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Monograph prepared in the context of the inclusion of the following active substance in Annex I of the Council Directive 91/414/EEC

ENDOSULFAN

Addendum Volume III

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THE ADDENDUM WAS PREPARED UNDER THE RESPONSIBILITY OF:

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CHAPTER B-1: Identity

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CHAPTER B-8: Environmental fate and behaviour

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ADDENDUM TO ANNEX B

ENDOSULFAN

B - 1: IDENTITY

B.1 Identity

The main notifier (Task Force Aventis/ Makhteshim) proposed a new list of GAP at the ECCO 106. **Cotton and tomatoes have been selected as representative uses for Annex I inclusion**. Although based on the annotation made by Aventis/Makhteshim, the task force supports all the uses listed in the previous list of GAP and intends to seek registrations in some Member States after Annex I listing of the active substance. **The previous list of GAP included citrus, hazelnut, pome fruits, stone fruits, grapes, sugar beet, pepper, potatoes and the following imported crops tea, soyabean, citrus, coffee. The RMS took into account all these uses in the risk assessment that was discussed during the ECCO Peer Review and several data GAPs were identified; a safe use was not identified in the ECCO Peer Review.**

The new risk assessment is made for **COTTON and TOMATO**, all the other uses are not supported by the available information.

The evaluation of the new information received from the main notifier have been included in the evaluation table.

LIST OF USES SUPPORTED BY AVAILABLE DATA – REPRESENTATIVE USES (DATE: 28.09.2001)

Active substance: **Endosulfan**

Crop and/ or situation (a)	**Member State or Country**	**Product name**	**F G or I** (b)	**Pests or Group of pests controlled** (c)	**Formulation**		**Application**				**Application rate per treatment**			**PHI** (days) (l)	**Remarks:** (m)
					Type (d-f)	Conc. of as (i)	method kind (f-h)	growth stage & season (j)	number min max (k)	interval between applicat-ions (min)	kg as/hl min max	water l/ha min max	kg as/ha min max		
Cotton	Southern Europe	Thiodan 35 EC	F	I, A	EC	350 g/l	Medium /high volume spray	Last application when balls are partly open	3	14 – 21 days	0.105	800	0.84	21	Short PHI of 21 days is required, if chem. agent is used for desiccation of foliage.
Tomatoes	Southern Europe	Thiodan 35 EC	F	I, A	EC	350 g/l	Medium /high volume spray	At any stage	2	14 days	0.053 – 0.105	500 - 1000	max. 0.53	3	
			G						2	14 days	0.053	1500	0.8	3	

Remarks:
(a) For crops, the EU and Codex classifications (both) should be used; where relevant, the use situation should be described (*e.g.* fumigation of a structure)
(b) Outdoor or field use (F), glasshouse application (G) or indoor application (I)
(c) *e.g.* biting and suckling insects, soil born insects, foliar fungi, weeds
(d) *e.g.* wettable powder (WP), emulsifiable concentrate (EC), granule (GR)
(e) GCPF Codes - GIFAP Technical Monograph No 2, 1989
(f) All abbreviations used must be explained
(g) Method, *e.g.* high volume spraying, low volume spraying, spreading, dusting, drench
(h) Kind, *e.g.* overall, broadcast, aerial spraying, row, individual plant, between the plants - type of equipment used must be indicated
(i) g/kg or g/l
(j) Growth stage at last treatment (BBCH Monograph, Growth Stages of Plants, 1997, Blackwell, ISBN 3-8263-3152-4), including where relevant, information on season at time of application
(k) The minimum and maximum number of application possible under practical conditions of use must be provided
(l) PHI - minimum pre-harvest interval
(m) Remarks may include: Extent of use/economic importance/restrictions

ADDENDUM TO ANNEX B

ENDOSULFAN

B - 8: ENVIRONMENTAL FATE AND BEHAVIOUR

B.8 Environmental fate and behaviour

The main concern after the ECCO Meeting 103 was that DT_{50} and DT_{90} values could not be established for the metabolite endosulfan sulphate from the submitted studies and further data were required.

With the studies included in the original dossier RMS concluded that the degradation of endosulfan in soil did not show any alteration of the hexaclor norboren 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 all together are a high amount of it. Therefore a wider investigation of the degradation routes of this compound was required.

The notifier has submitted an aerobic soil degradation study of the metabolite endosulfan sulphate and two field dissipation studies on cotton crop in Spain and Greece.

B.8.1 Aerobic soil degradation study

B.8.1.1 Aerobic soil degradation study of ENDOSULFAN SULPHATE

Study: endosulfan: [^{14}C]AE F051327: Soil Metabolism and degradation
Author: Dr. Frank Schnöder
Dated: 1 February 2002
Reference: C019647
GLP: Yes

An aerobic soil degradation study was performed with ^{14}C-ring labelled AEF051327 (endosulfan sulphate) (radiochemical purity 99.4-99.9%) in order to investigate the metabolism and degradation rate of the test item in four soils (LS 2.2, SLS, SP and HE) inflow-through test systems. In this study bicycle ring was ^{14} C labelled enabling to asses the complete degradation of this structure. On previous studies, with parent endosulfan, the labelling position did not allow to conclude the complete degradation of the bicycle that is the most stable and chlorinated part of the molecule.
The characteristics of the soils are summarised in table 8.1.1-1

Table 8.1.1-1: Characteristics of the soils

Parameters/ soil	**LS 2.2**	**HE**	**SP**	**SLS**
Origin/supplier	LUFA Spreyer/LUFA spreyer	Greece/Aventis Crop Science GmbH	Spain/Aventis Crop Science GmbH	Hattersheim/Aventis Crop Science GmbH
pH ($CaCl_2$)	6.4	7.4	6.2	7.0
Organic carbon (g/100 g soil)	2.1	1.6	0.5	1.0
CEC (meq/100 g soil)	11.7	26.2	9.8	13.8
Particle size distribution (BBA and UK)				
Soil type (BBA)	Sandy loam	Clay	Sandy silt loam	Clay loam
< 0.002 mm (clay) %	11	39	13	20
0.002-0.063 mm (silt) %	15	44	39	60
0.063-2.0 mm (sand) %	74	17	48	20
Particle size distribution (USDA)				
Soil type (USDA)	Sandy loam	Silty clay loam	Loam	Silt loam
Sand % (2000-53 µm)	75	18	50	21
Silt % (53-2 µm)	14	43	37	59
Clay % (<2µm)	11	39	13	20
MWC (g/100 g soil)	48.0	52.2	34.3	48.8
FC (g/100 g soil)	15.5	33.0	19.1	22.0
Biomass (µg C/100 g dry soil)				
Following collection	642	609	241	218
Start of study	501	n.a	141	119
Day 90	411	790	185	132
Day 180	630	409	123	272
Day 260	405	623	218	285
Day 365	274	472	66	173

n.a: no available. Biomass for this soil could no be re-determined due to limited amount of soil available.

Following a single application of the test item at a rate of 0.840 kg/ha (field application), the soil was incubated under aerobic conditions at 20±2º C and a moisture of 30 to 40% of the maximum water holding capacity in the dark for a period of 365 days in total. Soil samples of 150 g dry weight equivalent were prepared by weighing the sieved soil into individual 500 ml glass flasks. These flasks were placed in desiccators and a stream of moistened air was allowed to pass through the incubation system. Volatile components and $^{14}CO_2$ were collected by a system of traps. The first trap was empty and acted as a security trap, the second and third contained ethanediol and 2% liquid paraffin in decane to trap polar and non-polar volatiles, respectively, and the final two contained 2 M sodium hydroxide solution to trap liberated carbon dioxide. Effluent air from the desiccators was drawn through the traps.

In order to maintain the microbial activity throughout the incubation period all soil samples under incubation were fortified with 50 g fresh soil 3, 6 and 9 months after application and the samples were intensively mixed after fortification. As a consequence, the weight of samples worked up by day 120, 240 and 365 was 200 g, 250 g and 300 g soil in total, respectively. Duplicate samples were removed at different time intervals and analysed after extraction for parent molecule and degradation products by HPLC using UV- ^{14}C-flow through detection.

The soils extracts were also analysed for the expected transformation products, endosulfan diol (AE F051329), endosulfan lactone (AE F051328) and endosulfan hydroxy carboxylic acid (AE 0365278) by radio-HPLC.

The individual mass balances ranged from 82.48 % to 112.12%, 68.87% to 103.35%, 84.95% to 102.38% and 69.50% to 102.58% AR for soils LS2.2, HE, SP and SLS, respectively. The lowest recoveries (82.48%, 68.87%, 84.95% and 69.50% AR for soils LS2.2, HE, SP and SLS) were observed for the samples fortified with fresh soil at the later sampling intervals. The losses can be explained by an inhomogenic distribution of the test item and its residues in the samples as aliquots only were removed for the work-up. Therefore, data from later sampling should be taken with caution. Due to the metabolic conversion, the extractable radioactivity continuously decreased for all soils tested in the course of the experiment. The values are in a range from 109.32% to 19.79% AR, 98.88% to 22.22% AR, 98.68% to 54.84% AR and 90.71% to 13.40% AR in soils LS2.2, HE, SP and SLS by day 0 to day 365, respectively. In parallel, the formation of non- extractable radioactivity increased to 27.52%, 29.79%, 24.60% and 32.56% of the applied dose for soil LS2.2, HE, SP and SLS after 365 days, respectively. The volatile radioactivity was found in sodium hydroxide traps only. By the end of the study, the volatiles accounted for 34.97%, 16.67%, 4.95% and 23.40% AR for soils LS2.2, HE, SP and SLS, respectively. Their identity as ^{14}C-carbon dioxide was confirmed by a complete precipitation of radioactivity as barium carbonate for selected samples.

For all soils, the majority of radioactivity in the organic extracts was represented by the test item. The values for the test item decreased from 106.14%, 95.21%, 97.29% and 86.27% AR day 0 to 18.10%, 20.06%, 45.63% and 11.21% AR for soil LS2.2. HE, SP and SLS after 365 days, respectively. The soil extracts were also analysed for the expected transformation products endosulfan diol (AE F051329), endosulfan lactone (AE F051328) and endosulfan hydroxy carboxylic acid (AE 0365278) by radio-HPLC. However, none of these potential metabolites was detected at any sampling interval in the course of the study. A small portion of radioactivity in HPLC chromatograms was not assigned to a distinct peak. This "diffuse radioactivity" amounted to only 1.27% AR in soil LS2.2, 1.61% AR in soil HE 1.01% AR in soil SP and 1.15% AR in soil SLS in maximum.

An unknown metabolite was detected in all soils at a number of time points. The maximum values were 10.78% by day 30 (soil LS2.2), 28.3% by day 59 (soil HE) 2.32% by day 59 (soil SP) and 11.84% by day 59 (soil SLS) for the extractable radioactivity (organic and water phase). For all soils, the unknown component was not detected by HPLC in any sample by day 365. The unknown metabolite was subject of further investigation for the elucidation of its chemical structure. Selected HPLC fractions (soils LS2.2 and HE from day 30 and 120, and SLS, day 30, both replicates each) containing the unknown component were investigated by Covance Laboratories Ltd, Harrogate, UK (CLEH) and by the University of York, York, UK. Several mass spectroscopy (MS) techniques as well as derivation techniques and analyses of the isolated unknown were applied, however, there was not sufficient evidence to result in a distinct structural proposal. As a likely structure, a dicarboxylic acid, dihydrodiol metabolite is under discussion.

The notifier informed RMS in May 2002 and in the report OE02/089 that different laboratories made an attempt to identify the new and unknown soil metabolite. First of all, Schnoeder characterised this metabolite as polar on the basis of the elution times in the radio-RP-HPLC analysis. The soil metabolite did not co-elute with any known reference standard, but proofed to be more polar than the most polar metabolite endosulfan hydroxy carboxylic acid (Schnoeder 2002).

The derivatisation of the purified metabolite with diazomethane resulted in a methylation reaction indicating that the metabolite contained a carboxylic acid function. The hydrogenation with lithium aluminium hydride resulted in the reduction of the carboxylic acid group. An acetylation with acetic anhydride and pyridine failed. This indicated either the absence of a hydroxylic group or a strong steric (and electronic) hindrance of the acetylation reaction. The loss of radiocarbon during concentration of the soil extract with the unknown metabolite and the very short retention time in GC analysis indicated a potential volatility, that suggested a cleavage of the original bicyclus resulting in a smaller degradation product with a carboxylic acid group (Schwab, 2001). **This report has not been submitted to RMS.**

HPLC-MS investigations of the original extract with the unknown were performed by Pethen at the Covance Laboratories Ud. in UK and commissioned to the University of York, UK (Pethen and Schnoeder, 2001). Different MS techniques were applied, e.g. electron impact, chemical ionisation and tandem MS/MS including atmospheric pressure chemical ionisation and source collision induced dissociation. All of these methods failed due to the very low ionisation yield and the spread to the MS peaks into an isotopic peak pattern originating from the natural abundance of ^{35}Cl and ^{37}Cl isotopes reducing the intensity of the single MS signals. Only the presence of the carboxylic acid group could be confirmed by the elimination of carbon dioxide in a MS/MS experiment.

An additional attempt was made to prepare a butyl derivative with butan-1-ol and 2 % sulfuric acid at 100°C and a pentafluorobenzyl (PFB) derivative with PFB bromine in acetone and potassium carbonate. These derivatives were tried to analyse by GC/MS and by direct insertion probe MS analysis both with electron impact ionisation. However, the identification also failed, as chlorinated ions could not be detected.

The notifier informed in the report that attempts to identify the unknown soil metabolite will be continued. This information is essential to establish the residue definition in soil.

Table 8.1.1-2: Degradation products (organic extracts) from soil LS2.2 (%AR)

Time (days)	Sulphate	Diol	Lactone	Hydroxy carboxylic acid	Unknown	Unresolved	Volatiles	Soil residue	Total recovery %
0	104.39	< LOD	< LOD	< LOD	< LOD	0.98	0	2.53	108
7	93.21	< LOD	< LOD	< LOD	< LOD	1.16	0.19	4.07	99
14	86.21	<	< LOD	< LOD	3.54	1.27	0.59	5.34	97

		LOD							
30	74.57	< LOD	< LOD	< LOD	5.31	0.90	2.80	8.28	92
59	68.96	< LOD	< LOD	< LOD	7.70	1.19	6.29	12.64	97
120	47.88	< LOD	< LOD	< LOD	**9.15**	0.32	13.08	**19.94**	90
240	23.88	< LOD	< LOD	< LOD	4.34	0.12	26.73	**28.55**	84
365	14.82	< LOD	< LOD	< LOD	< LOD	0.18	35.00	27.52	78

Table 8.1.1-3: Degradation products (organic extracts) from soil HE (%AR)

Time (days)	**Sulphate**	**Diol**	**Lactone**	**Hydroxy carboxylic acid**	**Unknown**	**Unresolved**	**Volatiles**	**Soil residue**	**Total recovery %**
0	95.21	< LOD	< LOD	< LOD	< LOD	0.25	0	4.01	99.5
7	86.53	< LOD	< LOD	< LOD	0.67	0.63	0.20	6.13	94.16
14	85.24	< LOD	< LOD	< LOD	2.99	1.12	0.33	7.62	97
30	62.12	< LOD	< LOD	< LOD	**15.23**	1.61	1.35	11.18	94.5
59	56.67	< LOD	< LOD	< LOD	**14.38**	0.41	3.09	17.54	92
120	48.62	< LOD	< LOD	< LOD	6.88	0.41	6.67	**28.51**	91
240	30.17	< LOD	< LOD	< LOD	5.83	0.28	10.94	**32.97**	80
365	18.05	< LOD	< LOD	< LOD	< LOD	0.10	16.71	**29.79**	64.6

Table 8.1.1-4: Degradation products (organic extracts from) soil SP (%AR)

Time (days)	**Sulphate**	**Diol**	**Lactone**	**Hydroxy carboxylic acid**	**Unknown**	**Unresolved**	**Volatiles**	**Soil residue**	**Total recovery %**
0	95.10	< LOD	< LOD	< LOD	< LOD	0.97	0.00	2.60	98.7
7	84.94	<	< LOD	< LOD	< LOD	1.03	0.24	4.47	91

		LOD							
14	86.36	< LOD	< LOD	< LOD	< LOD	1.79	0.39	4.80	93
30	87.93	< LOD	< LOD	< LOD	< LOD	0.64	0.52	6.95	96
59	88.82	< LOD	< LOD	< LOD	< LOD	1.19	0.83	10.10	100.1
120	75.74	< LOD	< LOD	< LOD	< LOD	1.15	1.01	**15.02**	93
240	64.78	< LOD	< LOD	< LOD	2.19	0.56	1.95	**24.04**	93
365	45.55	< LOD	< LOD	< LOD	< LOD	0.04	4.95	**24.60**	75

Table 8.1.1-5: Degradation products (organic extracts from) soil SLS (%AR)

Time (days)	**Sulphate**	**Diol**	**Lactone**	**Hydroxy carboxylic acid**	**Unknown**	**Unresolved**	**Volatiles**	**Soil residue**	**Total recovery %**
0	86.65	< LOD	< LOD	< LOD	< LOD	1.11	0.00	2.11	90
7	85.84	< LOD	< LOD	< LOD	< LOD	1.14	0.25	4.95	92
14	89.26	< LOD	< LOD	< LOD	1.94	1.21	0.30	4.58	97
30	80.16	< LOD	< LOD	< LOD	6.37	0.54	1.03	8.59	97
59	72.93	< LOD	< LOD	< LOD	7.13	0.97	2.77	13.47	97
120	51.92	< LOD	< LOD	< LOD	4.98	0.69	6.18	**22.68**	86
240	24.43	< LOD	< LOD	< LOD	5.73	0.17	13.54	**33.61**	77
365	8.36	< LOD	< LOD	< LOD	< LOD	0.03	23.40	32.56	64

The disappearance times for 50% and 90% of the test item were calculated by applying a first order kinetics and a one compartment approach. The results are summarised in the table 8.1-6

Table 8.1.1-6: DT50 and DT 90 values according first order kinetics

Soil	**LS2.2**	**SLS**	**SP**	**HE**
DT_{50} (days)	123	141	391	147

DT_{90} (days)	409	468	1299	489
R^2	0.97	0.92	0.93	0.98

The calculations show consistent DT_{50} values for soils LS2.2, HE and SLS, but a significant higher value for soil SP. The degradation kinetics determined for the Spanish soil SP might indicate a certain persistence of endosulfan sulphate. The soil SP used in this study originated from the same site than the soil dissipation study described below (see B.8.1.2).

The non-extractable radioactivity in soil was investigated by treatment of aliquots of an extracted soil sample of soil HE sampling date 240d, replicates A and B, with aqueous acid and base. By acidic extraction, 28.43% (replicate A) and 28.31 % AR (replicate B) still remained unextractable in the soil. Minor amounts of 0.87% (replicate A) and 0.88% AR (replicate B) were detected in the acidic extract. Following the alkaline extraction, only 3.89% (A) and 4.08% of AR (B) were present in the basic extract, while 25.28% (A) and 26.41 % AR (B) remained unextracted in the soil.

A fortification of soil samples with fresh soil starting by day 90 after application was carried out to basically show the degradability of agro residues of endosulfan sulphate when microbial activity is maintained as in the field. The monitoring of microbial biomass showed that the microbial activity in samples of soil SP suffered more in the course of the experiment than in the other soils tested. In addition, a strong formation of clods was observed when trying moisturise the soil to a value of 40% of the maximum water holding capacity. Consequently, a reduced test moisture of 30% only was used. A lower soil moisture and the more sensitive microbial activity while handling the soil sample in the laboratory testing were presumably the two main factors responsible for the prolonged disappearance times observed in soil SP.

Evaluation and comments: The study is considered acceptable but further information is necessary to complete the assessment of soil fate of endosulfan. The study shows that endosulfan sulphate, is subject to a slow, but near complete degradation accompanied by a significant formation of carbon dioxide. The DT_{50} of endosulfan sulphate was calculated in a range of 123 – 391 days, the mineralization at 120 days was in a range of 1.01 - 13.08%. The bounded residues were < 70%.

The previous assays, included in the monograph, demonstrated that the mineralization of endosulfan were below 5% at 120 d. The mineralization of endosulfan sulphate measured in this study is in line with the previously reported mineralization of endosulfan. Based on the results of the previous studies and the result of the endosulfan sulphate aerobic degradation study it can be said that endosulfan is degraded to endosulfan sulphate and the mineralization of endosulfan sulphate at 120 days is in a range of 1.01 – 13.08% and at 365 days is in a range of 5 – 35% depending on the type of soil.

None of the metabolites detected and identified in previous assays (included in the monograph) were detected in this study. However there is an unknown metabolite that appeared at level above 10% AR. All the attempts made for the identification of this metabolite failed but as a likely structures dicarboxylic acid or dihydrodiol metabolite are suspected. **The identification of this metabolite is**

essential to establish the endosulfan degradation route and the residue definition and must be monitored on field dissipation studies. Furthermore, in the field dissipation studies previously submitted and included in the monograph the endosulfan diol was detected.

B.8.1.2 Field dissipation study

B.8.1.2.1 Field Soil dissipation study in Spain

Study: endosulfan: Field Soil dissipation study in Spain
Author: Hardy I.A.J.
Dated: 27 September 2001
Reference: C015651
GLP: Yes

The environmental behaviour of the insecticide endosulfan was studied in the field after summer application at one location in the cotton growing area of Andalucía, Spain. In June 2000 the plot was cultivated and twice irrigated by sprinkler over the next 15 days, prior to the sowing of cotton on the 10 Ju1y 2000. Spraying of the Endosulfan formulation, AE F002671 00EC33 C703 took place on the 11 July 2000 at a nominal application rate of 840 g a.i./ha. Soil samples from different depths to a maximum of 0.3 m below the surface were then collected at regular intervals over 9 months and analysed for α-endosulfan, β-endosulfan and endosulfan sulphate.

The soil has been characterised as a loam using the USDA system. The average organic carbon content in the surface soil was 0.5%. Soil microbial biomass was typical of an agricultural soil, varying from 130 to 172 μg C (g soil)$^{-1}$ throughout the study. The soil used in this study was the same SP-soil used in the aerobic soil degradation study of endosulfan sulphate described in point B.8.1.1. Soil characteristics are the following

Organic carbon	0.5 wt%
pH in H_2O	6.4
CEC	7.5 mEq (100g)$^{-1}$
USDA classification	Loam
Sand	46
Silt	44
Clay	10
Microbial bioamass	130 – 172 μg C (g soil)$^{-1}$
Water Holding capacity	37.5 – 43.9 %

The calibrated application rate of endosulfan was 840 g a.i./ha, with the calibrated rate from the spray measurements being 775 g a.i./ha. The application was confirmed by analysing the content of filter papers placed on the soil and by analysing soils taken immediately after application. The results from filter papers and immediate post-application soil samples were found to be lower than the calibrated application rate, being in the range 54 to 68%.

The raw residue data are presented in table 8.1.2.1-1, since laboratory recoveries are generally within the acceptable range of 70 to 110%, the measured residue values were used without correction. The concentration in wet soil were converted to dry weight values using the ration of soil wet weight to dry weight. Residue levels in mg/kg were converted to residue rates in g/ha, considering a density of soil of 0.0015 kg/cm^3. The resulting parent compound residue decay rate versus days after application was evaluated by a pesticide dissipation model (ModelManager), with endosulfan sulphate being evaluated using multicompartment kinetic model (TopFit) to determine a degradation half life.

Table 8.1.2.1-1: Raw soil residue data

DAT	**Hor**	**α-endosulfan**					**β-endosulfan**					**Endo-sulphate**				
		mg/kg					**mg/kg**					**mg/kg**				
	(cm)	1	2	3	4	**Av**	1	2	3	4	**Av**	1	2	3	4	**Av**
-1	0-30	<0.01	<0.01	<0.01	<0.01	**<0.01**	<0.01	<0.01	<0.01	<0.01	**<0.01**	<0.01	<0.01	<0.01	<0.01	**<0.01**
0	0-10	0.25	0.25	0.25	0.26	**0.25**	0.1	0.1	0.09	0.11	**0.1**	<0.01	<0.01	<0.01	<0.01	**<0.01**
1	0-10	0.1	0.14	0.13	0.08	**0.11**	0.07	0.09	0.09	0.05	**0.075**	<0.01	<0.01	<0.01	<0.01	**<0.01**
	10-20	<0.01	<0.01	<0.01	<0.01	**<0.01**	<0.01	<0.01	<0.01	<0.01	**<0.01**	<0.01	<0.01	<0.01	<0.01	**<0.01**
3	0-10	0.06	0.07	0.09	0.11	**0.082**	0.04	0.06	0.09	0.10	**0.072**	0.01	0.01	0.02	0.02	**0.015**
	10-20	<0.01	<0.01	<0.01	<0.01	**<0.01**	<0.01	<0.01	<0.01	<0.01	**<0.01**	<0.01	<0.01	<0.01	<0.01	**<0.01**
7	0-10	0.04	0.04	0.04	0.05	**0.042**	0.04	0.04	0.06	0.05	**0.047**	0.01	0.01	0.02	0.02	**0.015**
	10-20	<0.01	<0.01	<0.01	<0.01	**<0.01**	<0.01	<0.01	<0.01	<0.01	**<0.01**	<0.01	<0.01	<0.01	<0.01	**<0.01**
14	0-10	0.02	0.02	0.03	0.02	**0.022**	0.04	0.03	0.04	0.04	**0.037**	0.03	0.02	0.03	0.03	**0.027**
	10-20	<0.01	<0.01	<0.01	<0.01	**<0.01**	<0.01	<0.01	<0.01	<0.01	**<0.01**	<0.01	<0.01	<0.01	<0.01	**<0.01**
30	0-10	<0.01	<0.01	<0.01	<0.01	**<0.01**	0.02	0.02	0.01	0.01	**0.015**	0.02	0.02	0.01	0.02	**0.017**
	10-20	<0.01	<0.01	<0.01	<0.01	**<0.01**	<0.01	<0.01	<0.01	<0.01	**<0.01**	<0.01	<0.01	<0.01	<0.01	**<0.01**
60	0-10	<0.01	<0.01	<0.01	<0.01	**<0.01**	<0.01	<0.01	<0.01	<0.01	**<0.01**	0.02	0.02	0.02	0.01	**0.017**
	10-20	<0.01	<0.01	<0.01	<0.01	**<0.01**	<0.01	<0.01	<0.01	<0.01	**<0.01**	<0.01	<0.01	<0.01	<0.01	**<0.01**
120	0-10	<0.01	<0.01	<0.01	<0.01	**<0.01**	<0.01	<0.01	<0.01	<0.01	**<0.01**	0.01	0.02	<0.01	<0.01	**0.012**
	10-20	<0.01	<0.01	<0.01	<0.01	**<0.01**	<0.01	<0.01	<0.01	<0.01	**<0.01**	<0.01	<0.01	<0.01	<0.01	**<0.01**
180	0-10	<0.01	<0.01	<0.01	<0.01	**<0.01**	<0.01	<0.01	<0.01	<0.01	**<0.01**	<0.01	<0.01	<0.01	<0.01	**<0.01**
	10-20	<0.01	<0.01	<0.01	<0.01	**<0.01**	<0.01	<0.01	<0.01	<0.01	**<0.01**	<0.01	<0.01	<0.01	<0.01	**<0.01**

The decline kinetics were modelled, with Model manager, for α and β-endosulfan and total endosulfan (α + β-endosulfan) using both simple first order (SFO) and first order multi compartment (FOMC) models). The FOMC model giving the best fit for DT50 and DT90. The results of this calculation are showed in table 8.1.2.1-2

Table 8.1.2.1-2: Endosulfan degradation kinetic data produced by Model Manager

	ENDOSULFAN KINETICS			
	r^2	order	DT50 (days)	DT90(days)
α-endosulfan	0.91	SFO	**1.4** (1.1 to 1.7)	**4.6** (3.7 to 5.6)
	0.96	FMOC	1.4 (1.0 to 1.8)	8.9 (6.9 to 10.8)
β-endosulfan	0.87	SFO	**7.9** (6.1 to 9.8)	**26.4** (20.2 to 32.6)

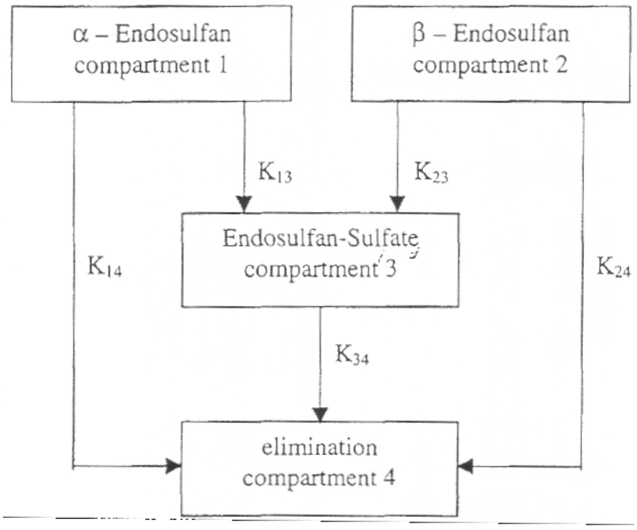
	0.97	FMOC	7.5 (6.0 to 9.1)	36.6 (31.6 to 41.6)
Total endosulfan (α+β)	0.87	SFO	**2.5** (1.9 to 3.0)	**8.2** (6.3 to 10.1)
	0.98	FMOC	3.5 (2.8 to 4.2)	17.7 (15.1 to 20.2)

Since FOMC is not a first order kinetic, and its results depend on the initial concentration the DT_{50} derived from this calculation is not validated by the RMS. The DT_{50} of dissipation considered valid is the DT_{50} from the first order kinetic adjust and the goodness of fit was considered valid by the RMS

Furthermore, a essential failure is detected in this calculation since a high dissipation of endosulfan is observed for the first 24 h after application in relation to the rest of the degradation. These initial fast dissipation is generally observed in field studies and is attributed to the initial volatilisation and homogenisation before product is incorporated into soil matrix. SCP opinion on fenamirol (November 19-2001) states that loss processes such as volatilisation need to be considered and that degradation in field studies should be calculated once the product has been incorporated in the soil matrix. **Therefore, DT_{50} and DT_{90} need to be recalculated from samples at day 1 and not day 0. Another option is recalculate a two phase curve and take the half life of the second phase for the assessment.** Rapporteur recalculated total degradation of endosulfan in this way obtaining a **DT_{50} for total endosulfan of 7.4 days**. (DT_{90} = 24.6 days; r^2 = 0.97) (Data points used corresponding to days 1-30, first order kinetics).

Endosulfan sulphate is derived from α and β-endosulfan and was therefore evaluated with TopFit 2.0, a multicompartment kinetic model, in order to determine a true degradation half-life (figure 8.1.2.1-1). However in this modelling the above consideration was not taken into account and all data points were employed. Furthermore, no flows were introduced to represent the equilibrium between alpha and beta endosulfan.

Figure 8.1.2.1-1: Top Fit Compartment model schematic



The results of the Top Fit compartment model are showed in table 8.1.2.1-3

Table 8.1.2.1-3: TopFit compartment model output

		K_{ij} (d^{-1})	**DT50 (d)**	**r^2**
α-endosulfan	Σk_{ij}	0.4849	1.4	0.939
	k_{13}	0.0249	-	-
	k_{14}	0.460	-	-
β-endosulfan	Σk_{ij}	0.0897	7.7	0.938
	k_{23}	0.0124	-	-
	k_{24}	0.0773	-	-
Endosulfan sulphate	Σk_{ij}	0.00922	75.2	0.891
	k_{34}	0.00922	-	-
All data sets	-	-	-	0.923

Evaluation and comments: Endosulfan dissipated moderately fast under field conditions (DT_{50} 7.4 days, DT_{90} 24.6 days). Total parent endosulfan residues were less than 10 % of applied within 1 month. The soil metabolite endosulfan sulphate achieved a maximum residue of 7.5 % of applied parent at 14 days and then declined (DT50 75.2 days, DT90 249.7 days) to leave no detectable residues after 6 months. As the concentration over the whole period was only slightly above the LOQ, the results of the kinetic modelling are influenced by a high element of uncertainty.

According to the Topfit compartment analysis one can say that the contribution of the degradation of α-β-endosulfan to the formation of endosulfan sulphate was lower than their contribution to the unknown compartment, since the degradation kinetic constants k_{14} and k_{24} were higher than k_{13} and k_{23}. However this may be the result of not considering the initial dissipation of endosulfan by volatilisation before its incorporation into soil matrix.

α-, β-Endosulfan and endosulfan sulphate were found to have low mobility under field conditions despite precipitation plus irrigation exceeding average local rainfall during the period of the study. No residues were found in the soil deeper than 10 cm, however LOQ = 0.01 mg/kg do not allow to quantify amounts of substance below 5 % of applied and slow leaching may not be completely excluded with this study.

Furthermore this study does not represent the current supported use in cotton in which three applications are considered, this study was made with only one application therefore the percentage of appearance of endosulfan sulphate of this study cannot be used for PEC calculation. The soil samples of this study was analysed for α-β-endosulfan and endosulfan sulphate, the other metabolites were not analysed in this study , in previous studies (included in the monograph) endosulfan diol was detected in the field dissipation studies after several applications of endosulfan (Hacker 1989 (A42193); Mester 1990

(A42997). **The endosulfan soil dissipation will be reassessed when the unknown metabolite of the aerobic soil degradation of endosulfan sulphate study will be identified.**

B.8.1.2.2 Field Soil dissipation study in Greece

Study: Field soil dissipation of endosulfan following single application to bare cotton plots at 1 location in Greece, 2000.
Author: Dr. Marcus Balluf
Dated: 10 December 2001
Reference: C018180
GLP: Yes

The objective of this study was to gain soil samples for the determination of residues and an estimation of the environmental behaviour of endosulfan after a single application of endosulfan on three bare soil plots at one site in Pilea (Thessaloniki), Greece. One day prior to application the site was cultivated with cotton.

Endosulfan was applied on the 30 June 2000 to three plots. A non-treated plot served as a control plot. The test item was applied with a calibrated boom sprayer at a rate of 840 g ai/ha in 800 L/ha water. Soil samples from the non-treated plot were taken immediately before the application, 6 months and 12 months after the application.

Soil samples from the treated plots were taken immediately after the application and 1 day, 3 days, 7 days, 14 days, 1 month, 2 months, 4 months, 6 months, 9 months and 12 months after the app1ication. Samples were taken from different depths to a maximum of 0.3 m below the surface. They were stored and shipped deep-frozen. Residue analysis was performed by lnstitut Fresenius Chemische und Biologische Laboratorien GmbH, Taunusstein, Germany on the three components: α-endosulfan, β-endosulfan and endosulfan-sulphate. The limit of quantification (LOQ) was 0.01 mg/kg soil for each of the components. The raw soil residue data are showed in table 8.1.2.2-1.

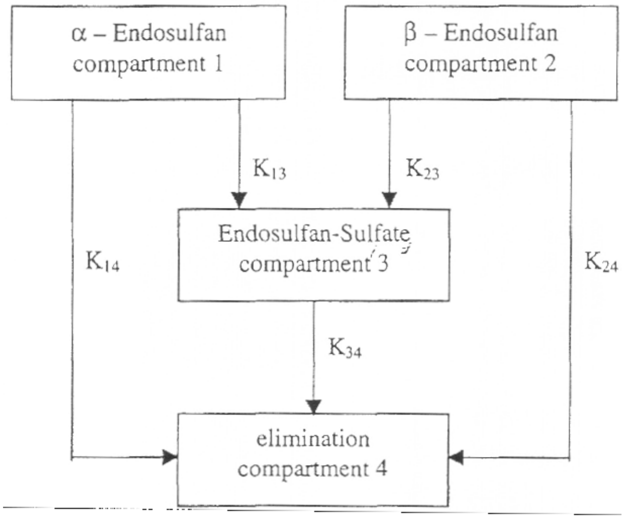
Table 8.1.2.2-1: Raw soil residue data (mg/kg dry soil)

DAT		**0**	**1**	**3**	**7**	**14**	**28**	**59**	**120**	**187**	**277**	**369**
Hor (cm)	Average											
0-10	α	0.483	0.183	0.167	0.140	0.117	0.063	<0.01	<0.01	0.003	<0.01	<0.01
	β	0.210	0.117	0.087	0.097	0.093	0.080	0.015	<0.01	<0.01	<0.01	<0.01
	sulphate	<0.01	<0.01	<0.01	0.033	0.040	0.047	0.037	0.027	0.01	0.018	0.01
	Total	**0.698**	**0.305**	**0.258**	**0.270**	**0.250**	**0.190**	**0.057**	**0.037**	**0.018**	**0.028**	**0.020**
10-20	α	none	0.020	0.005	0.005	0.010	0.037	0.005	0.005	0.002	0.003	0.002
	β	none	0.010	0.010	0.005	0.010	0.042	0.007	0.005	0.005	0.005	0.005
	sulphate	none	0.002	0.003	0.005	0.005	0.032	0.015	0.005	0.005	0.027	0.008
	Total	**none**	**0.032**	**0.018**	**0.015**	**0.025**	**0.110**	**0.027**	**0.015**	**0.012**	**0.035**	**0.015**
20-30	α	none	0.002	0.002	0.003	0.003	0.013	0.000	0.000	0.000	0.002	0.002

	β	none	0.005	0.005	0.005	0.005	0.015	0.003	0.007	0.000	0.003	0.002
	sulphate	none	0.003	0.005	0.005	0.003	0.015	0.002	0.003	0.002	0.005	0.003
	Total	**none**	**0.010**	**0.012**	**0.013**	**0.012**	**0.043**	**0.005**	**0.010**	**0.002**	**0.010**	**0.007**
g/ha												
0-30	α	725.0	307.5	260.0	222.5	195.0	170.0	15.0	15.0	7.5	15.0	12.5
	β	315.0	197.5	152.5	160.0	162.5	205.0	37.5	25.0	15.0	20.0	17.5
	sulphate	7.5	15.0	20.0	65.0	72.5	140.0	80.0	52.5	25.0	75.0	32.5
	Total	**1047.5**	**520.0**	**432.5**	**447.5**	**430.0**	**515.0**	**132.5**	**92.5**	**47.5**	**110.0**	**62.5**

Considering the results, the following dissipation behaviour were calculated. In model fit A the 277 DAT value of endosulfan-sulphate was included, in model fit B the 277 DAT was not considered, based on this different data sets the DT50 values were calculated . Endosulfan sulphate is derived from α and β-endosulfan and was therefore evaluated with TopFit 2.0, a multicompartment kinetic model, in order to determine a true degradation half-life (figure 8.1.2.2-1).

