6	22.7	<DL	99.3

Samples of pond water were collected one or two days before and the day of the pesticide applications and following a schedule of approximately 3, 7, 14, 28, 60, 90 and 180 days after the last application. Integrated water column samples were collected from the sampling zones using a pump with a stainless steel impeller and casing and Teflon tubing. Water was extracted with methylene chloride using a separator funnel, and the extract was concentrated to 1 mL after solvent exchange with hexane. The extract was analysed for endosulfan by capillary column gas chromatography using an electron capture detector. Sediment cores for residue analysis were obtained at the same scheduled intervals and locations as pond water. A 5cm cylinder was forced into the sediment and then carefully removed with the core intact. Water above the core was siphoned off and the top 5 cm of sediment placed in an aluminium container for layer separation and analysis. Sediment cores were analysed for endosulfan with a detection limit of 5 µg/kg. Approximately 50g of sediment was serially extracted by tumbling with acetone. The final extract was concentrated, solvent exchanged to hexane, and analysed for endosulfan by capillary column gas chromatography using an electron capture detector. Results obtained are summarised in the following tables (Tables 8.4.4-15 and 8.4.4-16).

Table 8.4.4-15: Concentrations (ng/L) of endosulfan in the treated pond waters

¡Error! Marcador	**Treated plot C271**					**Treated plot M558**				
¡Error! Marcador no definido.	**Date**	**Form**	**Mean**	**Minimum**	**Maximum**	**Date**	**Form**	**Mean**	**Minimum**	**Maximum**
Before first application	5/25	α endosulfan	<DL	<DL	<DL	5/25	α endosulfan	<DL	<DL	8
		β endosulfan	<DL	<DL	12.0		β endosulfan	5.5	<DL	12
		E sulphate	5.8	<DL	8.0		E sulphate	8.7	6	12
		Total	7.6	<DL	19.7		Total	16.3	5.8	29.6
First application 5/27	5/27	α endosulfan	42.1	32	58	5/27	α endosulfan	69.8	<DL	390
		β endosulfan	38.3	18	62		β endosulfan	54.3	<DL	310
		E sulphate	<DL	<DL	8		E sulphate	<DL	<DL	<DL
		Total	81.8	50	120		Total	124	<DL	700
	6/8	α endosulfan	22.2	18	25	6/8	α endosulfan	<DL	<DL	6
		β endosulfan	41.3	26	48		β endosulfan	<DL	<DL	<DL
		E sulphate	61.7	54	68		E sulphate	<DL	<DL	<DL
		Total	123	107	133		Total	<DL	<DL	6
						6/10	**RUNOFF EVENT**			
Second application 6/10 (C271) 6/11 (M558)	6/10	α endosulfan	120	63	180	6/11	α endosulfan	14.8	<DL	58
		β endosulfan	78	68	86		β endosulfan	5.2	<DL	15
		E sulphate	61.5	58	67		E sulphate	35	27	45
		Total	257	187	322		Total	53.7	29.8	103
	6/24	α endosulfan	9	<DL	18	6/22	α endosulfan	<DL	<DL	<DL
		β endosulfan	<DL	<DL	9		β endosulfan	<DL	<DL	5
		E sulphate	<DL	<DL	<DL		E sulphate	16.3	10	40
		Total	10.5	<DL	27		Total	16.5	9.6	43.5
Third application 6/27 (C271) 6/23 (M558)	6/28	**RUNOFF EVENT**				6/25	**RUNOFF EVENT**			
	6/29	**RUNOFF EVENT**								
	6/30	α endosulfan	377	130	1100	6/25	α endosulfan	255	120	460
		β endosulfan	413	130	1300		β endosulfan	196	87	350
		E sulphate	337	170	1000		E sulphate	138	115	150
		Total	1110	433	3360		Total	583	317	924
	7/2	α endosulfan	288	80	1000	6/28	α endosulfan	37.7	10	130
		β endosulfan	627	350	1600		β endosulfan	45	14	160
		E sulphate	415	200	1400		E sulphate	220	66	660
		Total	1310	691	3950		Total	294	130	924
	7/5	**RUNOFF EVENT**								
	7/5	α endosulfan	44.2	40	48	6/30	α endosulfan	<DL	<DL	6
		β endosulfan	59.7	47	65		β endosulfan	<DL	<DL	5
		E sulphate	223	200	240		E sulphate	30	<DL	50
		Total	319	294	343		Total	30.7	<DL	57
	7/11	α endosulfan	13.7	10	16	7/7	α endosulfan	7.8	<DL	47
		β endosulfan	<DL	<DL	8		β endosulfan	9.5	<DL	52
		E sulphate	128	120	130		E sulphate	5.1	<DL	31
		Total	141	126	148		Total	22.3	<DL	129
	7/12	**RUNOFF EVENT**								
	7/25	α endosulfan	12.5	9	20	7/21	α endosulfan	<DL	<DL	<DL
		β endosulfan	<DL	<DL	20		β endosulfan	<DL	<DL	6
		E sulphate	185	170	190		E sulphate	24.5	23	26
		Total	195	173	218		Total	26.4	23.1	29.1
	8/9	**RUNOFF EVENT**				8/3	**RUNOFF EVENT**			
	8/10	**RUNOFF EVENT**				8/9	**RUNOFF EVENT**			
	8/16	**RUNOFF EVENT**								
	8/23	α endosulfan	11.2	10	13	8/22	α endosulfan	<DL	<DL	<DL
		β endosulfan	<DL	<DL	15		β endosulfan	<DL	<DL	<DL
		E sulphate	136	130	140		E sulphate	10	8	16
		Total	145	135	153		Total	9.6	7.7	15.4
	9/5	**RUNOFF EVENT**								
	9/27	α endosulfan	8	7	9.7	9/21	α endosulfan	<DL	<DL	6
		β endosulfan	<DL	<DL	<DL		β endosulfan	<DL	<DL	<DL
		E sulphate	58.3	51	61		E sulphate	<DL	<DL	5
		Total	64.1	56.1	66.7		Total	<DL	<DL	10.8
	10/3	**RUNOFF EVENT**				9/28	**RUNOFF EVENT**			

¡Error! Marcador ¡Error! Marcador no definido.	Treated plot C271					Treated plot M558				
	Date	**Form**	**Mean**	**Minimum**	**Maximum**	**Date**	**Form**	**Mean**	**Minimum**	**Maximum**
	11/7	**RUNOFF EVENT**				10/3	**RUNOFF EVENT**			
						11/21	**RUNOFF EVENT**			
	12/17	α endosulfan	<DL	<DL	<DL	12/13	α endosulfan	<DL	<DL	<DL
		β endosulfan	<DL	<DL	<DL		β endosulfan	<DL	<DL	<DL
		E sulphate	12.7	12	15		E sulphate	<DL	<DL	<DL
		Total	12.2	11.5	14.4		Total	<DL	<DL	<DL

<DL = Less than detection limit of 5 ng/L.

Table 8.4.4-16: Concentrations (µg/kg) of endosulfan in the treated pond sediments

¡Error! Marcador no definido.**Application** ¡Error! Marcador no definido.	Treated plot C271					Treated plot M558				
	Date	**Form**	**Mean**	**Minimum**	**Maximum**	**Date**	**Form**	**Mean**	**Minimum**	**Maximum**
Before first application	5/26	α endosulfan	<DL	<DL	<DL	5/24	α endosulfan	<DL	<DL	<DL
		β endosulfan	<DL	<DL	<DL		β endosulfan	<DL	<DL	<DL
		E sulphate	<DL	<DL	<DL		E sulphate	<DL	<DL	<DL
		Total	<DL	<DL	<DL		Total	<DL	<DL	<DL
First application 5/27	5/28	α endosulfan	<DL	<DL	<DL	5/28	α endosulfan	25.8	<DL	130
		β endosulfan	<DL	<DL	<DL		β endosulfan	17.6	<DL	98
		E sulphate	<DL	<DL	6.2		E sulphate	<DL	<DL	6.4
		Total	<DL	<DL	6		Total	44.4	<DL	234
	6/8	α endosulfan	<DL	<DL	<DL	6/8	α endosulfan	<DL	<DL	5.6
		β endosulfan	<DL	<DL	<DL		β endosulfan	<DL	<DL	<DL
		E sulphate	<DL	<DL	<DL		E sulphate	<DL	<DL	<DL
		Total	<DL	<DL	<DL		Total	<DL	<DL	5.6
						6/10	**RUNOFF EVENT**			
	6/10	α endosulfan	<DL	<DL	<DL	6/11	α endosulfan	<DL	<DL	<DL
		β endosulfan	<DL	<DL	<DL		β endosulfan	<DL	<DL	8.2
		E sulphate	<DL	<DL	<DL		E sulphate	<DL	<DL	<DL
		Total	<DL	<DL	<DL		Total	<DL	<DL	8.2
Second application 6/10 (C271) 6/11 (M558)	6/25	α endosulfan	10.2	<DL	21	6/22	α endosulfan	<DL	<DL	<DL
		β endosulfan	11.4	<DL	52		β endosulfan	8	<DL	17
		E sulphate	7.2	<DL	43		E sulphate	<DL	<DL	<DL
		Total	28.5	6.8	73		Total	8	<DL	17
Third application 6/27 (C271) 6/23 (M558)	6/28	**RUNOFF EVENT**				6/25	**RUNOFF EVENT**			
	6/29	**RUNOFF EVENT**								
	6/30	α endosulfan	<DL	<DL	15	6/25	α endosulfan	37.7	<DL	63
		β endosulfan	5.2	<DL	20		β endosulfan	44.9	8.3	61
		E sulphate	<DL	<DL	8.1		E sulphate	17.5	6	28
		Total	10	<DL	42.8		Total	99.4	14.1	149.9
	7/5	**RUNOFF EVENT**								
	7/5	α endosulfan	6.6	<DL	20	6/30	α endosulfan	<DL	<DL	8
		β endosulfan	29.5	<DL	47		β endosulfan	9.3	<DL	17
		E sulphate	13.7	<DL	31		E sulphate	8.2	<DL	16
		Total	49.2	<DL	77.6		Total	19.5	<DL	38.4
	7/11	α endosulfan	<DL	<DL	<DL	7/7	α endosulfan	<DL	<DL	5.5
		β endosulfan	<DL	<DL	13		β endosulfan	<DL	<DL	19
		E sulphate	<DL	<DL	6.5		E sulphate	10.4	<DL	25
		Total	<DL	<DL	13		Total	15.1	<DL	48.6
	7/12	**RUNOFF EVENT**								
	7/25	α endosulfan	<DL	<DL	<DL	7/21	α endosulfan	<DL	<DL	<DL
		β endosulfan	<DL	<DL	12		β endosulfan	6.2	<DL	12
		E sulphate	6.4	<DL	17		E sulphate	12.7	<DL	27
		Total	9	<DL	24.5		Total	18.4	<DL	31.3
	8/9	**RUNOFF EVENT**				8/3	**RUNOFF EVENT**			
	8/10	**RUNOFF EVENT**				8/9	**RUNOFF EVENT**			
	8/16	**RUNOFF EVENT**								