Figure 8.1.2.2-1: Top Fit Compartment model schematic



The results of the Top Fit compartment model are showed in table 8.1.2.2-2 and table 8.1.2.2-3

Table 8.1.2.2-2: TopFit compartment model output (Model fit A)

		K_{ij} (d^{-1})	DT50 (d)	r^2
α-endosulfan	Σ k_{ij}	0.345	2.0	0.833
	k_{13}	0.02	-	-
	k_{14}	0.325	-	-
β-endosulfan	Σ k_{ij}	0.0488	14.2	0.810
	k_{23}	0.0114	-	-
	k_{24}	0.0374	-	-

Endosulfan sulphate	Σk_{ij}	0.00430	161	0.873
	k_{34}	0.00430	-	-
All data sets	-	-	-	0.839

Table 8.1.2.2-3: TopFit compartment model output (Model fit B)

		K_{ij} (d^{-1})	DT50 (d)	r^2
α-endosulfan	Σk_{ij}	0.3796	1.8	0.834
	k_{13}	0.00461	-	-
	k_{14}	0.375	-	-
β-endosulfan	Σk_{ij}	0.0436	15.9	0.813
	k_{23}	0.0256	-	-
	k_{24}	0.0180	-	-
Endosulfan sulphate	Σk_{ij}	0.0148	46.8	0.920
	k_{34}	0.0148	-	-
All data sets	-	-	-	0.856

Evaluation and comments: Again modelling has not taken into account alpha and beta equilibrium. Furthermore, many raw data used on the calculation are below the LOQ. (all data points later than 59 days). The use of these data should be avoided. Initial dissipation processes should also be excluded and therefore data on day 0. When data for **total endosulfan** from day 1 to day 59 (excluding day 28) are adjusted to first order degradation kinetics a **DT_{50} = 21 days** is obtained (Rapporteur calculation DT_{90} = 70 days; r^2 = 0.96). **Modelling should be recalculated by the notifier taking into account the above considerations to calculate formation and degradation constants of metabolite endosulfan sulphate. However it may be agreed that, depending on the evaluation method used, the DT50 for endosulfan-su1fate ranged between 47 and 161 days. Waiting for a more accurate modelling, RMS considers more appropriate to use the DT_{50} = 161 days from the model fitted A as a reasonable worst case for degradation of endosulfan sulphate.** This result is in agreement with data obtained from laboratory degradation study. Total endosulfan-sulphate residues remained less than 10 %, at maximum of applied amount. α-, β-endosulfan completely disappeared 2 months after application while residues of endosulfan-sulphate were still present after 12 months in concentrations very close to the LOQ of 0.01 mg/kg. As the concentration over the whole period was only slightly above the LOQ, the results of the kinetic modelling are influenced by a high element of uncertainty.

According to the Topfit compartment analysis one can say that the contribution of the degradation of α-β-endosulfan to the formation of endosulfan sulphate was lower than their contribution to the unknown compartment, since the degradation kinetic constants k_{14} and k_{24} were higher than k_{13} and k_{23}. However this may be the result of not considering the initial dissipation of endosulfan by volatilisation before its incorporation into soil matrix.

α-, β-Endosulfan and endosulfan-sulphate were found to have low mobility under field conditions despite precipitation plus irrigation exceeded average annual rainfall by 4.6 %. Residues were found occasionally below 10 cm in concentrations > LOQ demonstrating that leaching may not be excluded from this study.

Furthermore this study does not represent the current supported use in cotton in which three applications are considered, this study was made with only one application therefore the percentage of appearance of endosulfan sulphate of this study cannot be used for PEC calculation. The soil samples of this study was analysed for α-β-endosulfan and endosulfan sulphate, the other metabolites were not analysed in this study , in previous studies (included in the monograph) endosulfan diol was detected in the field dissipation studies after several applications of endosulfan (Hacker 1989 (A42193); Mester 1990 (A42997).

B.8.1.3 Overall assessment of the route and rate of degradation

In this section an overall assessment of the route and rate of endosulfan is included. We have included the conclusions of the studies assessed in the monograph and the three new studies.

- **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 lactone, 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 together and mineralization of endosulfan is expected to be low (<5%).

The degradation rate of endosulfan in soil laboratory studies can be summarised as follows (table 8.1.3-1).

Table 8.1.3-1: Summary of DT_{50} values (days) in soil from laboratory studies

COMPOUND	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

COMPOUND	TEMPERATURE	DT_{50}	DT_{90}	R^2	N
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 were not reliably established in any study due to the fact that no enough data on the degradation were available to do the calculation at the end of th study (365 days for the longest study). The DT_{50} and DT_{90} values of endosulfan sulphate were required (points 2.1 and 2.2 of the evaluation tables). In 2002 the notifier submitted an aerobic soil degradation study of endosulfan sulphate.

The study (Schnöder, 2002, C019647) showed that endosulfan sulphate, is subject to a slow, but complete degradation accompanied by a significant formation of carbon dioxide. The DT_{50} of endosulfan sulphate was calculated in a range of 123 – 391 days, the mineralization at 120 days was in a range of 1.01 - 13.08%. The bounded residues were < 70%. The results are showed in table 8.1.3-2.

Table 8.1.3-2: DT50 and DT 90 values of endosulfan sulphate according first order kinetics

Soil	LS2.2	SLS	SP	HE
DT_{50} (days)	123	141	391	147
DT_{90} (days)	409	468	1299	489
R^2	0.97	0.92	0.93	0.98

The previous assays, included in the monograph, demonstrated that the mineralization of endosulfan at 120 days were below 5%. The mineralization of endosulfan sulphate is in line with the mineralization of endosulfan. Based on the results of the previous studies and the result of the endosulfan sulphate aerobic degradation study it can be said that endosulfan is degraded to endosulfan sulphate and the mineralization of endosulfan sulphate at 120 days is in a range of 1.01 – 13.08% and at 365 days is in a range of 5 – 35% depending on the type of soil. However, none of the metabolites detected and identified in previous assays (included in the monograph) were detected in this study. However, there is an unknown metabolite that appeared at level above 10% AR, all the attempts made for the identification of this metabolite failed but as a likely structure, a dicarboxylic acid, dihydrodiol metabolite is suspected. **The identification of this metabolite is essential for the definition of the degradation route of endosulfan, for the residue definition and for the field dissipation studies**

required. Furthermore in the field dissipation studies included in the monograph the endosulfan diol was detected. The aerobic soil degradation study does not allow to produce a reliable DT_{50} and mineralization of metabolites, furthermore an unknown metabolite was detected at levels higher than 10% of AR.

- **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 8.1.3-3).

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 $\alpha+\beta$ 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 disappearance) were not considered together in the calculation.**

On March 2002 the notifier submitted two new soil dissipation studies under southern conditions. The studies were performed in Spain (Hardy 2001, C015651) and Greece (Balluff, 2001, C018180). A nominal application rate of 840 g a.i./ha was made in both studies. Soil samples from different depths to a maximum of 0.3 m below the surface were then collected at regular intervals over 9 months and analysed for α-endosulfan, β-endosulfan and endosulfan sulphate. The resulting parent compound residue decay rate versus days after application was evaluated by a pesticide dissipation model (ModelManager), with endosulfan sulphate being evaluated using multicompartment kinetic model (TopFit) to determine a degradation half life. The results of both studies showed that Endosulfan rapidly dissipated under field conditions with total parent endosulfan (a+β) residues also declining rapidly (DT$_{50}$ 7.4 - 21 days). Total parent endosulfan residues were less than 10 % of applied within 1 month. The soil metabolite endosulfan sulphate achieved a maximum residue of 7.5 % of applied parent at 14 days in the Spanish study and 13.4% at 28 days in the Greek study and then declined (DT$_{50}$ 75.2 – 161 days) to leave no detectable residues after 6 months. As the concentration over the whole period was only slightly above the LOQ, the results of the kinetic modelling are influenced by a high element of uncertainty.

According to the Topfit compartment analysis one can say that the contribution of the degradation of α-β-endosulfan to the formation of endosulfan sulphate was lower than their contribution to the unknown compartment, since the degradation kinetic constants k_{14} and k_{24} were higher than k_{13} and k_{23}. However this may be the result of not considering the initial dissipation of endosulfan by volatilisation before its incorporation into soil matrix.

The maximum of endosulfan sulphate level in the field could also be derived from the residue data of the field dissipation studies: In Spain, the maximum proportion of endosulfan sulphated accounted for 7.8% of the applied amount of endosulfan 14 days after application and in Greece 13.4% at mean in time interval 14-28 days after application followed by almost complete degradation till the end of the studies (one year after application). **However this studies do not represent the current supported use in cotton, because only one application of endosulfan was made instead of 3. From the soil dissipation studies reported in the monograph it can be consider that the higher amount of endosulfan sulphate was 60% of the applied concentration.**

α-, β-Endosulfan and endosulfan sulphate were found to have moderate mobility under field conditions despite precipitation plus irrigation exceeding average local rainfall during the period of the study. However, this field study may not be used to demonstrates the low potential for unsaturated zone movement and the potential for α-, β-Endosulfan or endosulfan sulphate to appear in groundwater.

DT$_{50}$ for α- β- Endosulfan and endosulfan sulphate values were estimated after each application in cropped and bare ground loamy sand soil (table 8.1.3-3).

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
α+β Endosulfan						
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

DT$_{50}$ (days)	**DT$_{90}$ (days)**	**R^2**	**n**	**Kinetic**	**pH**	**Reference**
α+β Endosulfan						
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 (Bare ground)
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 (Bare ground)
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 (Bare ground)
7.4	24.6	0.97	5	1st order	6.2	C015651 Sandy silt loam (bare ground)
21.03	70	0.96	5	1st order	7.7	C018180 Sandy silt (Bare ground)
Endosulfan sulphate						
75.2	249.7	0.89	10	1st order	6.2	C015651 Sandy silt loam (bare ground)
161		0.87	11	1st order	7.7	C018180 Sandy silt (Bare ground)

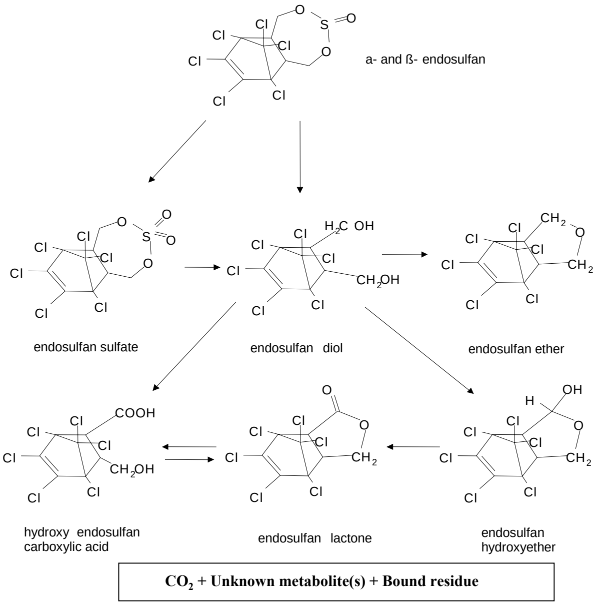
Soil residues were studied by Tiirma and Dorn, 1988 (A40218) in ten different soils after more than 3 years of use of formulated endosulfan. The maximum dosages per year were always higher than those proposed by GAP, from 0.5 to 3.2 kg as/ha. Monitoring was done 6 or 7 months after the last application. 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. Hence, 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.

All identified metabolites contain non-altered hexachlornorborene bicycle. The mineralization of endosulfan is < 5%. Main metabolite is endosulfan sulphate that has a mineralization between 11.01% and 13.08%. These facts suggest a potential 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 physicochemical 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.



B.8.2 Soil PEC calculation

A provisional PEC soil calculation can be made waiting for the final elucidation of the unknown metabolite observed in the aerobic soil degradation study of endosulfan sulphate.

The calculated PEC_s was for α+β Endosulfan and the main metabolite endosulfan sulphate.

The Table 8.2-1 shows the DT_{50} of α+β endosulfan calculated from the field studies.

Table 8.2-1: DT_{50} of α+β endosulfan (days) in soils from filed studies

DT_{50} (days)	DT_{90} (days)	R^2	n	Kinetic	pH	Reference
α+β Endosulfan						
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

DT_{50} (days)	DT_{90} (days)	R^2	n	Kinetic	pH	Reference
α+β Endosulfan						
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)
7.4	24.6	0.97	5	1st order	6.2	C015651 Sandy silt loam (bareground)
21.03	70	0.96	5	1st order	7.7	C018180 Sandy silt (Bareground)
Endosulfan sulphate						
75.2	249.7	0.89	10	1st order	6.2	C015651 Sandy silt loam (bareground)
161		0.87	11	1st order	7.7	C018180 Sandy silt (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 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 (May 2002).

Parent compound:

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 8.2-2 and 8.2-3 respectively.

Table 8.2-2: Calculation of PIEC values for endosulfan assuming a crop intercept of 0%

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
Cotton	0.84	3	14	1.12	3.03
Tomatoes	0.53	2	14	0.70	1.34

(field)					
Tomatoes (greenhouse)	0.8	2	14	1.06	2.02

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

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**
Cotton	0.84	3	14	0.56	1.52
Tomatoes (field)	0.53	2	14	0.35	0.67
Tomatoes (greenhouse)	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, one cases has been considered as a worst case: cotton. They are summarised in tables 8.2-4:

Table 8.2-4: 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	1.50	1.51
4	1.47	1.50
7	1.44	1.48
14	1.37	1.44
21	1.30	1.41
28	1.23	1.37
30	1.21	1.36
60	0.97	1.22
90	0.78	1.11
100	0.72	1.07
150	0.50	0.91
190	0.37	0.81
250	0.24	0.69
350	0.11	0.54

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.

Endosulfan sulphate:

Northern conditions:

From the soil dissipation studies in field (A53554) 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.

The higher value of the best fitted kinetics (R^2>0.8)was DT_{50} = 161 days, this DT_{50} represents a realistic worst case for all European condition.

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 8.2-5 and 8.2-6 respectively.

Table 8.2-5: Calculation of PIEC values for endosulfan assuming a crop intercept of 0% (northern conditions)

Crops	Maximum Single Treatment Rate kg a.s./ha	Number of Applications	Spraying interval	PIEC mg sa/kg several applications
Cotton	0.84	3	14	1.75
Tomatoes (field)	0.53	2	14	0.77
Tomatoes (greenhouse)	0.8	2	14	1.16

Table 8.3-6: Calculation of PIEC values for endosulfan assuming a crop intercept of 50% (northern conditions)

Crops	Maximum Single Treatment Rate kg a.s./ha	Number of Applications	Spraying interval	PIEC mg sa/kg several applications
Cotton	0.84	3	14	0.87
Tomatoes (field)	0.53	2	14	0.38
Tomatoes (greenhouse)	0.8	2	14	0.58

Based on these PIEC, the time weighted average predicted environmental concentration in soil (PEC_{TWA}) have been calculated, one cases has been considered as a worst case: cotton. They are summarised in tables 8.2-7:

Table 8.2-7: Estimated PECs and TWA-PECs of endosulfan sulphate after last application in cotton and assuming a crop intercept of 50% (northern conditions).

Days	PECs	TWA-PECs
0	0.870	0.870
1	0.866	0.868
2	0.862	0.866
4	0.855	0.862
7	0.844	0.857
14	0.819	0.844
21	0.794	0.831

Days	PECs	TWA-PECs
28	0.771	0.819
30	0.764	0.816
60	0.671	0.766
90	0.590	0.721
100	0.565	0.706
150	0.456	0.640
190	0.383	0.594
250	0.296	0.532
350	0.192	0.449

Southern conditions:

From the soil dissipation studies in field (C015651–Spain & C018180-Greece) it can be considered that the higher amount of the endosulfan sulphate was 13.4 % of the applied concentration (Initial PEC), multiplied by a factor of 0.9624.

The higher value of the best fitted kinetics (R^2>0.8)was DT_{50} = 161 days, this DT_{50} represents a realistic worst case for all European condition.

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 8.2-8 and 8.2-9 repectively.

Table 8.2-8: Calculation of PIEC values for endosulfan assuming a crop intercept of 0% (southern conditions)

Crops	Maximum Single Treatment Rate kg a.s./ha	Number of Applications	Spraying interval	PIEC mg sa/kg several applications
Cotton	0.84	3	14	0.39
Tomatoes (field)	0.53	2	14	0.17
Tomatoes (greenhouse)	0.8	2	14	0.26

Table 8.3-9: Calculation of PIEC values for endosulfan assuming a crop intercept of 50% (southern conditions)

Crops	Maximum Single Treatment Rate kg a.s./ha	Number of Applications	Spraying interval	PIEC mg sa/kg several applications
Cotton	0.84	3	14	0.19
Tomatoes (field)	0.53	2	14	0.08
Tomatoes (greenhouse)	0.8	2	14	0.13

Based on these PIEC, the time weighted average predicted environmental concentration in soil (PEC_{TWA}) have been calculated, one cases has been considered as a worst case: cotton. They are summarised in tables 8.2-10:

Table 8.2-10: Estimated PECs and TWA-PECs of endosulfan sulphate after last application in cotton and assuming a crop intercept of 50% (Southern conditions).

Days	PECs	TWA-PECs
0	0.190	0.190
1	0.189	0.189
2	0.188	0.189
4	0.186	0.188
7	0.184	0.187
14	0.178	0.184
21	0.173	0.181
28	0.168	0.179
30	0.167	0.178
60	0.146	0.167
90	0.129	0.157
100	0.123	0.154
150	0.099	0.139
190	0.083	0.129
250	0.064	0.116
350	0.042	0.098

However, an accumulation of the endosulfan sulphate can be expected in certain conditions due to a continuous use during several years of endosulfan.

B.8.3 Water/sediment studies

From the studies assessed in the monograph 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_{50} 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.

On May 2002 the notifier submitted a new water/sediment study and announced that the water/sediment study performed with pH<7 was available by August 2002.

Study: Degradation of [^{14}C] Endosulfan in two aerobic water/sediment systems
Author: Winfried Jones
Dated: May 2002
Reference: C022921
GLP: Yes

The degradation of the test substance [^{14}C]endosulfan, uniformly labelled at all chlorinated carbon atoms of the benzodioxathiepin ring, was investigated in two different water/sediment systems(Krempe/Ohlau) under aerobic conditions over a period of 120 days at 20ºC, following BBA Guideline IV, 5-1 and the draft OECD Guideline 308.

Two different water/sediment systems were used for these investigations. They were collected from the area North-West and North of Hamburg on September 05,2001. the properties of these systems comply with the respective requirements of the guidelines. The two sediments are specially different in the contents of organic carbon (3.2 / 0.1 %), and in the particle size distribution. The characteristics of these systems are summarised in table 8.3-1

Table 8.3-1: Characteristics of the water/sediment system

Parameter	**Krempe**		**Ohlau**	
	water	**sediment**	**water**	**sediment**
Temperature [ºC]	17		13	
PH	**7.3**	**6.6**	**6.8**	**6.1**
Redox potential [mV]	53		150	
O_2 content [mg/l]				
Surface	7.9		11.2	
5 cm above sediment	4.3		9.9	
Total N [mg/l] beginning	5.9		7.9	
End	1.1		1.3	
[%]		0.26		<0.01

Total P[mg/l] beginning	0.3		0.2	
End	0.1		0.1	
[mg/kg]		1580		137
DOC [mg/l]	17		12	
Organic carbon [%]		3.2		0.10
Water hardness [mmol/l]	2.0		1.5	
Dry matter [%]		36		84
Cation exchange				
Capacity [meq/100 g soil]		20.5		1.8
Particle size [%]				
<0.002 mm		21.8		1.2
0.002-0.006 mm		3.0		<0.1
0.006-0.020 mm		17.8		<0.1
0.020-0.063 mm		39.4		<0.1
0.063-0.200 mm		16.1		7.3
0.200-0.630 mm		1.4		78.8
0.630-2.0 mm		0.5		12.7
Det. Of biomass [mgC/100g]				
Beginning		61.6		2.3
End		46.7		7.0

According to German classification (DIN 4220) the sediment Krempe is characterised as a silty loam, whereas the sediment Ohlau is a sand; applying the USDA classification system by interpoling to 0.055 mm, the sediments are characterised as a clay loam and a sand , respectively. The principle difference between these water/sediment systems are the contents of organic carbon in the sediments (3.2 or 0.1 % respectively) and the particle size distribution.

The ^{14}C-labelled test substance, dissolved in approximately 0.4 ml acetone, was applied to each test flak, containing a 2.5 cm sediment layer and 6 cm supernatant water layer, resulting in a n application rate of 0.27 mg active ingredient per kg water. The test concentration was orientated to a target field application rate of 840 g/ha assuming a 100% overspray of a 30 cm deep water source.

The study was conducted at 20±2 ºC in the dark over a period of 120 days with 12 sampling dates (0h, 24h, 2d, 3d 7d, 10d, 14d, 30d, 45d, 58d, 93d and 120d). For most samples, only one replicate was collected. Two replicate were collected at the following dates: 0h, 14d, 58d, and 120 d.

For both water/sediment systems tested, the material balances were good to excellent with a range of 93.8 to 104.5 % of total applied dose (one outlier at 114%). The radioactivity applied was completely extractable (100%/88.1 % for Krempe and Ohlau, respectively) at the first sampling interval. By the end of the study, the sum of extractable radioactivity from water and the sediment had decreased to 81.0% and 89.6% accompanied by the formation of 0.7% and 1.1% ^{14}C-carbon dioxide. Other volatile radioactivity accounted to a maximum of 1.6% and 2.8% at any sampling interval. The non-extractable radioactivity in the sediment had increased to 19.0%/8.2% (Krempe/Ohlau) by the end of the study, day 120.

At termination (120 d after application) the amounts of radioactivity found in the water were 29 /55 % of applied dose (Krempe / Ohlau), whereas the amounts in the sediment were 71/43 %. This differences show that endosulfan and its metabolites adsorb with a higher adsorption rate to a silty loam as compared to a sand. The amount of parent compound at termination (120 d after application) had declined to 20 % of applied dose in the system Krempe (loamy sediment) and to 6 % in the system Ohlau (sandy sediment).

The degradation proceeded by hydrolytic and oxidative pathways to result in endosulfan sulphate AE F051327 and endosulfan diol AE F051329 as components early formed in metabolism. In the course of the incubation, endosulfan hydroxy ether AE F051326 and endosulfan hydroxy carboxylic acid AE F114151 were additionally observed as main metabolites. In the loamy Krempe system, the peak values were 7.1 %, 63.5%, 9.8% and 32.9% for the total samples (water+sediment), respectively (see table 8.3-2, Figures 8.3-1 and 8.3-2). In the sandy Ohlau system, the peak values were 25.6%, 34.6%,10.1% and 44.3% for the total samples, respectively (see table 8.3-3, Figures 8.3-3 and 8.3-4). Other components were found generally below 1.5% of total applied dose at any sampling interval. A comparison with the profiles of sterilised samples underlined that the degradation of endosulfan was an microbial induced process. The proposed metabolic pathway of endosulfan in aerobic water/sediment is proposed in figure 8.3-5

In the sterile samples the degradation of endosulfan was significantly retarded, however, spontaneous hydrolysis mainly to endosulfan diol was observed. The extracted sediments of day 120 were investigated by organic matter fractionation. In Krempe system , 12.8% of 19.6% residues in sediment could be extracted into aqueous sodium hydroxide solution. The remainders (6.8%) was assigned to humans. 7.4% of the 12.8% extract were analysed as humic acids, 3.9% were analysed as fulvic acids. In the Ohlau system, 7.4% of 9.6% residues in sediment could be extracted into NaOH. The remainder (2.2%) was assigned to humins. 2.2 % of the 7.4% extract were analysed as humic acids, 5.0% were analysed as fulvic acids.

Table 8.3-2: Metabolites formed during degradation of Endosulfan (System Krempe)

Test Period	**Radioactivity (% of total applied radioactivity)**																	
	α+βEndosulfan			**Endosulfan sulphate**			**Endosulfan diol**			**Endosulfan lactone**			**Endosulfan hydroxy ether**			**Endosulfan hydroxy carboxylic acid**		
	water	sediment	total	water	sediment	total	water	sediment	total	water	sediment	total	water	sediment	total	water	sediment	total
0	66.1	17.6	83.7	<0.1	<0.1	<0.1	16.3	<0.1	16.3	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	n.d.	<0.1
1	27.4	34.3	61.7	<0.1	<0.1	<0.1	31.0	8.3	39.3	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	n.d.	<0.1
2	6.1	41.2	47.3	<0.1	<0.1	<0.1	**35.0**	**15.0**	**50.1**	<0.1	<0.1	<0.1	1.4	<0.1	1.4	<0.1	n.d.	<0.1
3	4.3	34.1	38.4	0.8	<0.1	0.8	**24.6**	**21.3**	45.9	<0.1	<0.1	<0.1	1.3	2.0	3.3	0.9	n.d.	0.9
7	2.6	34.2	36.8	<0.1	<0.1	<0.1	**20.1**	**31.0**	51.0	<0.1	0.3	0.3	2.7	4.3	6.9	2.3	n.d.	2.3
10	1.5	20.4	21.8	<0.1	<0.1	<0.1	**22.0**	**41.5**	63.5	<0.1	<0.1	<0.1	**4.0**	**5.8**	**9.8**	3.5	n.d.	3.5
14	0.7	45.8	46.5	<0.1	<0.1	<0.1	**6.3**	**32.6**	38.9	<0.1	<0.1	<0.1	1.6	**6.7**	8.4	**2.5**	n.d.	2.5
30	0.5	**55.6**	56.1	<0.1	2.1	2.1	**1.0**	**22.7**	23.7	<0.1	<0.1	<0.1	0.4	**4.3**	4.7	**8.3**	n.d.	8.3
45	0.3	**23.1**	23.3	<0.1	**4.3**	4.3	**1.4**	**26.5**	27.9	0.1	1.7	1.8	0.5	**6.3**	6.8	**20.2**	n.d.	20.2
58	0.2	**20.9**	21.1	<0.1	**3.7**	3.7	**1.4**	**24.5**	25.9	<0.1	3.1	3.2	0.2	**4.5**	4.7	**24.9**	n.d.	24.9
93	0.2	**19.1**	19.3	0.1	**4.5**	4.6	**0.8**	**14.5**	15.3	0.1	2.9	3.0	0.2	**3.3**	3.5	**32.9**	n.d.	**32.9**
120	0.1	**19.4**	19.5	0.1	**7.0**	**7.1**	**1.2**	**15.2**	16.4	<0.1	2.2	2.3	0.2	**2.6**	2.8	**25.3**	n.d.	25.3
24h steril	32.5	65.9	98.4	0.3	<0.1	0.3	3.2	<0.1	3.2	<0.1	<0.1	<0.1	0.8	<0.1	0.8	<0.1	n.d.	<0.1
14d steril	6.8	82.3	89.2	<0.1	<0.1	<0.1	2.7	5.4	8.1	<0.1	<0.1	<0.1	0.4	<0.1	0.4	<0.1	n.d.	<0.1
58d steril	2.9	75.6	78.5	<0.1	<0.1	<0.1	4.9	15.4	20.3	<0.1	<0.1	<0.1	0.2	0.9	1.1	<0.1	n.d.	<0.1
120d steril	1.4	62.4	63.8	<0.1	<0.1	<0.1	5.8	28.7	34.5	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	n.d.	<0.1

Eliminado: total

Figure 8.3-1: Formation and dissipation of endosulfan in water phase, sediment and the whole system.

Krempe system

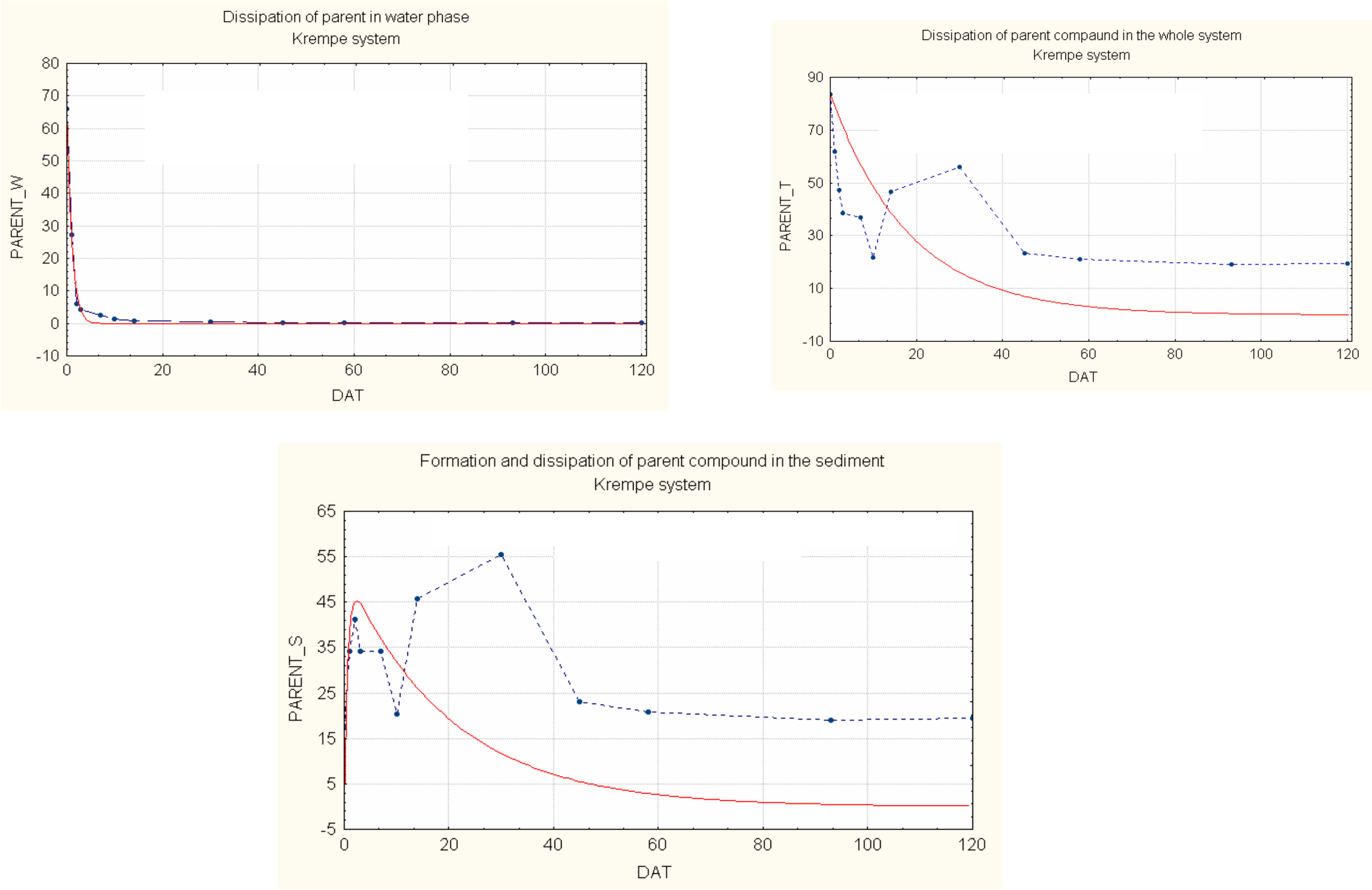


Figure 8.3-2 : Formation and dissipation of the main metabolites found in Krempe system

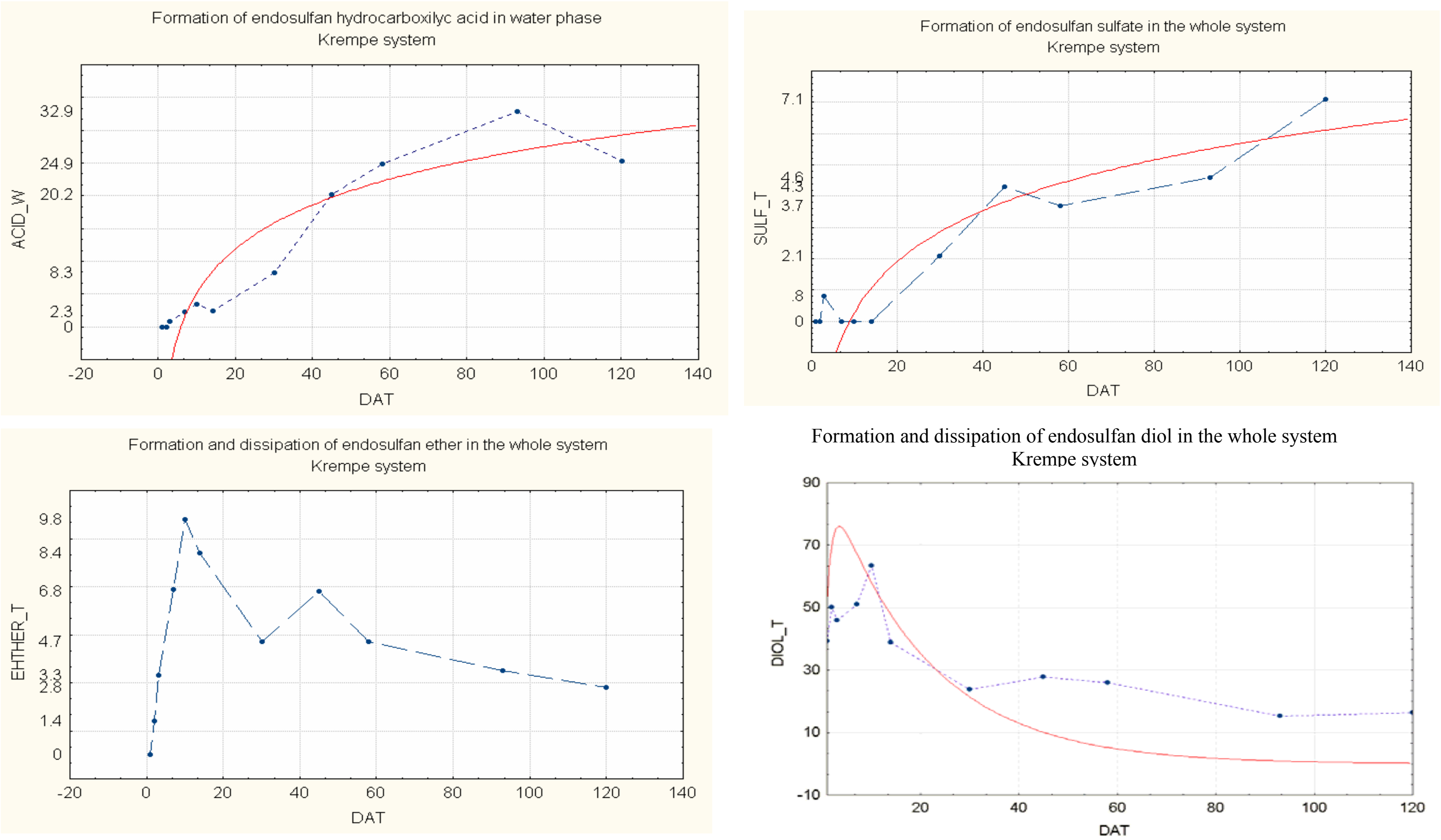


Table 8.3-3: Metabolites formed during degradation of Endosulfan (System Ohlau)

Test Period	**Radioactivity (% of total applied radioactivity)**																	
	α+βEndosulfan			**Endosulfan sulphate**			**Endosulfan diol**			**Endosulfan lactone**			**Endosulfan hydroxy ether**			**Endosulfan hydroxy carboxylic acid**		
	water	sediment	total	water	sediment	total	water	sediment	total	water	sediment	total	water	sediment	total	water	sediment	total
0	53.1	20.7	73.8	<0.1	<0.1	<0.1	11.4	<0.1	11.4	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	n.d.	<0.1
1	33.2	46.4	79.6	<0.1	<0.1	<0.1	18.1	<0.1	18.1	<0.1	<0.1	<0.1	1.0	<0.1	1.0	0.7	n.d.	0.7
2	23.0	45.9	68.9	<0.1	<0.1	<0.1	21.8	4.9	26.8	<0.1	<0.1	<0.1	1.5	<0.1	1.5	0.9	n.d.	0.9
3	17.0	49.0	66.0	<0.1	<0.1	<0.1	**23.66**	**5.4**	29.0	<0.1	<0.1	<0.1	1.8	<0.1	1.8	1.0	n.d.	1.0
7	7.8	50.3	58.1	<0.1	<0.1	<0.1	**22.9**	**11.7**	**34.6**	<0.1	<0.1	<0.1	3.0	2.0	5.0	1.4	n.d.	1.4
10	8.0	54.4	62.4	<0.1	<0.1	<0.1	**17.4**	**12.4**	29.8	<0.1	<0.1	<0.1	2.9	<0.1	2.9	1.8	n.d.	1.8
14	7.5	47.1	54.5	0.3	<0.1	0.3	**16.5**	**12.2**	28.7	<0.1	<0.1	<0.1	**5.5**	**4.7**	**10.1**	**2.5**	n.d.	2.5
30	4.3	35.5	39.8	2.4	8.5	10.9	**2.3**	**4.0**	6.4	0.2	<0.1	0.2	**2.5**	**2.6**	5.0	**24.3**	n.d.	24.3
45	1.7	**23.8**	25.5	**3.8**	**19.9**	23.7	**2.5**	**2.3**	4.8	0.2	<0.1	0.2	**0.8**	**1.7**	2.5	**31.7**	n.d.	31.7
58	0.5	**10.0**	10.5	**5.3**	**20.0**	**25.3**	**3.3**	**1.7**	5.0	0.1	0.3	0.4	0.7	1.0	1.7	**41.4**	n.d.	41.4
93	0.5	**6.5**	7.0	**3.5**	**21.2**	24.7	**4.3**	**1.7**	6.0	<0.1	0.7	0.7	0.5	0.7	1.2	**44.3**	n.d.	44.3
120	0.2	**6.2**	6.4	**3.3**	**22.3**	25.6	**2.8**	**1.7**	4.5	0.3	0.7	1.0	0.3	0.8	1.1	**44.1**	n.d.	44.1
24h steril	37.1	54.9	92.0	<0.1	<0.1	<0.1	4.6	<0.1	4.6	<0.1	<0.1	<0.1	1.1	<0.1	1.1	0.6	n.d.	0.6
14d steril	10.3	78.0	88.3	0.2	<0.1	0.2	5.9	2.1	8.0	<0.1	<0.1	<0.1	0.8	<0.1	0.8	0.9	n.d.	0.9
58d steril	8.7	47.1	55.8	<0.1	<0.1	<0.1	22.6	20.0	42.6	<0.1	<0.1	<0.1	<0.1	0.7	0.7	0.4	n.d.	0.4
120d steril	5.3	55.9	61.2	<0.1	<0.1	<0.1	<0.1	17.9	17.9	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	0.4	n.d.	0.4

Figure 8.3-3: Formation and dissipation of endosulfan in water phase, sediment and the whole system.

Ohlau system

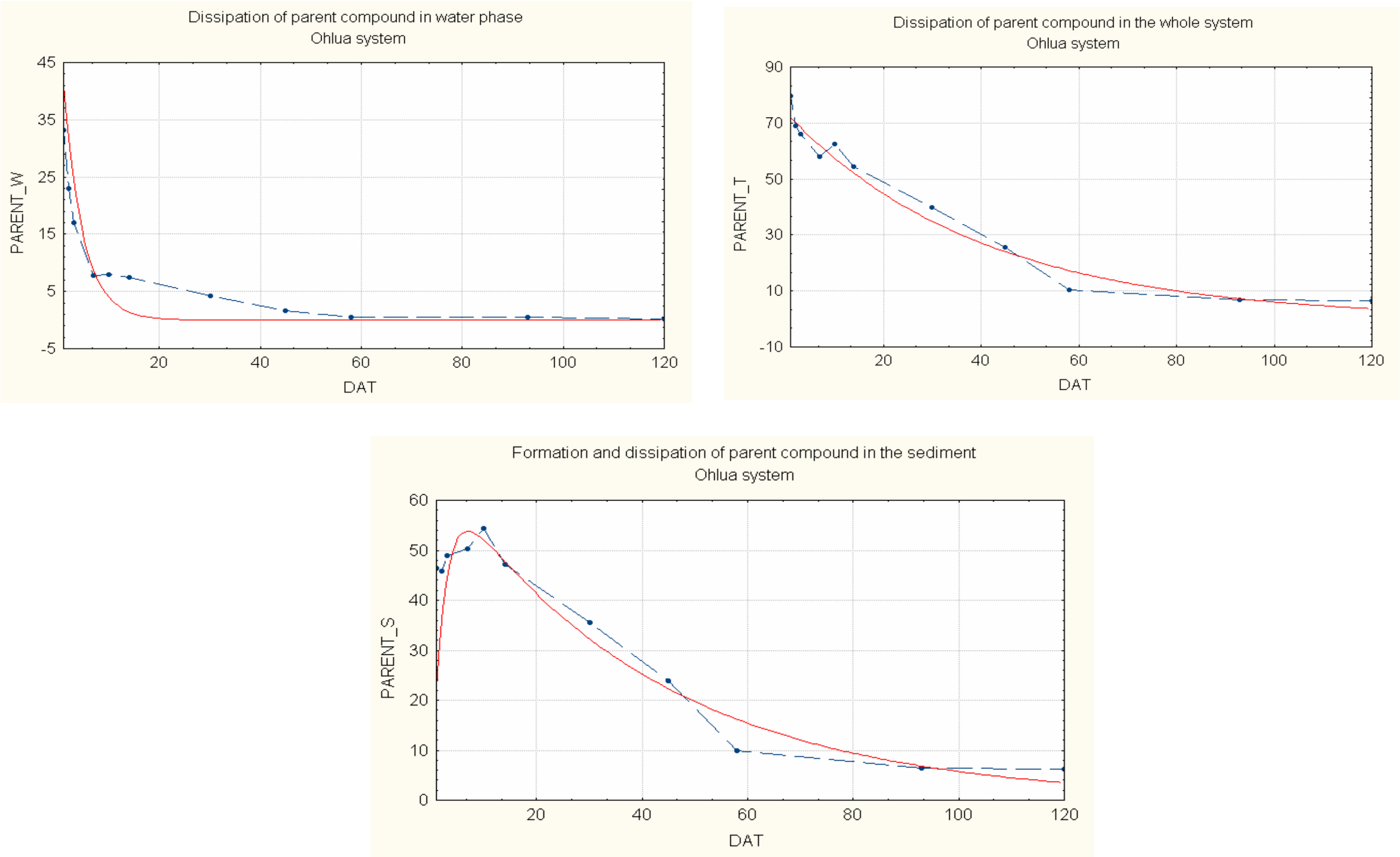


Figure 8.3-4: Formation and dissipation of the main metabolites found in.
Ohlua system

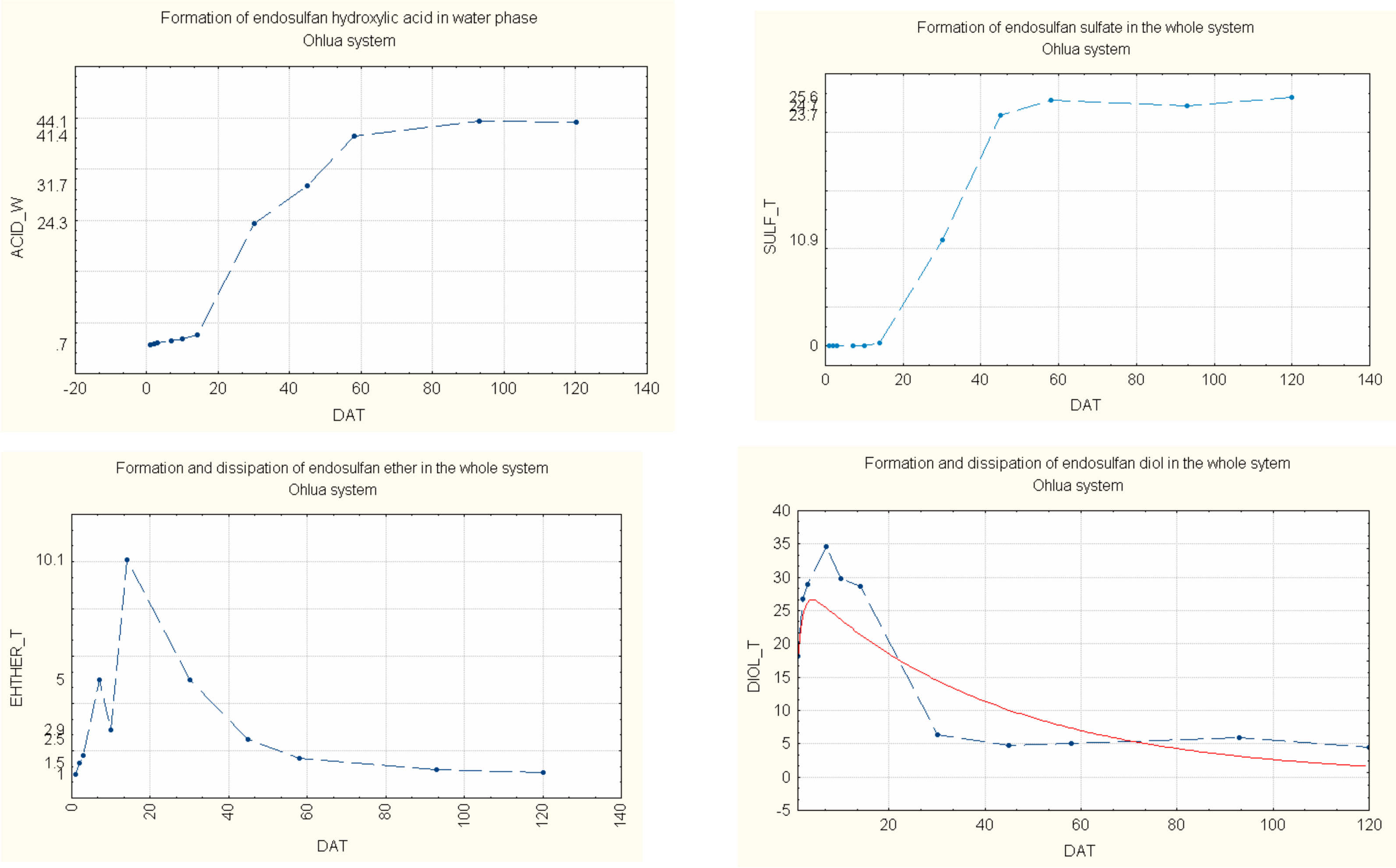
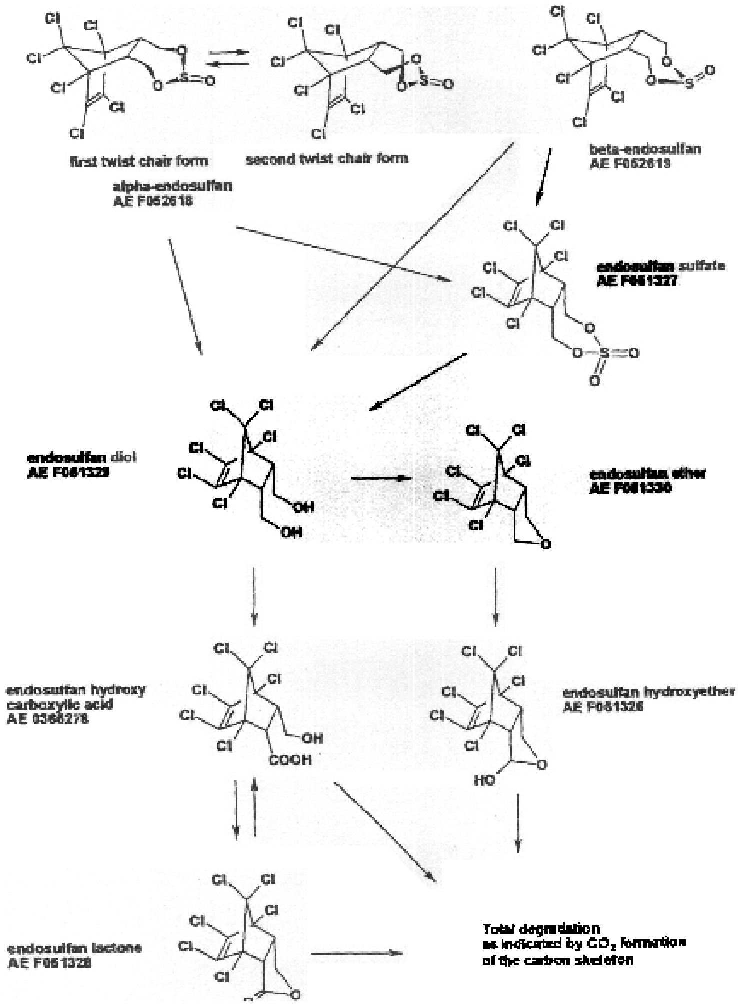


Figure 8.3-5: Metabolic pathway of endosulfan in aerobic water/sediment



Assessment:

The study is acceptable. The study shows that the degradation of endosulfan proceeded by hydrolytic and oxidative pathways to result in endosulfan sulphate and endosulfan diol as components early formed in metabolism. Also, endosulfan hydroxy ether and endosulfan hydroxy carboxylic acid have been observed as main metabolites. Endosulfan and endosulfan sulphate are absorbed to the sediment, endosulfan diol that must be considered as main metabolite, appeared at the beginning of the study in both systems and it is absorbed in the sediment with a peak in the whole system of 63.5% TAR at 10 days after application in the system Krempe and 34.6% TAR at 7 days after application in the system Ohlau. Endosulfan hydroxy carboxylic acid appeared 3 days after application in the System Krempe and 1 day after application in the Ohlau system, this metabolite was only detected in water its concentration

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increased during the study with a level at the end of the study of 25.3% TAR in the Krempe system and 44.1% TAR in the Ohlau system, the degradation of this metabolite was not observed.

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Notifier has proposed the following DT50 for endosulfan and total endosulfan:

System/substance	**Disappearance Times**					
	From total system			**From water**		
	DT_{50} (days)	**DT_{90} (days)**	**r^2**	**DT_{50} (days)**	**DT_{90} (days)**	**r^2**
KREMPE						
Endosulfan	3.5	11.6	0.65	**0.7**	2.4	0.99
Endosulfan (without 30 d outlier)	3.3	11.1	0.78			
Endosulfan+ endosulfan sulphate	3.6	11.9	0.62	0.7	2.4	0.99
Endosulfan+ endosulfan sulphate (without 30d outlier)	3.4	11.3	0.76			
OHLUA						
Endosulfan	**15.8**	52.6	0.92	**1.6**	6.1	0.96
Endosulfan+ endosulfan sulphate	35.1	116.5	0.87	1.8	6.1	0.94

The DT50s values for endosulfan sulphate have not been considered valid by the RMS, because no degradation of it has been observed in the study accumulating in the sediment (figures 8.3-2 and 8.3-4). On the other hand, endosulfan carboxylic acid, also accumulates but in the water phase at a concentration of 44% TAR at the end of the study . In the case of the endosulfan diol an attempt of estimation the DT50 was made by RMS taking into account first order kinetics. However the goodness of fit was less than 0.7 and it cannot be established. RMS proposed the following DT50 for endosulfan taking into account simple 1st order kinetics :

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Eliminado: only was considered endosulfan and endosulfan sulfate as the main residue when in both system endosulfan diol appeared at levels higher than endosulfan sulfate and in water Endosulfan hydroxycarboxylic acid appeared at levels of 40% at the end of the study. Notifier has not calculated the DT50 for endosulfan and for the main metabolites. This calculation should be performed, as was stated in the monograph. This water/sediment system does not give more information than the previously assessed in the monograph and its results will not be considered for the risk assessment.¶

system		k	confidence interval	r^2 (%)	DT50 (days)	DT90 (days)
Krempe system	water	0.967307	0.863779 1.07083	99	0.71	2.38
	whole			0		
Ohlau system	water	0.378167	0.282793 0.473541	94.8	1.83	6.09
	whole	0.024482	0.0202221 0.0282744	97.67	28.31	94.05

The fast dissipation rate of endosulfan from surface water is due to significant transfer of endosulfan to the sediment.

Conclusions:

-The water sediment study shows that the parent compound is not completely degraded in one of the water/sediment system since 19.4% TAR is identified as endosulfan in the sediment of Krempe system (figures 8.3-1 and 8.3-3). With regard to the metabolites, accumulation of endosulfan sulphate in the sediment and endosulfan carboxylic acid in the water phase was observed (figures 8.3-2 and 8.3-4) during the study in both systems, and their dissipation rates cannot have been established: The concentration was maintained in a plateau between 25.5 and 44% TAR in the case of carboxylic acid and of 25% in the case of endosulfan sulphate. In these cases, DT50 > 120 d has been demonstrated. On the other hand, formation and dissipation endosulfan diol was observed but t15% TAR was observed in the sediment of the Krempe system at the end of the study

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- Taking into account the experimental results of this study the definition of residue in the water systems is as follows:

- parent compound (19.5% TAR at 120 days in Krempe system),
- endosulfan sulphate (22% TAR in the sediment at 120 d in Ohlau system)
- endosulfan carboxylic acid (44.1% TAR in the water phase at 120 d in Ohlau system)
- endosulfan diol (35% TAR in the water phase at 2 days and 41.5% TAR in the sediment at 10 days in Krempe system)

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Water/sediment study under at pH below 7

Study: Degradation of [^{14}C] Endosulfan in two aerobic water/sediment systems (under acid conditions)
Author: Winfried Jonas
Dated: March 2003
Reference: C031060
GLP: Yes

The degradation of the test substance [^{14}C] endosulfan, uniformly labelled at all chlorinated carbon atoms of the norbonene ring, was investigated in two different water/sediment systems (Pinnsee lake /Tonteich lake), under aerobic conditions over a periods of 365 days at 20ºC following BBA Guideline IV,5-1 ant the draft of OECD Guideline 308. The nominal application was 0.28/l of water applied according to a maximum field application rate of 0.84 Kg as/Ha and by assuming 100% overspray. The pH of both water/sediment systems was kept below 7 throughout the study period.
The samples were collected on July 2, 2001 from the area East and North-East of Hamburg. Table 8.3-5 summarized the characteristics of the systems.

Table 8.3-5: Characteristics of the water/sediment systems

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Parameter	**Pinnsee lake** **59. 460º N 6.122º E**		**Tonteich lake** **59.845º N 5.845 ºE**	
	water	**sediment**	**water**	**sediment**
Temperature [ºC]	21		21	
PH	**6.7**	**7.2**	**4.5**	**4.9**
Redox potential [mV]	330		460	
O_2 content [mg/l]				

Surface	8.5		9.0	
5 cm above sediment	8.4		7.8	
Total N [mg/l] beginning	2.5		0.89	
End	5.5		0.19	
[%]		<0.022		<0.03
Total P[mg/l] beginning	0.49		0.1	
End	1.5		0.11	
[mg/kg]		51		247
DOC [mg/l]	17		12	
Organic carbon [%]		0.09		11.3
Water hardnes [mmol/l]	0.084		2.73	
Dry matter [%]		86.7		55.0
Cation exchange				
Capacity [meq/100 g soil]		1.9		11.3
Particle size [%]				
<0.002 mm		0.4		22.9
0.002-0.006 mm		0.0		3.7
0.006-0.020 mm		1.0		7.4
0.020-0.063 mm		1.4		13.8
0.063-0.200 mm		16.1		24.7
0.200-0.630 mm		59.5		24.2
0.630-2.0 mm		21.6		3.3
Det. Of biomass [mgC/100g]				
Beginning		1.4		21.2
End		0.0		0.0

According to German classification (DIN 4220) the sediment Pinnsee is characterised as a sand, whereas the sediment Tonteich is a sandy loam.

A volume of 0.46 ml (Pinnsee) and 0.43 ml (Tonteich) of a stock solution (0.392 mg of [^{14}C-endosulfan/ml) , was applied to each test flak, containing a 2-2.5 cm sediment layer (170/117 g [Pinnsee/Tonteich] dry sediment) and 6 cm supernatant water layer (528 g (Pinnsee) and 592 g (Tonteich)).

The study was conducted at 20±2 ºC in the dark over a period of 365 days with 15 sampling dates (0h, 24h, 2d, 3d 7d, 10d, 14d, 30d, 45d, 57d, 91d 118 d, 156d, 245d and 365d). For most sampling intervals, only one replicate was collected. Two replicates were collected at 0d,57d, 118d and 365d, Four further samples per system were sterilized before application and analysed at 1, 14, 57, 118 and 365 d after application.

The analysis procedure and the limits of detection are summarized on figure 8.3-6. and table 8.3-6, respectively . In the report the lowest percentage reported for radioactivity in extracts and individual substances was set in 0.1% related to the radioactivity applied to the test system.

Figure 8.3-6: Principle scheme of analysis

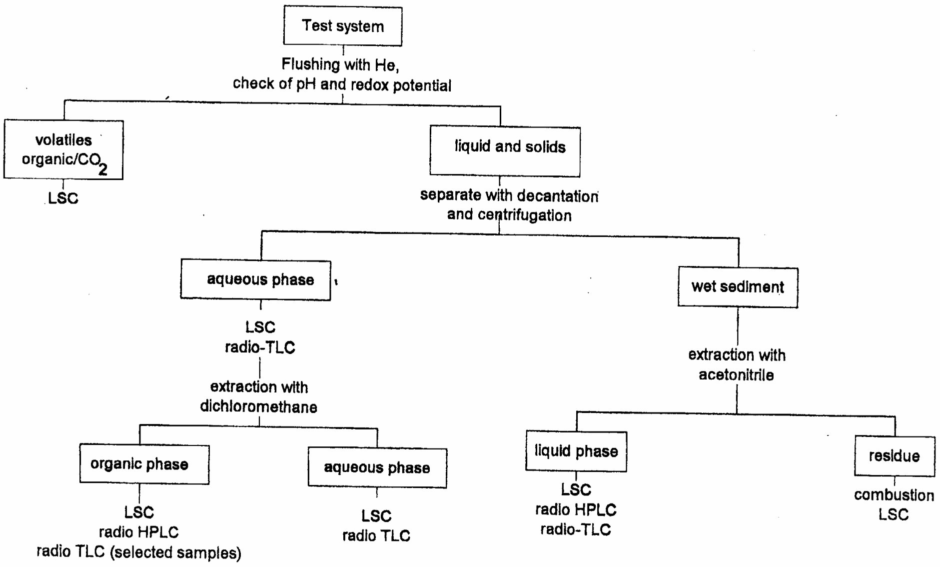

Table 8.3-6: LOD for measurements

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	LOD in total amount [%of applied]		
matrix	LSC	HPLC	TLC
water	0.007	0.49	0.12
dichloromethane	0.003	0.25	0.051
acetonitrile	0.012	0.17	0.069
Combustion	0.035		
Ethyl acetate	0.001		
carbsorb/Permafluor	0.0001		

The pH value, O_2-concetration and redox potential in the water were determined at each sampling date. Aerobic conditions in the water were observed during the entire study . Aerobic conditions in the water were observed during the entire study. The redox potential was in arrange of 117 and 280 mV and between 139 and 419 mV in Pinnsee water phase and Tonteich water phase, respectively. The pH after application varied between from 5.1 to 6.9 for Pinnsee water and 3.9 to 6.3 for Tonteich water phases . For Pinnsee, the Ph in water remained nearly constant throughout the test period (6.3-6.9) but dropped intermediately to pH 5.4 and 5.1 after 91 and 245 days respectively. For Tonteich the pH remained rather constant for the first 30 days, then increased slowly to pH 6.3 after 57 days, again followed by a subsequent decrease to 4.6 after 118 days and to 3.9 at the end of the test period. Compared to the water phase, the redox potential in the sediment phase was found to be much lower, indicating anaerobic conditions in parts o the system (see Figure 8.3-7)

The microbial biomass in the sediment was determined at the beginning and at the end of the study. The biomass decreased from 1.4 to 0.0 mg C/100g for Pinnsee system and from 21.3 to 0.0 mgC/100 g in the Tonteich system.

The total radioactivity recovered was in the range of 91.2 to 99.2% of total applied dose (the sterilised systems showed material balances in the range from 90.4-99.4%). Radiolabelled carbon dioxide formed during the degradation amounted to 3.0 and 1.8 % of applied dose for the systems Pinnsee and Tonteich at the end of the study period. Other organic volatiles were also found to a low extent of 0.7-0.8%. For sterilised samples, the values were 4.6% for the Pinnsee and 1.7 % for the Tonteich system.

For both systems the amounts of radioactivity detected in the water column decreased from 69/77% (Pinnsee/Tonteich) of the total applied dose for zero day to approximately 33/3.6% (Pinnsee/Tonteich) at the end of the study on day 365. Correspondingly, the amount of radioactivity found in the sediment increased from 25/15% (Pinnsee/Tonteich) to 58/92% by the end of the study. These differences revealed a stronger adsorption of endosulfan and its metabolites to the sediment with higher organic matter content. The non-extractable residues in the sediment increased to 18.3/15.5% (Pinnsee/Tonteich) on days 156 and 365, respectively.

The parent compound was degraded to a higher extent in the Pinnsee system (from 84 by day 0 to 3.1% on day 365) than in Tonteich one (from 84.4 on day 0 to 24.1% on day 365).

The degradation proceeded by hydrolytic and oxidative pathways to result in endosulfan sulphate AE F051327 and endosulfan diol AE F051329 as components early formed in metabolism. In the course of the incubation, endosulfan lactone AE F051328, endosulfan hydroxy ether AE F051326 and endosulfan hydroxy carboxylic acid AE F114151 were additionally observed as main metabolites.

Considering the water phase the maximum levels of formed metabolites were 7.1% (sulphate), 5.8% (diol), 2.0% (OH-ether) and 15.6% (OH acid) in Pinnsee system. And in the Tonteich system the maximum levels found were, 0.9% (sulphate), 3.2 (diol), 1.8% (lactone, 1.4% (OH-ether)and 2.0 (OH-acid). Unknown degrades did not exceed 2.4% of the applied radioactivity in the both systems

In the sandy Pinnsee sediment, these metabolites achieved maximum levels of 46.2% (sulphate), 10.7% (diol), 2.2 (OH-ether) and 3.6 (OH-acid). In the sandy loam Tonteich sediment, the maximum levels accounted were 28.55 (sulphate), 11.3 (diol), 13.3% (lactone), 3.7 (Oh-ether) and 3.8 (OH-acid). . The experimental results are summarized in tables 8.3-7 and 8.3-8

It should be noted that endosulfan lactone was only detected at a relevant level in the sediment of the Tonteich system with high organic matter (11.3%) and pH range of 3.9-55. It appears thath the hydroxy carboxylic acid dominates over lactone at lower carbon contents and higher pH values as indicated by Pinnsee system and by the previous study conducted at pH 7-8. Figures 8.3-8 and 8.3-9

A comparison with the profiles of sterilised samples suggests that degradation of endosulfan in natural water and sediment is a microbial induced process. The proposed metabolic pathway of endosulfan in aerobic water/sediment is proposed in figure 8.3-4

Assessment: **The study is acceptable.** The study shows that the degradation of endosulfan proceeded by hydrolytic and oxidative pathways (figure 8.3-10) to result in **endosulfan sulphate and**

endosulfan diol as components early formed in metabolism. Also, **endosulfan lactone and endosulfan hydroxy carboxylic** acid have been observed **as main metabolites.**

No accumulation of endosulfan was observed in Pinnseen system (pH 6.2-7.2) , but 23.8% TAR was identified as endosulfan in the sediment of Tonteich system (pH 4.5-4.9)

Endosulfan sulphate appears to be the main metabolite with a peak in the whole system of 51.6% at 118 days (figure 8.3-10). On the other hand, in the water phase endosulfan sulphate attained up to 7% of TAR no reaching a plateau in Pinnsee system. However, in the water phase of Tonteich system it up a plateau of 0.18-0.19 %TAR. **Regarding to the fate of endosulfan sulphate in the sediment, it appears to reach a plateau in Pinnsee system between 40 and 35% TAR. In the case of Tonteich system, endosulfan sulphate reach up to 28.5% TAR at the end of the study no reaching a plateau (Figures 8.3-8 and 8.3-9)**.

Endosulfan diol, appeared at the beginning of the study in both systems and it is absorbed in the sediment with a peak of approximately 11% in the two system at day 45 in Pinnsee system and at day 91 in Tonteich system, amount that decreased to <0.1% TAR and 6.2 % TAR at the end of the study, respectively (Figures 8.3-8 and 8.3-9).

Endosulfan hydroxy carboxylic acid appeared 7days after application in the Pinnsee System and 91 days after application in the Tonteich system. This metabolite was detected as well in water phase as the sediment. The concentration found in the water phase differs in the two systems. **In Pinnsee system, the concentration increased during the study with a level at the end of the study of 15.6% TAR in the water phase no reaching a plateau**. **In Tonteich system, the maximum concentration found was 2% TAR , decreasing to <0.1 at the end of the study. The amount in the sediment was maintained constant at the end of the study in the two system at a level of 3.1-3.6% TAR (Figures 8.3-8 and 8.3-9)**

It should be noted that **endosulfan lactone was detected at a relevant level in the sediment of the Tonteich system (11.3% TAR), (pH range of 4.5-4.9). In this case the amount of endosulfan lactone found in the whole system at the end of the study was 13.3 % TAR no reaching a plateau. Therefore, under acid conditions pH (4.5-5) it should be noted that endosulfan lactone dominates over hydroxy carboxylic acid.**

On the other hand in Pinnsee system the highest concentration found in the whole of the system was 8.8% TAR. At the end of the study, the concentration increased up to 4.4% in the water phase no reaching a plateau whereas in the sediment , the concentration decreased from 6.4% to 2.2 % . **(Figures 8.3-8 and 8.3-9)**

Finally, endosulfan hydroxy ether was not found as relevant metabolite (<5%TAR) in this study,

The notifier has proposed the following DT50 for endosulfan and total endosulfan:

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Eliminado: **3.9**

Eliminado: **5**

Eliminado: In the water phase

Eliminado:

Eliminado: at the end of the study

Eliminado: Meanwhile

Eliminado: **maybe due to the decreasing microbial biomass seen throughout the study.¶**
¶
Comments: No information was given with regard to the caractherisation of bounded residues.

System/substance	**Disappearance Times**					
	From total system			**From water**		
	DT_{50} (days)	**DT_{90} (days)**	**r^2**	**DT_{50} (days)**	**DT_{90} (days)**	**r^2**
PINNSEE						
Endosulfan	**24.5**	81.5	0.9618	**0.81**	2.68	0.7148
Endosulfan (without 30 d outlier)				0.61	2.68	0.7344
Endosulfan+ endosulfan sulphate	173	>365	0.62	0.7	2.4	0.99
TONTEICH						
Endosulfan	132	>365	0.9869	1.25	4.15	0.8721
Endosulfan+ endosulfan sulphate	273	>365	0.9861	1.254.15	4.15	0.8688

DT50 values for endosulfan sulphate have not been considered valid by the RMS, because the DT_{50} values for the total residue in water, sediment and in the whole system should be calculated correctly taking into account the process of formation and degradation. However, **in the case of endosulfan sulphate degradation process has not seen in this study (it accumulates in the sediment) and DT50 > 120 d has been demonstrated**

Eliminado: These DT50s have not been considered valid by the RMS, because the DT_{50} 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.

Moreover, only endosulfan and endosulfan sulphate were considered in the estimations when, endosulfan diol ,endosulfan hydroxy carboxylic acid and endosulfan lactone also appeared at relevant levels.

RMS proposed the following DT50 for endosulfan taking into account simple 1st order kinetics :

system		k	confidence interval	r^2 (%)	DT50 (days)	DT90 (days)
Pinnsee system	water	0.441792	0.259282 0.024302	82.52	1.56	5.211
	whole	0.019933	0.0158056 0.020605	96.3782	34.7	115
Tonteich system	water	0.334398	0.258193 0.410603	94.841	2.072	6.8
	whole	0.00421523	0.00335278 0.00507768	93.56	164	546.25

The fast dissipation rate of endosulfan from surface water is due to significant transfer of endosulfan to the sediment.

Comments: No information was given with regard to the characterisation of bounded residues.

Conclusions:

-The water sediment study shows that the parent compound is not completely degraded in one of the water/sediment system since 23.8% TAR is identified as endosulfan in the sediment of Tonteich system (figures 8.3-9 and 8.3-10).

- With regard to the metabolites, accumulation of endosulfan sulphate in the sediment was seen in the both systems (figures 8.3-9 and 8.3-10) and endosulfan carboxylic acid in the water phase in Pinnsee system (figure 8.3.8), and their dissipation rates cannot have been established. In these cases, DT50> 120 d has been demonstrated. On the other hand, formation and dissipation endosulfan diol was observed . RMS attempted to estimate its degradation rate according to first order kinetics. However, the goodness of fit was less than 0.7

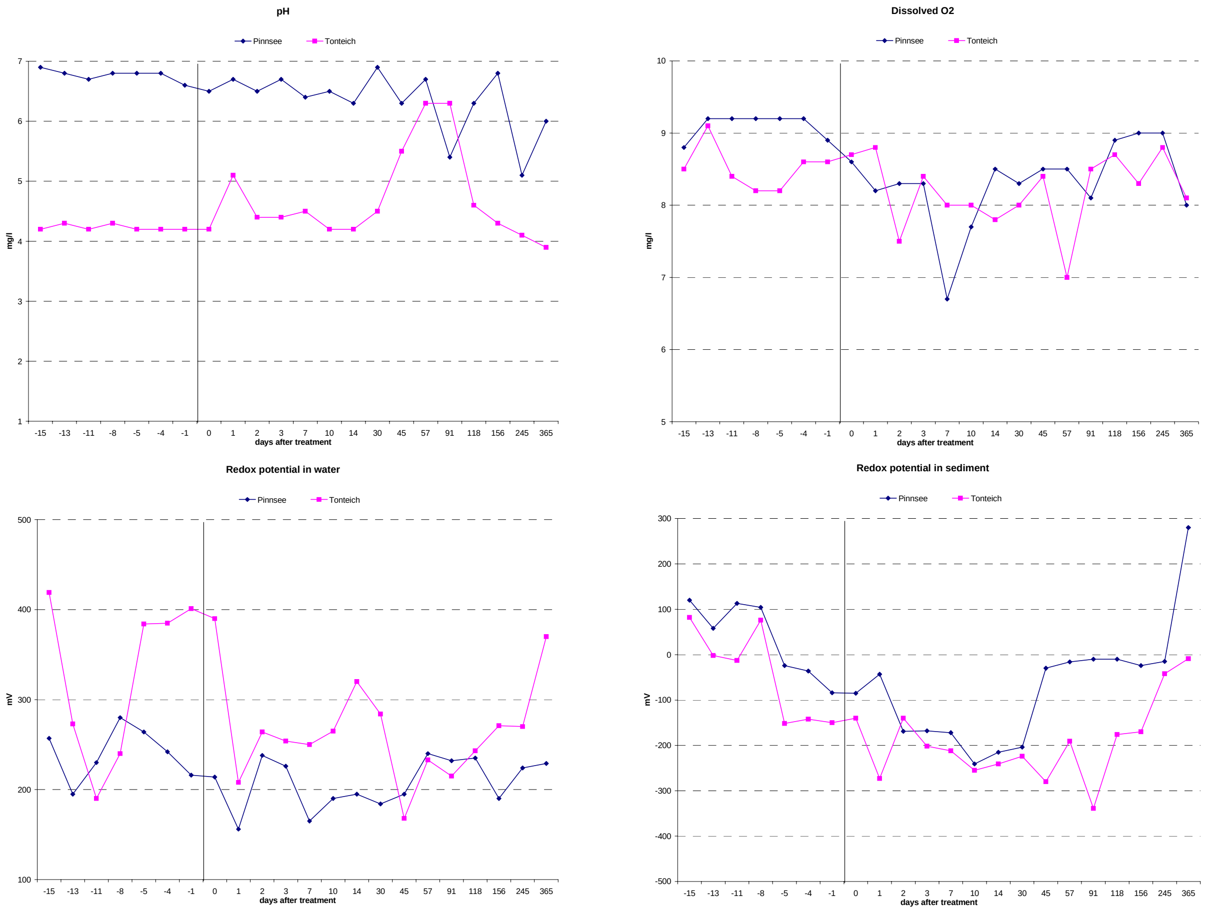
- Under acid conditions accumulation of endosulfan lactone has been observed (13.3% TAR in the sediment at the end of the study no reaching a plateau).

- Taking into account the experimental results of this study the definition of residue in the water systems is as follows:

  - parent compound (23.8% TAR at 365 days in the sediment of Tonteich system).
  - endosulfan sulphate (35.4% TAR at 365 days in the sediment of Pinnsee system)
  - endosulfan carboxylic acid (15.6% TAR in the water phase at 365 d in Pinnsee system)
- endosulfan diol (11.5% TAR in the sediment of Tonteich system at 91 days and 10.7% TAR in the sediment at 45 days in Pinnsee system)
  - endosulfan lactone (13.3% TAR in the sediment of Tonteich system at 365 days in Tonteich system).