¡Error! Marcador no definido.**Application** ¡Error! Marcador no definido.	**Treated plot C271**					**Treated plot M558**				
	Date	**Form**	**Mean**	**Minimum**	**Maximum**	**Date**	**Form**	**Mean**	**Minimum**	**Maximum**
	8/23	α endosulfan	<DL	<DL	<DL	8/22	α endosulfan	<DL	<DL	<DL
		β endosulfan	5.2	<DL	17		β endosulfan	5.2	<DL	16
		E sulphate	20.5	6.7	38		E sulphate	24.8	15	28
		Total	25	6.4	50.7		Total	29.1	14.4	42.9
	9/5	**RUNOFF EVENT**								
	9/27	α endosulfan	<DL	<DL	<DL	9/21	α endosulfan	<DL	<DL	<DL
		β endosulfan	<DL	<DL	9		β endosulfan	<DL	<DL	<DL
		E sulphate	9.4	<DL	17		E sulphate	<DL	<DL	9.8
		Total	11.5	<DL	24.4		Total	<DL	<DL	9.4
	10/3	**RUNOFF EVENT**				9/28	**RUNOFF EVENT**			
	11/7	**RUNOFF EVENT**				10/3	**RUNOFF EVENT**			
						11/21	**RUNOFF EVENT**			
	12/17	α endosulfan	<DL	<DL	<DL	12/13	α endosulfan	<DL	<DL	<DL
		β endosulfan	<DL	<DL	<DL		β endosulfan	<DL	<DL	<DL
		E sulphate	<DL	<DL	8.4		E sulphate	<DL	<DL	7.7
		Total	<DL	<DL	8.1		Total	<DL	<DL	7.4

<DL = Less than detection limit of 5 µg/kg.

The results obtained in both treatment plots were as follows:

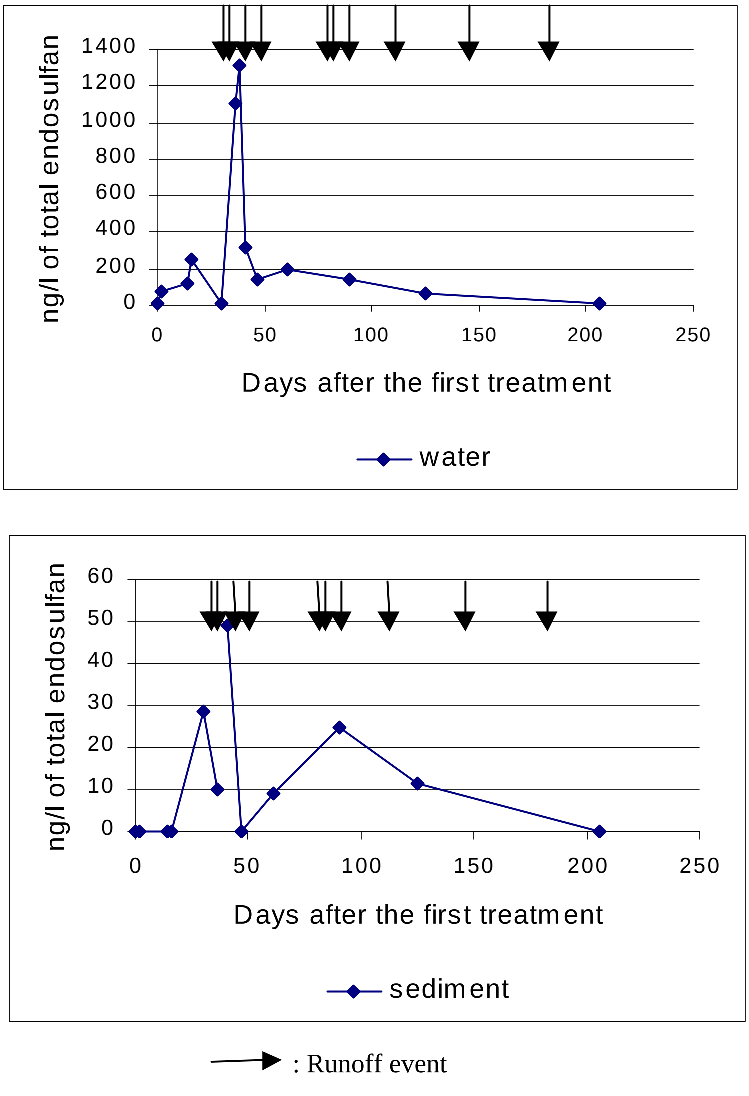
Pond treatment C271: The aerial drift contribution to pond water in C271 was demonstrated by the presence of endosulfan after the first and second endosulfan applications, even though no rainfall or runoff occurred in this test system until after the third applications. Mean total endosulfan concentrations were:

81.8 ng/L immediately after the first application
123 ng/L 12 days after the first application and two days before the second application
257 ng/L immediately after the second application
10.5 ng/L 13 days after the second application and three days prior the third application
1.110 ng/L 3 days post third application.

As can be observed, mean total endosulfan in this pond water peaked after the first runoff event induced via irrigation. Pond water from C271 averaged 1,110 ng/L total endosulfan three days post-application and the day after the forced runoff event and peaked two days later at 1,310 ng/L. These concentrations decreased sharply to 319 ng/L three days later, steadily declined thereafter, and only small quantities of endosulfan sulphate were detectable in C271 pond water six months after the final application.

Endosulfan in pond sediment entered via runoff through pond water and sedimentation of suspended particles to the pond bottom. Mean total endosulfan concentrations in C271 sediment increased to a maximum of 49.2 µg/kg 8 days after the third application, following a forced runoff event. One explanation for the lower peak sediment concentrations was reported by the author. They could occur because of the high turbidity caused by the May 10, storm event at this watershed. Fine particulate sediments remained suspended in C271 for approximately two months. Endosulfan may have selectively adsorbed to the fine suspended sediment and remained suspended in the water column rather than settling to the pond bottom as for M558. Total endosulfan concentrations in C271 sediment ranged from bellow the detection limits (<5 µg/kg) to 25 µg/kg between mid July and late-August, declining to below detection limits by December.

Figure 8.4.4-5: Evolution of the total endosulfan residue in water and sediment of the pond C271



Pond treatment M558: This treatment received approximately half the endosulfan dose observed for treatment pond C271 pond water. Mean total endosulfan concentrations in M558 were:

124 ng/L immediately after the first application, which was attributable wholly to aerial drift.

<5 ng/L 12 days after the first application and three days before the second application

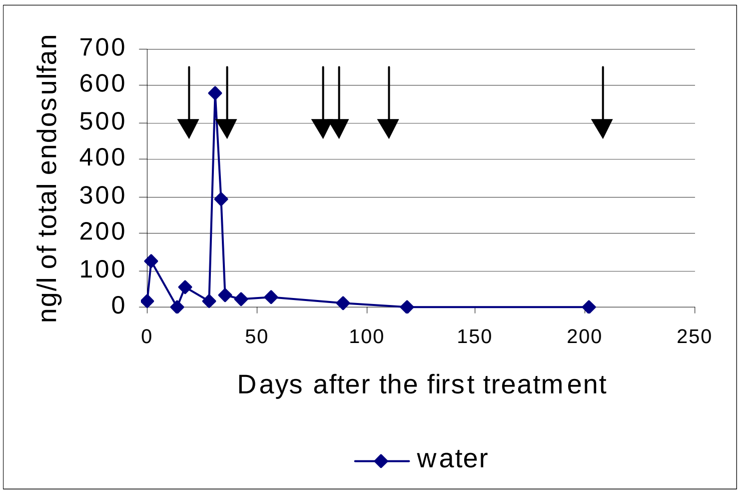
53.7 ng/L immediately after the second application. This measured mean concentration could not be wholly attributed to aerial drift. A natural runoff event occurred at M558 on June 10.