In table 3.8-9 a summary of the percent of the metabolites found in the water/sediment studies assessed in this addendum is given

Figure 8.3-7: Physo-chemical observations in the test systems



Eliminado: R

Eliminado: A

Eliminado: R

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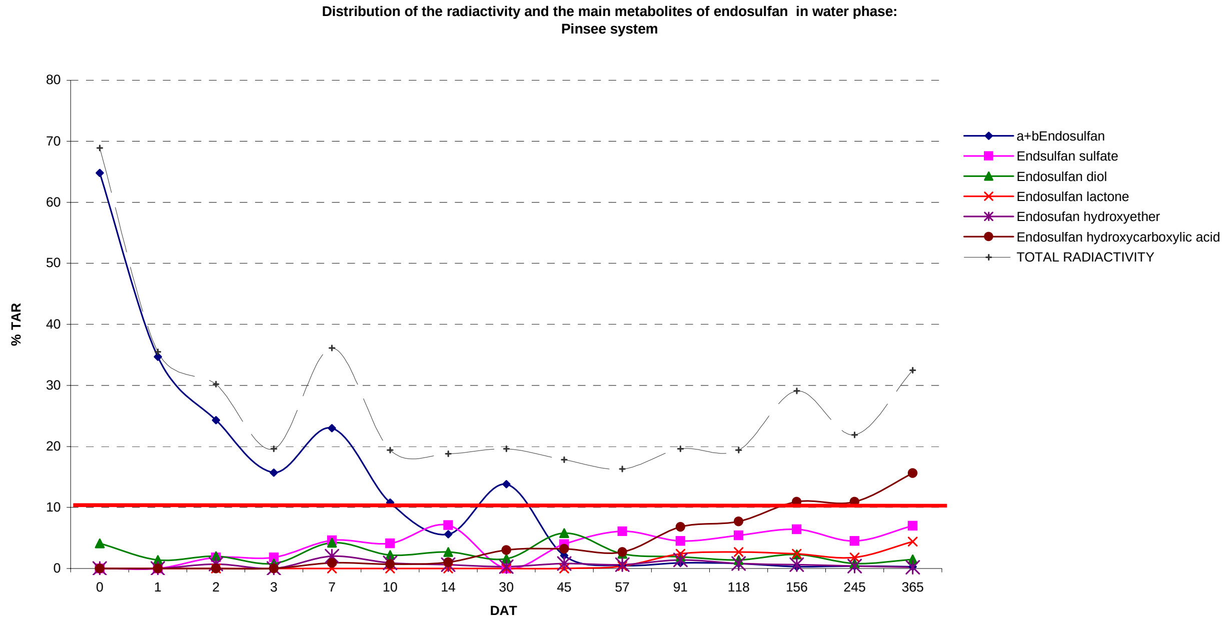
Table 8.3-7: Metabolites formed during degradation of Endosulfan (System Pinnsee)

DAT	Radioactivity (% of total)																												
	α+β Endosulfan			**Endosulfan sulphate**			**Endosulfan diol**			**Endosulfan lactone**			**Endosulfan hydroxy ether**			**Endosulfan hydroxy carboxylic acid**			**Unknown 1 (R.T 4.5-5.8 min)**			**Unknown 2 (RT <2.5 min)**			**Unknown 3 (RT 10 min)**	**Bounded**	**volatiles**	**total identified**	**total recovered**
	water	sediment	total	water	sediment	total	water	sediment	total	water	sediment	total	water	sediment	total	water	sediment	total	water	sediment	total	water	sediment	total	total				
0	**64.8**	**19.2**	**84**	<0.1	<0.1	<0.1	4.1	0.2	4.3	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	5.5	nd	93.8	93.8
1	34.7	52.6	87.3	<0.1	0.3	0.3	1.4	0.9	2.3	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	4.4	nd	94.3	93.7
2	24.3	56.4	80.7	1.8	4.1	5.9	2	1.2	3.2	<0.1	<0.1	<0.1	0.7	<0.1	0.7	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	4.8	nd	95.3	96.7
3	15.7	**66.6**	82.3	1.8	3.2	5	0.8	1.9	2.7	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	0.4	<0.1	0.4	<0.1	<0.1	<0.1	<0.1	5.2	nd	95.6	96.1
7	23	44.6	67.6	4.6	8.3	12.9	4.2	1.2	5.4	<0.1	<0.1	<0.1	2	<0.1	2	0.9	<0.1	0.9	<0.1	<0.1	<0.1	0.4	<0.1	0.4	<0.1	9.4	nd	98.6	99.6
10	10.8	57.7	68.5	4.1	10.7	14.8	2.2	2.5	4.7	<0.1	<0.1	<0.1	0.9	1.1	2	0.7	<0.1	0.7	1	<0.1	1	0.2	<0.1	0.2	<0.1	5.3	nd	97.2	96.7
14	5.6	42.7	48.3	7.1	23	30.1	2.7	3.5	6.2	<0.1	<0.1	<0.1	0.6	<0.1	0.6	1	<0.1	1.1	0.3	<0.1	0.3	0.2	<0.1	0.2	<0.1	4.6	0.3	91.4	93
30	13.8	44.1	57.9	<0.1	19.1	19.1	1.6	7.3	8.9	<0.1	<0.1	<0.1	0.3	**2.2**	**2.5**	3	<0.1	3	1.1	<0.1	1.1	0.3	<0.1	0.3	<0.1	4.5	0.9	97.3	97.6
45	2.1	32	34.1	**4**	29.8	33.8	**5.8**	**10.7**	**16.5**	<0.1	<0.1	<0.1	0.8	<0.1	0.8	3.2	<0.1	3.2	0.8	<0.1	0.8	0.4	<0.1	0.4	0.1	7.9	0.8	98.4	99
57	0.5	19.6	20.1	**6.1**	41.1	47.2	2.4	3.2	5.6	0.4	<0.1	0.4	0.6	<0.1	0.6	2.7	<0.1	2.7	2.4	<0.1	2.4	1	<0.1	1	<0.1	16.3	1	97.3	97.6
91	0.9	15.7	16.6	**4.5**	**38.8**	**43.3**	1.9	4.9	6.8	2.4	**6.4**	**8.8**	1.4	<0.1	1.4	**6.8**	**3.1**	**9.9**	0.9	<0.1	0.9	0.3	<0.1	0.3	<0.1	8.7	1.3	97.1	98.5
118	0.8	11.9	12.7	**5.4**	**46.2**	**51.6**	1.4	2.1	3.5	2.7	**2.1**	**4.8**	0.8	<0.1	0.8	**7.7**	**1.2**	**8.9**	<0.1	<0.1	<0.1	0.5	<0.1	0.5	<0.1	11.9	1.2	95.9	96
156	0.3	3.4	3.7	**6.4**	**36.7**	**43.1**	2.3	2.2	4.5	2.4	**2.4**	**4.8**	0.6	1.1	1.7	**10.9**	**2.1**	**13**	2.7	<0.1	**2.7**	1.4	1.1	3.5	0.5	**18.3**	1.7	97.5	98
245	0.4	4.5	4.9	**4.5**	**40.2**	**44.7**	0.8	2.4	3.2	1.8	**2.6**	**4.4**	0.4	0.6	1	**10.9**	**1.4**	**12.2**	0.8	<0.1	0.8	1.7	1.8	3.6	0.2	13.2	3.1	91.3	91.7
365	**0.3**	**2.8**	**3.1**	**7**	**35.4**	**42.4**	1.5	<0.1	**1.5**	**4.4**	**2.2**	**6.6**	0.2	0.7	1	**15.6**	**3.6**	**19.2**	2.1	<0.1	2.1	0.5	0.5	1	0.4	13.3	3.6	94.2	94.5
Sterile conditions																													
1	39.5	43.8	83.3	<0.1	<0.1	<0.1	1.2	0.7	1.9	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	3.7	nd	88.9	90.3
14	20.1	60.4	80.5	<0.1	<0.1	<0.1	2.5	1.1	3.6	<0.1	<0.1	<0.1	0.2	0.7	1.2	<0.1	<0.1	1.2	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	6.7	nd	93.2	92.7
57	16.3	49.6	65.9	<0.1	5.7	5.7	4.7	6.8	11.5	<0.1	<0.1	<0.1	0.4	0.5	0.9	<0.1	0.1	0.9	0.3	<0.1	0.3	<0.1	<0.1	<0.1	<0.1	6.1	1.9	94.5	93.2
118	11.3	64.2	75.5	<0.1	<0.1	<0.1	6.9	5.7	12.6	<0.1	<0.1	<0.1	0.4	<0.1	0.4	<0.1	<0.1	0.4	0.4	<0.1	0.4	<0.1	<0.1	<0.1	<0.1	1.6	3	100.5	94.2
365	6	44.6	50.6	<0.1	<0.1	<0.1	17.1	14	31.1	<0.1	<0.1	<0.1	0.3	<0.1	0.3	0.2	<0.1	0.3	0.3	<0.1	0.3	<0.1	<0.1	<0.1	<0.1	6.6	4.7	87.3	94.7

Table 8.3-8: Metabolites formed during degradation of Endosulfan (System Tonteich)

DAT	Radioactivity (% of total)																												
	α+βEndosulfan			**Endosulfan sulphate**			**Endosulfan diol**			**Endosulfan lactone**			**Endosulfan hydroxy ether**			**Endosulfan hydroxy carboxylic acid**			**Unknown 1 (R.T 4.5-5.8 min)**			**Unknown 2(RT <2.5 min)**			**Unknown 3 (RT 10 min)**	**Bounded residues**	**volatiles**	**total identified**	**total recovered**
	water	sediment	total	water	sediment	total	water	sediment	total	water	sediment	total	water	sediment	total	water	sediment	total	water	sediment	total	water	sediment	total	total				
0	74.1	10.3	84.4	<0.1	<0.1	<0.1	2.8	<0.1	2.8	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	4.4	nd	91.6	91.6
1	41.5	40.2	81.7	<0.1	<0.1	<0.1	**3.2**	1	4.2	<0.1	3.4	3.4	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	0.11	0.11	<0.1	2.9	nd	92.31	93.3
2	36.8	53	89.8	<0.1	<0.1	<0.1	0.18	1.2	1.38	<0.1	<0.1	<0.1	**1.4**	<0.1	1.4	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	2.2	nd	94.78	95.5
3	28.4	61.5	89.9	<0.1	<0.1	<0.1	1.4	1.6	3	<0.1	<0.1	<0.1	0.15	<0.1	0.15	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	2.5	nd	95.55	96.1
7	15	75.7	90.7	<0.1	<0.1	<0.1	0.18	1.9	2.08	<0.1	<0.1	<0.1	0.14	<0.1	0.14	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	1.9	nd	94.82	96.1
10	8.5	81.8	90.3	0.13	<0.1	<0.1	1	1.8	2.8	<0.1	<0.1	<0.1	0.14	<0.1	0.14	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	3.4	nd	96.64	97.5
14	6.3	81.2	87.5	**0.15**	2.1	2.25	1.2	2.4	3.6	<0.1	<0.1	<0.1	0.13	<0.1	0.13	<0.1	<0.1	<0.1	0.12	<0.1	0.12	<0.1	<0.1	<0.1	<0.1	2	0.6	92.82	97.3
30	4.5	79.4	83.9	**0.14**	4.1	4.24	1.4	4.2	5.6	<0.1	<0.1	<0.1	0.12	<0.1	0.12	<0.1	<0.1	<0.1	0.11	<0.1	0.11	<0.1	<0.1	<0.1	<0.1	2.7	0.5	97.17	99
45	4	**86.2**	**90.2**	**0.15**	<0.1	0.15	1.8	<0.1	1.8	<0.1	<0.1	<0.1	0.13	<0.1	0.13	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	2.8	0.5	95.58	97
57	4.4	**69.2**	**73.6**	**0.17**	6.2	6.37	2.4	8.5	10.9	<0.1	<0.1	<0.1	0.14	<0.1	0.14	<0.1	<0.1	<0.1	0.12	<0.1	0.12	<0.1	<0.1	<0.1	<0.1	3.5	0.7	95.33	97.4
91	2.4	**52.4**	**54.8**	**0.18**	**11.4**	**11.58**	1.8	**11.3**	**13.1**	**1.3**	3.4	**4.7**	1.1	**3.2**	**4.3**	**2**	1.3	3.3	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	**5.3**	0.5	97.58	98.5
118	1	**50.2**	**51.2**	**0.18**	**17.6**	**17.78**	1.3	**10.3**	**11.6**	**1.8**	7.6	**9.4**	0.15	<0.1	0.13	0.18	<0.1	0.18	0.12	<0.1	**0.12**	<0.1	<0.1	<0.1	<0.1	**6.1**	1.1	97.49	99.5
156	0.17	**40.1**	**40.27**	**0.18**	**19.1**	**19.28**	0.16	**9.1**	**9.26**	**1.8**	**8.8**	**10.6**	0.13	2.7	2.83	0.13	**3.8**	**3.93**	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	**7.6**	0.9	94.67	97.5
245	0.14	**29.6**	**29.74**	**0.19**	**27.6**	**27.79**	0.13	**7.2**	**7.33**	**1.8**	**12.2**	**14**	0.12	1.5	1.62	0.13	**3.3**	**3.43**	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	**9.4**	1.5	94.81	97
365	0.13	**23.8**	**23.93**	**0.18**	**28.5**	**28.68**	0.13	**6.2**	**6.33**	**1.5**	**13.3**	**14.8**	0.11	1.1	**1.21**	<0.1	**3.3**	**3.3**	<0.1	<0.1	<0.1	<0.1	0.13	**0.13**	<0.1	**15.5**	2.6	96.48	98.1
Sterile conditions																													
1	19.6	63.1	82.7	<0.1	<0.1	<0.1	1.8	0.19	1.99	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	1.7	nd	86.39	92.4
14	6.3	84.1	90.4	<0.1	<0.1	<0.1	0.18	1.9	2.08	<0.1	<0.1	<0.1	0.13	<0.1	0.13	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	1.6	nd	94.21	95.5
57	3	86	89	<0.1	<0.1	<0.1	0.15	3.1	3.25	<0.1	<0.1	<0.1	0.11	<0.1	0.11	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	3.8	0.6	96.76	97.7
118	2.2	87.3	89.5	<0.1	<0.1	<0.1	0.16	5.1	5.26	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	2.8	1.2	98.76	99.6
365	0.17	78.2	78.37	<0.1	<0.1	<0.1	<0.1	10.3	10.3	<0.1	<0.1	<0.1	1.2	0	1.2	0.1	0	0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	3.6	1.9	95.47	96.3

Figure 8.3-8: Distribution of the radioactivity and the main metabolites of endosulfan in water phase



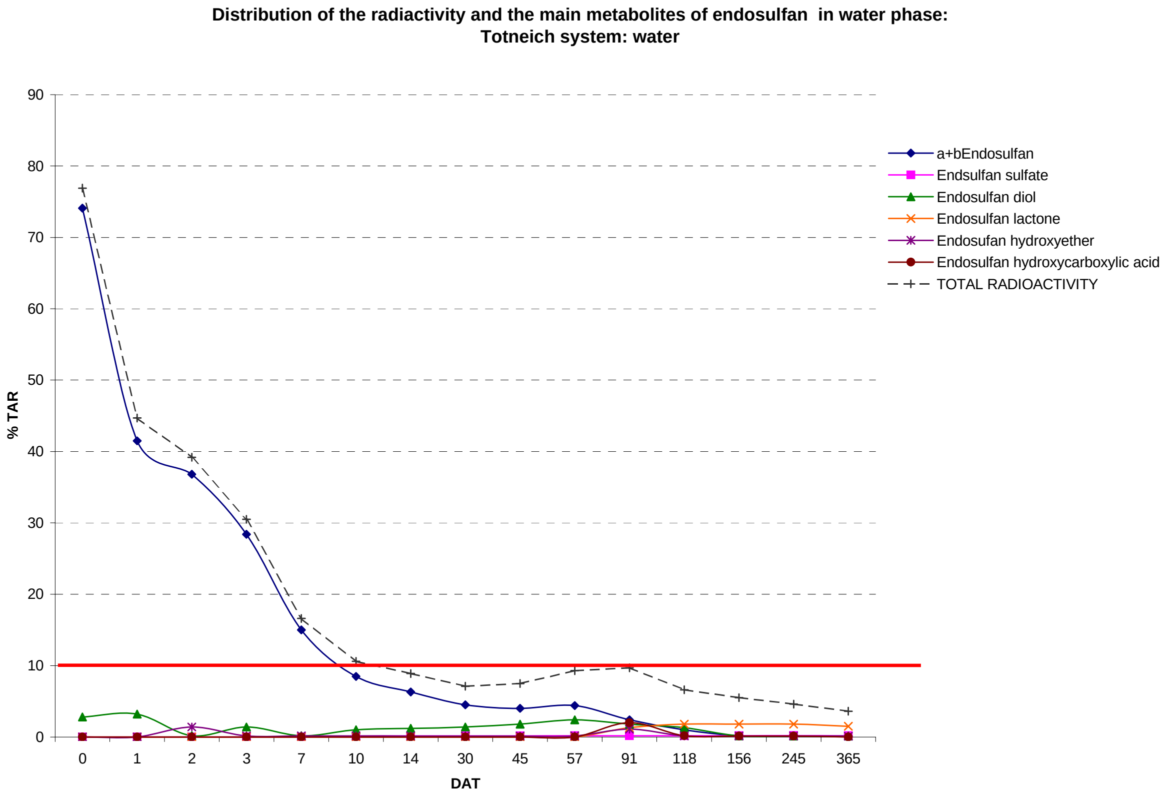
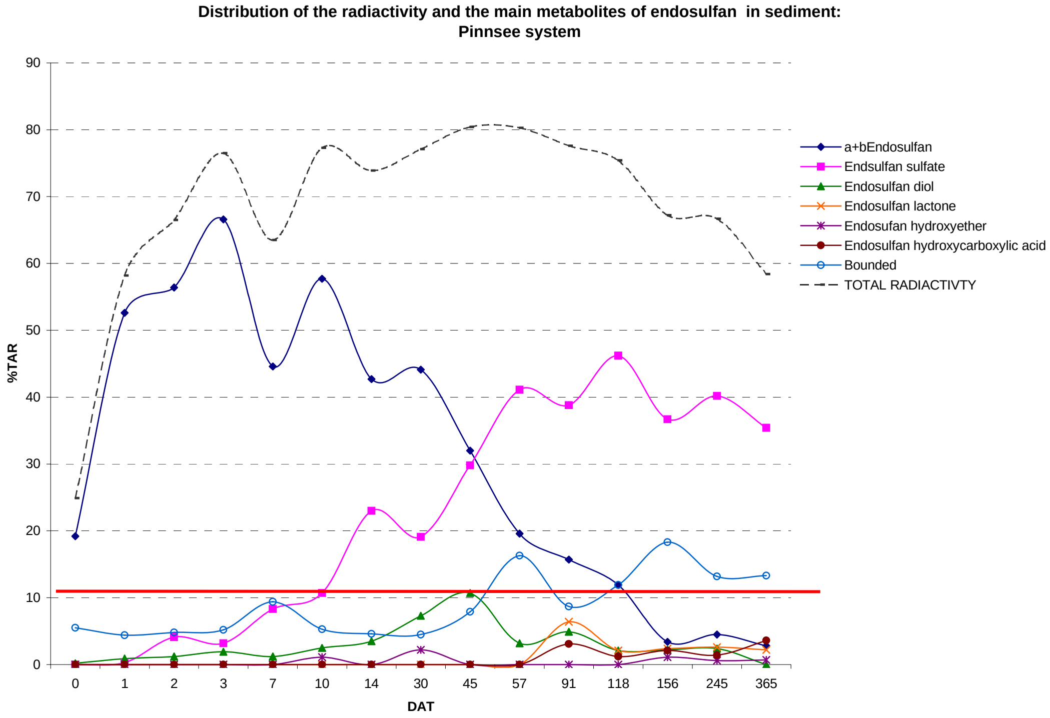


Figure 8.3-9: Distribution of the radioactivity and the main metabolites of endosulfan in sediment



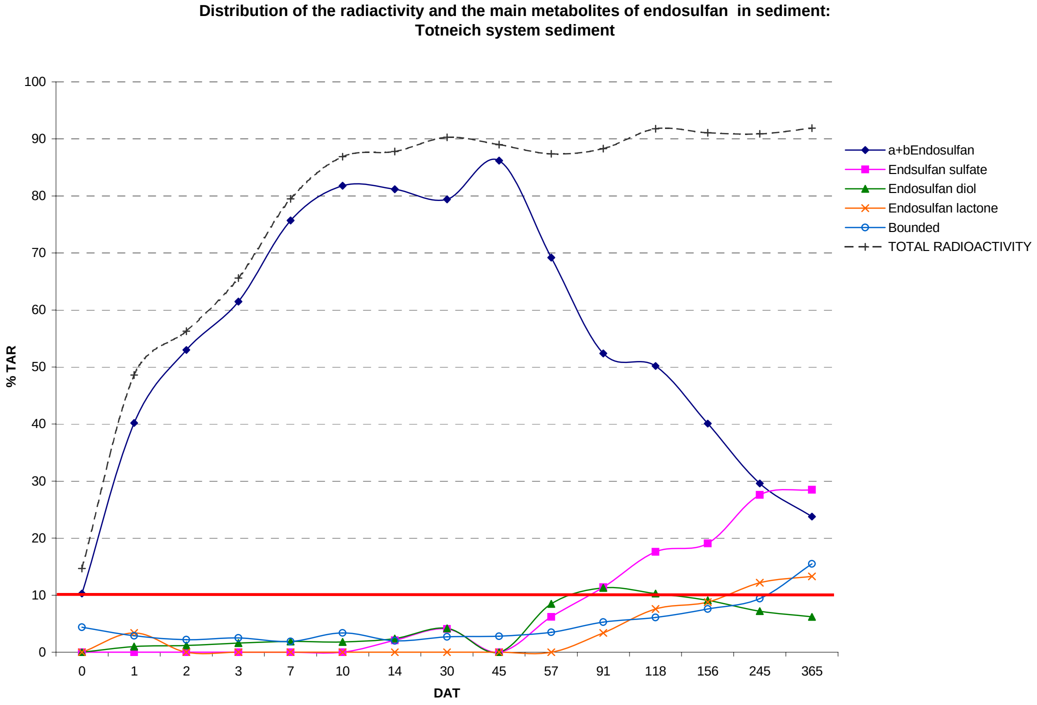


Figure 8.3-10: Accumulation of endosulfan and endosulfan sulphate .
(Tonteich system pH in water 4.5 pH in sediment 4.9
Pinnsee system pH in water 6.7 pH in sediment 7.2)

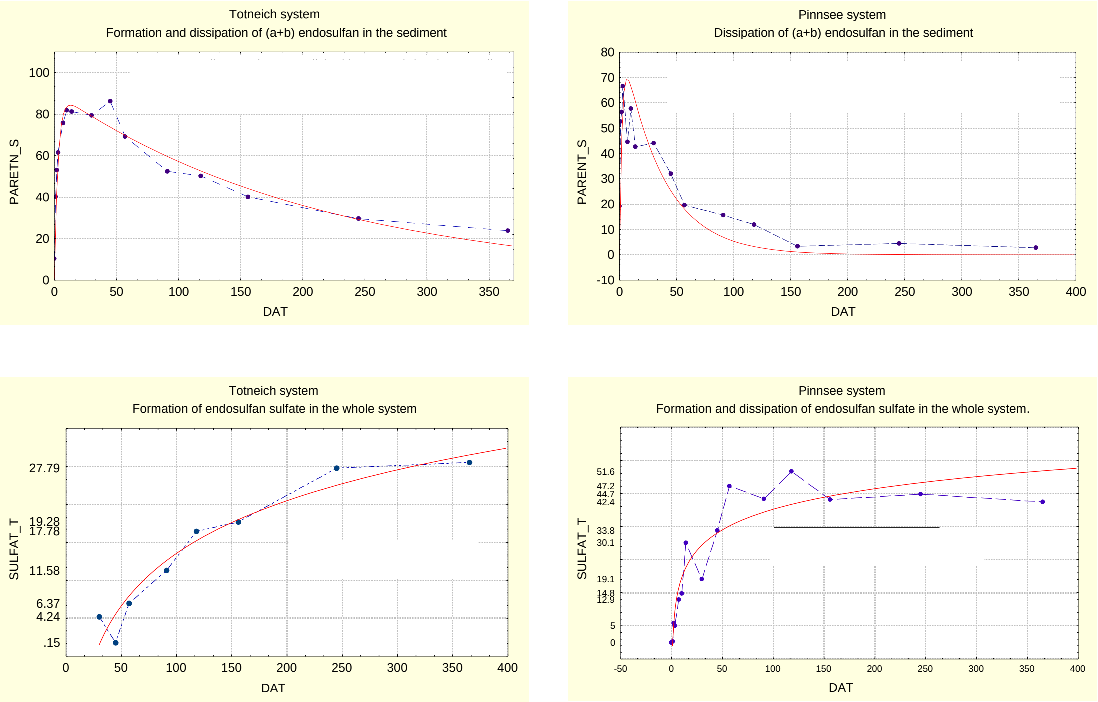


Table 8.3-9: Main metabolites found in the water sediment studies as percentage of total applied radioactivity (days after treatment)

	(a+b) endosulfan			**endosulfan sulphate**			**endosulfan diol**			**endosulfan lactone**			**endosulfan dihydroxy ether**			**endosulfan hydrocarboxylic acid**		
system	water	sediment	whole system	water	sediment	whole system	water	sediment	whole system	water	sediment	whole system	water	sediment	whole system	water	sediment	whole system
Krempe																		
max.	66.1 (0)	55.6 (30)	83.4 (0)	0.8 (3)	7.0 (120)	7.1 (120)	35 (2)	41.5 (10)	63.5 (10)	<0.1	3.1 (58)	3.2 (58)	4 (10)	6.7 (14 d)	9.8 (10)	32.9 (93)	nd	32.9 (93)
at the end (120)	0.1	19.4	**19.5**	0.1	7.0	**7.1**	1.2	**15.2**	16.4	<0.1	2.2	2.3	0.2	2.6	2.8	**25.3**		25.3
Ohlau																		
max.	53.1 (0)	54.4 (10)	79.6 (1)	5.8 (58)	22.3 (120)	25.6 (120)	23.66 (3)	12.2 (14)	34.6 (7)	0.3 (120)	0.7 (93)	1.0 (120)	5.5 (14)	4.7 (14)	10.1 (14)	44.3 (93)	nd	44.3
at the end (120)	0.2	6.2y	**6.4**	3.3	22.3	**25.6**	2.8	1.7	4.5	0.3	0.7	1.0	0.3	0.8	1.1	**44.1**		44.1
Pinnsee																		
max.	64.8 (0)	66.6 (3)	84 (0)	7.1(14)	46.2 (118)	51.6 (118)	5.8 (45)	10.7 (45)	16.5 (45)	4.4 (365)	6.4 (91)	8.8 (91)	2 (7)	2.2 (30)	2.5 (30)	15.6 (365)	3.6 (365)	19.2 (365)
at the end (365)	0.3	2.8	3.1	7	35.4	**42.4**	1.5	<0.1	1.5	4.4	2.2	**6.6**	0.2	0.7	1	**15.6**	3.6	19.2
Tonteich																		
max.	74.1 (0)	86.2 (45)	90.7 (7)	0.18 (91)	28.5 (365)	28.68 (365)	3.2 (1)	11.3 (91)	13.1 (91)	1.8 (118)	13.3 (365)	14.8 (365)	1.4 (3)	3.2 (91)	4.3 (91)	2 (91)	3.8 (156)	3.93 (156)
at the end (365)	0.13	23.8	**23.93**	0.18	28.5	**28.68**	0.3	**6.2**	6.33	1.5	13.3	**14.8**	0.11	1.1	1.21	<0.1	3.3	3.3

Table 8.3-10: pH in the water systems tested

system	**Krempe**	**Ohlau**	**Pinnsee**	**Tonteich**
pH in water	**7.3**	**6.8**	**6.7**	**4.5**
pH in sediment	**6.6**	**6.1**	**7.2**	**4.9**

RMS Overall assessment of water /sediment studies

From the studies assessed in the monograph it can be concluded that the main degradation routes for endosulfan in water are hydrolysis since photolysis is not observed under environmental conditions. In the study of hydrolysis, a pH dependence of endosulfan degradation was seen., thus the rate was higher at pH >7 .

From the water/sediment study (ph 7.3-7.8) assessed in the monograph RMS concluded:

- 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.

- DT_{50} can be expected to range from 10 to 12 days for parent endosulfan. The DT_{50} values for the total residue (endosulfan+ endosulfan sulphate), 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.

- 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.

On the other hand, the pH of water/sediment system study assessed in the monograph ranged between 7.3 and 7.8 and the ECCO 103 meeting noted that the study was performed at too high a pH to use the results for risk assessment (given the rapid hydrolysis at pH 7 and above).

On May 2002 the notifier has submitted a new water/sediment study and announced that the water/sediment study performed with pH<7 will be available by August 2002. The pH of these studies are shown in the table 8.3-10, and from these studies RMS has concluded:

- Fast dissipation rate of endosulfan from surface water was observed due to significant transfer of endosulfan to the sediment (DT50 0.7-6.8 days). On the other hand, DT50 values of dissipation in the whole system ranged between 28.31 and 164.4 days, the latter corresponds to the a water sediment at pH 5 according to the RMS estimations.

- Regarding to the metabolites, accumulation of endosulfan sulphate in the sediment and of endosulfan hydroxy carboxylic acid in the water phase has been seen throughout the study and the rate of degradation could not be estimated . In these cases DT50 > 120 d has been demonstrated. Endosulfan diol also has been seen at levels over 10% TAR, but dissipation has been seen. However, its dissipation rate could not be established according to first order kinetics (good ness of fit <0.7)

- Under acidic conditions endosulfan lactone seems to accumulate in the sediment (13.3% TAR at 365 d no reaching a plateau).

- These studies demonstrate that the degradation rate of endosulfan and the abundance of one or other degradation products seems to be influenced by the pH and other properties of the water/sediment system.

Taking all this into account the following conclusions are made:

1.- Dissipation of endosulfan is seen in the water/sediment system but the dissipation rate of endosulfan and the abundance of one or other degradation products seems to be influenced by the pH and other properties of the water/sediment system.

2.- Regarding to the metabolites, accumulation of endosulfan sulphate in the sediment and of endosulfan hydroxy carboxylic acid in water has been seen throughout the studies and the rate of degradation could not be estimated . In these cases DT50 > 120 d has been demonstrated.

4.- Endosulfan diol was also detected at levels over 10% TAR, but dissipation was observed. However, its dissipation rate could not be established according to first order kinetics (good ness of fit <0.7)

3.- Under acidic conditions endosulfan lactone seems to accumulate in the sediment (13.3% TAR at 365 d no reaching a plateau).

Therefore, the definition of residue is as follows:

Water phase: α + β endosulfan , hydroxy carboxylic acid and endosulfan diol
Sediment: α + β endosulfan, endosulfan sulphate, endosulfan diol and endosulfan lactone.

On May 2003 Notifier addressed an additional report Code: C032555 comparing the experimental results found in the laboratory water sediment studies conducted under different physico-chemical characteristics.

Study: Endosulfan-fate in water sediment Comparision of different water-sediment studies conducted with pure 14C-labelled test substance
Author: Buerkle, Leo W.
Dated: 2003
Reference: C032555
GLP: N/A

In this report the following conclusions are made:

1.- parent endosulfan very rapidly dissipated from the water phase with a half life generally less than 2 days

2.- Total Endosulfan (parent plus endosulfan sulphate) rapidly dissipated from the water phase with a half lifer also less than two days

3.- In the whole system the dissipation of parent and total endosulfan (endosulfan+ endosulfan sulphate) is rapid to moderate (DT50<35 days) under neutral to slightly alkaline conditions. In acid water system dissipation may be slower, but cannot be derived from the third study conducted under acidic conditions due to a total decrease of the microbial activity to zero.

4.- The pH survey (see above) showed that acidic surface waters in the region of intended use of endosulfan (Southern Europe) are very rare. Therefore, the fate of endosulfan is more represented by studies conducted under neutral and slightly alkaline conditions.

5.- Major metabolites observed in the water and sediment were endosulfan sulphate, endosulfan diol and endosulfan hydroxy carboxylic acid. Their composition was influenced by the biological activity and consequently by the sampling interval after the beginning of the incubation and last but not least by the pH system.

Assessment:

Taking into the account the assessment made above of the water sediment studies and the pH survey below RMS has the following remarks of the modifier's conclusions :

1.- DT 50 of endosulfan ranged between 3.2 and 132 days (this latter value corresponds at pH of 5).

2.- The conclusions with regard to the DT50 of total endosulfan (endosulfan +endosulfan sulphate) are not considered valid since no dissipation of endosulfan sulphate was observed in the whole system in any study.

3.- Endosulfan lactone should be added to the major metabolites.

4.- The abundance of one or other degradation products seems to be influenced by pH and other properties of the water/sediment system

5.- The pH survey of the surface water has not taken into account the sediment pH and in same cases the number of the samples is low (Portugal) and finally, no information regarding the litology of the sampling places is given and its relationship with the crops proposed in the GAP (see below)

On November 2003, notifier submitted, out of deadline, a recalculation of DT50 for endosulfan an its main metabolites based on the experiment found in the study coded as C022921. The assessment is shown below.

Study: Kinetic evaluation of the dissipation of endosulfan and its metabolites endosulfan sulfate, endosulfan diol and endosulfan hydroxy carboxylic acid in aerobic water-sediment test systems
Author: Hammel, Klaus
Dated: October, 2003
Reference: C036633
GLP: N/A

The simple first order kinetic (SFO) showed that this procedure has to be modified in order to achieve reliable kinetic parameter estimates.

Trials runs demonstrated that the two data sets had to be pooled and that for endosulfan diol only total amounts could be considered.

All attempts to obtain satisfactory results for the parent and the metabolites by simultaneous fit failed. Therefore the kinetic parameters for the metabolites and the parent had to be determined by separate optimisations.

It occurred further that specific degradation processes in the surface water and in the sediment can be well described by identical half life values. Using different half life parameters has led to unreliable estimates and no superior agreement between measured and calculated values. This was found for all compounds for which amounts in surface water and sediment were considered separately.

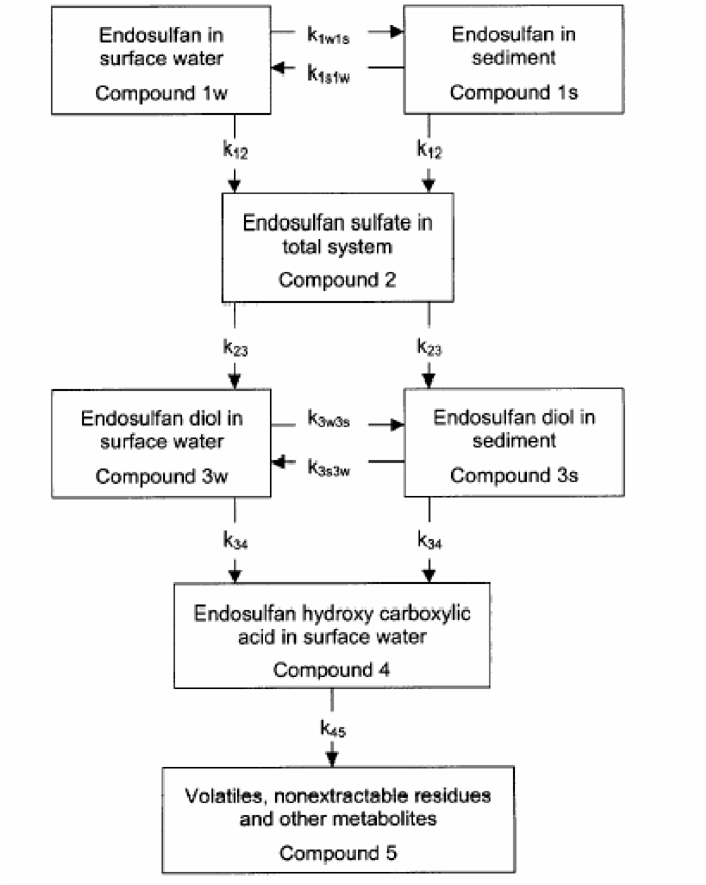
The estimations were made taking into account the pathway given in figure 8.3-11 using the numerical software package ACLS Optimize 1.2 (ACLS, 1996). ACLS Optimize uses as object function maximum likelihood which describes the probability to obtain a given set of data assuming that model and model parameter are correct. This includes a submodel of experimental error which can be additionally adjusted by the optimisation procedure. This submodel essentially determines how the assumed experimental error is related to the experimental value. It may be constant, that is independent of the experimental value or proportional to it.

The input differential equations were integrated using a 4th Runge-Kutta method. The optimisation method was chosen by ACLS Optimise according to the number of parameter. For few parameters the Nelder-Mead algorithm is sued for more the Generalize Reduced Gradient method.

For the following evaluations it was assumed that all reaction follow 1st order kinetics. The scheme of transformation of endosulfan in water sediment system as shown in figure 8.3-11 was translated to corresponding ACLS compartment model .

Separate optimisation had to be performed for endosulfan and its metabolites as it was said before.

Figure 8.3-11 Metabolic pathway for endosulfan and its metabolites in water-sediment system used fort the evaluation of kinetic parameters



The system of reaction equations characterising the comportment model for the total system may be written as:

$$\frac{dC_{1w}}{dt} = -(k_{12} + k_{1w1s}) \times C_{1w} + k_{1s1w} \times C_{1s} \qquad (1)$$

$$\frac{dC_{1s}}{dt} = -(k_{12} + k_{1s1w}) \times C_{1s} + k_{1w1s} \times C_{1w} \qquad (2)$$

$$\frac{dC_{2}}{dt} = k_{12}(C_{1w} + C_{1s}) - k_{23} \times C_{2} \qquad (3)$$

$$\frac{dC_{3w}}{dt} = k_{23} \times C_{2} - (k_{34} + k_{3w3s}) \times C_{3w} + k_{3s3w} \times C_{3s} \qquad (4)$$

$$\frac{dC_{3s}}{dt} = k_{23} \times C_2 - (k_{34} + k_{3s3w}) \times C_{3s} + k_{3w3s} \times C_{3w} \qquad (5)$$

$$\frac{dC_4}{dt} = k_{34}(C_{3w} + C_{3s}) - k_{45} \times C_4 \qquad (6)$$

where C is the amount of a compound in percentage of applied radioactivity and kij are rate constant. The subscripts of C and kij correspond to the compartment number as defined in figure 8.3-11 . Inspection of the equations above shows that for endosulfan (compound 1) and endosulfan diol (compound 3), surface water and sediment were considered individually.

Because at zero time already significant amounts of endosulfan and endosulfan diol were measured the corresponding initial values were fitted. The initial of all other compounds were set to zero.

Results: For the fit of the whole metabolic scheme to the data an overall value of $r^2 = 0.63$ was obtained, the values measured in surface water were generally better reproduced than those measured in the sediment. The results are given in the table 8.3-11

Assessment:

With regard to the rates obtained for the parent for the whole system, they agrees those obtained by SFO by RMS for the system at pH >5 (max. 34.7d, r^2= 96.37% for Pinnsee system) , although in the present study the variance explained is only of the 75.5% . The Fast dissipation rate of endosulfan from surface water (DT50 1.01 days) would be explained by the significant transfer of endosulfan to the sediment.