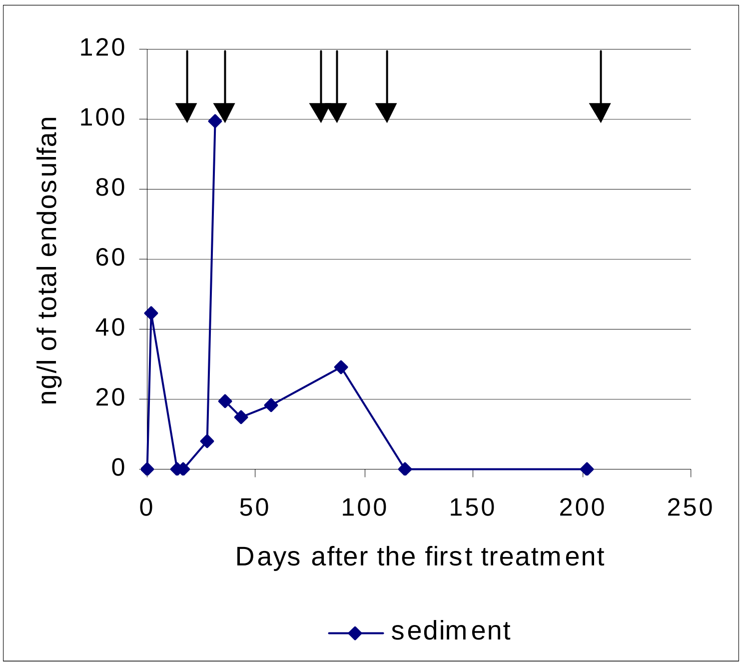
16.5 ng/L 11 days after the second application and one day prior the third application

583 ng/L two days post third application.

As can be observed, the highest concentrations occurred after third application when a combination of irrigation and rainfall (June 24) driven a runoff event. The mean total concentration immediately after the third application (583 ng/L) declined to 30.7 ng/L on June. On July, 24 days after the application, only minute quantities (<10 ng/L) of endosulfan were detected. Thereafter, endosulfan declined to below detection limit.

Figure 8.4.4-7: Evolution of the total endosulfan residue in water and sediment of the pond M-55-8





: Runoff event

The study including a large amount of information on both fate and behaviour and ecotoxicity. The main results from the environmental fate aspects are summarised in Table 8.4.4-17.

Table 8.4.4-17: Summary of the main events related environmental fate and behaviour of endosulfan in the firs treatment pond.

Day	Parameter/Observation	Result	Comments
0	First application		
0	Spray drift on pond surface during first application	α-E 114±59 µg/m^2 β-E 52±32 µg/m^2 E-sulf <0.6 µg/m^2	Corresponds to aprox. 0.2% of the amount applied to 1 ha.
1	Soil concentration after first application	α-E 178±235 µg/kg β-E 132±155 µg/kg E-sulf 21±20 µg/kg	mean ± sd
1	Water concentration after first application	α-E 42±10 ng/l β-E 38±17 ng/l E-sulf <5±3 ng/l	Corresponds to aprox. 36% (α-E) and 73% (β-E) of the concentration estimated according to spray drift.
1	Sediment concentration after first application	α-E <5 µg/kg β-E <5 µg/kg E-sulf <5 µg/kg	mean ± sd
14	Second application		
14	Spray drift on pond surface during second application	α-E 169±52 µg/m^2 β-E 50±17 µg/m^2 E-sulf <0.6 µg/m^2	Corresponds to aprox. 0.2% of the amount applied to 1 ha.
14	Soil concentration after second application	α-E 405±228 µg/kg β-E 400±195 µg/kg E-sulf 81±25 µg/kg	mean ± sd
14	Water concentration after second application	α-E 120±41 ng/l β-E 78±7 ng/l E-sulf 61±3 ng/l	mean ± sd
14	Sediment concentration after second application	α-E <5 µg/kg β-E <5 µg/kg E-sulf <5 µg/kg	mean ± sd
31	Third application		
31	Spray drift on pond surface during third application	α-E 22±25 µg/m^2 β-E 7±8 µg/m^2 E-sulf <0.6µg/m^2	Corresponds to aprox. 0.04% of the amount applied to 1 ha.
32	Soil concentration after third application	α-E 870±130 µg/kg β-E 1260±313 µg/kg E-sulf 158±66 µg/kg	mean ± sd
32	Run-off (20-30 mm) is induced after third application		
33	Run-off (20-30 mm) is induced Concentrations in run-off	α-E 30000±67000 ng/l β-E 45000±120000 ng/l E-sulf 6700±20000 ng/l	There are the highest concentrations measured in the run-off
34	Water concentration after third application and run-off	α-E 377±361 ng/l β-E 413±444 ng/l E-sulf 337±326 ng/l	The α-E concentrations correspond to a run-off of about 0.01% of the total applied amount or 0.05% of the amount remaining in the soil top 5 cm.
34	Sediment concentration after third application and run-off	α-E <5 µg/kg β-E 5±9 µg/kg E-sulf <5 µg/kg	mean ± sd
36	Water concentration 2 days after run-off	α-E 288±356 ng/l β-E 627±486 ng/l E-sulf 415±482 ng/l	Highest concentrations measured in water.

Day	Parameter/Observation	Result	Comments
39	Sediment concentration after run-off	α-E 7±8 µg/kg β-E 30±17 µg/kg E-sulf 14±9 µg/kg	Highest concentrations measured in sediment.
39	Precipitation (18 mm)		
46	Precipitation (22 mm)		
	Additional run-off events		

In summary, the mean peak dose of endosulfan in pond water was approximately 1.3 µg/L in C271, with a concomitant value of approximately 0.6 µg/L for M558. Concentrations of endosulfan in pond water declined to background concentration in six months at C271 and three months in M558. Endosulfan concentrations in pond systems were influenced by runoff events. Endosulfan sediment concentration in C271 and M558 peaked immediately following the first major runoff events after the third application at both ponds. Mean total endosulfan concentrations in sediment in M558 (99.4 µg/kg) peaked at approximately twice those encountered in C271 (43.5 µg/kg). However, by late summer, sediment in both ponds had similar amounts of endosulfan (10-30 µg/kg) which declined to less than the detection limit by December.

Endosulfan residue data from both treatment ponds indicated that the runoff event immediately following the third application provided the critical dose to the ponds.

The study confirms that run-off is the more relevant exposure route when very large buffer zones are required to avoid the level of contamination due to spray drift when the generic EU scenario is used. Therefore, for a higher tier assessment, proper scenarios for the risk assessment of endosulfan in the crops and conditions included in the intended uses should be required.

B.8.4.5 Saturated zone degradation

No information has been submitted.

B.8.4.6 Summary

- ¡Error! Marcador no definido.**Hydrolysis**

The hydrolysis half live of endosulfan was studied by Goerlitz and Kloeckner, 1982 (A31069) and this study was considered unacceptable. A second study carried out by Goerlitz and Rutz, 1989 (A40003) was considered acceptable and studies the hydrolysis of endosulfan at different pH (5, 7 and 9). The rate of hydrolysis of α endosulfan and β endosulfan was extremely dependent of pH. Under acidic conditions no hydrolysis could be observed (>200 days), in a neutral medium the rate was moderate (10-19 days) and in an alkaline environment, it was very rapid (<1 day). In all cases, the only hydrolysis product identified was endosulfan diol, which occurred at >50% of the applied radioactivity.

- ¡Error! Marcador no definido.**Photolysis**

The photolytic degradation route of endosulfan at a wavelenght of <290 nm, was studied by Schumacher et al, 1973 (A25698); Dujera and Mukerjee, 1982 (A27138); Stumpf and Schink, 1988 (A37588) and Stumpf, 1988 (A37588). Results from these studies showed that photolysis can not be considered as an important degradation route due to the fact that both isomers are photolytically estable. In consequence, no relevant metabolites were detected.

- ¡Error! Marcador no definido.**Biological degradation**

None study was submitted concerning the biological degradation of endosulfan. The degradation in natural water (river and sea water) was studied in three trials, it is concluded that the main degradation route of endosulfan in water is the hydrolysis and that it is pH dependent.

- ¡Error! Marcador no definido. **Water /sediment studies**

Water /sediment studies have been provided by Gildemeister, 1985 (A31182); Stumpf, 1990b (A44231) and Cotham and Bidleman, 1989 (A41218), this last study was considered not valid since no data about degradation kinetics was submitted. All of them showed low DT_{50} values (Table 8.4.6-1).

Table 8.4.6-1: Summary of DT_{50} values from water/sediment studies

¡Error! Marcador no definido.**Study** ¡Error! Marcador no definido. ¡Error! Marcador no definido.	**System**	**Total system**						**Water phase**		
		Total endosulfan			**Parent endosulfan**			**Total endosulfan**		
		DT_{50} (days)	**R^2**	**n**	**DT_{50} (days)**	**R^2**	**n**	**DT_{50} (days)**	**R^2**	**n**
Gildemeister, 1985 (A31182)	River main	-	-	-	12	0.92	7	-	-	-
	Gravel pit	-	-	-	9.5	0.85	6	-	-	-
Stumpf, 1990b (A44231)*	River main	21	0.82	8	12	0.70	8	15	0.86	8
	Gravel pit	18	0.83	8	10	0.87	8	12	0.85	8

* = Data presented by Stumpf, 1990 (A44231) were based on results from Gildemeister, 1985 (A31182).