On the other hand, the scheme followed to estimate the rates for the metabolites (figure 8.3-11) does not seem to be the most suitable for the estimation, according to the route proposed in the water sediment studies (figure 8.3-5). Thus, endosulfan diol and endosulfan carboxylic acid are produced before endosulfan sulphate. This might mean a faster production of endosulfan diol from the parent , which would transform into endosulfan carboxylic acid. Even more, no degradation was observed of endosulfan sulphate in the sediment and endosulfan carboxylic in the water phase.

Finally, the overall goodness of fit of the model is so low : 62.74%, less than the value established by the current guidelines (70%). Therefore they cannot be considered valid.

Observation: in the estimations the experimental results of the study coded as C031060 were not taking into account

Table 8.3-11 New rates for endosulfan and its main metabolites reported by notifier on October 2003

Endosulfan

	paramenter estimates		stnd deviation	DT50	DT90
	initial	final			
k1w1s	1.05E-08	0.68226	0.089218	1.015958	3.374938
k1s1w	1.05E-08	0.065929	0.026564	10.51354	34.92522
k12	0.010159	0.018253	0.0036803	**37.97443**	126.1483
C1w0	0.56035	0.56036	0.030589		
c1s	0	0.074218	0.043282		
Log Likelihood	-18.096	61.587			
Stadistical sumary					
	Maxmized log likelihood	WT Resid sum of squares	Weighted residual sum	Percentage varition explained	weighting parameter
C1w	41.61	4.38E-02	-3.32E-02	53.88	0
C1s	19.98	2.66E-01	1.11E-01	51.44	0
Overall	61.59	3.10E-01	7.82E-02	**75.49**	

Metabolites

	paramenter estimates		stnd deviation	DT50	DT90
	initial	final			
k1w1s	0.03	0.69462	8.50E-02	0.99788	3.314885
k1s1w	0.03	0.060862	2.52E-02	11.38883	37.83289
k3w3s	0.03	0.039095	1.26E-02	**17.72982**	58.89718
k12	0.03	0.0089109	1.91E-03	**77.78644**	258.401
k23	0.03	0.013034	5.30E-03	**53.17993**	176.6599
k34	0.03	0.023483	4.12E-03	**29.51698**	98.05328
k45	0.03	0.0065135	4.03E-03	**106.417**	353.5096
ciw0	0.56	0.55772	2.44E-02		
c3w0	0.37	0.27302	2.23E-02		
c3s0	0.05	0.10516	3.32E-02		
k3s3w	0.03	1.00E-06	NaN		
Log Likelihood	79.239	174.24			
Stadistical sumary					
	Maxmized log likelihood	WT Resid sum of squares	Weighted residual sum	Percentage varition explained	weighting parameter
C1w	40.89	4.65E+01	-1.68E-02	93.5	0
C1s	15.9	3.73E-01	-2.81E-01	31.81	0
C2	31.67	1.00E-01	-4.36E-01	48.33	0
C3w	34.62	7.84E-02	-1.91E-01	70.64	0
C3s	18.92	2.91E-01	-3.20E-01	10.38	0
C4	32.24	9.57E-02	-3.09E-01	83.88	0
Overall	174.2	9.85E-01	-1.55E+00	**62.74**	

B.8.3.1 Summary of pH conditions in surface waters in southern Europe

On May 2002 notifier submitted a report regarding the pH conditions in surface waters in southern Europe.

Study: Summary of pH conditions in surface waters in southern Europe

Author: Neil Mackay
Dated: 2002
Reference: C022977
GLP: N/A

Data were obtained from three sources:

- European Topoic Centre for Inland Waters, European Environment Agency (data extracted from Eurowaternet database for major monitorin stations)
- Universita Cattolica del Sacro Cuore, Piacenza, Italy
- Spanish Ministry of the Environment Office of Water Quality Monitoring

Results demonstrate that, when considering the average pH observations from sets obtained from diverse locations in five Member States over many years, the typical pH conditions are consistently in alkali range.

There are, however, circumstances where the minimum pH observations in individual sets of observations falls bellow neutral. However, this is relatively rare. In Italy, as few as 4% of these minimum pH observations are in the acidic range. The worst-case would appear to be Portuguese surface water conditions. When the most relevant regional water body is considered up to 19% of the minimum observations are in the acidic range. However, it must be remembered that, even in this Member State, all observations set average values remain above netral.

Table 8.3.1-1: Summary of pH conditions in Southern European Member States from Eurpean Topic Centre for Inland Waters, European Environemt Agency

	Mean of average values (Range)	**Mean of minimum values (Range)**	**Mean of maximum values (Range)**	**Rivers monitored**
France (314 sets)	7.92 ± 0.24 (7.3-8.51)	7.53 ± 0.32 (5.6-8.0)	8.32 ± 0.43 (7.5-10)	Seine, Garonne, Saone Rhone Loire
Greece (78 sets)	7.76 ± 0.30 (7.00-8.4)	7.24 ± 0.38 (6.5-8.2)	8.14 ± 0.27 (7.5-8.8)	Nestos Strymon Axios Aliakmon Pinios Acheloos
Italy (208 sets)	7.83 ± 0.26 (7.1-8.5)	7.54 ± 0.35 (6.4-8.5)	8.09 ± 0.31 (7.1-9.1)	Arno Tevere Adige Po Metauro
Portugal (16 sets)	8.10 ± 0.34 (7.3-8.54)	7.38 ± 0.54 (6.2-8.2)	8.76 ± 0.26 (8.2-9.1)	River Guadiana
Spain (147 sets)	7.87 ± 0.20	7.27 ± 0.40	8.46 ± 0.53	Duero Guadalquivir Ebro Tajo Guadiana
Overal range of means	7.76 – 8.10	7.24 – 7.54	8.09 – 8.76	

Table 8.3.1-2: Summary of acidic pH observations frequency in Southern European Member States from European Topic Centre for Inland Waters, European Environemnt Agency

	Average values	**Minimun values**	**Maximum values**
	Percentage of sets with acidic pH observations		
France (314 sets)	0%	<5%	0%
Greece (78 sets)	0%	<18%	0%
Italy (208 sets)	0%	<4%	0%
Portugal (River Guadianaç;16 sets)	0%	<19%	0%
Spain (147 sets)	0%	<16%	0%
Overal range of means	0%	*Ca* 4% - *ca*19%	0%

In addition to this database, further detailed data were obtained for Italy and Spain. The result of these assessment are broadly consistent with the data base summarised above. It is noted that in the more detailed Italian database for Emilia Romagna the frequency of acidic pH observations was less than o.1%. There are more frequent observations of acidic pH observations in the Spanish database provided by the Ministry of Enviroment. However, it was concluded that pH measurements as low as pH 2.2 and 3.8 are most unlikely to be accurate reflections of natural surface water pH conditions and may be associated with inaccurate measurement or monitoring of nearby industrial processes or discharges. The mean pH observations from this dataset remain in the alkali range (pH 7.74).

On this basis it can be concluded that the frequency of occurrence of acidic surface waters in Southern Europe are overwhelmingly in the alkali range. There are circumstances where acidic pH conditions are encountered, but these are comparatively rare (on average *ca* 8% of minimum observations are in the acidic range). Where acidic conditions are encountered the majority are only slightly acidic.

Assessment

- In this survey no information regarding the lithology of the sampling places is given and its relationship with the crops proposed in the GAP.
- No information with regard to the pH in the sediment is given
- In the case of Portugal only 16 sets were analysed.
- The pH range varied widely and the pH value of the water sediment assessed in this addendum are included in them, and the possibility of this pH under field conditions cannot be rejected.

B 8.4 Exposure for Aquatic risk assessment.

In the monograph, the PEC in surface water for endosulfan were calculated according to BBA draft guide based on

- the maximum single application rates, the number of treatments and the intervals between for each crops.
- a buffer zone from 0 to 50 m
- A deep water medium of 30 cm and 1m
- DT50 of 15 days. This value was stimated as the high value of the total endosulfan concentrations ($\alpha+\beta$ endosulfan + endosulfan sulphate) in the water phase of two different sediment water system (Stumpf, 1990 A44231)

From the estimation of PECsw , RMS concluded that the highest 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 submitted by applicant, 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.

Regarding to the PECs in sediment, they cannot be estimated due to DT50 for parent was not submitted

In 2003 applicant submitted a higher tiered aquatic risk assessment, that was conducted via a detailed analysis of landscape in Spain (**C019471, C019472**, C019473). Also a refined risk assessment was submitted (C021321, C021146, C021344, **C021352**).
Based on the risk assessment for the use of endosulfan in cotton in Spain a scenario is proposed for Greece (C023003)
Finally, an aquatic risk assessment for use of endosulfan in tomato was also provided (C022617)

B 8.4.1 Estimation of PECsw via drift

B 8.4.1.1 Tier I

Study: Aquatic ecological risk assessment for endosulfan uses on cotton in Spain par 1: characterising risks associated with spray drift
Author: Neil Mackay
Dated: February 2002
Reference: C021321
GLP: N/A

The risk assessment presented in the report used a stepwise strategy . Within in the first tier risk assessment simplistic assumptions regarding fate and exposure were compared with conservative deterministic effect thresholds to all calculation of TER values as indices of risk. This was then superseded in Tier II through the introduction of a more sophisticated exposure assessment based on a detailed geographical analysis of one representative area of use of endosulfan on cotton in Spain.

This refined exposure assessment was then compared with deterministic ecotoxycological endpoints. to provide a risk profile for a number of highly relevant surface water bodies. A further refinement was introduced at Tier III in the form of a probabilistic effects assessment. The final risk assessment for aquatic organisms was performed by comparing the predictive percentiles of exposure and the sensitivity distribution.

According to the GAP, usage on cotton is based on an application rate of 0.84 Kg as/Ha with up to 3 applications per crop occurring in Mid-June to Mid-August in Greece and Spain with an application interval of 14-21 days.

A comparison of the interval between applications and the DT50 in water sediment described in the report suggested the negligible quantities of endosulfan would be expected to remain by the time of the next application . This suggested it was appropriate to base the first tier drift estimates upon single application drift rates.
Table 8.4.1.1-1 shows the notifier assumptions for the estimations of PEC sw in Tier I

Table 8.4.1.1-1 Notifier assumption for the estimations of PECsw in Tier I

	DT50 Report N A5100	max observed Report Nº A5100	drift values
endosulfan	0.58 (2)	negligible(3)	based upon single application drift values
total endosulfan residue (α+β endosulfan+ endosulfan sulphate)	15(1)	45% (4)	

<u>RMS assessment:</u>

(1) DT50 no valid for endosulfan sulphate.
(2) DT50 for endosulfan in the water is in the range of the values estimated in the studies assessed in this studies. However, due to the partitioning into sediment, the maximum half life found in the whole system water/sediment (sediment pH between 6 –7) was 34.7 days according to the RMS estimations.
(3) The maximum amount found in the water at 14 DAT was 7.5% TAR in the water/sediment assessed in the present addendum. The maximum amount of endosulfan observed in the sediment (sediment pH between 6 –7) in the studies assessed in this addendum was 66% (at 3 DAT).
(4) The percentage for endosulfan sulphate is in the range of the experimental results of the studies assessed in the present addendum.

Assessment: The calculation of PEC in surface water was made taking into account the previous version of SANCO/3268/2001. It had into account that the application rate was assumed to be the maximum season’s usage applied as a single dose, unless the **DT50 in water** for the compound is less than the interval between treatments. This assumption cannot be considered valid according to the results of the water/sediment studies assessed in the present addendum since up to 66.6% TAR has been observed in the sediment at a pH (sediment) 7.3 . Therefore, RMS has recalculated the PECsw and the initial PEC in sediment taking into account the following assumptions:

Table 8.4.1.1-2 Assumptions for the recalculation of PECsw

Application rate g/ha	840
Application/crop type	cotton
Number of application per season	3
Application interval (d)	14
Drift %	2.01
DT50 water/sediment (d)	34

The results for water are given in the table 8.4.1.1-3. **In the case of the sediment** maximum would be **28.1 μg/kg**, taking into account a bulk density of 0.8 g/cc a depth of 5 cm and a maximum of 66.6% observed in the water/sediment system at pH >5 .

Table 8.4.1.1-3 Actual and TWA PEC for endosulfan in surface water (μg/l) due to drift loading (3 applications, 14 days interval)

DAT	PEC	PECtwa
0	16.88400	16.88400
1	16.54328	16.71306
2	16.20943	16.54442
4	15.56181	16.21392
7	14.63857	15.73459
10	13.77010	15.27419
14	12.69176	14.68830
21	11.00386	13.73478
28	9.54044	12.86478
60	4.96874	9.74105
100	2.19833	7.20356
120	1.46223	6.30386
250	0.10328	3.29249
350	0.01345	2.36437
365	0.00990	2.26768

In the case of the metabolites, notifier only has estimated the PEC in surface water for the endosulfan sulphate as 81.4% of the maximum PEC of endosulfan, being the initial PEC of 6.53 μg/l. Taking into account a DT50 of 15 days and a minimum interval period between the applications of 14 days, 91.4% would be expected at 14 days after the third application.

However, no degradation was observed of endosulfan sulphate in the sediment and neither of endosulfan carboxylic acid in the water phase. Therefore, the following initial PEC were estimated by RMS taking into account the initial PEC (maximum amount) calculated for the parent in the water phase and in the sediment (Table 8.4.1.1-3) , the maximum observed in the water sediment studies for each metabolites and their molecular weight . The results are given in the table 8.4.1.1-4.

Table 8.4.1.1-4 Initial actual PEC for endosulfan metabolites in surface water (µg/l) and sediment (µg/kg) due to drift loading

PEC	water phase	sediment
endosulfan sulphate	<10 %	13.49300123
endosulfan diol	5.241003	10.34249809
endosulfan carboxylic acid	7.148493	<10 %
endosulfan lactone (1)	-	3.277553317
endosulfan hydroxyether (2)	-	2.478246663

(1) estimated taking into account 13.3% TAR

(2) estimated taking into account the maximum amount found in the whole system

B.8.4.1.2 Tier II Estimation of PECsw based on landscape analysis

B.8.4.1.2.1 Selection of scenarios for the risk assessment (drift and runoff) of endosulfan in the crops and conditions included in the intended uses.

Study: Site-Specific evaluation of realistic usage conditions for endosulfan in Greece, Spain and Portugal

Author: Neil Mackay

Dated: February 2002a

Reference: C021352

GLP: N/A

An assessment was conducted of regional data in order to evaluate agricultural suitability of specific sites that could potentially form the basis for a site-specific simulation scenario based on regional production statistics (where available), regional climate and regional soil and landscape characterisation. Upon selection of an appropriate site, more detailed information was obtained as follows:

- weather data
- soil lithology considerations
- soil characteristics
- irrigation
- associated water bodies

On the basis of this evaluation three scenarios were identified as providing an agriculture realistic basis for evaluating risk associated with usage of endosulfan:

- usage on cotton in Greece (“Thessaloniki” scenario)
- usage on cotton in Spain (”Sevilla” scenario)
- usage on tomatoes in Portugal (“Evora” scenario”).

In table 8.4.1.2.1-1 a summary of the description of each scenario is shown

Table 8.4.1.2.1-1 Sites summaries

Site	**GREECE**	**SPAIN**	**PORTUGAL**
crop	**cotton**	**cotton**	**tomatoes**

Site	**GREECE**	**SPAIN**	**PORTUGAL**
crop	**cotton**	**cotton**	**tomatoes**
Ann average precipitation	470 mm	564 mm	656 mm
elevation	7.4 m	10 m	309 m
pro file location	close to Péllа and Mikron Monastírion, situated ca 35-40 km to the northwest of Thessalonki	Casablanquilla	Evora
soil type	Agnic ustipsamment Sff02	Clacaric regosol	Typically orthic luvisols with associations of Eutric cambisols and Lithosols with inclusions of Chromic Luvisols
soil texture	sandy silt loam	sandy clay loam	sand
Lithology	Quaternary alluvium, Clayey and sandy tertiary sediment, marl, gneiss, amphibolites, quartzite, marble	Fluvial an marine alluvia	Shale, quartz diorite, granite, schist, porphyry, gneiss, conglomerate
Slope	0-8% Pélla<0.5%	2-8% Casablanquilla 2.0%	Hilly to sep topography
Soil pH	7.5	7.7	6.3
Soil organic carbon content	0.41%	0.95%	0.35%
Irrigation requirements	A significant deficit (average: 69.5 mm/y ca 15% of annual average precipitation) must be made up for by irrigation	A significant deficit (average: 55.0 mm/y ca 10% of annual average precipitation) must be made up for by irrigation	Avarege of 250 mm/y additional irrigation water (ca 38% of annual average precipitation) applied during simulated 20 y period
Irrigation method	Drip irrigation (10%) canon irrigation (70%) multi-splinker system (10%) flooding (10%)	Typically irrigation is applied through the furrows 10% via drip irrigation, canon irrigation, multi splinker system and flooding. Irrigation is typically carried out over 8 h at rate of 1000 m^3 /Ha	The most frequently used irrigation method (used over 90% farm units) is drip irrigation . In the remaining farms, flooding, sprinklers and pivot irrigation are used. When fruits are forming and especially in more freely draining soils irrigation may occur for up to 10 h/a. It is more common for irrigation to occur for ac 4 h/days
number of irrigation events	up to 6	up to 6	the frequency of irrigation used varies considerably due to wide differences in climate and soil characteristics
Irrigation timimg	1 plant emergence 2 plant development 3 plant development (1st and 2nd square) 4 Ball development 5 Ball development 6 Ball development	Starting on or about June 15 and the n again typically at 15 days intervals as required	The timing of irrigation used varies considerably due to wide difference in climate and soil characteristics
Treatment of excess of water	Discharge to irrigaton/drainage ditches	A 5% of the surplus irrigation water is discharged to surface water bodies or drain. it is typical for discharge water to be released to water bodies that are they themselves	In general, all of the irrigation water is taken up form soil and direct discharges to surface water are uncommon.

Site	GREECE	SPAIN	PORTUGAL
crop	**cotton**	**cotton**	**tomatoes**
		used to irrigate rice paddies further downstream.	
Drainage	well drained, deep natural drainage	well drained, water table not observed	NA
Runoff mitigation measures		Fields are typically bounded at the lower boundary with ditches to retain irrigation water	trenches are dug to retain any excess water and prevent accidental contamination of nearby natural water bodies.
Typical field size	ca 4-5 Ha	30-40 Ha	supposed to be 2 Ha
Water body description	Irrigation channels seasonal water bodies	Ditches seasonal water bodies	Ditches seasonal water bodies
Endosulfan application rate	0.84 kg/Ha (assuming 20-40% interception by foliage)	0.84 kg/Ha (assuming 50% interception by foliage)	0.53 Kg/Ha
number of applications of endosulfan	3	2	2
Application interval	14-21 d	14-21 d	7-14 d
Application timing	Mid-June to Mid Aug	Mid-June to Mid August	June-July

B.8.4.1.2.2 Detailed landscape characterisation for Seville Cotton-growing region. Mitigation factors to directional drift refinement and mitigation associated with interaction with vegetation

Study: Characterization and analysis of potential vulnerability of aquatic habits near agriculture Volume I: Sevilla Spain
Authors: Steve Kay
Year: 2001
Doc Nº C019473

Objectives: The main objectives of this study are to determine:

- how often is cotton within a certain distance of aquatic environments
- percentage of cotton within the study site potentially exposes water
- how often cotton crops are directly adjacent to water bodies
- the width (min, max, mean and 90th percentile) of the naturally occurring vegetative filter strips the composition of vegetative filter strips (VFS)

Based on these data, a probabilistic distribution of exposure concentrations in different classes of water bodies was determined for exposure via spray drift. Several relevant mitigation factors were considered, such as naturally occurring margin between the fields and the water bodies, natural vegetated filter strips and the effect of wind direction on spray deposition.

Study site: An evaluation of the major use areas of endosulfan in EU agriculture indicates that application to cotton and to a lesser tree crops are important. One key region in the southern EU where this mixture of crops is common in south-western Spain. Based on agricultural statistics for the region, the province of Seville accounted for over 65% of the cotton production in the andalusian plain of

Spain . Once the general study are was selected, the exact position of the study site was determined by the availability of suitable satellite imagery and detailed knowledge of local cropping patterns. The final study site encompasses approximately 350 000 Ha of land in the agricultural plains to the northeast of Seville

Material: The data sets used in this study are:

- Corine land cover (coarse resolution): used to help in the identification and placement of individual study sites that are areas of intense agriculture with a large degree of surface water. The selected site was studied in more detail using an acquired satellite image and other GIS data sets.
- Multi-spectral satellite Imagery (medium resolution 10 m to 20 m): was used to identified and examine the land cover interaction within the study site. The satellite image used for the classification was acquired on July 5, 200 by the SPOT –4 satellite using both the multi-spectral and panchromatic sensors. Since the imagery was acquired when agricultural vegetation was growing vigorously, different crop types were separated spectrally with little difficulty.
- Aerial imagery (Fine resolution (0.25 m^2): 0.25 m ground resolution aerial images were acquired for selected sub areas of the study site and known to have a close proximity between agriculture and water. The resolution of theses image permitted detailed quantification of the presence, width, and composition of buffer between agriculture and water bodies, as well as, improved identification of smaller land cover groups, such as cluster tree.
- topographic maps: 1:50 000 scale topographic maps acquired from the national Geographical Institute (ING) were used to geo reference the satellite and aerial images, to generate digital hydrology information, and as general reference material during the satellite image classification stage. Information for all static and flowing water bodies were digitised from the maps and placed into the GIS for processing and analysis.

Methodology: After the geo-referencing process the medium resolution imagery, a classification process was made to identify the actual land cover types. To do it a ground –truthing process was followed (see studies coded as C019471 and C019472) . It consists in identify the land cover types of a small subset of pixels and then extrapolate these known regions to the rest of the image. Data collected during the process were recorded on paper maps generated form the geo referenced satellite imagery. Ten ground truth maps were create, each encompassing apporx 32 Km^2 and distributed across the entire satellite image to capture the diversity of the land covers within the imagery.

The image classification process assigns each pixel within the satellite imagery to pre-defined land cover classes. The first step uses statistical clustering algorithms to group pixels that are spectrally similar, and in the second step the ground truth information is used to assign those groups to the appropriate land cover class. The overall classification accuracy was 87% . Figure 8.4.1.2.1-1 shows the final medium resolution land cover classification. A total of 21,401 Ha of cotton were identified (19% of the total national production area for Spain , representing 6.1% of the total classified land coverage and 7.5 % of the total agricultural land coverage. A summary is provided in table 8.4.1.2.1-1

Figure 8.4.1.2.1-1 Final Medium-resolution land cover classification

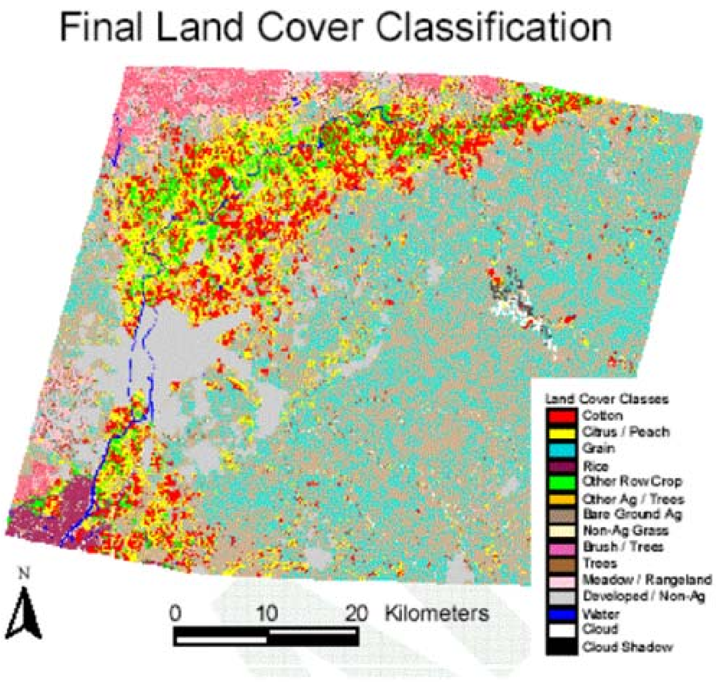


Table 8.4.1.2.1-1 Land cover area statistics for Spanish assessment region

Description	**Area (ha)**	**Class (%)**
Water	2,352	0.5%
Trees	4,871	1.4%
Trees/Brush	9,121	2.6%
Meadow/Rangeland	13,118	3.8%
Non-Agricultural Grass	2,283	0.7%
Developed/Urban	30,220	8.7%
Clouds	703	0.2%
Shadow	531	0.2%
Non-Agricultural Classes Sub-Total	***63,198***	***18.1%***
Cotton	21,401	6.1%
Other irrigated crops	12,872	3.7%
Citrus/Peach	31,543	9.1%
Other Tree Crops	641	0.2%
Rice	5,234	1.5%
Grains/Sunflowers	84,946	24.4%
Fallow/Bareground Agriculture	128,455	36.9%
Agricultural Classes Sub-Total	285,092	81.9%
Total	348,289	100.0%

The medium resolution image analyses provide an extremely large sample population of water bodies (see table 8.4.1.2.1-2) . Mainly, four water bodies types were identified and characterised on basis of digitised hydrology mapping. These are:.

- ponds
- rivers
- streams
- canals

But they are limited by the spatial resolution of the source image . Thus, For the spatial location, physical characteristics of surface water and their interactions between agriculture and specific water bodies in the study, a higher resolution digital data was used since the medium resolution imagery pixel size (10 m) was longer than the width of the flowing water bodies considered for the aquatic risk assessment (< 5m).

These water bodies were selected form the overall set of water bodies in a stratified-random sampling process designed to ensure statistically significant sampling of each water body class. Therefore, the results of these refinement resolution analyses (performed on a subset of the medium resolution water bodies) can be extrapolated to all bodies included in the medium resolution analysis.

60 aerial photographs were selected to obtain a sample size large enough to provide 95% confidence that buffer width measurements from the approx 0.25 m resolution imagery are within ± 1 m of actual. A summary of the water bodies that were intensely characterised from the aerial photographs is provided in table 8.4.1.2.1-3

Table 8.4.1.2.1-2 Water Body Summary by Class and Size (form medium resolution imagery)

Water Body	**Count**	**Length**	**Percentage of Total**
Ponds < 1 ha	246	71,989	1.6
Ponds 1-5 ha	75	65,539	1.5
Ponds >5 ha	15	50,083	1.8
Ponds Sub-Total	***336***	***187,611***	***4.2***
Rivers	16	294,170	6.5
Rivers Sub-Total	***16***	***294,170***	***6.5***
Intermittent Streams	2050	2,182,365	48.4
Permanent Streams	251	286,264	6.3
Stream Sub-Total	***2301***	***2,468,629***	***54.7***
Canals <2 m	1896	1,327,607	29.4
Canals 2-4 m	83	92,708	2.1
Canals >4 m	94	140,088	3.1
Canals Sub-Total	***2073***	***1,560,403***	***34.6***
TOTAL	**4726**	**4,510,813**	**100**

Table 8.4.1.2.1-3 Distribution of water bodies characterised from aerial photographs (detailed resolution)

Water Body	**Segment* Count**	**Percentage of Total**
Canals <2 m wide	1979	19.5
Canals 2-4 m wide	732	7.2
Canals >4 m wide	336	3.3
Canals Sub-Total	***3047***	***30.0***
Streams <2 m wide	1139	11.2
Streams >2 m wide	661	6.5

Water Body	**Segment* Count**	**Percentage of Total**
Stream Sub-Total	***1800***	***17.7***
Rivers	119	1.2
Rivers Sub-Total	***119***	***1.2***
Ditches	5101	50.2
Ditches Sub-Total	***5101***	***50.2***
Ponds < 1 ha area	33	0.32
Ponds 1-5 ha area	59	0.58
Ponds Sub-Total	***92***	***0.91***
TOTAL	**10,159**	**100**

* Segment lengths are 10 m

Interpretation of detailed aerial photography allowed for the characterisation of the naturally existing margins between agriculture and surface water. The margin analysis was designed to examine the land cover composition within five specific margin distances of surface water in order to assess the potential risk of exposure to aquatic environments from endosulfan applications to target crops. Within the study site, the areas (margins) around both surface water and crop were examined to quantify the proportion of target crop in close proximity to water , and the proportion of surface water in close proximity to target crop. Margins were generated at five distances (10, 20, 30, 50 and 100 m) around both water bodies and target crops from the land cover data derived from the medium resolution imagery. Table 8.4.1.2.1-4a shows selected percentile values for naturally existing margin width for each water body class analysed. For example, 90% of streams in the 2-4 m size class have naturally occurring buffers that are at least 7 m wide. A second way of seeing this information is presented in table 8.4.1.2.1-4b where key buffer widths between 5-10 m are listed with their percentile rankings. In table 8.4.1.2.1-4c Percent of Margin area composed of cotton is shown

Table 8.4.1.2.1-4a Selected Percentile Values from the Distribution of Natural Margin Widths for All Water Bodies by Water Body Type and Size Class

Water Body	**Segment Count**	**Natural Margin Width (m)**				
		50th	**75th**	**90th**	**95th**	**99th**
Canals <2 m	1979	6	5	2	1	0
Canals 2-4 m	732	8	7	5	2	1
Canals >4 m	336	16	12	7	2	1
Canals Sub-Total	***3047***					
Streams <2 m	1139	9	8	6	4	0
Streams >2 m	661	13	11	7	5	0
Stream Sub-Total	***1800***					
Rivers	119	23	15	8	6	1
Rivers Sub-Total	***119***					
Ditches	5101	6	5	3	2	0
Ditches Sub-Total	***5101***					
Ponds < 1 ha	33	12	9	8	7	6
Ponds 1-5 ha	59	18	11	10	8	7
Ponds Sub-Total	***92***					
TOTAL	**10,159**					

Table 8.4.1.2.1-4b Percentile values for buffer widths between 5-10 m for all water bodies by water body type and size class

Water bodies	**Canals**			**Streams**		**Rivers**	**Ditches**	**Ponds**	
Size Class	**< 2 m**	**2 – 5 m**	**> 5 m**	**<2 m**	**2 – 4 m**	**All**	**All**	**<1 ha**	**1-5 ha**
Segment Count	**1979**	**732**	**336**	**1139**	**661**	**119**	**5101**	**33**	**59**
Margin Width (m)									
5	75	90	95	93	95	98	75	99	99
6	50	86	94	90	92	95	50	99	99
7	39	75	90	87	90	95	42	95	99
8	26	50	87	75	84	92	36	90	95
9	21	38	81	50	75	89	31	75	93
10	13	27	76	43	64	88	26	66	90

Table 8.4.1.2.1-4c Percent of Margin area composed of cotton is shown

Class	margin	% composed of cotton
Streams	10	5
	20	1
	30	1
	50	2
	100	3
Rivers	10	1
	20	1
	30	2
	50	4
	100	13
Canals	10	19
	20	6
	30	4
	50	6
	100	11
Ponds	10	1
	20	1
	30	1
	50	3
	100	6

All of the buffer delineated through this process were analysed for composition with the results presented in table 8.4.1.2.1-5 below. For example 53% of the area separating cropland from stream <2 m wide is composed of dense brush.

Table 8.4.1.2.1-5 .- Percent Composition of Margins for all Water Bodies by Water Body Type and Size Class

Water Body	**Segment Count**	**Dense Trees**	**Sparse Trees**	**Dense Brush**	**Sparse Brush**	**Grass or Bare**
Canals <2 m	1979	0%	0%	64%	29%	7%
Canals 2-4 m	732	0%	1%	76%	8%	15%
Canals >4 m	336	1%	3%	32%	36%	28%
Canals Sub-Total	***3047***					
Streams <2 m	1139	1%	2%	53%	30%	14%
Streams >2 m	661	2%	7%	44%	28%	19%
Stream Sub-Total	***1800***					
Rivers	119	5%	14%	38%	22%	21%
Rivers Sub-Total	***119***					
Ditches	5101	0%	2%	77%	8%	13%
Ditches Sub-Total	***5101***					
Ponds < 1 ha	33	0%	0%	0%	16%	84%
Ponds 1-5 ha	59	0%	0%	3%	21%	76%
Ponds Sub-Total	***92***					
TOTAL	**10,159**					

The drift exposure analysis was designed to account for the spatial relationships (direction and distance) between the target crop and the water body and is called the directional method. Sample points were placed on the perimeter of each water body and from these points lines extended in each of the 8 primary compass directions (N, NE, E, SE, S, SW, W and NW). These lines were then examined for the presence of crop with the distance to the first occurrence of crop recorded an d an appropriate drift value determined based on distance for that direction. The study area contained both flowing and static water bodies. The aquatic concentration arising from drift onto a flow water body will change in time depending upon the flow rate. For simplicity it was assumed that all flow water bodies had a zero flow rate . In practice, different fields will be sprayed at different times according to type of crop and the necessity of providing crop protection. To simplify the calculations, it was assumed that all arable cropland in the study area were sprayed at the same time.

The following summary outlines the strategy employed within the higher-tier exposure assessment. The maximum potential drift deposition is based upon the Ganzelmeier drift rate for direct adjacency. This provides as Concentration Limit (CL) for a given water body segment. The relationship between crop and surface waters (distance and direction) provides a means of modifying the Concentration Limit.

A drift deposition estimate less than the maximum based upon direct adjacency will result if either only a proportion of the water body is exposed to spray drift, or if crop is not directly adjacent to the water body. The Directional Method uses two ratios called the *Affected Ratio* and *Drift Ratio* to estimate these two factors. The *Affected Ratio* estimates the proportion of the water body that experiences spray drift, the *Drift Ratio* estimates the proportion of drift onto the water body in relation to the maximum. The way in which these ratios are calculated is detailed below:

To establish a spatial link between the water body surrounding crop and wind direction, each water body had a number of sampling points placed at regular intervals on the water body perimeter. The high resolution dataset had points placed at 5 m intervals on the perimeter of all water bodies. Each sample point was taken to represent a specific length of perimeter (i.e., if sample points were separated by 10 m intervals then each point represented 10m of water body perimeter and it was assumed that drift calculated at that point was the same over the 10 m).

Once points had been placed, a 50m line was drawn against the direction of the wind as shown in Figure 8.4.1.2.1-2. Lines that crossed the water body (identified by a unique water body ID) were disregarded because exposure would be accounted for by points elsewhere on the perimeter. The number of points that could potentially expose the water body were then counted, this number was called NPE. For example, in Figure 8.4.1.2.1-2, there are 41 points on the water body perimeter but only 13 could cause exposure when the wind is in the direction shown. The number of segments that could actually expose the water body (because the line intersected crop somewhere along its 50m length) were counted and this number was called NAE (NAE = 9 in Figure 8.4.1.2-2). The Affected Ratio is given by the ratio of NAE to NPE . For the water body in Figure 8.4.1.2-2 the Affected Ratio is 9/13 or about 0.7, indicating that approximately 70% of the water body experiences drift.

Each line segment was then examined to measure the distance between the water body and the nearest crop. For example in Figure 8.4.1.2-2, say that the distance between the water body and crop for each of the points NAE were as shown in Table 8.4.1.2.1-6 . If the water body is 10m wide, then the corresponding width integrated or Width Averaged Drift (WAD) would be as shown in Table 8.4.1.2.1-6, resulting in a total WAD of 2.54% and an average WAD of 0.28%. If the crop was directly adjacent to the water body for all points (NAE), then the average WAD would be 0.81% i.e. the value for direct adjacency averaged over 10 m. The Drift Ratio for this water body, with the wind in this direction, is given by 0.28/0.81 or 0.35 i.e. the portion of the water body that does receive drift receives 35% of the maximum. The Affected Ratio and Drift Ratio are then multiplied by the Concentration Limit (Max PEC) based upon direct adjacency to give provide the PEC for that water body segment and wind direction.

PEC = Max PEC * Affected Ratio * Drift Ratio

For the water body in Figure 2 this would be:

PEC = Max PEC * 0.70* 0.35 = 20 * 0.25= 5.00 ng/l

Being the max PEC:

$$PEC(g/l) = \frac{AveDrift\% * Apprate\ (g/ha) * SurfaceArea\ (Ha)}{SurfaceArea\ (Ha) * 10000\ (m^2/Ha) * depth\ (m) * 1000\ (l/m^3)}$$

In order to calculate drift at any distance from an application area, an analytical function of drift versus distance was required. Ganzelmeier data were fitted to a power law function (drift=A*(distance)^b). The best fit line was obtained from the following function: Drift%= 4* distance$^{-1.142}$

Therefore Average drift between the point A and the point B is given by the integration of the function:

$$Drift\% = \frac{28.2 * \left[A^{-0.142} - B^{-0.142}\right]}{B - A}$$

To calculate the average drift onto the water body the total drift must be divided by the water body width

Figure 8.4.1.2.1-2.- Line Segments Drawn for a Water Body for a Single Wind Direction

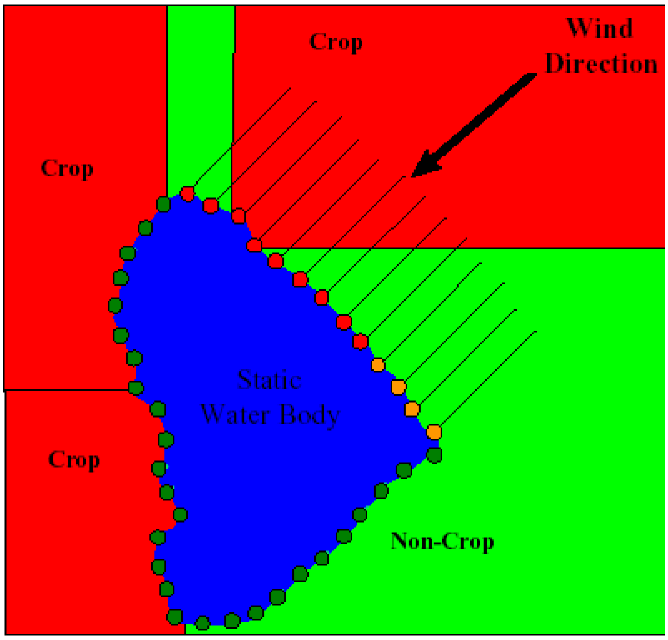


Table 8.4.1.2.1-6 Distances and drift for 10m wide water body shown in Figure 8.4.1.2.1-2

Distance at point from water body to crop (m)	Interval for width average drift (m)	Width averaged drift (%)
20	20-30	0.10
10	10-20	0.18
0	1-11	0.81
0	1-11	0.81
5	5-15	0.28
12	12-22	0.15
22	22-32	0.09
30	30-40	0.07
38	38-48	0.05
	TOTAL	**2.54**
	AVERAGE	**0.28**

The width of the water body is required to calculate the average drift across the water body. Flowing water body widths were determined by grouping into width classes during the hydrology processing phase. To estimate the widths of ponds, an assumption was made that all ponds were square-shaped and the width of the pond was determine by the square root of its surface area.