The route of degradation was studied by Gildemeister, 1985 (A31182). Under these conditions two relevant metabolites were identified, endosulfan sulphate and endosulfan hydrocarboxylic acid which were accounted for >10% of applied radioactivity. Other different metabolites as endosulfan lactone, endosulfan diol, endosulfan ether and an unidentified compound were individually accounted at <10%

of the applied radioactivity. The $^{14}CO_2$ detected in the traps throughout the study was < 0.1%. Volatile compounds were always lower than 10% of the applied radioactivity (2-4%). Endosulfan and its metabolites showed a quick adsorption to sediment. **The DT values for the parent compound and the metabolites in sediment were not calculated, the residue is strongly adsorbed to the sediment and this fact can affect to its bioavailability. Moreover the detected metabolites were the extractable an effort should be done to characterize the bound residues that they were 20% of the applied radioactivity and the plateau were not got.**

Additional information has been provided by a field study (Cornaby *et al*, 1989 (A41298). After three applications of endosulfan (1.12 kg as/ha) in a field cropped with tomatoes, the concentrations of α endosulfan, β endosulfan and endosulfan sulphate were determined in two experimental ponds after spray and runoff events. Immediately after spray drift events, 0.257-0.053 µg/L of total endosulfan were found in the water phase. Only after forced runoff events concentrations rose levels of 1.31-0.583 µg/L. They decreased to about 0.011 µg/L after 3-6 weeks. The concentrations were noticeably higher in the sediments. Thus, 49.2-99.1 µg/mg were determined 0-1 week after the runoff event. Based on these results, it can be stated that high endosulfan concentrations in water could mainly occur after runoff events. In all concentration ranges a relatively rapid degradation of endosulfan looked to occur. However, concentrations in the sediment should be expected for longer periods of time (more than two months). The run-off is the more relevant exposure route when very large buffer zones are used to avoid the water contamination due to spray drift.

It can be concluded that the main degradation routes for endosulfan in water are hydrolysis since photolysis is not observed under environmental conditions. Its half life shows variability related to the water conditions, mainly pH. Under typical environmental conditions (pH = 7 and water/sediment systems) endosulfan DT_{50} can be expected to range from 10 to 12 days for parent endosulfan. **The DT values for the total residue in water, sediment and in the total system should be calculated correctly taking into account the process of formation and degradation a good kinetic should be proposed.**

Two main metabolites were identified under these conditions, endosulfan sulphate and endosulfan hydroxylic acid. Endosulfan diol, which was accounted for >10% of applied radioactivity in the hydrolysis degradation route, was only observed at lower rates in the water/sediment studies. However, poor information is available about fate and behaviour of endosulfan for this compartment. So, this process still need to be further investigated.

A correct determination of DT_{50} and DT_{90} values of parent endosulfan and its metabolites in water, sediment and total system should be required, a correct degradation kinetics (route and rates) should be proposed. The field studies submitted clearly showed the importance of the run-off in the endosulfan concentrations in water, therefore proper scenarios for the risk assessment of endosulfan in the crops and conditions included in the intended uses should be required.

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

Taking into account that conventional and natural water treatment procedures generally maintain alkalinic conditions in the medium, the endosulfan degradation rate is expected to be quick (4-7 hours) for the compound present in the medium. Therefore, endosulfan can be significatively degraded and diluted before arriving to the treatment system.

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

B.8.6.1 Surface water (PEC_{SW})

The environmental concentrations in surface water (PEC_{sw}) for endosulfan have been calculated from the BBA draft guide based on:

The maximum single application rates, the number of treatments and the intervals in between for each crop (SI).

A buffer zone from 0 to 50 m.

A deep water medium of 30 cm and 1 m.

DT_{50} = 15 days. This value has been estimated as the high value of the total endosulfan concentrations ($\alpha + \beta$ + endosulfan sulfate) in the water phase of two different sediment water systems (Stumpf, 1990 (A44231)).

According to this scenario, the initial PIEC values were estimated. Based on these results, actual concentrations (Ct) at different times and time weighted average concentrations were estimated as:

$$C_t = C_0 \text{ x } e^{-kt}$$
$$C_{TWA} = C_0 \text{ x } (1-e^{-kt})/kt$$

For crops with multiple applications, initial concentrations after each endosulfan use (PIECn) were estimated as:

$$\text{PIECn} = \text{PIEC} + \text{concentration of endosulfan after Spray Interval } (C_{t=SI})$$

Additionally, actual concentrations (Ct) at different times and time weighted average concentrations after each application were also calculated.

Due to the high quantity of data, a summary of the most representative crops and conditions and their respective PIEC values and C_t, C_{TWA} concentrations after last application are expressed in tables 8.6.1-1 and 8.6.1-2.

Table 8.6.1-1: $PIEC_{sw}$ values for the selected crops after the last application

Crop	Application rate	Nº	SI days	Distance m	Drift %	Initial PECsw (µg as/L) 0.3 m depth	1 m depth
Citrus	1.05	2	14	0	100.0	350.00	105
				3	15.5	54.25	16.275
				5	10.0	35.00	10.5
				10	4.5	15.75	4.725
				15	2.5	8.75	2.625
				20	1.5	5.25	1.575
				30	0.6	2.10	0.63
				40	0.4	1.40	0.42
				50	0.2	0.70	0.21
Vineyards	1.05	2	14	0	100.0	350.00	105
				3	7.5	26.25	7.875
				5	5.0	17.50	5.25
				10	1.5	5.25	1.575
				15	0.8	2.80	0.84
				20	0.4	1.40	0.42
				30	0.2	0.70	0.21
				40	0.2	0.70	0.21
				50	0.2	0.70	0.21
Arable crops (cotton)	0.84	3	14	0	100.0	280.00	84.00
				1	4.0	11.20	3.36
				3	1.0	2.80	0.84
				5	0.6	1.68	0.50
				10	0.4	1.12	0.34
				15	0.2	0.56	0.17
				20	0.1	0.28	0.08
				30	0.1	0.28	0.08
Arable crops (Cucumber)	0.53	3	7	0	100.0	176.67	53
				1	4.0	7.07	2.12
				3	1.0	1.77	0.53
				5	0.6	1.06	0.318
				10	0.4	0.71	0.212
				15	0.2	0.35	0.106
				20	0.1	0.18	0.053
				30	0.1	0.18	0.053

Table 8.6.1-2: TWA-PEC$_{sw}$ values at 48h, 96 h and 21 days for the selected crops after the last application

Crop	Water distance (m)	**TWA-PEC$_{sw}$ (µg as/L)** Days after last treatment								
		0	**1**	**2**	**4**	**7**	**14**	**21**	**28**	**42**
Citrus fruit	0	533.28	521.14	509.38	486.89	455.62	392.66	341.30	299.14	235.32
	3	82.66	80.78	78.95	75.47	70.62	60.86	52.90	46.37	36.47
	5	53.33	52.11	50.94	48.69	45.56	39.27	34.13	29.91	23.53
	10	24.00	23.45	22.92	21.91	20.50	17.67	15.36	13.46	10.59
	15	13.33	13.03	12.73	12.17	11.39	9.82	8.53	7.48	5.88
	20	8.00	7.82	7.64	7.30	6.83	5.89	5.12	4.49	3.53
	30	3.20	3.13	3.06	2.92	2.73	2.36	2.05	1.79	1.41
	40	2.13	2.08	2.04	1.95	1.82	1.57	1.37	1.20	0.94
	50	1.07	1.04	1.02	0.97	0.91	0.79	0.68	0.60	0.47
Vineyards	0	533.28	521.14	509.38	486.89	455.62	392.66	341.30	299.14	235.32
	3	40.00	39.09	38.20	36.52	34.17	29.45	25.60	22.44	17.65
	5	26.66	26.06	25.47	24.34	22.78	19.63	17.07	14.96	11.77
	10	8.00	7.82	7.64	7.30	6.83	5.89	5.12	4.49	3.53
	15	4.27	4.17	4.08	3.90	3.64	3.14	2.73	2.39	1.88
	20	2.13	2.08	2.04	1.95	1.82	1.57	1.37	1.20	0.94
	30	1.07	1.04	1.02	0.97	0.91	0.79	0.68	0.60	0.47
	40	1.07	1.04	1.02	0.97	0.91	0.79	0.68	0.60	0.47
	50	1.07	1.04	1.02	0.97	0.91	0.79	0.68	0.60	0.47
Cotton	0	503.4	491.9	480.8	459.6	430.1	370.7	322.2	282.4	222.1
	1	20.14	19.68	19.23	18.38	17.2	14.83	12.89	11.3	8.885
	3	5.034	4.919	4.808	4.596	4.301	3.707	3.222	2.824	2.221
	5	3.02	2.952	2.885	2.758	2.581	2.224	1.933	1.694	1.333
	10	2.014	1.968	1.923	1.838	1.72	1.483	1.289	1.13	0.889
	15	1.007	0.984	0.962	0.919	0.86	0.741	0.644	0.565	0.444
	20	0.503	0.492	0.481	0.46	0.43	0.371	0.322	0.282	0.222
	30	0.503	0.492	0.481	0.46	0.43	0.371	0.322	0.282	0.222
Cucumber	0	397	388	379.2	362.5	339.2	292.3	254.1	222.7	175.2
	1	15.88	15.52	15.17	14.5	13.57	11.69	10.16	8.908	7.008
	3	3.97	3.88	3.792	3.625	3.392	2.923	2.541	2.227	1.752
	5	2.382	2.328	2.275	2.175	2.035	1.754	1.525	1.336	1.051
	10	1.588	1.552	1.517	1.45	1.357	1.169	1.016	0.891	0.701
	15	0.794	0.776	0.758	0.725	0.678	0.585	0.508	0.445	0.35
	20	0.397	0.388	0.379	0.362	0.339	0.292	0.254	0.223	0.175
	30	0.397	0.388	0.379	0.362	0.339	0.292	0.254	0.223	0.175

As can be observed from the tables above, the higher concentrations of endosulfan in water should be expected for orchards and cotton. In fact, they are treated with the highest application rates and show the highest drift values.

Based on the results of the field study the main exposure route for endosulfan is the runoff, therefore proper scenarios for the risk assessment of endosulfan in the crops and conditions included in the intended uses should be required.

B.8.6.2 Ground water (PEC_{GW})

As a result of laboratory studies on leaching and adsorption/desorption from soil, endosulfan and endosulfan sulfate can be regarded as immobile in soil. A complete and rapid adsorption to the sediment is observed in water/sediment studies. So, a ground water contamination by parent endosulfan is not expected. **However, as the degradation route in soil is not well defined and complete, it may not be discarded the formation of more polar metabolites able to reach ground water.**

B.8.6.3 Sediment (PECs)

Predicted environmental concentrations in sediment can not be estimated due to DT_{50} for parent or total endosulfan have not been studied by the applicant.

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

Kloepffer, 1992a (A49537)

The study was performed according to the Freon 113 method and GLP. The bimolecular OH-rate constant of α endosulfan (99.4% purity) was determined. The substance showed no measurable reaction with OH-radicals by photolysis of H_2O_2 during the reaction time. From the results obtained k_{OH} is smaller than the k_{OH} of the reference substance toluene. Therefore, the chemical lifetime of α endosulfan was estimated to be τ_{OH} > 4 days, corresponding to a half-life time $t_{1/2}$ > 2.7 days.

Kloepffer, 1992b (A49538)

The study was performed according to the Freon 113 method and GLP. The bimolecular OH-rate constant of β endosulfan (99.0% purity) was determined. From the results obtained k_{OH} is smaller than the k_{OH} of the reference substance toluene. Therefore, the chemical lifetime of β endosulfan was estimated to be τ_{OH} > 22 days, corresponding to a half-life time $t_{1/2}$ > 15 days.

Kloepffer, 1992c (A49536)

The study was performed according to the Freon 113 method and GLP. The bimolecular OH-rate constant of endosulfan sulfate (97.5% purity) was determined. The substance showed no measurable reaction with OH-radicals by photolysis of H_2O_2 during the reaction time. From the results obtained k_{OH} is smaller than the k_{OH} of the reference substance toluene. Therefore, the chemical lifetime of endosulfan sulfate was estimated to be τ_{OH} > 4 days, corresponding to a half-life time $t_{1/2}$ > 2.7 days.

Zetzsch, 1992 (A48146)

The study was performed according to OECD guidelines and GLP. The photochemical-oxidative degradation of α endosulfan (99% purity) was determined. The global mean concentration of HO in the air was 500 000 radicals/cm^3 and the chemical half lifetime of α endosulfan was $t_{1/2}$ 27±1 days.

Palm and Zetzsch, 1991 (A48681)

The study was not conducted under international guidelines. Rate constants for the reaction of α and β endosulfan with 0H radicals (photochemical oxidative degradation) were estimated by the incremental procedure of Atkinson. The reaction rate constant for the reaction of α- and β-endosulfan with OH radicals in the atmosphere was $1.8x10^{-12}$ $molecule.s/cm^3$ when the method of ATKINSON was employed, and the constant 24 hour average concentration of OH radicals was assumed to be $5x10^5$ $molecules/cm^3$ .This determination yielded a half life of about 8.5 days for endosulfan in the atmosphere.

Parlar, 1988 (A39963)

The study was not carried out under any guideline. The photochemical degradability of α endosulfan, β endosulfan and endosulfan sulfate in air were determined under simulated sunlight conditions (wavelength 290 nm). Results showed different photolysis products: H_2O, CO_2, CO, HCl, SO_2 and SO_4.

Hewitt and Harrison, 1984 (A47125)

The study was not conducted under any international guideline. Tropospheric concentrations of the hydroxyl radical were estimated using photochemical methods and measurement techniques. The global mean concentration of HO in the air was 500000 $radicals/cm^3$. The seasonal variation estimated by model studies was 3-fold.

- **Field Studies**

Bidleman *et al*., 1990 (A57282)

The study was not carried out under international guidelines. Air samples from Canadian Arctic were examined during two years to detect α endosulfan and β endosulfan. The concentration of α endosulfan in the air ranged from 2.7 to 9.7 pg/m^3 in 1986 and 1.8 to 5.0 pg/m^3 in 1987. β endosulfan was not detected. Nevertheless, the authors conceded that their data should be considered upper limits since only the non-specific electron capture detection was used for determination and other organochlorides may interfere with the GC/ECD peak of endosulfan.

Hoff *et al*., 1991 (A57281)

The study was not carried out under international guidelines. Air samples from Ontario, Canada were examined during two years to detect endosulfan. The data indicate a significant variation of the aerial concentration of endosulfan as a result of pesticide in agriculture. Concentration in air was reported from a blank level of 3.4 pg/m^3 to a maximum of 3.7 pg/m^3 with a mean of 350 pg/m^3. The maximum amounting to 1800 pg/m^3 is reached in July. Before May and after September, the concentration was too low for showing a mark. In conclusion, endosulfan is only detectable to a certain extent close to the time of application.

Bidleman *et al*., 1992 (A57283)

The study was not carried out under international guidelines. Air samples from Stable Island, Canada were examined during two years to detect endosulfan. Endosulfan (sum of 2 isomers) was detected at concentrations of 24-159 pg/m^3 in summer samples. This concentration dropped to 1.4-3.0 pg/m^3 (endosulfan α only) during the winter season. Therefore, endosulfan air concentrations resulted in large summer-winter differences which probably results from its current use in North America.

Scharf, 1992 (A49836)

The study was not carried out under international guidelines. Precipitation samples were collected at three locations in Germany (two of them being far from places of agricultural or industrial activities) during two years to detect endosulfan. Endosulfan could not be detected in any of the samples collected from rain and snow.

B.8.7.1 Evaporation behaviour

- **Plant Protection Product**

Ruedel, 1992a (A56571)

The study was performed according to BBA directives and GLP. Thiodan 35% was sprayed to the surface of thin layers of light soil at a rate of about 400 g a.s./ha. An air stream of 1.0 m/s was passed over the trays for 24 hours at a temperature of 21.3 to 21.9ºC and a relative humidity of 47 to 52%. The air was analysed at intervals for total radioactivity (α and β endosulfan). In the soil also extractable and non-extractable total radioactivity and the separate isomers were determined. In 24 hours 25 to 29% of the applied radioactivity evaporated. Evaporation of α endosulfan was faster than the isomer β endosulfan. The initial ratio in the soil of α to β endosulfan changed from 66/34 ratio to 56/44, while in the air-stream the a ratio of 85/15 was detected in the 6-24 h interval.

Ruedel, 1992b (A56887)

The study was performed according to BBA directives and GLP. Thiodan 35% was sprayed to the surface of flowering phaseolus-beans (covered soil = 70-80%) at a rate of about 500 g a.s./ha. An air stream of 1.2 m/s was passed over the trays for 24 hours at a temperature of 20.8 to 21.0ºC and a relative humidity of 43 to 44%. The air was analysed at intervals for total radioactivity (α and β endosulfan). In the leaf surfaces and plants also extractable and non-extractable total radioactivity and the separate isomers were determined. In 24 hours 63.6 to 63.7% of the applied radioactivity evaporated. Evaporation of α endosulfan was faster than the isomer β endosulfan. The initial ratio in the leaf surfaces and extracted from the plants changed from 66/34 ratio to 35/65 and 52/48, respectively. In the air-stream the a ratio of 90/10 was detected in the 0-1 h interval.

B.8.7.2 Summary

Endosulfan is expected to be evaporated from soil. Atmospheric concentrations resulted in large summer-winter differences where the highest concentrations are always detectable close to the time of application. It is mainly due to after spraying endosulfan (α isomer > β isomer) is quickly evaporated (25 to 63.7%). Its half life in air (DT_{50} value) ranges from 8.5 to 27 days.

A high rates of endosulfan are expected to be evaporated from soil.

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

Information about predicted environmental concentrations have not been submitted by the applicant. However, a high rate of evaporation should be expected.

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

In light of all data obtained on degradation of endosulfan in soil and water, residues can be provisionally defined as both isomers of the active substance (α endosulfan and β endosulfan) as well as their common metabolite endosulfan sulphate.

However this definition must be considered incomplete. The degradation of endosulfan did not show any alteration of the hexaclor norborene bicycle and showed a very low mineralization (<5%). These two facts suggest a high persistence of a soil residue constituted by a number of chlorinated metabolites, which may not account individually for more than 10% of applied dose but that all together may represent high amount of it. Based on their chemical structure it may be expected that the physico-chemical properties of these compound will be similar and generally persistent and bio-accumulable. Therefore, a wider investigation of the degradation routes of this compound must be done in order to establish a proper residue definition.