No depth information was available during the hydrology processing phase, so depth assumption had to be made to estimate exposure. Depth assumptions are collected in table 8.4.1.2.1-7.

Table 8.4.1.2.1-7 The width and depth assumptions used in the spray drift analysis

Water body class	water body size (m)	Nominal characteristics	
		Width (m)	Depth (m)
Canals	<2	1	0.3
	2-5	2	0.5
	>5	10	1.00
Streams	<2	1	0.5
	2-4	2	0.5
Rivers	All	10	1.00
	> 12m	12	0.3
Ditches	All	1	0.3
Ponds	All	$\sqrt{area}$	1.00

Results: PEC were calculated for every water body in the study area the fine resolution dataset (10159 water bodies samples). Results were summarized by ranking the PEC in order of increasing concentration and calculating percentiles. Percentiles 50th 75th 90th 95th 99th levels were reported. This was performed utilizing the eight no-spray zones (0, 5, 6,7, 8, 9, 10, 15 and 20 meters). The set of PECs for all water bodies was then broken down into results for different water body classes. Percentiles for PEC corresponding to each non spray zone were then calculated as above. The water body classes were then subdivided into a number of width categories and the resulting percentiles calculated for each these categories.

The directional method examines for the presence of crop within the 40 m in eight directions from each water body. Whereas each water body is examined in all eight directions an eight direction average is used for reporting purposes. It is important to note that the eight direction average is calculated for each water body and this value is input into a distribution from which the percentiles appearing in the table are derived. The results are shown in table 8.4.1.2.1-8.

- In addition to the standard results computed as described above, PECs were computed by taking into account the potential mitigation of intervening buffer vegetation on spray drift.

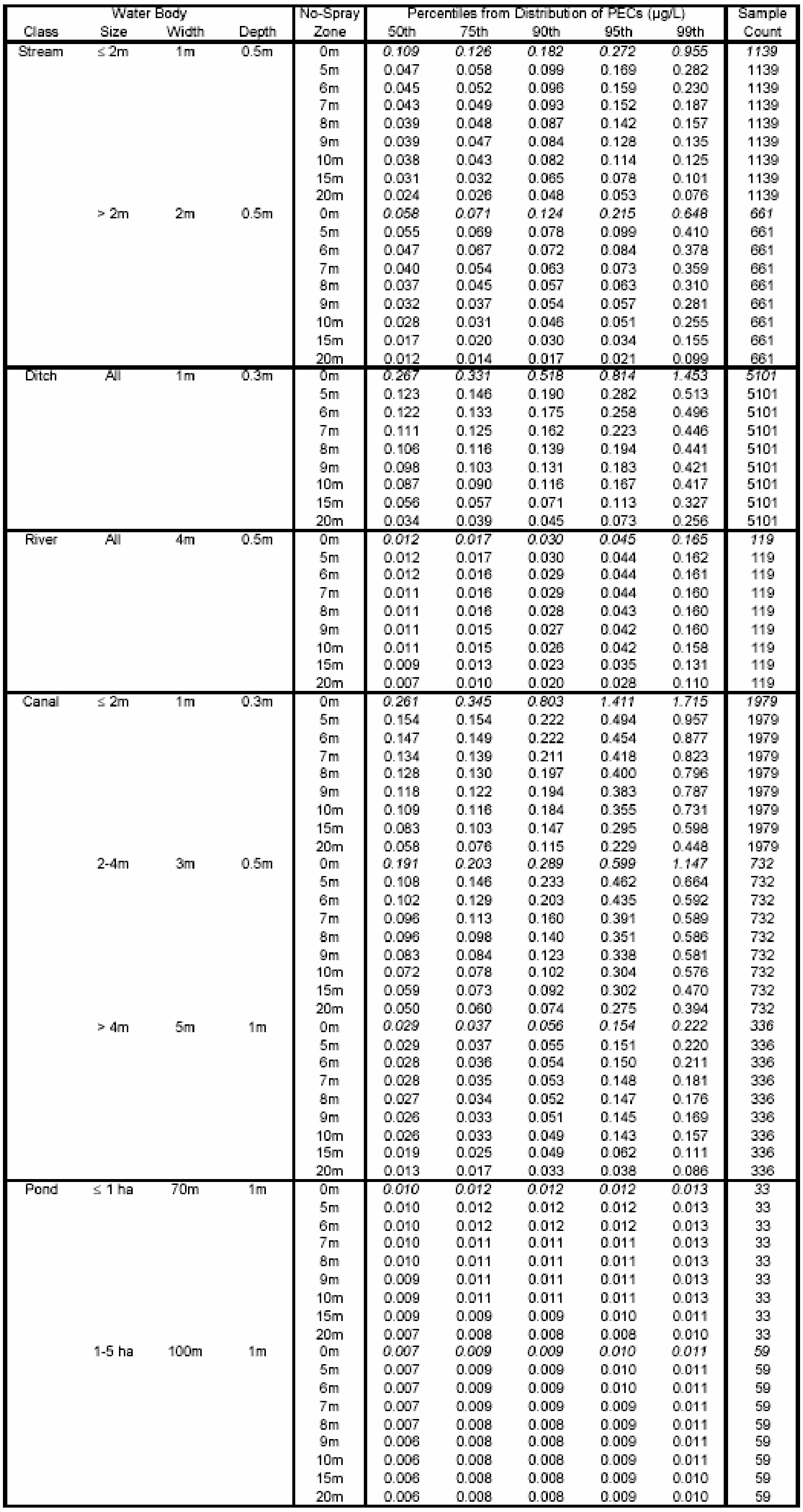
The mitigation afforded by a margin comprised of grass and wild flower mixture with a base canopy height of 700 mm with elements extending to 1300 mm high was on the order of 60 – 85% relative to drift observed with a 150 mm mown grass margin (Miller *et al.*, 2000). It is likely that dense brush such would be characterised by minimum mitigation efficiencies on the order of >85%. The sparse forms, with less density and height, but greater porosity are likely to be characterised by minimum mitigation efficiencies on the order of >60%. Mitigation factors also need to be estimated for sparse and dense trees. Evidence from windbreak studies conducted as a component of the research exercise commissioned by UK MAFF on behalf of UK PSD may provide useful benchmarks. Studies conducted with dense structures of alder (Alnus sp.) were characterised by mitigation efficiencies of ca 75% (Miller, pers. comm.). Sparse tree structures will provide less effective mitigation of drift, but this is largely dependent upon canopy height, leaf structure etc… It is suggested that a mitigation efficiency relative to the observations with tall grasses (already discussed) and Alder of ca 50% may be justified. Since it was not possible to estimate the height and, therefore, effectiveness of grass surfaces they have simply been grouped with bare surfaces and have been assumed, conservatively, to offer no drift mitigation.

Taking all this into account, the drift mitigation efficiencies used in the analysis were:

- Dense trees: 75%
- Sparse trees: 50%
- Dense brush: 85%
- Sparse
- Brush: 65%
- Grass and/or bare: 0%

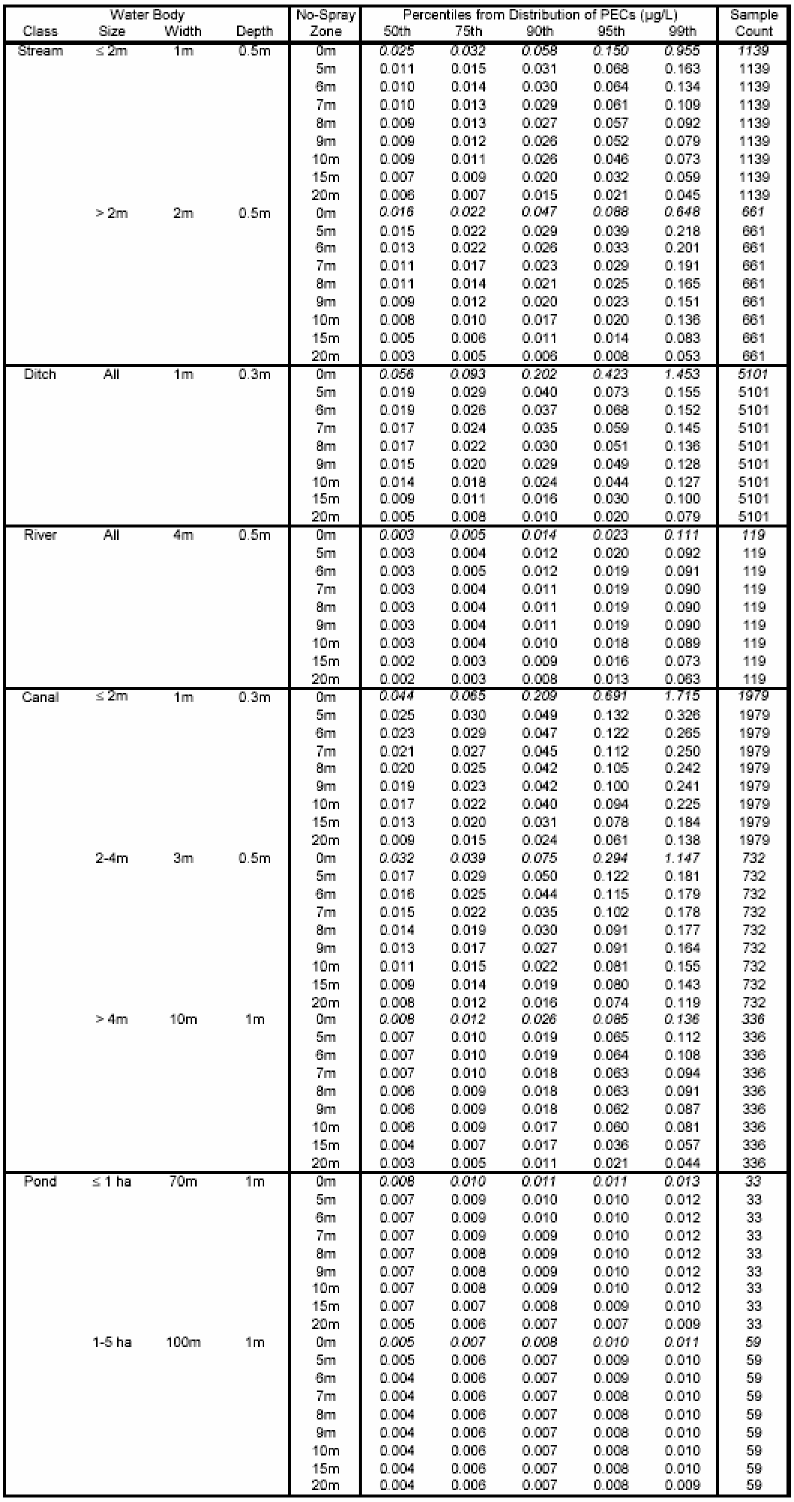
A land cover was considered dense if the canopy closure was complete or nearly so, otherwise the land cover was considered sparse. The % reduction in spray drift was applied for each meter land cover that the directional drift analysis indicated existed between the crop and water. For example, if the directional line being analysed passed through one meter of dense brush, one meter of sparse brush and 3 meters of grass, the spray drift would be reduced 65% for the sparse brush and then reduced a further 85% for the dense brush before being integrated across the width of the water body. The results of the spray drift analysis incorporating the mitigating effects of intervening vegetation are presented in table 8.4.1.2.1-9.

Table 8.4.1.2.1-8 Selected Percentile Values from the Distribution of PECs for All Water Bodies from the Directional Drift Method Averaged over 8 Wind Directions



Water Body				No-Spray	Percentiles from Distribution of PECs (µg/L)					Sample
Class	Size	Width	Depth	Zone	50th	75th	90th	95th	99th	Count
Stream	≤ 2m	1m	0.5m	0m	*0.109*	*0.126*	*0.182*	*0.272*	*0.955*	*1139*
				5m	0.047	0.058	0.099	0.169	0.282	1139
				6m	0.045	0.052	0.098	0.159	0.230	1139
				7m	0.043	0.049	0.093	0.152	0.187	1139
				8m	0.039	0.048	0.087	0.142	0.157	1139
				9m	0.039	0.047	0.084	0.128	0.135	1139
				10m	0.038	0.043	0.082	0.114	0.125	1139
				15m	0.031	0.032	0.065	0.078	0.101	1139
				20m	0.024	0.026	0.048	0.053	0.076	1139
	> 2m	2m	0.5m	0m	*0.058*	*0.071*	*0.124*	*0.215*	*0.648*	*661*
				5m	0.055	0.069	0.078	0.099	0.410	661
				6m	0.047	0.067	0.072	0.084	0.378	661
				7m	0.040	0.054	0.063	0.073	0.359	661
				8m	0.037	0.045	0.057	0.063	0.310	661
				9m	0.032	0.037	0.054	0.057	0.281	661
				10m	0.028	0.031	0.046	0.051	0.255	661
				15m	0.017	0.020	0.030	0.034	0.155	661
				20m	0.012	0.014	0.017	0.021	0.099	661
Ditch	All	1m	0.3m	0m	*0.267*	*0.331*	*0.518*	*0.814*	*1.453*	*5101*
				5m	0.123	0.146	0.190	0.282	0.513	5101
				6m	0.122	0.133	0.175	0.258	0.496	5101
				7m	0.111	0.125	0.162	0.223	0.446	5101
				8m	0.106	0.116	0.139	0.194	0.441	5101
				9m	0.098	0.103	0.131	0.183	0.421	5101
				10m	0.087	0.090	0.116	0.167	0.417	5101
				15m	0.056	0.057	0.071	0.113	0.327	5101
				20m	0.034	0.039	0.045	0.073	0.256	5101
River	All	4m	0.5m	0m	*0.012*	*0.017*	*0.030*	*0.045*	*0.165*	*119*
				5m	0.012	0.017	0.030	0.044	0.162	119
				6m	0.012	0.016	0.029	0.044	0.161	119
				7m	0.011	0.016	0.029	0.044	0.160	119
				8m	0.011	0.016	0.028	0.043	0.160	119
				9m	0.011	0.015	0.027	0.042	0.160	119
				10m	0.011	0.015	0.026	0.042	0.158	119
				15m	0.009	0.013	0.023	0.035	0.131	119
				20m	0.007	0.010	0.020	0.028	0.110	119
Canal	≤ 2m	1m	0.3m	0m	*0.261*	*0.345*	*0.803*	*1.411*	*1.715*	*1979*
				5m	0.154	0.154	0.222	0.494	0.957	1979
				6m	0.147	0.149	0.222	0.454	0.877	1979
				7m	0.134	0.139	0.211	0.418	0.823	1979
				8m	0.128	0.130	0.197	0.400	0.796	1979
				9m	0.118	0.122	0.194	0.383	0.787	1979
				10m	0.109	0.116	0.184	0.355	0.731	1979
				15m	0.083	0.103	0.147	0.295	0.598	1979
				20m	0.058	0.076	0.115	0.229	0.448	1979
	2-4m	3m	0.5m	0m	*0.191*	*0.203*	*0.289*	*0.599*	*1.147*	*732*
				5m	0.108	0.146	0.233	0.462	0.664	732
				6m	0.102	0.129	0.203	0.435	0.592	732
				7m	0.096	0.113	0.160	0.391	0.589	732
				8m	0.096	0.098	0.140	0.351	0.586	732
				9m	0.083	0.084	0.123	0.338	0.581	732
				10m	0.072	0.078	0.102	0.304	0.576	732
				15m	0.059	0.073	0.092	0.302	0.470	732
				20m	0.050	0.060	0.074	0.275	0.394	732
	> 4m	5m	1m	0m	*0.029*	*0.037*	*0.056*	*0.154*	*0.222*	*336*
				5m	0.029	0.037	0.055	0.151	0.220	336
				6m	0.028	0.036	0.054	0.150	0.211	336
				7m	0.028	0.035	0.053	0.148	0.181	336
				8m	0.027	0.034	0.052	0.147	0.176	336
				9m	0.026	0.033	0.051	0.145	0.169	336
				10m	0.026	0.033	0.049	0.143	0.157	336
				15m	0.019	0.025	0.049	0.062	0.111	336
				20m	0.013	0.017	0.033	0.038	0.086	336
Pond	≤ 1 ha	70m	1m	0m	*0.010*	*0.012*	*0.012*	*0.012*	*0.013*	*33*
				5m	0.010	0.012	0.012	0.012	0.013	33
				6m	0.010	0.012	0.012	0.012	0.013	33
				7m	0.010	0.011	0.011	0.011	0.013	33
				8m	0.010	0.011	0.011	0.011	0.013	33
				9m	0.009	0.011	0.011	0.011	0.013	33
				10m	0.009	0.011	0.011	0.011	0.013	33
				15m	0.009	0.009	0.009	0.010	0.011	33
				20m	0.007	0.008	0.008	0.008	0.010	33
	1-5 ha	100m	1m	0m	*0.007*	*0.009*	*0.009*	*0.010*	*0.011*	*59*
				5m	0.007	0.009	0.009	0.010	0.011	59
				6m	0.007	0.009	0.009	0.010	0.011	59
				7m	0.007	0.009	0.009	0.009	0.011	59
				8m	0.007	0.008	0.008	0.009	0.011	59
				9m	0.006	0.008	0.008	0.009	0.011	59
				10m	0.006	0.008	0.008	0.009	0.011	59
				15m	0.006	0.008	0.008	0.009	0.010	59
				20m	0.006	0.008	0.008	0.009	0.010	59

Table 8.4.1.2.1-9 Selected Percentile Values from the Distribution of PECs for All Water Bodies using the Directional Drift Method Averaged over 8 Wind Directions and Accounting for Mitigation by Naturally Occurring Vegetation



Water Body				No-Spray	Percentiles from Distribution of PECs (µg/L)					Sample
Class	Size	Width	Depth	Zone	50th	75th	90th	95th	99th	Count
Stream	≤ 2m	1m	0.5m	0m	*0.025*	*0.032*	*0.058*	*0.150*	*0.955*	*1139*
				5m	0.011	0.015	0.031	0.068	0.163	1139
				6m	0.010	0.014	0.030	0.064	0.134	1139
				7m	0.010	0.013	0.029	0.061	0.109	1139
				8m	0.009	0.013	0.027	0.057	0.092	1139
				9m	0.009	0.012	0.026	0.052	0.079	1139
				10m	0.009	0.011	0.026	0.046	0.073	1139
				15m	0.007	0.009	0.020	0.032	0.059	1139
				20m	0.006	0.007	0.015	0.021	0.045	1139
	> 2m	2m	0.5m	0m	*0.016*	*0.022*	*0.047*	*0.088*	*0.648*	*661*
				5m	0.015	0.022	0.029	0.039	0.218	661
				6m	0.013	0.022	0.026	0.033	0.201	661
				7m	0.011	0.017	0.023	0.029	0.191	661
				8m	0.011	0.014	0.021	0.025	0.165	661
				9m	0.009	0.012	0.020	0.023	0.151	661
				10m	0.008	0.010	0.017	0.020	0.136	661
				15m	0.005	0.006	0.011	0.014	0.083	661
				20m	0.003	0.005	0.006	0.008	0.053	661
Ditch	All	1m	0.3m	0m	*0.056*	*0.093*	*0.202*	*0.423*	*1.453*	*5101*
				5m	0.019	0.029	0.040	0.073	0.155	5101
				6m	0.019	0.026	0.037	0.068	0.152	5101
				7m	0.017	0.024	0.035	0.059	0.145	5101
				8m	0.017	0.022	0.030	0.051	0.136	5101
				9m	0.015	0.020	0.029	0.049	0.128	5101
				10m	0.014	0.018	0.024	0.044	0.127	5101
				15m	0.009	0.011	0.016	0.030	0.100	5101
				20m	0.005	0.008	0.010	0.020	0.079	5101
River	All	4m	0.5m	0m	*0.003*	*0.005*	*0.014*	*0.023*	*0.111*	*119*
				5m	0.003	0.004	0.012	0.020	0.092	119
				6m	0.003	0.005	0.012	0.019	0.091	119
				7m	0.003	0.004	0.011	0.019	0.090	119
				8m	0.003	0.004	0.011	0.019	0.090	119
				9m	0.003	0.004	0.011	0.019	0.090	119
				10m	0.003	0.004	0.010	0.018	0.089	119
				15m	0.002	0.003	0.009	0.016	0.073	119
				20m	0.002	0.003	0.008	0.013	0.063	119
Canal	≤ 2m	1m	0.3m	0m	*0.044*	*0.065*	*0.209*	*0.691*	*1.715*	*1979*
				5m	0.025	0.030	0.049	0.132	0.326	1979
				6m	0.023	0.029	0.047	0.122	0.265	1979
				7m	0.021	0.027	0.045	0.112	0.250	1979
				8m	0.020	0.025	0.042	0.105	0.242	1979
				9m	0.019	0.023	0.042	0.100	0.241	1979
				10m	0.017	0.022	0.040	0.094	0.225	1979
				15m	0.013	0.020	0.031	0.078	0.184	1979
				20m	0.009	0.015	0.024	0.061	0.138	1979
	2-4m	3m	0.5m	0m	*0.032*	*0.039*	*0.075*	*0.294*	*1.147*	*732*
				5m	0.017	0.029	0.050	0.122	0.181	732
				6m	0.016	0.025	0.044	0.115	0.179	732
				7m	0.015	0.022	0.035	0.102	0.178	732
				8m	0.014	0.019	0.030	0.091	0.177	732
				9m	0.013	0.017	0.027	0.091	0.164	732
				10m	0.011	0.015	0.022	0.081	0.155	732
				15m	0.009	0.014	0.019	0.080	0.143	732
				20m	0.008	0.012	0.016	0.074	0.119	732
	> 4m	10m	1m	0m	*0.008*	*0.012*	*0.026*	*0.085*	*0.136*	*336*
				5m	0.007	0.010	0.019	0.065	0.112	336
				6m	0.007	0.010	0.019	0.064	0.108	336
				7m	0.007	0.010	0.018	0.063	0.094	336
				8m	0.006	0.009	0.018	0.063	0.091	336
				9m	0.006	0.009	0.018	0.062	0.087	336
				10m	0.006	0.009	0.017	0.060	0.081	336
				15m	0.004	0.007	0.017	0.036	0.057	336
				20m	0.003	0.005	0.011	0.021	0.044	336
Pond	≤ 1 ha	70m	1m	0m	*0.008*	*0.010*	*0.011*	*0.011*	*0.013*	*33*
				5m	0.007	0.009	0.010	0.010	0.012	33
				6m	0.007	0.009	0.010	0.010	0.012	33
				7m	0.007	0.009	0.009	0.010	0.012	33
				8m	0.007	0.008	0.009	0.010	0.012	33
				9m	0.007	0.008	0.009	0.010	0.012	33
				10m	0.007	0.008	0.009	0.010	0.012	33
				15m	0.007	0.007	0.008	0.009	0.010	33
				20m	0.005	0.006	0.007	0.007	0.009	33
	1-5 ha	100m	1m	0m	*0.005*	*0.007*	*0.008*	*0.010*	*0.011*	*59*
				5m	0.005	0.006	0.007	0.009	0.010	59
				6m	0.004	0.006	0.007	0.009	0.010	59
				7m	0.004	0.006	0.007	0.008	0.010	59
				8m	0.004	0.006	0.007	0.008	0.010	59
				9m	0.004	0.006	0.007	0.008	0.010	59
				10m	0.004	0.006	0.007	0.008	0.010	59
				15m	0.004	0.006	0.007	0.008	0.010	59
				20m	0.004	0.006	0.007	0.008	0.009	59

Assessment: The design of the study is considered so suitable and valid by RMS. However, the PEC values submitted must be carefully taken into account . Thus it seems that only an application has been considered in the estimations whereas three applications are considered in the GAP for cotton. As it was said in the tier I exposure assessment, it cannot be considered valid to estimate the PEC values based on a single application based on the experimental results of the water sediment studies evaluated in this addendum, in which up to 66.6% TAR has been observed in the sediment at a pH (sediment) 7.3. Therefore, the values shown in tables 8.4.1.2.1-8 and 8.4.1.2.1-9 should be multiple by 3 for the risk assessment, considering it as an worst case since dissipation of endosulfan is not supposed. It was observed that the percentiles of drift values are based on Ganzelmeier 1995 and not in Rautmann 2001, who provides drift values up to 50 m. No information regarding to the PEC in the sediment was provided when in the water sediment studies up to 66.6 % TAR was identified as endosulfan in the sediment at pH (sediment) = 7.3

Finally, no information regarding to the PEC estimation for endosulfan metabolites was given in the report.

In the report coded as C021321 Tier II assessment is made in two steps:

1.- an initial assessment taking into account naturally existing margin as mitigation

2.- A more complex assessment taking into account wind direction and the role vegetative filter strip mitigating drift. The assessment made above concerns to this last step.

As well as in the step II, it seems that only an application has been considered in the estimations for step I. Only PEC estimation was made for endosulfan sulphate but no information was given with regard to the other relevant metabolites found in the water sediment studies as endosulfan diol or endosulfan carboxylic acid . No information is given regarding to the PEC in the sediment for endosulfan and its metabolites. On the other hand, estimations of PECsw for endosulfan sulphate is provided estimated as 84.1% of the comparable values for endosulfan. But the amounts found in the water phase was always below 10% in the water sediment studies. However, its accumulation in the sediment was observed throughout the studies (see point B8.3 of this addendum).

In the following paragraphs a summary of the assessment of the step 1 is shown.

Within the remote sensing exercise water bodies with at least 1% of the 50 m margin composed of crop are considered potentially at risk (see table 8.4.1.2.1-4c). The following assumptions were made within this initial characterisation exposure:

Manner of application: It is assumed within this assessment of exposure that applications are typically carried out with standard spray nozzles. This is consistent with the data outlined within Tables 3.4 and 3.5, as summarised by Ganzelmeier et al. (1995) and Rautmann (2001). Accordingly, it should be recognised that this is a relatively conservative assumption. In many cases, drift reducing nozzles may be employed or other spray application techniques may used to reduce the scale of drift losses from the field.

Wind speed: It is assumed that applications would be carried out under weather conditions in which wind speed would be between 0.8 – 3.6 m/s. This is consistent with the data summarised by Ganzelmeier et al. (1995).

Wind direction: It is assumed within the assessment of exposure that drift deposition always occurs based upon the shortest transect between crop and surface water. As wind direction potentially has a very significant mitigation role, this will be considered in greater detail within the higher-tier risk assessment.

Interaction with vegetative interfaces: It is assumed within the assessment of exposure that drift does not interact and is not impeded in any way by vegetation within the margin between crop and surface waters.

Assumption regarding surface water bodies : For simplicity, simplistic exposure calculations are based upon nominal representatives of each water body class. These assumptions are outlined in Table 8.4.1.2.1-7. It is further assumed within this assessment of exposure that all water bodies are subject to spray drift loadings.

The information presented in Tables 8.4.1.2.1-4a and 8.4.1.2.1-4b, allows for the development of spray-drift loading estimates. Based upon the assumptions outlined earlier and the proximity of surface waters to crop, exposure assessments are then presented in Tables 8.4.1.2.1-10 and 11 for endosulfan. Where direct adjacency was observed a surrogate drift rate based upon a minimum 1 m buffer was assumed. Where direct adjacency was observed, a surrogate drift rate based upon a minimum 1 m buffer was assumed.

Table 8.4.1.2.1-10 PEC Estimates for Endosulfan for Selected Natural Margin Widths and Associated Percentiles for All Water Bodies by Water Body Type and Size Class

Water bodies	**Canals**			**Streams**		**Rivers**	**Ditches**	**Ponds**	
Size Class	**< 2 m width***	**2 – 5 m width***	**> 5 m width**	**<2 m width***	**2 – 4 m width**	**All**	**All***	**<1 ha area**	**1-5 ha area**
Segment Count	**1979**	**732**	**336**	**1139**	**661**	**119**	**5101**	**33**	**59**
Margin Width (m)	**Concentration (µg/l)**								
5	1.61	1.47	1.18	0.96	0.88	0.38	1.61	0.09	0.07
6	1.33	1.23	1.01	0.80	0.74	0.32	1.33	0.08	0.06
7	1.13	1.05	0.88	0.68	0.63	0.28	1.13	0.07	0.06
8	0.97	0.92	0.78	0.58	0.55	0.25	0.97	0.07	0.05
9	0.86	0.81	0.70	0.51	0.49	0.22	0.86	0.07	0.05
10	0.77	0.73	0.64	0.46	0.44	0.20	0.77	0.06	0.05

* It is anticipated that these water bodies are typically not exposed to drift or drift is of limited relevance due to seasonality or utility

Table 8.4.1.2.1-11 PEC Estimates for Endosulfan for Selected Percentile Values from the Distribution of Natural Margin Widths for All Water Bodies by Water Body Type and Size Class

Class	Size*	Concentration (µg/l)				
		50th	75th	90th	95th	99th
Canals	< 2 m**	1.33	1.61	4.00	7.40	7.40
	2 m – 5 m	0.92	1.05	1.47	3.35	5.70
	> 5 m	0.40	0.54	0.88	1.18	3.55
Streams	< 2 m**	0.51	0.58	0.80	1.21	4.44
	2 m – 4 m	0.33	0.49	0.63	0.88	3.42
Rivers	> 4 m	0.09	0.13	0.25	0.32	0.78
Ditches	All**	1.33	1.61	2.70	4.00	7.40
Ponds	< 1 ha	0.06	0.07	0.07	0.07	0.09
	1 – 5 ha	0.04	0.05	0.05	0.05	0.07

* width or area

** It is anticipated that these water bodies are typically not exposed to drift or drift is of limited relevance due to seasonality or utility.

Exposure assessments are then presented in Tables 8.4.1.2.1-12 and 8.4.1.2.1-13 for endosulfan sulphate. PEC values for endosulfan sulphate in static surface waters was simplified estimated as 84.1% of the comparable values for endosulfan.

Tables 8.4.1.2.1-12 PEC Estimates for Endosulfan Sulphate for Selected Percentile Values from the Distribution of Natural Margin Widths for All Water Bodies by Water Body Type and Size Class.

Class	Size*	Concentration (µg/l)				
		50th	75th	90th	95th	99th
Canals	< 2 m**	1.12	1.35	3.36	6.22	6.22
	2 m – 5 m	0.77	0.88	1.24	2.82	4.79
	> 5 m	0.34	0.45	0.74	0.99	2.99
Streams	< 2 m**	0.24	0.27	0.37	0.57	2.07
	2 m – 4 m	0.16	0.23	0.29	0.41	1.60
Rivers	> 4 m	0.04	0.06	0.12	0.15	0.37
Ditches	All**	1.12	1.35	2.27	3.36	6.22
Ponds	< 1 ha	0.05	0.06	0.06	0.06	0.08
	1 – 5 ha	0.03	0.04	0.04	0.04	0.06

* width or area

** It is anticipated that these water bodies are typically not exposed to drift or drift is of limited relevance due to seasonality or utility

Tables 8.4.1.2.1-13 PEC Estimates for Endosulfan Sulphate for Selected Percentile Values from the Distribution of Natural Margin Widths for All Water Bodies by Water Body Type and Size Class

Water bodies	**Canals**			**Streams**		**Rivers**	**Ditches**	**Ponds**	
Size Class	**< 2 m width**	**2 – 5 m width**	**> 5 m width**	**<2 m width**	**2 – 4 m width**	**All**	**All**	**<1 ha area**	**1-5 ha area**
Segment Count	**1979**	**732**	**336**	**1139**	**661**	**119**	**5101**	**33**	**59**
Margin Width (m)	**Concentration (µg/l)**								
5	1.35	1.24	0.99	0.45	0.41	0.18	1.35	0.08	0.06
6	1.12	1.03	0.85	0.37	0.34	0.15	1.12	0.07	0.05
7	0.95	0.88	0.74	0.32	0.29	0.13	0.95	0.06	0.05
8	0.82	0.77	0.66	0.27	0.26	0.12	0.82	0.06	0.04
9	0.72	0.68	0.59	0.24	0.23	0.11	0.72	0.06	0.04
10	0.65	0.61	0.54	0.22	0.21	0.09	0.65	0.05	0.04

* It is anticipated that these water bodies are typically not exposed to drift or drift is of limited relevance due to seasonality or utility

Study : Field observation on water bodies and agricultural Practices Volume I- Spain (Seville) Study Site.

Authors: Steve Kay and Chris Holmes

Year: 2000

Doc No: C019471

Approximately 50 observations of water bodies in the Seville were documented in September 2000. These observation are quality and were made to assist researches in understanding the nature of the water bodies at the site, not to scientifically quantify them. This report provides general commentary and records the observations made in the Seville site.

The entire area is intensely agricultural with tree crops (oranges, peaches and olives) and cotton dominating production. There was more citrus and peach production than originally anticipated, and the trend is towards expanding this production because of demand in the new EU market place.

Erosion was extensive and in some cases quite substantial. Ditch maintenance is a never-ending task because of the extensive runoff. Another noticeable contributor to the runoff problem is often relatively close proximity of agriculture to water bodies, especially in the non irrigated areas. While there was usually a VFS (vegetated filter strips) between crop and drainage in the irrigated areas, pressure to maximize production and the dryness of the environment leads growers to plant close to drainage in non irrigated areas.

Regional irrigation practices are to provide irrigation water via canals until mid-July, after which only citrus and greenhouse uses are provided with irrigation water, and only if the growers have remaining “irrigation credit”, some growers provide irrigation to their crops after mid-July cut-off using wells.

Most irrigation is either flood or drip irrigation, and there is a movement towards expanding drip irrigation, especially on tree crops. Field and row crops are predominantly flood irrigated. All observed canals were raised (0.5-3 m) above the natural landscape soil levels making it virtually impossible for runoff from the fields into the canals to occur. There is some spray/sprinkler irrigation but its use appears to be very limited. With one exception, all but largest irrigation canals were dry. No vegetation was observed in any of the canals, and this was to be expected as the canals are maintained over the winters. Most of the drainage from fields drainage from fields was also dry.

In agricultural there is almost no natural landscape left, with the few rare instances observed occurring near larger rivers and streams where small stands of trees and brush might be found. few hawks were observed, or any birds for that matter, even in irrigated agricultural areas. There were no fish observed in any water bodies and in only two cases were frogs observed. The area was very dry and even some irrigated orchards showed signs of water stress. Most of the rainfall occurs in late fall/early winter followed by another period of significant rain in the early spring. Out site of these two periods, rain is infrequent ad, as note earlier, the region as a whole is extremely dry.

Assessment: These observation are quality and were made not to scientifically quantify them. It should be taken into account that the observations were made on the month of September, when the irrigation period had finished yet. However, the application of endosulfan and the irrigation are at the same period of the year. Therefore, it cannot confirm that the canals are dry during the application period.

The authors affirms that all the canals were raised (0.5-3 m) above the natural landscape soil making it virtually impossible for runoff from the fields into the canals to occur. However, according to the photographs submitted, this is only true for the smallest field distribution canals. Therefore runoff risk cannot be rejected for large and mid size canals.

In the document coded as C021321 and C021344 a characterisation of the water bodies and their ecological relevance is made based on the results obtained in the study coded as C019473 and in the summary of the ground truthing exercise, assessed above.

Canals: According to applicant the smallest canals can be effectively discounted as a relevant route of entry into these surface waters. Although mid-sized distribution canals are likely to be flooded more frequently to fulfil the needs of the tertiary distribution network there is evidence that even these systems are dry a substantial proportion of the time. Both the smaller field irrigation canals and the mid-sized distribution canals may be discounted from consideration of spray-drift impacts.

RMS note: However, it should be taken into account that irrigation season and application period of endosulfan are at the same time. Therefore, spray risk into smaller and mid size canals cannot be rejected.

Larger canals are often permanently flooded through pumping or open connection with the Guadalquivir River system. Because of their greater degree of permanence exposure of these water bodies are considered to be relevant with respect to potential for loadings derived from spray drift.

According to applicant, There is evidence from the ground-truthing exercise that even the largest class of canals has a very limited ecological significance. The system has been characterised during the ground-truthing exercise as a shallow, very turbid, slowly flowing system. Temperature conditions are likely to be very high in these turbid, shallow systems compared with other natural surface waters. Elevated temperature, combined with an absence of emergent and submerged aquatic plants is likely to greatly reduce the dissolved oxygen concentration. An absence of significant aquatic plant life as primary production would reduce the ecological significance of this system with respect to both aquatic invertebrates and fish. Low dissolved oxygen content would have the effect of further reducing the significance of these systems as habitat for fish.

RMS note: However, no information was provided with regard to water quality from the large canals of the irrigation system.

Secondly, spray loadings cannot be rejected, and the ecological relevance should be taken into account since loadings may reach from the surrounding crops throughout the canals until its outlet.

Regarding to runoff loadings it must be taken into account that endosulfan sulphate accumulates in the sediment and the contribution of this via cannot be rejected into mid size and large canals, which do not raise above natural landscape.