B.8.10 References relied on

Annex IIA, Annex IIIA point(s)	Year	Author (s) Title Company (insert name) Report No. Source (where different)	GLP GEP Y / N	Published Y / N	Owner	Data Protection
IIA, 7	1985	Paterson, S. Equilibrium Models for the Initial Integration of Physical and Chemical Properties The Dow Chemical Company, USA. Report No.: A46554 Experimental Exposure From Chemicals, 1985, Vol I, Chapter 9, 217-231	No	Yes	Publ.	No
IIA, 7.0/01	1982	Goebel, H., *et. al.* Properties, effects, residues and analytics of the insecticide endosulfan. Residues review, vol. 83, item VI	No	Yes	Publ.	No
IIA, 7.0/02; 7.1/04		Endosulfan: Its effects on environmental quality. Report No.: 11, Item 3 and 4, 22-63, Annex I-8, 77-83 National Research Council Granada	No	Yes	Publ.	No
IIA, 7.1/01		Excel Industries Ltd. Fate and behaviour in Environment	No	No	Excel	No
IIA, 7.1/02/04	1984	Who Environmental Health Criteria 40. Endosulfan World Health Organization, Geneva, Item 3.	No	Yes	Publ.	No
IIA, 7.1/03; 5.6.2/01		Gorbach, S. Fate of pesticides in environmental. Terminal residues of endosulfan. Fate of pesticides in environment, vol. VI, 283-285	No	Yes	Publ.	No
IIA, 7.1.1/01; 7.2.1/04	1979	Miles, J.R.W.; Moy, P. Degradation of Endosulfan and its metabolites by a mixed culture of soil microorganisms. Bull. Environm. Contam. Toxicol. 23, 013-019	No	Yes	Publ.	No
IIA, 7.1.1/01; 7.1.3/01	1974	Stewart, D.K.R.; Cairns, K.G. Endosulfan persistance in soil and optake by potato tubers. J. Agr. Food Chem., vol. 22, No. 6: 984-86	No	Yes	Publ.	No
IIA, 7.1.1/02	1985	Akther; Siddiqui, P.M.A. Degradation of endosulfan (technical and formulation) by soil microorganism. Kar. Iniv. J. Sc. 13(2): 191-197	No	Yes	Publ.	No
IIA, 7.1.1/03	1981	Beit, O.D.E., *et. al* Factors involved in the dynamics of pesticides in soil: The effect of pesticide concentration on leachbility and adsorption. Intern. J. Environmental Studies. Vol. 16, 181-187	No	Yes	Publ.	No
IIA, 7.1.1/03	1981	El Beit, I.O.D.; Wheelock, J.V.; Cotton, D.E.	No	Yes	Publ.	No

Annex IIA, Annex IIIA point(s)	Year	Author (s) Title Company (insert name) Report No. Source (where different)	GLP GEP Y / N	Published Y / N	Owner	Data Protection
		Pesticide – microbial interaction in the soil. Intern. J. Environmental Studies, vol. 16: 171-180				
IIA, 7.1.1/04	1977	Martens, R. Degradation of [8,9-^{14}C] Endosulfan by soil under different condicondictions. Bull. Environm. Contam. Toxicol. Vol. 17	No	Yes	Publ.	No
IIA, 7.1.1/05	1976	Martens, R. Degradation of [8,9-^{14}C] Endosulfan by soil microorgasnism. Applied and environmental. Microbiology, 853-858	No	Yes	Publ.	No
IIA, 7.1.1/06	1989	Hodapp, D.M.; Winterlin, W. Pesticide degradation in model soil evaporation beds. Bull. Environm. Contam. Toxicol., 43, 36-44	No	Yes	Publ.	No
IIA, 7.1.1.1.1/7.1.1.2.1	1984	Gildemeister, H.; Jordan, H.J. Aerobic Soil Metabolism Study of the Insecticide Hoe 002671 (Endosulfan) Hoechst Analyt.Labor., Germany. Report No.: A29680	No	No	AgrEvo	No
IIA, 7.1.1.1.1/ 7.1.1/02	1977	Martens, R. Degradation of ENDOSULFAN-8,9-^{14}C in Soil under Different Conditions FAL, Germany. Report No.: A12501 Bulletin Environ. Contam. Toxicol. Vol. 17, No. 4. pages 438-446. 1977	No	Yes	Publ.	No
IIA, 7.1.1.1.1; 7.1.1.2.1	1988	Stumpf, K.; Gildemeister, H.; Dambach, P. Hoe 002671-^{14}C, Aerobic Metabolism of Endosulfan in Soil and the Influence of Increased Microbial Biomass at 28 °C Hoechst Analyt.Labor., Germany. Report No.: A39429	Yes	No	AgrEvo	No
IIA, 7.1.1.1.1; 7.1.1.2.1; 7.1.1.1	1995	Stumpf, K.; Dambach, P.; Lenz, O. Code: Hoe 002671, Hoe 052618, Hoe 052619 Metabolism of ^{14}C-labelled Endosulfan in Five Soils under Aerobic Conditions Hoechst Schering AgrEvo, Frankfurt, Germany. Report No.: A53618	Yes	No	AgrEvo	Yes
IIA, 7.1.1.1.2	1983	Gildemeister, H.; Jordan, H.J.	No	No	AgrEvo	No

Annex IIA, Annex IIIA point(s)	Year	Author (s) Title Company (insert name) Report No. Source (where different)	GLP GEP Y / N	Published Y / N	Owner	Data Protection
		Photolytic Degradation of the Insecticide Endosulfan on Soil Covered Thin Layer Plates under Simulated Sunlight Hoechst Analyt.Labor., Germany. Report No.: A25805				
IIA, 7.1.1.1.2 / 7.1.1.2.1	1988	Gildemeister, H.; Stumpf, K.; Scheinkoenig, U. Hoe 002671-^{14}C. Anaerobic Metabolism of Endosulfan in a Sandy Loam and a Silt Loam Soil Hoechst Analyt.Labor., Germany. Report No.: A37589	Yes	No	AgrEvo	No
IIA, 7.1.1.1.2	1988	Ruzo, Luis O.; McGovern, Patricia A.; Shepler, Kathryn Soil Surface Photolysis of (^{14}C)Endosulfan in Natural Sunlight FMC, United States. Report No.: A41608	Yes	No	AgrEvo	No
IIA, 7.1.1.2.2	1992a	Baedelt, H.; Idstein, H.; Krebs, B. Endosulfan - emulsifiable concentrate - (352 g/l) (Code: Hoe 002671 00 EC33 B317) Investigation of the degradation behaviour in soil under field conditions (Stufe 2 in accordance with the BBA Guideline Part IV, 4-1) Hoechst C Produktentwicklung Oekologie 2, Germany. Report No.: A53554	Yes	No	AgrEvo	No
IIA, 7.1.1.2.2	1992b	Baedelt, H.; Idstein, H.; Krebs, B. Endosulfan - emulsifiable concentrate 352 g/l (Code: Hoe 002671 00 EC33 B317). Investigation of the degradation behaviour in soil under field conditions Hoechst C Produktentwicklung Oekologie 2, Germany. Report No.: A54025	Yes	No	AgrEvo	No
IIA, 7.1.1.2.2 / IIIA, 9.1.1.2	1992	Czarnecki, J.J.; Mayasich, J.M. Terrestrial Field Dissipation of Endosulfan Applied to Cropped and Bareground Plots in California Biodynamics, United States. Report No.: A51819	Yes	No	AgrEvo	No
IIA, 7.1.1.2.2	1995	Fuchsbichler, G. Hoe 002671 (endosulfan), Hoe 051327 (endosulfansulfate) and Hoe 051329 (endosulfandiol) Storage stability in soil Bayerische Hauptversuchsanstalt für Landwirtschaft, Germany. Report No.: A53652	Yes	No	AgrEvo	Yes

Annex IIA, Annex IIIA point(s)	Year	Author (s) Title Company (insert name) Report No. Source (where different)	GLP GEP Y / N	Published Y / N	Owner	Data Protection
IIA, 7.1.1.2.2 / IIIA, 9.1.1.2	1989	Hacker, L.A. Endosulfan (Thiodan 3EC) field dissipation study of terrestrial uses on tomatoes in Georgia/U.S.A. Landis Assoc., United States. Report No.: A42193 Southern Agriculture Research, Inc. (field test)	Yes	No	AgrEvo	No
IIA, 7.1.1.2.2 / IIIA, 9.1.1.2	1990	Mester, Thomas C. Final Report Endosulfan (LX165-03) Terrestrial/Runoff. Study on Cotton in California with Furrow Irrigation Landis Assoc., United States. Report No.: A42997	Yes	No	AgrEvo	No
IIA, 7.1.1.2.2 / IIIA, 9.1.1.2	1988	Tiirmaa, H.; Dorn, E. Endosulfan (Hoe 002671) Worldwide monitoring of Soil Dissipation Hoechst LEA, Germany; Hoechst Analyt.Labor, Germany. Report No.: A40218	No	No	AgrEvo	No
IIA, 7.1.1.2.2 / IIIA, 9.1.1.2	1993	Tiirmaa, H.; Krebs, B., Sochor, H. Degradation of endosulfan in soil after application of Thiodan 50 WP over several seasons in an apple orchard Hoechst C Produktentwicklung Oekologie 2, Germany. Report No.: A53771	No	No	AgrEvo	No
IIA, 7.1.1.2.2 / IIIA, 9.1.1.1; 9.1.1.2	1986	Timme, G.; Frehse, H.; Laska, V. Statistical interpretation and graphic representation of the degradational behaviour of pesticide residues. II. Bayer AG, Germany. Report No.: A53503 Pflanzenschutz-Nachrichten Bayer. Vol. 39. pages 187-203. 1986	No	Yes	Publ.	No
IIA, 7.1.2	1988a	Goerlitz, G.; Eyrich, U. Endosulfan (Hoe 002671) Adsorption / Desorption in the System Soil / Water. Part I: Hoe 052618 (= alpha-Endosulfan), Hoe 052619 (= beta-Endosulfan) Hoechst Analyt.Labor., Germany. Report No.: A37591	Yes	No	AgrEvo	No

Annex IIA, Annex IIIA point(s)	Year	Author (s) Title Company (insert name) Report No. Source (where different)	GLP GEP Y / N	Published Y / N	Owner	Data Protection
IIA, 7.1.2	1988b	Goerlitz, G.; Eyrich, U. Endosulfan (Hoe 002671) Adsorption/Desorption in the System Soil/Water part II: Metabolites of Hoe 002671: Hoe 051327 (= Endosulfan-sulfate),Hoe 051329 (= Endosulfan-diol) Hoechst Analyt.Labor., Germany. Report No.. A39353	Yes	No	AgrEvo	No
IIA, 7.1.2/01	1981	Beit, O.D.E., *et. al.* Factors affecting soil residues of Dieldrin, endosulfan, y-HCH, Dimethoate and Pyrolan. Ecotoxicology and environmental safety 5, 135-160	No	Yes	Publ.	No
IIA, 7.1.3.1	1985	Gildemeister, H.; Grundschoettel, P. Hoe 002671-14 C. Leaching Study Hoechst Analyt.Labor., Germany. Report No.: A31700	Yes	No	AgrEvo	No
IIA, 7.1.3.1	1975	Thier, W. Leaching behaviour of the agrochemical product Hoechst Analyt.Labor., Germany. Report No.: A49270	No	No	AgrEvo	No
IIA, 7.1.3.2	1982	Gildemeister, H.; Jordan, H.J. Leaching behaviour of the crop protection product Hoe 02671 0I AS 101 (5, 9a-^{14}C) (endosulfan) after an aging period of one half-life Hoechst Analyt.Labor., Germany. Report No.: A49273	Yes	No	AgrEvo	No
IIA, 7.1.3.2	1983	Gildemeister; Remmert, U. Leaching Study of the Insecticide Hoe 002671 and its Degradates Hoechst Analyt.Labor., Germany. Report No.: A27287	No	No	AgrEvo	No
IIA, 7.1.3.2	1986	Goerlitz; Asshauer Solubility in Water Hoechst Analyt.Labor., Germany. Report No.: A34274	Yes	No	AgrEvo	No
IIA, 7.1.3.2	1987	Sarafin, R.; Asshauer, J. Hoe 052619 and Hoe 052619 (alpha- und beta-Endosulfan) Solubility in Water Hoechst Analyt.Labor., Germany. Report No.: A36704	No	No	AgrEvo	No
IIA, 7.2/01	1978	Ronal, C.C.; *et. al.* Water Pesticides Monitering Journal, Vol. 12, No. 3	No	Yes	Publ.	No

Annex IIA, Annex IIIA point(s)	Year	Author (s) Title Company (insert name) Report No. Source (where different)	GLP GEP Y / N	Published Y / N	Owner	Data Protection
IIA, 7.2/02		Gorbach, S.; *et. al.* Residue analyses in the water systeem of East-Java Bull. Environ. Contam. & Toxicol. Vol 6, No. 1, 40-47	No	Yes	Publ.	No
IIA, 7.2/02; 7/03; 5/02; 8.0/01	1979	Gepta, P.K.; Gupta, R.C. Phaarmacology, toxicology and degradation of endosulfan, a review. Toxicology, 13, 115-130	No	Yes	Publ.	No
IIA, 7.2.1/01	1971	Eichelberger, J.W.; Lichtenberg, J.J. Persistence of pesticides in river water. Environmental Sci. Technol., vol. 5, no. 6: 541-544	No	Yes	Publ.	No
IIA, 7.2.1/02	1992	Armbrust, K.; Crosby, D.G. The degradation of endosulfan, chlorothanil and dichlorethan in seawater. 203 Rd. American Chemical Society National meeting, California. Vol. 203 (1-3) 70	No	Yes	Publ.	No
IIA, 7.2.1/02; 7.2.2/01	1971	Greve, P.A. Persistence of endosulfan in surface water. Meded. Fac. Landbouwwet. Rijksuniv. Gent, vol. 36: 439-447	No	Yes	Publ.	No
IIA, 7.2.1/03	1974	El Zorgani, G.A.; Omer, M.E.H. Metabolism of endosulfan isomers by Asperguillus niger. Bul. Environmental Cont. & Tox., vol 12: 182-182	No	Yes	Publ.	No
IIA, 7.2.1.1	1982	Goerlitz, G.; Kloeckner, Ch. Hydrolysis of Hoe 02671 (Endosulfan) Hoechst Analyt.Labor., Germany. Report No.: A31069	No	No	AgrEvo	No
IIA, 7.2.1.1	1984	Goerlitz, G. Hoe 002671, Endosulfan. Material Balance of the Hydrolysis Reaction - Addendum to Report (B)90/82 Hoechst Analyt.Labor., Germany. Report No.: A28825	No	No	AgrEvo	No
IIA, 7.2.1.1	1989	Goerlitz, G.; Rutz, U. Hoe 002671 Abiotic hydrolysis of the two isomers Hoe 052618 (alpha-Endosulfan) Hoe 052619 (beta-Endosulfan) as a function of pH Hoechst AG, Analytisches Laboratorium, Germany. Report No.: A40003	Yes	No	AgrEvo	No
IIA, 7.2.1.2	1982	Dureja, P.; Mukerjee, S.K.	No	Yes	Publ.	No

Annex IIA, Annex IIIA point(s)	**Year**	**Author (s)** **Title** **Company (insert name) Report No.** **Source (where different)**	**GLP GEP** **Y / N**	**Published** **Y / N**	**Owner**	**Data Protection**
		Photoinduced Reactions: Part IV. Studies on Photochemical Fate of 6,7,8,9,10-Hexachloro-1,5,5a,6,9,9a-hexahydro--6,9-methano-2,4,3-benzo(e)dioxathiepin-3-oxide (Endosulphan), an Important-Insecticide Div. of Agric. Chemicals, IARI, India. Report No.: A27138 Indian J. of Chem. Vol. 21B, May. pages 411-413. 1982.				
IIA, 7.2.1.2	1973	Schumacher, H.G.; Parlar, H.; Klein, W.; Korte, F. Photochemische Reaktionen von Endosulfan Univ.Bonn. Report No.: A25698 Chemosphere. Vol. 2. pages 65 - 68. 1973	No	Yes	Publ.	No
IIA, 7.2.1.2	1991	Stumpf, K.; Jordan, H.J. Hoe 052618-^{14}C and Hoe 052619-^{14}C (alpha- and beta-Endosulfan), Photodegradation in Acetate Buffer Solution and in Surface Water Hoechst AG, Produktentwicklung Oekologie 1, Germany. Report. No.: A49585	Yes	No	AgrEvo	No
IIA, 7.2.1.2	1988	Stumpf, K.; Schink, C. Hoe 002671-^{14}C. Photodegradation of alpha-Endosulfan (Hoe 052618) and beta-Endosulfan (Hoe 052619) in Water Hoechst Analyt.Labor., Germany. Report No.: A37588	Yes	No	AgrEvo	No
IIA, 7.2.1.3.1 / IIIA, 9.2.2	1990a	Stumpf, K. Hoe 002671, endosulfan, trade name "Thiodan". Potential degradability in water Hoechst C Produktentwicklung Oekologie 1, Germany. Report No.: A45100	No	No	AgrEvo	No
IIA, 7.2.1.3.2	1989	Cornaby, B.W.; Maciorowski, A.F.; Griffith, M.G. et al. Assessment of the Fate and Effects of Endosulfan on Aquatic Ecosystems Adjacent to Agricultural Fields Planted with Tomatoes (Pont study) Battelle, Columbus Laboratory, USA; Hickey´s Agri-Services Inc., USA. Report No.: A41298	Yes	No	AgrEvo	No
IIA, 7.2.1.3.2/ IIA, 7.2.1/01	1989	Cotham, William E.; Bidleman, Terry F. Degradation of Malathion, Endosulfan, and Fenvalerate in Seawater and Seawater/Sediment Microcosms Univ.South Carolina, United States. Report No.: A41218 J. Agric. Food Chem. Vol. 37. pages 824-828. 1989	No	Yes	Publ.	No

Annex IIA, Annex IIIA point(s)	Year	Author (s) Title Company (insert name) Report No. Source (where different)	GLP GEP Y / N	Published Y / N	Owner	Data Protection
IIA, 7.2.1.3.2 / IIIA, 9.2.3	1985	Gildemeister, H. Hoe 002671-14-C Aerobic Aquatic Metabolism Study with the Insecticide Endosulfan Hoechst Analyt.Labor., Germany. Report No.: A31182	Yes	No	AgrEvo	No
IIA, 7.2.1.3.2 / IIIA, 9.2.3	1990b	Stumpf, K. Comments Regarding the Dutch Hazard Assessment of Endosulfan Concerning the Bioavailability in Water/Sediment Systems Hoechst C Produktentwicklung Oekologie 1, Germany. Report No.: A44231	No	No	AgrEvo	No
IIA, 7.2.2	1988	Altshuller, A. P. Ambient air hydroxyl radical concentrations: Measurements and model predictions USEPA, Research Triangle Park, USA. Report No.: A47124 JAPCA; 39; 704 - 708; 1989	No	Yes	Publ.	No
IIA, 7.2.2	1987a	Atkinson, R. Estimation of gas-phase hydroxyl radical rate constants for organic chemicals University of California, USA. Report No.: A47123 Environm. Toxicology and Chemistry; 7; 435 - 442; 1988	No	Yes	Publ.	No
IIA, 7.2.2	1987b	Atkinson, R. A Structure-Activity Relationship for the Estimation of Rate Constants for the Gas-Phase Reactions of OH Radicals with Organic Compounds Univ. of California, USA. Report No.: A57325 Intern. Journal of Chem. Kinetics; 1987; 19; 799 - 828	No	Yes	Publ.	No
IIA, 7.2.2	1990	Bidleman, T. F.; Patton, G. W.; Hinckley, D. A.; et al. Chlorinated Pesticides and Polychlorinated Biphenyls in the Atmosphere of the Canadian Arctic Report file No: A57282 Lewis Publishers, Inc.; 1990; 347 - 372üöä	No	Yes	Publ.	No
IIA, 7.2.2	1992	Bidleman, T. F., Cotham, W. E., Addison, R. F., {Abs}Zinck, M. E. Organic Contaminants in the Northwest Atlantic Atmosphere at Sable Island, Nova Scotia, 1988-89 University of South Carolina, USA, and Bedford Institute of Oceanography; Canada. Report No.: A57283 Chemosphere; 1992; 24; 1389 - 1412	No	Yes	Publ.	No