Streams According to applicant, The vast majority of smaller stream systems are seasonal or intermittent. These systems are typically seasonal systems that dry out during the spring and summer months and reappear as flowing water bodies during the winter months when evapotranspiration decreases, excess soil moisture increases and groundwater recharge begins. The timing of re-establishment of these streams varies considerably and depends upon weather conditions, topography, soil type and local groundwater characteristics. It can safely be suggested that these water bodies are typically dry at the time of recommended endosulfan application between mid-June and mid-August. This coincides with the period of greatest evapotranspiration and greatest soil moisture deficit. Dry stream beds may be periodically rewetted following prolonged or intense rainfall and may infrequently receive run-off waters from neighbouring fields. However, the duration of these periods of rewetting is typically very short (in the range of hours or days) as a result of very rapid evaporation or infiltration into soil. As a consequence it is submitted that during summer months the connectivity, extent, volume and quality of water in these intermittent systems are insufficient to support fish populations. As a consequence, it can be argued with great confidence that these water bodies can effectively be discounted when considering impacts to fish associated with spray drift. It is recognised, however, that up to perhaps 10% of the larger streams may exist permanently within the landscape and need to be considered with respect to impacts from spray drift. However, there is a degree of uncertainty surrounding the figure since the ground-truthing exercise demonstrated that many streams identified as permanent systems on topographical maps were actually found to be dry at the time of the survey. It is suggested, therefore, that by addressing concerns associated with larger streams there is an in-built degree of conservatism within the risk assessment.

RMS note: Although the intermediate streams cannot be relevant for spray drift, they can be with regard to the runoff loadings after wettering due to a rainfall period. Thus, accumulation of endosulfan sulphate in the sediment was observed in the water sediment studies. Notifier recognises that a larger proportion of the larger streams may exist permanently within the landscape and need to be considered with respect to impacts from run-off. The importance of run-off to these systems may need to be considered throughout the year but is heavily mitigated by dilution within a flowing system and the recognition that there is a high degree of conservatism in the assumption that these systems can be treated as permanent.

RMS note: However, if they are treated as permanent an unreal factor of dilution is considered.

Ditches: As with the small intermittent streams, ditches are dry throughout most of the summer period. Rewetting will occur very infrequently following intensive rainfall but the majority of the water is expected to retained within the field by irrigation bunding. It should also be pointed out that such ditches are intensively managed and subject to regular dredging as a consequence of erosion. Local contacts advised that these systems were dry for all but a few weeks of the year, depending upon weather, soil and topography. As a consequence, it can be argued with great confidence that these water bodies can effectively be discounted when considering impacts to fish associated with spray drift. The primary role for these systems is to drain agricultural land during winter months and act as a man made subdivision of the landscape.

With regard to runoff loadings In the past it has been typical for farmers to plough furrows in parallel with the direction of slope to assist with gravity-fed flood irrigation (a worst-case, with respect to run-off and erosion potential). However, these irrigation practices are gradually being phased out in favour of approaches allowing a greater degree of control and conservation on scarce water resources. Nonetheless, tillage practices to minimise erosion and run-off (agricultural mitigation measures) remain unusual. However, it is common for farmers to retain water (derived from irrigation or rainfall) within the field by building soil barriers at the end of the furrows to make most effective use of available water. This would have the effect of also retaining run-off water and would act as a significant mitigation measure. Channels are often cut in these systems to allow drainage during the winter months. As a consequence it is argued that ditches are of only seasonal relevance with respect to run-off loadings.

Ponds: They are highly ecologically relevant and the need to address potential for spray-drift and run-off loadings is recognised within the risk assessment. The potential for impact from these two routes of entry is heavily mitigated by dilution within a large volume. In a large proportion of cases, these ponds are bunded systems that will preclude entry of run-off. Nonetheless, spray-drift and run-off are both considered although, in the case of run-off

A summary of the relevance of each water body with respect to spray drift and run off is provided in tables 8.4.1.2.1-14 and 8.4.1.2.1-15

Table 8.1.2.1.1-14 Summary of relevance of spray-drift and run-off and ecological significance of various water body types

Water Body	**Segment Count**	**Percentage of Total**	**Spray Drift Relevance**	**Run Off Relevance**	**Ecological Significance**
Canals <2 m width	1979	19.5	Low	Irrelevant	Low
Canals 2-4 m width	732	7.2	Low	Irrelevant	Low
Canals >4 m width	336	3.3	High	Irrelevant	Low
Canals Sub-Total	***3047***	***30.0***			
Streams <2 m width	1139	11.2	Low	Seasonal	Seasonal
Streams >2 m width	661	6.5	High	High	High
Stream Sub-Total	***1800***	***17.7***			
Rivers	119	1.2	High	High	High
Rivers Sub-Total	***119***	***1.2***			
Ditches	5101	50.2	Low	Seasonal	Seasonal
Ditches Sub-Total	***5101***	***50.2***			
Ponds < 1 ha area	33	0.32	High	Moderate	High
Ponds 1-5 ha area	59	0.58	High	Moderate	High
Ponds Sub-Total	***92***	***0.91***			
TOTAL	**10,159**	**100**			

Table 8.4.1.2.1-15 Summary of the Most Relevant Routes of Entry for Various Water Body Types

Water Body	**Segment Count**	**Percentage of Total**	**Relevant Scenario**
Canals <2 m width	1979	19.5	None
Canals 2-4 m width	732	7.2	None
Canals >4 m width	336	3.3	Spray Drift
Canals Sub-Total	***3047***	***30.0***	
Streams <2 m width	1139	11.2	Seasonal Run-off
Streams >2 m width	661	6.5	Spray Drift
Stream Sub-Total	***1800***	***17.7***	
Rivers	119	1.2	Spray Drift
Rivers Sub-Total	***119***	***1.2***	
Ditches	5101	50.2	Seasonal Run-off
Ditches Sub-Total	***5101***	***50.2***	
Ponds < 1 ha area	33	0.32	Spray Drift
Ponds 1-5 ha area	59	0.58	Spray Drift
Ponds Sub-Total	***92***	***0.91***	
TOTAL	**10,159**	**100**	

Study: Field observation on water bodies and agricultural Practices Volume II- Greece (Thessaloniki) Study Stie.
Authors: Steve Kay and Chris Holmes
Year: 2000
Doc Nº C019472

Approximately 45 observations of water bodies in Thessalonica were documented in October 2000. These observation are quality and were made to assist researches in understanding the nature of the water bodies at the site, not to scientifically quantify them. This report provides general commentary and records the observations made in the Greece site.

Thessalonik represents one of the most important agricultural region in Greece and is extensively cropped and irrigated. There was a large variety of crops found in the area with cotton, peaches and rice comprising the primary crops.

Overall, the field sizes were quite small (50 mx 100 mx or 50 m x 200 m being common sizes) and there was incredible diversity of planted crops with each consecutive field often containing a different crop from the previous one. The Greece site had little erosion evidence, due in part to the relatively flat landscape and the somewhat wetter climate that leads to permanent drainage supporting more robust vegetated filter strips (VFS).

Regional irrigation practices are to provide irrigation water via canals year-round, but only if the growers have “ irrigation credit”. Wells as a source of irrigation water are very rare, as are retaining ponds. Almost all irrigation is introduced to the fields by flooding. All observed canals were raised (0.5- 3m) above the natural landscape ground level making it virtually impossible for runoff from the fields into the canals to occur.

Many of the irrigation canals contained water and most of the larger ones have water year-round. Aquatic vegetation was observed in most of the larger canals , as were many frogs and in some cases even small fish. Approximately one-third of the observed drainage ditches from fields were dry or almost , but all permanent streams encountered contained water.

Most of the rainfall occurs in late fall/early winter followed by another period of significant rain in the early spring. Out site of these two periods, rain is infrequent but does occur periodically throughout the year.

Assessment: These observation are quality and were made not to scientifically quantify them.
Although notifier refers to the analysis landscape in Greece, no information about it was submitted. According to notifier the reason was that “The Greek site was not analysed due to restrictions by the Greek government”.

B.8.4.2 Estimation of PEC via runoff

In the monograph a field study to measure the runoff of endosulfan was carried out in a tomato field . Two watershed/ pond systems served as treatment sites (C271 and M558), with two additional watershed/pond system as reference sites. Tomatoes planted in the reference watershed received no endosulfan.

In summary, the mean peak dose of endosulfan in pond water was approx 1,3 µg/l in C271, with a concomitant value of approx 0.6 µg/l for M558. Concentrations o endosulfan in pond water declined to background concentration in six months at C721 and three months in M558. Endosulfan concentrations in pond system 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 the sediment in M558 (99.4 µg/kg) peaked at approx twice those encountered in C721 (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 the critical dose to the ponds

Based on the results the main exposure route for endosulfan is the runoff.
In 2003, applicant submitted a simulation of run-off carried out with PRZM software to estimate the amount of endosulfan and endosulfan sulphate that may be eroded.

B.8.4.2.1 Runoff loadings

Study: Estimations of run-off loadings and surface water exposure associated with representative endosulfan usage sites in Southern Europe
Author: Neil Mackay
year: 2002b
Doc Nº C021146
Simulation of run-off and surface water exposure have been carried out for endosulfan in three sites of Southern European Member States (Greece, Spain and Portugal). The sites are identified as follows :

- usage on cotton in Greece (“Thessaloniki” scenario)
- usage on cotton in Spain (”Sevilla” scenario)
- usage on tomatoes in Portugal (“Evora” scenario”).

A summary of the characteristics of each site are given in table 8.4.1.2.1-1. These scenarios were then used as a basis for generating input files to allow PRZM based simulation of runoff. The resulting runoff data were then used to generate estimates of surface water concentration in each relevant water bodies (see point 8.4.2.2 of this addenda). Under certain circumstances, there may be significant mitigation of runoff due to the presence of bounding at the field boundary. Where appropriate these measures were incorporated in to the simulation.

In table 8.4.2.1-1 the parameters introduced in the model are shown. A 50th percentile run-off potential year was identified for each chemical and scenario combination taking into account dissipation. For example, in the case of endosulfan usages on cotton, the 50th percentile run-off potential year was identified from a database of 20 years weather data based upon a time window between the first application (in mid-June) and the final application (in mid-August) plus an additional time window equivalent to one DT50 (14 days) for endosulfan. This provided a time window of 76 days. In the case of endosulfan sulfate, two 50th percentile run-off potential years were identified for best case dissipation (DT50 = 75 days) and worst case dissipation (DT50 = 161 days). As with endosulfan, total precipitation was characterised between the first application (in mid-June) and the final application (in mid-August) plus an additional time window equivalent to one DT50 (either 75 or 161 days). This provided total time windows of 137 and 223 days. This is proposed as providing a meaningful basis for identifying a context for evaluating realistic run-off potential that is consistent with the draft recommendations of FOCUS. (see table 8.4.2.1-1)

In each year simulated irrigation was added up to six times, typical for the agricultural practices associated with cultivation of cotton in Greece and Spain. Irrigation events (10 mm) were separated by approximately two weeks depending upon rainfall conditions and anticipated irrigation requirements.
Soil and hydrology assumptions for each scenario are given in table 8.4.1.2.1-1. Two cases were simulated in each scenario in order to represent best case and worst case soil hydrological conditions. This assists in identifying a range of likely run-off conditions and concentrations for the region as a whole.

The characteristics of the water bodies are summarised in table 8.4.2.1-2. A first-tier assumption was used that a treated 20 m wide strip existed at the interface between the field ditch, stream or river contributes run-off. In the case of the pond simulations a 5:1 ratio of contributing field to surface water area was assumed.

In each simulation it was assumed that soluble runoff is the primary immediate contributor to exposure within the water column. The majority of eroded material is assumed to remain entrapped at the margin of the field by either bounding (typical in order to more efficiently manage and conserve irrigation and rain water in cotton cultivation) or presence of vegetative filter strips. The comparatively small amount of eroded material that may still arrive in the surface water bodies was primarily assumed to be deposited to sediment where it would then undergo degradation and gradual re-partitioning with the water column.

It is apparent that following large-scale rainfall and runoff events that drained water in these small water system (except ponds) will rise and flow. In order to accommodate this dynamic behaviour within the assessment calculation the following approach was carried out dealing with dynamic hydrology.
The mass of chemical in runoff is calculated with the runoff volume and runoff concentration. This mass is then added to the surface water system and diluted into total volume of the ditch plus the volume of added runoff water. The ditch volume is then returned to the volume defined by the defeault depth (30 cm, 50 cm or 1 m). On a daily basis the concentration remaining is calculated based on 1st order kinetics and a DT_{50} of 0.58 d for endosulfan or 15 days for endosulfan sulphate (see foot note of

table 8.4.1.2.1-1). Run off events are checked and any additions are calculated in the manner described above. This calculation is then repeated on a daily basis throughout the simulation

In simulations of flowing systems (ditches, streams and rivers) additional background dissipation due to dilution is taken into account. The residence time for ditch is used to estimate a 1st order dilution rate that is included in the above calculations with the 1st order degradation rate in order to estimate overall dissipation. The contribution of dilution to overall dissipation varies between surface water bodies with larger systems such as rivers offering a greater potential for dilution than ditches. Similary, the extent of dilution varies between runoff events depending upon the scale of runoff. In some cases, with small system (such ditches) the contribution of dilution to dissipation may be actually very small when large runoff events occur (ie the ration of run off volume to ditch volume is very high).

Findings: Two sets of hydrological conditions were simulated to effectively describe the range of run-off conditions experienced at each site. With hydrological conditions favouring leaching rather than run-off (Case 1; PRZM Hydrological Class A) and with less favourable hydrological conditions (Case 2; PRZM Hydrological Class B). The results of runoff volume for each scenario are summarized on table 8.4.2.1-3 . The peak concentration s for each water body are shown in tables 8.4.2.1-4 to 8.4.2.1-9

Assessment: Endosulfan and endosulfan sulphate runoff was estimated taking into account the soluble fraction based on a 50th percentile run-off potential year identified for each chemical and scenario combination taking into account dissipation. In the case of endosulfan usages on cotton, the 50th percentile run-off potential year was identified from a database of 20 years weather data based upon a time window between the first application (in mid-June) and the final application (in mid-August) plus an additional time window equivalent to one DT50 (14 days) for endosulfan. This provided a time window of 76 days. In the case of endosulfan sulphate, two 50th percentile run-off potential years were identified for best case dissipation (DT50 = 75 days) and worst case dissipation (DT50 = 161 days). As with endosulfan, total precipitation was characterised between the first application (in mid-June) and the final application (in mid-August) plus an additional time window equivalent to one DT50 (either 75 or 161 days). This provided total time windows of 137 and 223 days plus an additional time window equivalent to one DT50 (14 days) for endosulfan.

The DT50 values used in these estimation were taken from a field dissipation study in which only one application rate was used. Based on the values of Koc and the experimental results observed in other field studies assessed in the monograph, the accumulation of endosulfan sulphate in soil cannot be rejected (Tiirmaa, 1993). Moreover, in the water sediment studies assessed in this addendum up to 66.6% of AR was identified as endosulfan in the sediment and accumulation of endosulfan sulphate was observed in this phase.

Taking into account all this, it should have been more suitable to estimate the runoff based on eroded soil for the parent and endosulfan sulphate. On the other hand, as accumulation of endosulfan hydroxy carboxylic acid was observed during the water sediment, it could have estimated the runoff of this metabolite from the amount of the parent content in the soil solution.

Finally , accumulation of run off concentration of the endosulfan sulphate was observed at the end of the simulation time (2 years) in some simulations . The results should be carefully taken into account since the application of endosulfan was only made in the first year.

Table 8.4.2.1-1 crop parameters used in the modelling

	Greece			Spain			Portugal	
number of application	3			3			2	
application number	1st	2nd	3th	1st	2nd	3th	1st	2nd
nominal application date	June 15	July 15	Aug 15	June 15	July 15	Aug 15	June 14	June 28
Foliar interception %	20	40	40	20	40	40	80	80
Application rates Kg/Ha	0.67	0.5	0.5	0.67	0.5	0.5	0.106	0.106
irrigation events (10 mm)	6 separated by 15 d			6 separated by 15 d				
Soil	sandy silt			sandy clay loam			sand	
Slope	<0.5%			<2%			2	
Koc range (1)	endosulfan				endosulfan sulphate			
	124747				8431			
endosulfan DT50 f (2)	14							
endosulfan sulphate DT50f (2)	best case. 75d (Spain) and worst case 161 d (Greece)							
time window to evaluate runoff (from the first application) (3)	endosulfan: 76 days endosulfan sulfate: 137 days (best case); 223 days (worstcase)							
DT50 w/s (4)	endosulfan 0.58 d endosulfan sulfate 15 days							

RMS notes:

(1) arithmetic mean of each four single values for alpha and beta endosulfan measured with four agricultural soils and one with a sediment; arithmetic mean of four values for endosulfan sulphate measured with agricultural soils (Goerlitz, Eyrich 1987; Sarfin et al 1989; Goerlitz, Eyrich 1988).

(2) The field studies are based only on one application (see point 8.1.2 of this addendum)

(3) the 50th percentile run-off potential year was identified from a database of 20 year weather data based upon a time window between the first application and the final application plus an additional time equivalent to one DT50

(4) there are new DT50 values available that have been assessed in this addendum. The DT50 of endosulfan sulphate is not considered valid since accumulation in the sediment was observed during the study.. Moreover, accumulation of endosulfan hydroxy carboxylic acid in the water phase was observed . See assessment made in point 8.3

Table 8.4.2.1-2 water bodies parameters use in the modelling

Water body	With or Area	depth (m)	Volume (l)	residence time (d)	Tier I
ditch	1 m	3	30 000*	Static	a treated 20 m wide strip existed at the interface between the field ditch contributes runoff
small stream	1m	0.5	50 000*	0.1	
large stream	2 m	0.5	100 000*	0.1	
River	4 m	1	400 000*	0.1	
Small pond	0.7 Ha	1	7 000 000	Static	a 5:1 ratio of contributing field to surface water area was assumed
Large pond	1 Ha	1	10 000 000	Static	

* Assumes 100 m long water body segment

Table 8.4.2.1-3 Summary of results of runoff volume for each scenario

<table>
<tr><td></td><td colspan="3">Thessaloniki site</td><td colspan="2">Seville site</td><td colspan="2">Evora site</td></tr>
<tr><td>Precipitation profile source</td><td colspan="3">Hellenic National Meteorological Service for Thessaloniki (Hellenic National Meteorological Service, 1999).</td><td colspan="2">Instituto Nacional de Meteorología for Seville</td><td colspan="2">Instituto de Meteorología for Evora</td></tr>
<tr><td>Selected period for simulations</td><td colspan="3">endosulfan: 1980-81
endosulfan sulphate (DT50 f= 75d): 1995-96
endosulfan sulphate (DT50 f= 161 d): 1985-86</td><td colspan="2">endosulfan: 93-94
endosulfan sulphate (DT50f= 75d): 88-89
endosulfan sulphate (DT50 f= 161 d): 85-86</td><td colspan="2">endosulfan: 91-92
endosulfan sulphate (DT50f= 75d): 87-88
endosulfan sulphate (DT50 f= 161 d): 88-89</td></tr>
<tr><td rowspan="2">Runoff volume following the first application</td><td>case A</td><td colspan="2">case B</td><td>case A</td><td>case B</td><td>case A</td><td>case B</td></tr>
<tr><td>19.74 mm (80-81)
11.05 mm (95-96)
25.35 mm (85-86)</td><td colspan="2">30.51 mm (80-81; 54.5 mm)
18.77 mm (95-96; 36.5 mm)
36.05 mm (85-86; 56.6 mm)</td><td>2.35 mm (93-94)
17.04 (88-89)
12.26 (85-86)</td><td>7.09 mm (93-94; 27 9 mm)
27.35 mm (88-89; 51.5 mm)
21.17 mm (85-86; 44 mm)</td><td>2.87 mm (91-92)
14.68 mm (87-88)
2.45 mm (88-89)</td><td>6.06 mm (91-92; 32.1 mm)
23.43 mm (87-88; 43.2 mm)
6.71 mm (88-89; 23.9 mm)</td></tr>
<tr><td rowspan="3">soluble to eroded ratio</td><td>endosulfan</td><td colspan="2">endosulfan sulphate</td><td colspan="4" rowspan="3">no given</td></tr>
<tr><td rowspan="2">8 to 1.368</td><td>DT50 75 d</td><td>DT50= 161 d</td></tr>
<tr><td>22 to 318005</td><td>20 to 79217</td></tr>
</table>

Table 8.4.2.1-4 Peak PECsw Values for Thessaloniki – Best Case Hydrological Conditions

	Peak PEC (ppb)		
	Endosulfan **DT_{50} = 14 d** **K_{oc} = 12,474** **SW DT_{50} = 0.58 d**	**Endosulfan sulfate** **DT_{50} = 75 d** **(formed at 13.4% of parent)** **K_{oc} = 8431** **SW DT_{50} = 15 d**	**Endosulfan sulfate** **DT_{50} = 161 d** **(formed at 13.4% of parent)** **K_{oc} = 8431** **SW DT_{50} = 15 d**
Small stream	4.16×10^{-2}	0.19	0.58
Large stream	2.69×10^{-2}	0.13	0.44
River	9.93×10^{-3}	4.10×10^{-2}	0.18
Small pond	1.70×10^{-4}	9.13×10^{-4}	3.25×10^{-3}
Large pond	1.19×10^{-4}	6.39×10^{-4}	2.28×10^{-3}
Ditch	5.75×10^{-2}	0.31	0.69

Table 8.4.2.1-5 Peak PECsw Values for Thessaloniki – Worst Case Hydrological Conditions

	Peak PEC (ppb)		
	Endosulfan **DT_{50} = 14 d** **K_{oc} = 12,474** **SW DT_{50} = 0.58 d**	**Endosulfan sulfate** **DT_{50} = 75 d** **(formed at 13.4% of parent)** **K_{oc} = 8431** **SW DT_{50} = 15 d**	**Endosulfan sulfate** **DT_{50} = 161 d** **(formed at 13.4% of parent)** **K_{oc} = 8431** **SW DT_{50} = 15 d**
Small stream	5.47×10^{-2}	0.25	0.67
Large stream	3.87×10^{-2}	0.18	0.53
River	1.46×10^{-2}	6.67×10^{-2}	0.24
Small pond	2.74×10^{-4}	1.79×10^{-3}	5.02×10^{-3}
Large pond	1.92×10^{-4}	1.26×10^{-3}	3.52×10^{-3}
Ditch	7.05×10^{-2}	0.38	0.78

Table 8.4.2.1-6 Peak PECsw Values for Sevilla – Best Case Hydrological Conditions

	Peak PEC (ppb)		
	Endosulfan **DT_{50} = 14 d** **K_{oc} = 12,474** **SW DT_{50} = 0.58 d**	**Endosulfan sulfate** **DT_{50} = 75 d** **(formed at 13.4% of parent)** **K_{oc} = 8431** **SW DT_{50} = 15 d**	**Endosulfan sulfate** **DT_{50} = 161 d** **(formed at 13.4% of parent)** **K_{oc} = 8431** **SW DT_{50} = 15 d**
Small stream	1.48×10^{-4}	0.16	0.18
Large stream	7.42×10^{-5}	0.11	0.12
River	1.86×10^{-5}	4.09×10^{-2}	3.92×10^{-2}
Small pond	2.71×10^{-7}	5.82×10^{-4}	5.48×10^{-4}
Large pond	1.90×10^{-7}	8.30×10^{-4}	7.82×10^{-4}
Ditch	2.50×10^{-4}	0.22	0.26

Table 8.4.2.1-7 Peak PECsw Values for Sevilla – Worst Case Hydrological Conditions

	Peak PEC (ppb)		
	Endosulfan **DT_{50} = 14 d** **K_{oc} = 12,474** **SW DT_{50} = 0.58 d**	**Endosulfan sulfate** **DT_{50} = 75 d** **(formed at 13.4% of parent)** **K_{oc} = 8431** **SW DT_{50} = 15 d**	**Endosulfan sulfate** **DT_{50} = 161 d** **(formed at 13.4% of parent)** **K_{oc} = 8431** **SW DT_{50} = 15 d**
Small stream	5.69×10^{-3}	0.20	0.23
Large stream	2.95×10^{-3}	0.15	0.17
River	7.59×10^{-4}	6.11×10^{-2}	6.38×10^{-2}
Small pond	1.13×10^{-5}	1.06×10^{-3}	1.11×10^{-3}
Large pond	7.90×10^{-6}	1.51×10^{-3}	1.59×10^{-3}
Ditch	9.30×10^{-3}	0.30	0.32

Table 8.4.2.1-8 Peak PECsw Values for Evora – Best Case Hydrological Conditions

	Peak PEC (ppb)		
	Endosulfan **DT_{50} = 14 d** **K_{oc} = 12,474** **SW DT_{50} = 0.58 d**	**Endosulfan sulfate** **DT_{50} = 75 d** **(formed at 13.4% of parent)** **K_{oc} = 8431** **SW DT_{50} = 15 d**	**Endosulfan sulfate** **DT_{50} = 161 d** **(formed at 13.4% of parent)** **K_{oc} = 8431** **SW DT_{50} = 15 d**
Small stream	4.93×10^{-7}	2.38×10^{-2}	6.28×10^{-3}
Large stream	2.49×10^{-7}	1.47×10^{-2}	3.26×10^{-3}
River	6.26×10^{-8}	4.44×10^{-3}	8.52×10^{-4}
Small pond	8.97×10^{-10}	7.62×10^{-5}	1.52×10^{-5}
Large pond	6.28×10^{-10}	5.33×10^{-5}	1.07×10^{-5}
Ditch	8.11×10^{-7}	3.50×10^{-2}	1.24×10^{-2}

Table 8.4.2.1-9 Peak PECsw Values for Evora – Worst Case Hydrological Conditions

	Peak PEC (ppb)		
	Endosulfan **DT_{50} = 14 d** **K_{oc} = 12,474** **SW DT_{50} = 0.58 d**	**Endosulfan sulfate** **DT_{50} = 75 d** **(formed at 13.4% of parent)** **K_{oc} = 8431** **SW DT_{50} = 15 d**	**Endosulfan sulfate** **DT_{50} = 161 d** **(formed at 13.4% of parent)** **K_{oc} = 8431** **SW DT_{50} = 15 d**
Small stream	3.23×10^{-4}	3.55×10^{-2}	1.96×10^{-2}
Large stream	1.63×10^{-4}	2.44×10^{-2}	1.10×10^{-2}
River	4.09×10^{-5}	8.52×10^{-3}	3.05×10^{-3}
Small pond	5.85×10^{-7}	1.75×10^{-4}	8.52×10^{-5}
Large pond	4.10×10^{-7}	1.22×10^{-4}	5.96×10^{-5}
Ditch	5.33×10^{-4}	5.03×10^{-2}	4.53×10^{-2}

B.8.4.2.2 Estimation of PECsw due to runoff

Study: Aquatic ecological risk assessment for endosulfan uses on cotton in Spain-Part 2: Characterizing risks associated with run-off

Author: Neil Mackay

Year: 2002c

Doc Nº C0211344

In a standard worst case assessment the exposure via run-off is assumed to be fixed loss of 10% of the application rate, which is introduced in a static shallow standard ditch with a depth of 30 cm . For use of endosulfan in cotton, this highly conservative approach results in a potential risk to aquatic organisms.

Therefore a higher-tiered aquatic exposure assessment was performed which relied on a statistical analysis of multi year rainfall events as origin of runoff events, the simulation of runoff with a leaching model and detailed geographical analysis of one representative area of use of endosulfan on cotton (see the assessment above).

The risk assessment presented in this document has used a stepwise strategy. Within the first tier risk assessment simplistic assumptions regarding fate and exposure were compared with conservative deterministic effect thresholds to calculate TER values as indices of risk. This was then superseded in Tier II through introduction of a more sophisticated exposure assessment based upon remote sensing data and the role of natural margins and buffer zones in reducing exposure and risk. In this addendum the exposure assessment is only evaluated.

Tier I exposure assessment. The first tier basis for evaluating exposure associated with run-off is an assumption of direct adjacency of applications to a standard 30 cm deep ditch system. According to the standard assumptions made by FOCUS sw, Run-off is considered as a single, non-specific loading fixed at a value of 10% of application to the standard 30 cm ditch. Where the DT50 of the chemical in water is less than one third of the interval between treatments calculations are carried out on a single treatment basis.

The dissipation rate for endosulfan in water-sediment systems has been obtained from the results of a study conducted by Gildemeister (1985; and subject to further interpretation as outlined by Stumpf, 1990). Within this study radiolabelled α- and β-endosulfan were observed to dissipate rapidly from the water column, mainly as a result of the combined actions of hydrolysis and partitioning into sediment. DT50 values of 10-14 hours were observed for α- and β-endosulfan and 12-15 days for the total endosulfan residue (α- and β-endosulfan and endosulfan sulfate). The DT50 of 14 hours (0.58 d) was selected as a basis for estimating endosulfan dissipation in water-sediment systems. A comparison of the interval between application (14-21 days) and the DT50 in water-sediment systems described here suggests that negligible quantities of endosulfan would be expected to remain by the time of the next application. This suggests it is appropriate to base the first-tier run-off estimates upon single application rates.

Based on a single application rate of 0.84 kg a.s./ha the worst-case first tier loading from a 20 m wide, 100 m long strip at the interface between ditch and field (0.2 ha) would be 16.8 g. This is then diluted into a 100 m long, 1 m wide and 30 cm deep water body (30,000 l) to provide a worst-case first tier instantaneous PEC of 0.56 mg/l. This value actually lies above the solubility of endosulfan. As a consequence a worst-case first tier instantaneous PEC based on the limit of solubility (0.30 mg/l at 22°C and pH 5) is employed in these preliminary calculations. Dissipation in surface water is assumed to occur based upon a DT50 of 0.58 days, as discussed earlier.

On the basis of these simplistic calculations and the observations made in the water-sediment study conducted by Gildemeister (1985) a maximum PEC for endosulfan and endosulfan sulphate can be estimated as follows:

Nominal initial (maximum) PEC for endosulfan = 0.30 mg/l

= 7.37 x 10-7 mol/l x 45% transformation

= 3.32 x 10-7 mol/l endosulfan sulfate

= 0.14 mg/l endosulfan sulfate

Tier II exposure assessment. This part is collected in the study coded as C021146 which was assessed above. The results for Spain are given in tables 8.4.2.1-6 and 8.4.2.1-7

Mitigation and refinement of exposure. The only mitigation considered was the likehood of entrapment of the vast majority of eroded material within the bunded field boundaries or within the thatch of any vegetative filter strip (VFS). No other mitigation was assumed. As a refinement in the understanding of exposure the results of the remote exercise carried out in Seville (see above) were taken into account to provide evidence of spatial mitigation associated with naturally existing margin widths. These factors were employed as a basis for mitigating runoff loadings upon the standard Exposit framework employed by the BBA. It consists on the following percentage of mitigations of runoff:

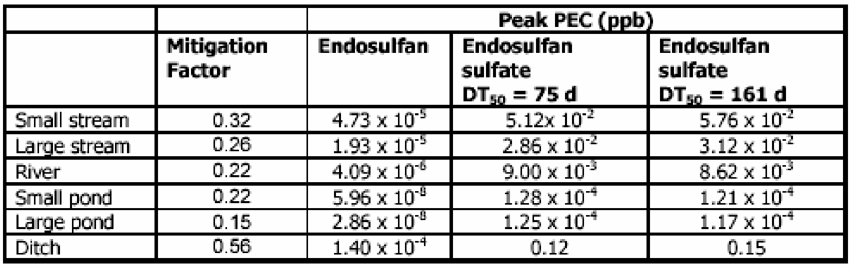
- 50 % reduction with a 5 m buffer zone
- 90 % reduction with a 10 m buffer zone
- 97.5 % reduction with a 20 m buffer zone

In order to estimate reductions for any margin width this relationship was described empirically by the following equation:

$$proportion\ of\ reduction = 100 - 10^{(-0.083 * margin\ width + 2.00)}$$

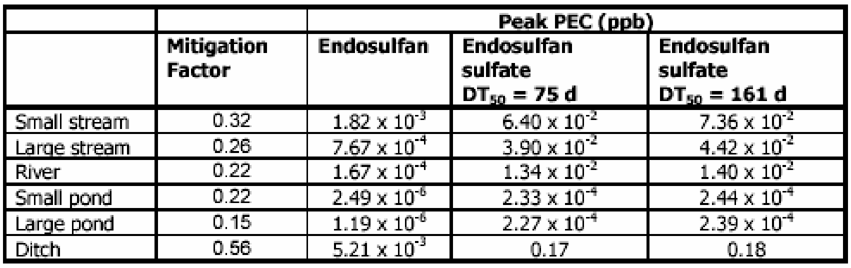
Based on this assumption and the proximity of surface waters to crop a step I in the refinement is presented in tables **8.4.2.1-10** and **8.4.2.1-11** for PECsw values taking into account the 90th percentile margin widths for each water body (table 8.4.1.2.1.4a).

Table 8.4.2.1-10 Mitigation factors and Peaksw values for 90th percentile margin widths for Seville – Best case hydrological conditions



		Peak PEC (ppb)		
	Mitigation Factor	**Endosulfan**	**Endosulfan sulfate DT_{50} = 75 d**	**Endosulfan sulfate DT_{50} = 161 d**
Small stream	0.32	4.73×10^{-5}	5.12×10^{-2}	5.76×10^{-2}
Large stream	0.26	1.93×10^{-5}	2.86×10^{-2}	3.12×10^{-2}
River	0.22	4.09×10^{-6}	9.00×10^{-3}	8.62×10^{-3}
Small pond	0.22	5.96×10^{-8}	1.28×10^{-4}	1.21×10^{-4}
Large pond	0.15	2.86×10^{-8}	1.25×10^{-4}	1.17×10^{-4}
Ditch	0.56	1.40×10^{-4}	0.12	0.15

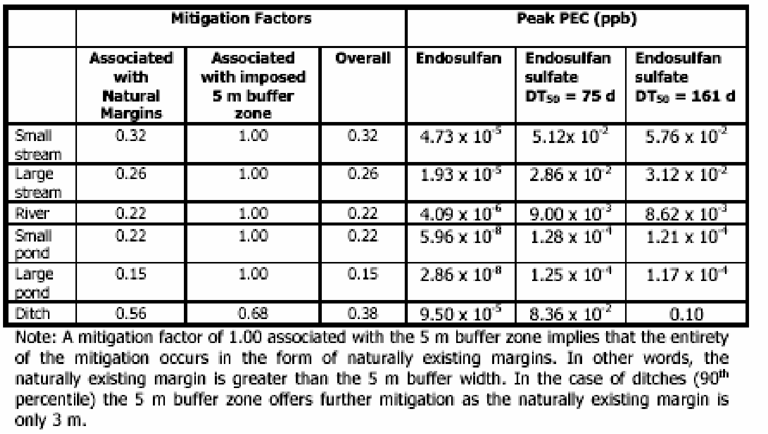
Table 8.4.2.1-11 Mitigation factor and peak PECsw values for 90th percentile margin for Seville- worst case hydrological conditions



		Peak PEC (ppb)		
	Mitigation Factor	Endosulfan	Endosulfan sulfate DT_{50} = 75 d	Endosulfan sulfate DT_{50} = 161 d
Small stream	0.32	1.82×10^{-3}	6.40×10^{-2}	7.36×10^{-2}
Large stream	0.26	7.67×10^{-4}	3.90×10^{-2}	4.42×10^{-2}
River	0.22	1.67×10^{-4}	1.34×10^{-2}	1.40×10^{-2}
Small pond	0.22	2.49×10^{-6}	2.33×10^{-4}	2.44×10^{-4}
Large pond	0.15	1.19×10^{-6}	2.27×10^{-4}	2.39×10^{-4}
Ditch	0.56	5.21×10^{-3}	0.17	0.18

A revised set of Peak PEC values in which additional mitigation associated with 5 m and 8 m buffer zones is presented in Tables 8.4.1.2-12 -8.4.1.2-15. Within these tables the overall mitigation figures are divided into that proportion associated with natural existing margins and additional imposed mitigation associated with the buffer zones of 5 and 8 m.

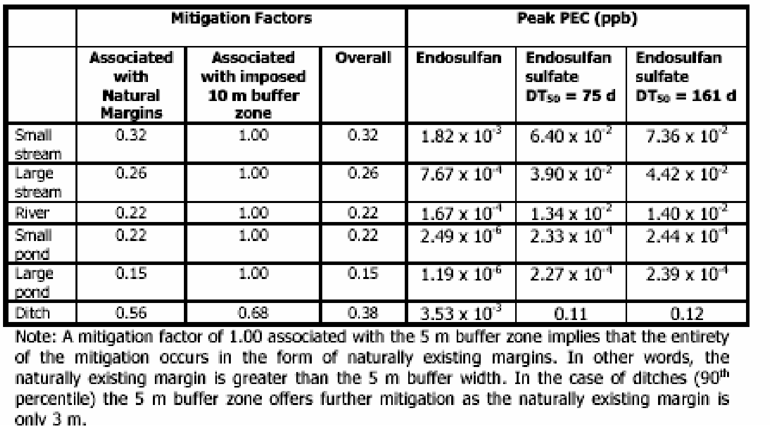
Table 8.4.1.2-12 Mitigation factors and peack Pecsw values for 90th percentile margin widths for Seville- Best case hydrological conditions- 5 m buffer proposal.



	Mitigation Factors			Peak PEC (ppb)		
	Associated with Natural Margins	Associated with imposed 5 m buffer zone	Overall	Endosulfan	Endosulfan sulfate DT_{50} = 75 d	Endosulfan sulfate DT_{50} = 161 d
Small stream	0.32	1.00	0.32	4.73×10^{-5}	5.12×10^{-2}	5.76×10^{-2}
Large stream	0.26	1.00	0.26	1.93×10^{-5}	2.86×10^{-2}	3.12×10^{-2}
River	0.22	1.00	0.22	4.09×10^{-6}	9.00×10^{-3}	8.62×10^{-3}
Small pond	0.22	1.00	0.22	5.96×10^{-8}	1.28×10^{-4}	1.21×10^{-4}
Large pond	0.15	1.00	0.15	2.86×10^{-8}	1.25×10^{-4}	1.17×10^{-4}
Ditch	0.56	0.68	0.38	9.50×10^{-5}	8.36×10^{-2}	0.10

Note: A mitigation factor of 1.00 associated with the 5 m buffer zone implies that the entirety of the mitigation occurs in the form of naturally existing margins. In other words, the naturally existing margin is greater than the 5 m buffer width. In the case of ditches (90th percentile) the 5 m buffer zone offers further mitigation as the naturally existing margin is only 3 m.