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IIA, 7.2.2 / IIIA, 9.3	1987	Goerlitz, G. Hoe 051327, vapour pressure Hoechst Analyt.Labor., Germany. Report No.: A38805 unpublishedüöä	No	Yes	Publ.	No
IIA, 7.2.2	1984	Hewitt, C. N.; Harrison, R. M. Tropospheric concentrations of the hydroxyl radical - A review University of Lancaster, UK. Report No.: A47125 Atmosphere Environment; 1985; 19; 545 - 554	No	Yes	Publ.	No
IIA, 7.2.2	1991	Hoff, R. M.; Muir, D. C. G.; Grift, N. P. Annual Cycle of Polychlorinated Biphenyls and Organohalogen Pesticides in Air in Southern Ontario. 1. Air Concentration data Atmospheric Environment Service and {Abs}Freshwater Inst., Canada. Report No.: A57281 Environm. Sci. Technology; {Abs}1992; 26; 2; 266 - 175	No	Yes	Publ.	No
IIA, 7.2.2	1993	Indranignsih, McSweeney, C.S., Ladds, P.W. Residues of endosulfan in the tissues of lactating goats University of North Queensland, Australia. Report No.: A51447 Australian Vet. Journal. Vol. 70. pages 59 - 62. 1993	No	Yes	Publ.	No
IIA, 7.2.2	1992a	Kloepffer, W. Determination of the kOH Rate Constant of alpha-Endosulfan According to the Freon 113 Method C.A.U. GmbH, Germany. Report No.: A49537	Yes	No	AgrEvo	No
IIA, 7.2.2	1992b	Kloepffer, W. Determination of the kOH Rate Constant of beta-Endosulfan According to the Freon 113 Method C.A.U. GmbH, Germany. Report No.: A49538	Yes	No	AgrEvo	No
IIA, 7.2.2	1992c	Kloepffer, W. Determination of the kOH Rate Constant of Endosulfansulfate According to the Freon 113 Method C.A.U. GmbH, Germany. Report No.: A49536	Yes	No	AgrEvo	No
IIA, 7.2.2	1989	Leist, K.-H. Amendment to Report No. HST 289/881067 (Doc No. A40440) Endosulfan, active ingredient technical (Code: Hoe 002671 0I ZD97 0003) combined chronic toxicity / carcinogenicity study (104-week feeding in rats) Residue Determination Hoechst AG, Pharma Research, Toxicology and Pathology, Germany. Report No.: A41265	Yes	No	AgrEvo	No

Annex IIA, Annex IIIA point(s)	Year	Author (s) Title Company (insert name) Report No. Source (where different)	GLP GEP Y / N	Published Y / N	Owner	Data Protection
IIA, 7.2.2 / IIIA, 9.3	1991	Palm, W.-U.; Zetzsch, C. Estimation of the rate constants for the reaction of alpha- and beta-endosulfan with 0H radicals by the incremental procedure of Atkinson Fraunhofer-Inst., Germany. Report No.: A48681	No	No	AgrEvo	No
IIA, 7.2.2 / IIIA, 9.3	1988	Parlar, H. Photochemical Degradability of alpha-, beta-Endosulfan and Endosulfan sulfate in Air Generated by: Univ.Kassel, Germany. Report No.: A39963	No	No	AgrEvo	No
IIA, 7.2.2 / IIIA, 9.3	1992a	Ruedel, H. Testing for volatility of ^{14}C-endosulfan (formulated as the product Thiodan 35EC): Volatilisation from soil Fraunhofer-Inst., Germany. Report No.: A56571	Yes	No	AgrEvo	No
IIA, 7.2.2 / IIIA, 9.3	1992b	Ruedel, H. Testing for volatility of 14 C-endosulfan (formulated as the product Thiodan 35EC): Volatilisation from plant surfaces Fraunhofer-Inst., Germany. Report No.: A56887	Yes	No	AgrEvo	No
IIA, 7.2.2 / IIIA, 9.3	1992c	Ruedel, H. Testing for volatility of ^{14}C-endosulfan sulfate (formulated as the product Thiodan 35EC): Volatilisation from plant surfaces Fraunhofer-Inst. fuer Umweltchemie, Germany. Report No.: A57248	Yes	No	AgrEvo	No
IIA, 7.2.2 / IIIA, 9.3	1992d	Ruedel, H. Testing for volatility of ^{14}C-endosulfan sulfate (formulated as the product thiodan 35EC): Volatilisation from soil Fraunhofer-Inst. fuer Umweltchemie, Germany. Report No.: A57247	Yes	No	AgrEvo	No
IIA, 7.2.2 / IIIA, 9.3	1987	Sarafin, R. Hoe 002671 (Endosulfan), Hoe 052618 (alpha-Endosulfan), and Hoe 052619 (beta-Endosulfan) - Vapour Pressures Hoechst Analyt.Labor., Germany. Report No.: A36734	No	No	AgrEvo	No

Annex IIA, Annex IIIA point(s)	Year	Author (s) Title Company (insert name) Report No. Source (where different)	GLP GEP Y / N	Published Y / N	Owner	Data Protection
IIA, 7.2.2	1992	Scharf, Juliane Untersuchungen zur Verteilung und zum Verhalten von Pflanzenschutzmitteln (PSM) in der Atmosphaere Univ.Darmstadt, Germany. Report No.: A49836 Thesis for doctorate. Technische Hochschule Darmstadt. 1992	No	Yes	Publ.	No
IIA, 7.2.2	1995	Simonich, S. L., Hites, R. A. Global Distribution of Persistent Organochlorine Compounds Indiana University; USA. Report No.: A57280 Science; 1995; 269; 1851 - 1854	No	Yes	Publ.	No
IIA, 7.2.2	1990	Weller, O. Henry-constants of: Hoe 052618 (alpha-Endosulfan), Hoe 052619 (beta-Endosulfan) Hoechst C Produktentwicklung Oekologie 1, Germany. Report No.: A43544		No	AgrEvo	No
IIA, 7.2.2	1992	Zetzsch, C. Photochemisch-oxidativer Abbau von alpha-Endosulfan in der Gasphase Fraunhofer-Inst., Germany. Report No.: A48146	Yes	No	AgrEvo	No
IIA, 7.2.2/01	1992	Ferrando, M.O., *et. al.* Persistence of some Pesticides in the Aquatic Environment. Bull. Environmental Contam. Toxicol. 48, 747-755	No	Yes	Publ.	No
IIIA, 9.1.1.2	1992b	Baedelt, H.; Idstein, H.; Krebs, B. Endosulfan - emulsifiable concentrate 352 g/l (Code: Hoe 002671 00 EC33 B317). Investigation of the degradation behaviour in soil under field conditions Hoechst C Produktentwicklung Oekologie 2, Germany. Report No.: A54025	Yes	No	AgrEvo	No
IIIA, 9.1.1.2	1992a	Baedelt, H.; Idstein, H.; Krebs, B. Endosulfan - emulsifiable concentrate - (352 g/l) (Code: Hoe 002671 00 EC33 B317) Investigation of the degradation behaviour in soil under field conditions (Stufe 2 in accordance with the BBA Guideline Part IV, 4-1) Hoechst C Produktentwicklung Oekologie 2, Germany. Report No.: A5335554	Yes	No	AgrEvo	No

Annex IIA, Annex IIIA point(s)	Year	Author (s) Title Company (insert name) Report No. Source (where different)	GLP GEP Y / N	Published Y / N	Owner	Data Protection
IIIA, 9.1.4	1995	Ganzelmeier, H.; Rautmann, D. et al. Studies on the spray drift of plant protection products - Results of a test programm carried out throughout the Federal Republic of Germany, Mitteilungen aus der Biologischen Bundesanstalt für Land- und Forstwirtschaft, Berlin-Dahlem, Heft 305, Backwell Wissenschafts-Verlag GmbH Berlin/Wien Landesanstalt fuer Pflanzenschutz, Stuttgart. Fraunhofer Institut fuer Umweltchemie und Oekotoxikologie, Schmallenberg. Report No.: A56850	No	Yes	Publ.	No
IIIA, 9.2.2 / 9.2.3	1989	Cornaby, B.W.; Maciorowski, A.F.; Griffith, M.G. et al. Assessment of the Fate and Effects of Endosulfan on Aquatic Ecosystems Adjacent to Agricultural Fields Planted with Tomatoes (Pont study) Battelle, Columbus Laboratory, USA; Hickey´s Agri-Services Inc., USA. Report No. A 41298	Yes	No	AgrEvo	No
	1984	World Health Organisation IPCS (International Programme on Chemical Safety), environmental Health Criteria, 40, endosulfan. World Health Organisation, Geneva		Yes	Publ.	No
	1994	British Crop Protection Council The pesticide Manual, incorporing the agrochemicals handbook, 10th edition, page 388-390		Yes	Publ.	No

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