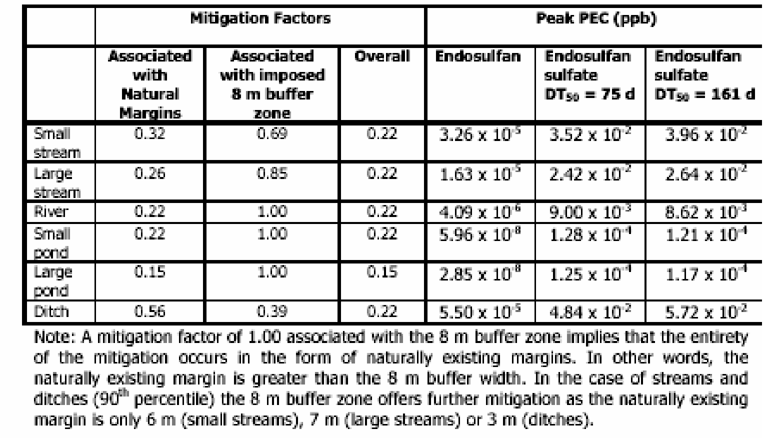
Table 8.4.1.2-13 Mitigation factors and peack Pecsw values for 90th percentile margin widths for Seville- worst case hydrological conditions- 5 m buffer proposal.



	Mitigation Factors			Peak PEC (ppb)		
	Associated with Natural Margins	Associated with imposed 10 m buffer zone	Overall	Endosulfan	Endosulfan sulfate DT_{50} = 75 d	Endosulfan sulfate DT_{50} = 161 d
Small stream	0.32	1.00	0.32	1.82×10^{-3}	6.40×10^{-2}	7.36×10^{-2}
Large stream	0.26	1.00	0.26	7.67×10^{-4}	3.90×10^{-2}	4.42×10^{-2}
River	0.22	1.00	0.22	1.67×10^{-4}	1.34×10^{-2}	1.40×10^{-2}
Small pond	0.22	1.00	0.22	2.49×10^{-6}	2.33×10^{-4}	2.44×10^{-4}
Large pond	0.15	1.00	0.15	1.19×10^{-6}	2.27×10^{-4}	2.39×10^{-4}
Ditch	0.56	0.68	0.38	3.53×10^{-3}	0.11	0.12

Note: A mitigation factor of 1.00 associated with the 5 m buffer zone implies that the entirety of the mitigation occurs in the form of naturally existing margins. In other words, the naturally existing margin is greater than the 5 m buffer width. In the case of ditches (90th percentile) the 5 m buffer zone offers further mitigation as the naturally existing margin is onlv 3 m.

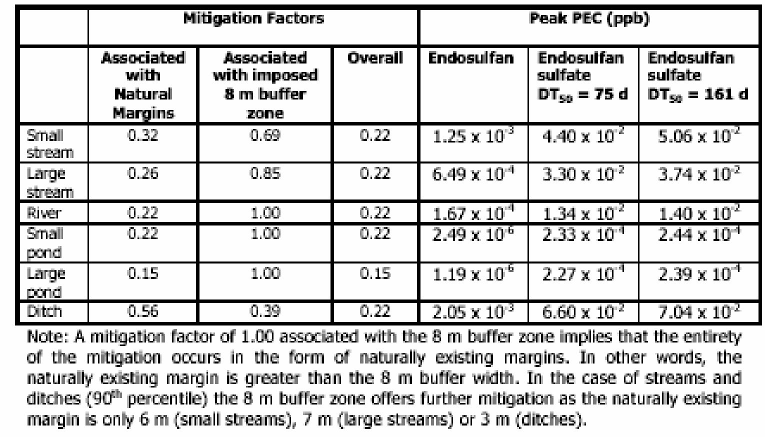
Table 8.4.1.2-14 Mitigation factors and peack Pecsw values for 90th percentile margin widths for Seville- Best case hydrological conditions- 8 m buffer proposal.



	Mitigation Factors			Peak PEC (ppb)		
	Associated with Natural Margins	**Associated with imposed 8 m buffer zone**	**Overall**	**Endosulfan**	**Endosulfan sulfate DT_{50} = 75 d**	**Endosulfan sulfate DT_{50} = 161 d**
Small stream	0.32	0.69	0.22	3.26×10^{-5}	3.52×10^{-2}	3.96×10^{-2}
Large stream	0.26	0.85	0.22	1.63×10^{-5}	2.42×10^{-2}	2.64×10^{-2}
River	0.22	1.00	0.22	4.09×10^{-6}	9.00×10^{-3}	8.62×10^{-3}
Small pond	0.22	1.00	0.22	5.96×10^{-8}	1.28×10^{-4}	1.21×10^{-4}
Large pond	0.15	1.00	0.15	2.85×10^{-8}	1.25×10^{-4}	1.17×10^{-4}
Ditch	0.56	0.39	0.22	5.50×10^{-5}	4.84×10^{-2}	5.72×10^{-2}

Note: A mitigation factor of 1.00 associated with the 8 m buffer zone implies that the entirety of the mitigation occurs in the form of naturally existing margins. In other words, the naturally existing margin is greater than the 8 m buffer width. In the case of streams and ditches (90th percentile) the 8 m buffer zone offers further mitigation as the naturally existing margin is only 6 m (small streams), 7 m (large streams) or 3 m (ditches).

Table 8.4.1.2-15 Mitigation factors and peack Pecsw values for 90th percentile margin widths for Seville- worst case hydrological conditions- 8 m buffer proposal.



	Mitigation Factors			Peak PEC (ppb)		
	Associated with Natural Margins	**Associated with imposed 8 m buffer zone**	**Overall**	**Endosulfan**	**Endosulfan sulfate DT_{50} = 75 d**	**Endosulfan sulfate DT_{50} = 161 d**
Small stream	0.32	0.69	0.22	1.25×10^{-3}	4.40×10^{-2}	5.06×10^{-2}
Large stream	0.26	0.85	0.22	6.49×10^{-4}	3.30×10^{-2}	3.74×10^{-2}
River	0.22	1.00	0.22	1.67×10^{-4}	1.34×10^{-2}	1.40×10^{-2}
Small pond	0.22	1.00	0.22	2.49×10^{-6}	2.33×10^{-4}	2.44×10^{-4}
Large pond	0.15	1.00	0.15	1.19×10^{-6}	2.27×10^{-4}	2.39×10^{-4}
Ditch	0.56	0.39	0.22	2.05×10^{-3}	6.60×10^{-2}	7.04×10^{-2}

Note: A mitigation factor of 1.00 associated with the 8 m buffer zone implies that the entirety of the mitigation occurs in the form of naturally existing margins. In other words, the naturally existing margin is greater than the 8 m buffer width. In the case of streams and ditches (90th percentile) the 8 m buffer zone offers further mitigation as the naturally existing margin is only 6 m (small streams), 7 m (large streams) or 3 m (ditches).

In the document a summary of the water body caractheristics is shown. It was reviwed above in the assessment made for the report coded C019471 corresponding to the thruthting

B.8.6 Assessment of endosulfan and metabolites against the POP and PBT classification criteria

In May 2001 notifier addressed an assessment of endosulfan and its relevant metabolites using POP criteria (C13092). In that moment RMS concluded that there was not sufficient amount of information regarding to the route of degradation of endosulfan to make the assessment against the POP classification criteria.

In May 2003 notifier addressed a new assessment against PBT and vPvB criteria in the context of the European PBT strategy (C028892). Additionally, a paper which stated that endosulfan does not meet the UN –ECE POP criteria was submitted.

Study: Endosulfan and its environmentally Relevant metabolites- Assessment using the criteria for classification as a persistent Organic Pollutant.
Author: Leo W. Buerkle
Dated: May 2001
Reference: C013092
GLP: n/a

Endosulfan, its isomers and the major metabolites were assessed against criteria for classification of a chemical as POP as agreed in the fifth session of UNEP Intergovernmental National Committee in Johannesburg at 4-9 December 2000. From the results of this assessment notifier concluded neither parent alpha- and beta-endosulfan nor relevant metabolites in the environment , i.e endosulfan sulphate and endosulfan hydroxylic acid do, apart from single transgresses of the individual trigger values, met the mentioned criteria for the assessment of a hemeical as POP (Table 8.4-1)

Table 8.4-2 summarizes the data used in the assessment submitted for the parent compound .
Table 8.4-3 summarizes the data used in the assessment submitted for endosulfan sulphate.
Table 8.4-4 collects the comments of notifier with regard to endosulfan hydroxycarboxlic acid.

Table 8.4-1 Criteria according to UN ECE-Protocol

Potential long range atmospheric transport	Vapour pressure< 1000Pa and atmospheric half life >2 days Or monitoring evidence in remote regions Or environmental propietird and/or model results that demonstrate that the chemical has a potential for transfer to receiving environmental transport through the air , water or migratory species with potential to transfer to a receiving environment in locations distant from the sources of its release.
Toxicity	Potential to adversely affect human health and/or the environment
Persistence	Half life in water > 2months or half life in sediment > 6 months or half life in soil > 6 months Or evidence that the substance is otherwise sufficiently persistent to be of concern within the scope of the protocol
Bioaccumulation	logKow >5 or bioconcetration factor (BCF) > 5000 or bioaccumulation factor (BAF) > 5000 Other factors such as the high toxicity of the substance, that make it of concern within the scope of the protocol. Monitoring data in biota indicating that the bioaccumulation potential of the chemical is sufficient to justify its consideration within the scope of the Convention

Eliminado: **Overall assessment of water sediment systems ¶**
¶
Four water sediment tests were submitted. Degradation of endosulfan proceeded by hidrolytical and oxidative pathways to result in endosulfan sulfate and endosulfan diol as componenets early formed in metabolisim (Figure 8.3-5). Endosulfan hydroxy ether and endosulfan hydroxy carboxylic acid were also observed as main metabolites. ¶
Under acid conditions, also endosulfan lactone apeeared above 10% but endosulfan dihydroxy ether was not detected, maybe due to the decreasing biomass to zero throughout the study.¶
Degradation of endosulfan sulfate was not seen in three of four system, it was accumulated in the sediment. Accumulation of endosulfan was seen in two systems ≥20%TAR at the end of the test.¶
Table 8.3-9 summarizes the maximum detected for each metabolite in water phase and sediment.¶
DT50s values have not been considered valid by the RMS, because the DT_{50} values for the total residue in water, sediment and in the whole system should be calculated correctly taking into account the process of formation and degradation. A good kinetic should be proposed. ¶

Table 8.4-2: Data and conclusions *made by notifier* in the assessment of a + b endosulfan against POP criteria

(Cod study)	alfa endosulfan	beta endosulfan
Dt50 in water hydrolysis pH 5 pH 7 pH9 **(A40003)**	 >200d 19 d 6.2 h	 >200d 10.7d 4.1 h
DT50 in water/sediment study **(A31182) (1)**	15 resp. 12 d for the dissaparence of the sum of a+b+endosulfan sufate from water body pH water: 7.3-7.8 pH sediment: 7.2-7.9	
DT50 sediment (1)	21 resp 18 for the disappearance of the sum of a+b+endosulfan sulphate from both water and sediment **(A31182)**	
DT50 in lab soil degradation studies	98, 128, 90, 92, 80 d **(A53618)** 25.6, 37.5 d **(A29680)** for the sum a+ b isomers	
DT50 in field soil degradation studies	91.6, 35.9, 38.5, 16.5, 75.9, 92.9, 85.9 d **(A53554, A54025)**	
Conclusions regarding to persisitence: the half lives of the sum of alpha beta endosulfan are generally shorter than the POP criteria. In addtion alpha endosulfan is generally faster degraded in soil than in beta isomer (A53618) indicating that alpha isomer has a lower overall persistence in the environment although it has a higher vapour pressure and therefore a higher potential for long range transport . On the other hand the beta isomer is less degradable in soil, but has a lower long range transport potential.		
Kow	4.74 pH=5.1 (A36576)	4.79 pH=5.1 (A36576)
BCF	2755 (A22871) 2650 (A50529) 11583 $t_{1/2}$=2.01-1.74 d (A49919);	
Bioaccumulation in mammals	mouse, 2 yr feeding with 18 mg/kg diet. highest residues detected in kidneys 0.14/0.23 mg/kg (m/f) and in liver 0.67/1.1 mg/kg (m/f) identified as endosulfan sufate (C005880) rat, 2 year feeding with 75 mg/kg diet. highest residues detected in liver 00.21/0.35 mg/kg (m/f) identified as endosulfan sufate (C005880) and no residues detected in kidneys an other organs or tissues (C005878) lactating cow, 28 day feeding study with 4/12/30 mg/kg diet highest residues identified as endosulfan sulphate and detected in fat were 1.4/4.7/9.9 mg/kg resulting in the highest transfer factors of 0.35*0.39/0.33 (C003624)	
Conclusion regarding to bioaccumulation criteria: The log Kow is below the POP trigger. One aquatic BFC in yellow tetra fish is higher than POP triggered bioaccumulation. However the biological half life of elimination determined was only of 2 days. Therefore, a bioaccumulation under field conditions is not constant as in the mentioned lab study rather than it follows a pulse pattern with several days intervals Residues in long term feeding studies with mouse, rat and cow did not indicate any bioaccumulation potential, because all transfer factors were smaller than unity. The results for mammals particularly did not show any potential of magnification in the food chain. There is no indication of bioaccumulation from available monitoring data.		
DT50 in air (2)	2 d	
Vapour pressure (3)	9.6 10^{-4} Pa(20ºC)	0.4 10^{-4} Pa(20ºC)
Water solubility (4)	0.33 mg/l (22 C pH 5)	0.32 mg/l (22 C pH 5)

(Cod study)	alfa endosulfan	beta endosulfan
Monitoring data from locations distant from th sources	several publication reported findings of predominately alpha endosulfan in the air or artic regions 2.7-9.7 pg/m^3 in 1986;1.8-5 pg/m^3 in 1987 beta endosulfan no detected **(A57281**,**A57282, A57283,)** This extremely low level does not pose any adverse effect to human or environment as illustrated by the following estimation of the molecule concentration in air : 1 pg/m^3= 10^{-12} g/m^3 = 10^{-18} g/ml Using the molar mass – 8406.9g/mol) and the Losch midt number (6.20*10^{23} molecules/mol) 1 pg/m^{3}is equivalent to 1480 molec/ml . For comparison this level is significantly lower than the low concentration assumed for the mean ozone (4.2 10^{13} $^{O}{}_{3}$/ml) or OH radical level in air (500 000 radicals/ml in an Atkinson calculation.	
Transport via migratory animals	it is unlikely due to low transfer factors (terrestrial animals) resulting in an absence of bio-magnification and very short depuration half life (fish)	
	The POP criteria do not contain fixed trigger values for adverse effects needed for a clear assessment of the potential damage to human health or to environment. There is only anecdotal and insufficient evidence of adverse effects to humans or environment . investigations of such allegations revealed in most cases misuse of the product Toxicity and ecotxicity data need to be compared with the potential exposure data to determine the potential damage to human health and the environment. Such comparisons do not result in an unacceptable risk for human health and the environment.	

(1) DT50 values no validated by RMS.

(2) According to Evaluation table SANCO/4326/2001 rev2-2 (01.04.02)

(3) the vapour pressures mentioned in the list of end points are in the similar range 1.05 10-3/ 1.8 10-4 Pa for alpha/beta endosulfan.

(4) the water solubilities mentioned in the list of end points are in the similar range 0.33/0.32 mg/l for alpha/beta endosulfan.

Table 8.4-3: Data and conclusions *made by notifier* in the assessment of endosulfan sulphate against POP

Criterium	**properties of the chemical**
Persistence $^{(1)}$	**water:** $t_{1/2}$ (water/sediment study): 15 resp 12 d for the disappearance of the sum of alpha +beta endosulfan sulphate from water body (Doc A31182) **soil:** $_{T1/2}$ (field dissipation studies) for the sum of alpha+ beta +endosulfan sulphate: 169,126 resp. 169, 193 d. calculated from the 0-20 cm residue data of A53554 resp A54025 using first order degradation kinetics. (Kinetics data on degradation of pure endosulfan sulphate are actually not available; however lab and field studies with respect to the degradation of sulphate are currently ongoing) Repeated application in a apple orchard over a period of 4 years did not show an enrichment of total residues (sum of alpha+ beta+ endosulfan sulphate) in soil indicating degradation rather than persistence in soil (Doc A53771) **Sediment:** $t_{1/2}$ (water sediment study); 21 resp. 18 d for the disappearance of the sum of alpha+ beta endosulfan from both water and sediment (Doc A31182)
	Conclusion: The half lives of the sum of alpha and beta endosulfan and endosulfan sulphate are generally shorter than POP-triggered persistence (Kinetics data on the degradation of pure endosulfan sulphate are actually not available).
Bioaccumulation	**Octanol/water partition coefficient ,** log Kow= 4.37 Ph 7 (Doc A 42638) **Bioconcentration factor in aquatic species :** no data available **Bioaccumulation in mammals.** Mouse 2 year feeding with 18 mg/kg diet (highest dose group): highest residues detected in kidneys 0.14/0.23 mg/kg (m/f) and in liver 0.21/0.35 (m/f) identified as endosulfan sulphate and no residues detected in kidneys and other organs and tissues (Doc C005978) lactating cow, 28 days feeding study

	with 4/12/30 mg/kg diet highest residues identified as endosulfan sulphate and detected in fat were 1.4/4.7/9.9 mg/kg resulting in the highest transfer factors of 0.35/0.39/0.33 (Doc C003624)
	Conclusion: The log Kow is below that of the parent substances and less than the POP trigger Residues in long term feeding studies with mouse, rat and cow did not indicate any bioaccumulation potential, because all transfer factors were smaller than unity . The results from mammals particularly did not show any potential of a magnification in the food chain.
potential for long-range environment transport	**Transport via air:** $t_{1/2}$ 2 days according anAtkinson calculation using an upgraded version of AOPWIN programme (Doc C012732) **Vapour pressure**: 10×10^{-5} Pa (20ºC) (Doc A38805) indicates a lower volatility than alpha or beta endosulfan **Transport via water:** is unlikely due to the very low water solubility of 0.5 mg/l at pH 5 and 20ºC (Doc A34274) **Transport via migrating animals** is also unlikely due to lower amounts available to animals compared to the parent substances and moderate log Kow **Monitoring data from locations distant from sources:** no findings reported
Adverse effefcts	**T** The POP criteria do not contain fixed trigger values for adverse effects needed for a clear assessment of the potential damage in human health or to the environment. Toxicity and ecotoxicity data need to be compared with potential exposure data to determine the potential to human health and the environment . Such comparisons do not result in an unacceptable risk for human health and environment.

(1) DT50 values no validated by RMS.

Table 8.4-4: Data and conclusions *made by notifier* in the assessment of endosulfan hydroxy carboxylic acid against POP

	The only environmental compartment where this metabolite had been detected was in the water body of a surface water study with two different water sediment inoculum (A31182). I ttopped 16-32 days after beginning of the incubation and dropped from the top portion of approximately 30% of the initial residues to 5-8% by day 51. it can therefore derived a very crude half-life of 20 days for the disappearance in both water sediment systems This half life is far below the POP persistence trigger for water Persistence in soil is not relevant because it is not formed in soil degradation studies. A potential bioaccumulation is very unlikely due to the polar character of the molecule, which is confirmed by the predominant occurrence in water body of the mentioned water sediment study Long range transport through the water is unlikely due to its rapid degradation. A transport through the air is also unlikely due to the polar character and consequently the very low volatilisation potential. A transport through migrating species is also unlikely due to the improbable bioaccumulation Adverse effects to human health and to the environment cannot be expected due to the low portion formed and the relatively polar character that restrains bioaccumulation.

RMS Assessment regarding the results of the evaluation proposed by notifier against POP criteria

- *Persistence criterion:*

Soil:

Parent: The DT50 obtained in the laboratory studies are summarized in table 8.3.1-1. In this table it can be observed that alpha endosulfan (worst case: 39 days) is generally faster degraded in soil than in beta isomer (worst case 264 days). The worst case observed for the sum of the two isomers was 128 days. Despite of this values, **it should taken into account that *the degradation of endosulfan did not show any alteration of the hexaclor norborne bicycleand showed very low mineralization (<5%; 120 DAT). These two facts suggest a high persistence of a soil residue constituted by a number of chlorinated metabolites.***

The main metabolite formed was endosulfan sulphate at a rate higher than 10% of applied radioactivity (18-40% at 60 days (A29680) and 46.1% at 365 days (A53618)). This compound was slowly degraded to the more polar metabolites which appeared at < 10% of the applied radioactivity . Non extractable residues were lower than 50% in the study A229680 and lower than 25% in the study coded A53618.

These results were confirmed under field conditions (A53554, A54025) . In all cases residues of parent compound were lower than 10% of the applied concentration and there was no evidence of leaching . However, residues of endosulfan sulphate (>10% of the initial concentration) were observed.

In soil accumulation study (A53771) total residues 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 concentration 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 this addenda two additional field dissipation studies have been assessed . The resulting parent compound residue decay rate versus days after application was evaluated by a pesticide dissipation model (ModelManager), with endosulfan sulphate being evaluated using multicompartment kinetic model (TopFit) to determine a degradation half life. The results of both studies showed that Endosulfan rapidly dissipated under field conditions with total parent endosulfan (a+β) residues also declining rapidly (DT_{50} 7.4 - 21 days). Total parent endosulfan residues were less than 10 % of applied within 1 month. The soil metabolite endosulfan sulphate achieved a maximum residue of 7.5 % of applied parent at 14 days in the Spanish study and 13.4% at 28 days in the Greeke study and then declined to leave no detectable residues after 6 months. As the concentration over the whole period was only slightly above the LOQ, the results of the kinetic modelling are influenced by a high element of uncertainty. **However**

these studies do not represent the current supported use in cotton, because only one application of endosulfan was made instead of 3.

Endosulfan sulphate : A laboratory study has been assessed in this addendum**. Four soils were tested and DT50 values ranged between 123-391 days.** The amount of endosulfan sulphate at the end of the study (365 days) varied between **8.3 and 45.55 % TAR.** In this study an unknown metabolite was identified above 10% but no those detected in the studies assessed in the monograph. **It seems that the rate of dissipation of the endosulfan sulphate depends on the soil type and it cannot be rejected that the rate fulfils the POP criteria .**

Water:

Parent: The rate of hydrolysis of α and β endosulfan is extremely dependent of pH. Under acidic conditions no hydrolysis could be observed (>200d), in a neutral medium the rate was moderate (10-19d) and in alkaline environment, it was very rapid (<1 d).

From the water sediment study evaluated in the monograph (pH>7), two main metabolites were identified under these conditions, **endosulfan sulphate and endosulfan hydroxylic acid** and mainly in the water phase, at >10% of the applied radioactivity. **The concentration of endosulfan sulphate in the sediment at the end of the study (51days) was 10.6 and 9.5 %TAR no reaching a plateau.**

Other different metabolites as endosulfan diol,, endosulfan lactone, endosulfan ether and unidentified metabolite were detected a very low levels. CO_2 detected and volatile compounds were < 4%.

Regarding to the DT_{50} values RMS concluded that 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.

In the present addendum two water sediment studies have been assessed at pH range 4.9-7.3. In conclusion**, the accumulation of parent and the endosulfan sulphate in the sediment and endosulfan hydroxy carboxylic acid in the water phase was observed. Endosulfan diol, was also observed as main metabolite. (see figures 8.3-1 to 8.3-4 and figures 8.3.-8 to figure 8.3-10). Finally, under acid conditions also endosulfan lactone appeared above 10% in the sediment at the end of the study period no reaching a plateau,**

DT_{50}s values for endosulfan sulphate have not been considered valid by the RMS, because the DT_{50} values for the total residue in water, sediment and in the whole system should be calculated correctly taking into account the process of formation and degradation of metabolites. However, in the case of endosulfan sulphate and endosulfan carboxylic acid, degradation process has not

Eliminado: endosulfan dihydroxy ether and endosulfan hydroxy carboxylic acid

Eliminado: er

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Eliminado: ¶
U

Eliminado: but endosulfan dihydroxy ether was not detected, maybe due to the decreasing biomass to zero throughout the study.¶

Eliminado: A good kinetic should be proposed.

seen, they accumulate in the sediment and in the water phase, respectively, and DT50 >120 d has been shown

In conclusion*, although degradation of endosulfan is seen it did not show any alteration of the hexaclor norborne bicycle. This suggest a high persistence residue constituted by a number of chlorinated metabolites.*

Eliminado: *and showed very low mineralization. These two facts*

Eliminado: *of a soil*

Thus, it seems that the rate of dissipation of the endosulfan sulphate in soil depends on the soil type and it cannot be rejected that the rate fulfils the POP criteria . Moreover, in the water sediment studies the accumulation of endosulfan sulphate in the sediment and endosulfan hydroxy carboxylic acid in the water phase was observed. In these cases DT50 >120 d has been shown. In the study under acidic conditions endosulfan lactone also appeared above 10% in the sediment at the end of the study period no reaching a plateau.

Eliminado: *but endosulfan dihydroxy ether was not detected, maybe due to the decreasing biomass to zero throughout the study.¶*

Eliminado: .

- *Bioaccumulation criterium*

The log Pow of endosulfan is 4.7. The studies presented by the notifier confirm the bioaccumulation potential of endosulfan, with BCF in fish between 2500 and 10000.

However, the clearance is very rapid, with a CT50 of about two days indicating no risk of biomagnification through the food chains.

Thus, endosulfan fulfils the B-criterion of the PBT-criteria, however the real risk of biomagnification is negligible due to the rapid clearance.

- *Potential for long range environmental transfer*

Air: Regarding to the half life of endosulfan in air the following conclusion was made in the evaluation table SANCO/4326/2001 rev2-2 (01.04.02): Half life of Endosulfan (report C012614) and Endosulfan sulphate (C012732) exposed to photochemical reaction with OH· radicals under European scenario ([OH·]=0.5 10^6 radicals / cm^3; 24 h per day) was calculated to be 47.1 h (2 days). Under USA scenario ([OH·]=1.5 10^6 radicals / cm^3; 12 h per day) was calculated to be 15.7 h (1.3 days) (AOPWIN program v. 1.88). Program yields the same result for both compounds due to similar chemical structure. ***According UN document on POPs (Montreal 1998) compounds with a persistence in the atmosphere with a half life equal or superior to 2 days are candidates to be considered POP.***

Monitoring data from locations distant from the sources : In the monograph of December 1999, RMS concluded that ***Endosulfan is expected to be evaporated from soil. Atmospheric concentration 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%)***

On the other hand, several publication reported findings of predominately alpha endosulfan in the air or artic regions2.7-9.7 pg/m3 in 1986;1.8-5 pg/m3 in 1987. Beta endosulfan was not detected

No information was submitted regarding to the main metabolites

- *Toxicity*.

For toxicity, no quantitative criterion is given in the EB decision 1998/2. Therefore, the division into three mammalian and ecotoxicity classes from the PBT-proyect were applied. This division is based on results from acute toxicity, reproduction and carcinogenicity for mammalian toxicity and acute and chronic ecotoxicity.

Endosulfan

Rat LD_{50} oral	10-22.7 mg/kg bw (f) R28 category 3
Rat LC_{50} inhalation	0.0126 mg/l air for 4 hours (f) R26 category 3
Rat LD_{50} dermal	500 mg/kg bw (f) R21 category 1
Carcinogenicity	No carcinogenic potential
Effects on reproduction	no effects on reproduction and no teratogenicity have been identified

Endosulfan-sulphate

Rat LD_{50} oral	25-50 mg/kg bw (f) R25 category 2
Rat LC_{50} inhalation	No data
Rat LD_{50} dermal	280 mg/kg bw (f) R24 category 2
Carcinogenicity	No data
Effects on reproduction	No data

Endosulfan hydroxycarboxylic acid

Rat LD_{50} oral	200 and 2000 mg/kg R 22 category 1
Rat LC_{50} inhalation	No data
Rat LD_{50} dermal	No data
Carcinogenicity	No data
Effects on reproduction	No data

Endosulfan is an insecticide that acts via the GABA receptor system. The lowest NOEC for chronic studies corresponds to a NOEC of 0.05 ug/l for fish. The 21 d chronic test on aquatic invertebrates resulted in a NOEC value of 63 ug/l. The NOEC for algae was 560 ug/l (72 hours NOEC).

This indicates that endosulfan fulfils the T-criterion of the PBT criteria.

Study: Selecting chemical substances for the UN_ECP POP protocol
Author: D. Lerche et al
Dated: Chemosphere 47 (2002) 617-630
Reference: C025221

The paper describes the results of a Dutch project with the aim of selection possible POP candidates for the UN_ECE-POP Protocol. The selection method is discussed as well as the so-called "preliminary risk profiles" for the selected candidates. Finally, future developments within the UN-ECE POP frame work and other international POP for a like UNEP and OSPAR will be discussed.

In order to select possible POP candidates PBT database created by HASKONING Consulting Engineers and Architects was used. This resulted in 300 substances meeting the criteria. For selecting POP candidates for UN ECE POP protocol . First, substances already included in the UN ECE POP Protocol and closely related substances were omitted. second, also other substances appearing already high on the agenda of the UN ECE were excluded: these were brominated flame retardants and chlorinated paraffins. Thereafter the selection was carried out applying the criteria of UN ECE POP Protocol (Table 8.4-1).

Estimation methods were used to calculate several of these PTB (persistence, toxicity and bioaccumulation potential) proprieties **as collecting and evaluating all available scientific literature was considered too time consuming for this phase**. For the same reason **the " non quantitative criteria** (i.e. the alternative evidence which can bw used, e.g. monitoring data showing that the substance is detected in remote regions) **for the criterion long-range atmospheric transport were not applied**. The quantitative criteria for potential for long range atmospheric transport, persistence and bioaccumulation were applied as follows:

Potential for long range atmospheric transport: persistence in air was predicted **using Atmospheric Oxidation Program (AOP)**. AOP estimates rate constants for the atmospheric gas-phase reaction between photochemically produced hydroxyl radicals and organic substances. it also estimates the rate constant for the gas-phase reaction between ozone and olefinnic/acetylinic substances. These rate constants are then used to calculate atmospheric half-lives based upon average atmospheric concentrations of hydroxyl reactions and ozone. Internal validation of AOP shows that from a list of 647 organic chemicals over 90% of the estimated gas phase hydroxyl radical rate constants are within a factor of two of the experimental values.

Persistence water, sediment and soil: biodegradation potential was predicted based on molecular fragments using **Biodegradation Probability program (BIODEG).** BIODEG gives the **probability for fast degradation** >0.5 are expected to degrade rapidly. BIODEG also includes a model that predicts the appropriate time required from ultimate degradation. The method is based upon molecular weight and 36 fragment constants. Internal validation of the model shows that for 295 chemicals 90% was correctly predicted. For the selection of POP candidates it was assumed that substances with non persistent character, defined as time required for complete degradation is less than n a month, do not meet the criteria from the UN ECE-POP Protocol.

Bioaccumulation the octanol-water partition coefficient was used as a predictor for the bioaccumulation potential. **BCFwin model** was applied, which uses a fragment constant methodology based on fragments and correction factors.

For toxicity no quantitative criterion is given in the EB decision 1998/2 (Table 8.4-1) **. The division into three mammalian and ecotoxicity classes from PTB –project were applied**. This division is base don results for acute toxicity, reproductions and carcenogenicity for mammalian toxicity and acute and chronic ecotoxicity **.**The (eco)toxicity data were obtained using ISIS/Risk line database. In the first place R-phrases according to EU 67/548/EEC were searched for acute toxicity, repro-toxicity and carcinogenety or International Angency of research on Cancer classifications for carcinogenicity . If this information could be found , toxicity data from IRIS/Risline were selected and the same classification criteria were applied.

Assessment

In table 8.4-5 the results obtained for endosulfan are showed . Endosulfan is presented by the authors as a substance which almost met the POP criteria , considering the uncertainties involved in the estimation of several criteria . Using actual data may lead to other-lower or higher-values.

Under RMS' opinion is more suitable to assess endosulfan against POP criteria using the whole scientific information collected and evaluated in the monograph and the following addenda than using the values estimated from several modelling.

On the other hand, it should be taken into account that although endosulfan seems to be no persistent in environment, this does not occur with the metabolites (see the assessment made in the point of soil and water degradation route).

Table 8.4-5: Results for endosulfan collected in the paper

CAS N	Chemical name	log Kow	Biodegradation (1)	vapour pressure Pa	Atmospheric half life (3)	Toxicity category (2)	
						Human	ecotox
115-29-7	Endosulfan	3.8	>m	3.5 E-5	1.3 d	1	1

(1) > m:longer, more than months

(2) category 1 according to PTB projet:

Mammalian toxicity

Oral LD50 rat (mg/Kg bw)	R22 or 200<LD50< 2000
Inhalation LC 5o rat (mg/14 h)	R20 or 2<LC50< 20
dermal LD 50 rat7rabitt (mg/Kg bw)	R21 or 400 < LD50< 2000

Ecotoxicity

Acute toxicity (mg/l)	0.1<L)E)C50<1
Chronic toxicity (mg/l)	0.01<NOEC< 0.1

(3) The endpoint given in this monograph is 2 days

Study: Assessment against PBT and VPVB criteria in the context of the European PBT strategy

Author: Leo W. Buerkle

Dated: December 2002

Reference: C028892

GLP: n/a

With its PBT strategy the European Union intends to identify potential persistent, bioaccumulating and toxic substances (PBTs) as well as very persistent and very bioaccumulating substances (vPvBs) among the high production volume chemicals (HPVCs). The European Commission, Joint Research Centre, Institute for Health and Consumer Protection, toxicology and Chemical substances, European Chemicals Bureau (ECB) published a PBT strategy report with screening results of corresponding substances based on entries in the IUCLID (International Uniform Chemical information Database (ecb41402-rev1, 2002). Among these substances endosulfan was classified as potential PBT and vPvB. This classification was justified by collection of physicochemical property data given in Annex 5, Table 3 (factsheet of potential PBT/vPvB, pages18-20). However, according to notifier, some data in the factsheet used for classification are inaccurate or difficult to interpreter or do not meet the P and B criteria of the Technical guidance document, revision II chapter 3-environmental risk assessment, section 4:4 PBT assessment. (Table 8.4-6).

Notifier does not agree with the proposed classification in the PBT strategy report and justifies its assessment by a compilation of the data reported in the document C028892

Table 8.4-6 Criteria of identification of PBT and vPvB substances

Criterion	PBT criteria	vPvB criteria
P	Half-life > 60 d in marine water or > 40 d in freshwater* or half-life > 180 d in marine sediment or > 120 d in freshwater sediment*	Half-life > 60 d in marine- or freshwater or >180 d in marine or freshwater sediment.
B	BCF > 2,000	BCF > 5,000
T	Chronic NOEC < 0.01 mg/l or CMR or endocrine disrupting effects.	Not applicable

* For the purpose of marine environmental risk assessment half-life data in freshwater and freshwater sediment can be overruled by data obtained under marine conditions.

Assessment:

Persistence criterion

Regarding to the Persistence criterion the data provided have been collected from the studies: A40003, A31182, A44231, C022921 , which have already been assessed in the monograph or in the present addendum.

According to the assessment made, DT50s values have not been considered valid by the RMS, because they should be calculated correctly for the total residue in water, sediment and in the whole system taking into account the process of formation and degradation.

In the present addendum two water sediment studies have been assessed at pH range 4.9-7.3. In conclusion, **in the case of endosulfan sulphate and endosulfan carboxylic acid degradation process**

has not seen. Thus, endosulfan sulphate accumulates in the sediment and endosulfan carboxylic acid in the water phase. Therefore, DT50 > 120 d hast been demonstrated in these cases . Finally, accumulation of endosulfan lactone is observed in the sediment under acidic conditions.

In conclusion: ***Degradation of parent compound is seen in water/sediment systems but , it did not show any alteration of the hexaclor norborne bicycle. This suggest a high persistence of a residue constituted by a number of chlorinated metabolites. Thus, endosulfan sulphate accumulates in the sediment and endosulfan carboxylic acid in the water phase. In these cases, DT50 > 120 d has been demonstrated. Finally, accumulation of endosulfan lactone is observed in the sediment under acidic conditions no reaching a plateau at the end of the period of test (365 days).***

Eliminado: Under acid conditions (pH 5), also endosulfan lactone apeeared above 10%

Eliminado: but endosulfan dihydroxy ether was not detected, maybe due to the decreasing biomass to zero throughout the study.¶

Eliminado: *ruote of endosulphan is not clear*

Eliminado:

Eliminado: ***and showed very low mineralization. These two facts***

Eliminado: *Under acid conditions (pH 5), also endosulfan lactone apeeared above 10%*

Bioaccumulation criterion

The log Pow of endosulfan is 4.7. The studies presented by the notifier confirm the bioaccumulation potential of endosulfan, with BCF in fish between 2500 and 10000.

However, the clearance is very rapid, with a CT50 of about two days indicating no risk of biomagnification through the food chains.

Thus, endosulfan fulfils the B-criterion of the PBT-criteria, however the real risk of biomagnification is negligible due to the rapid clearance.

Toxic criterion

Endosulfan is an insecticide that acts via the GABA receptor system. The lowest NOEC for chronic studies corresponds to a NOEC of 0.05 ug/l for fish. The 21 d chronic test on aquatic invertebrates resulted in a NOEC value of 63 ug/l. The NOEC for algae was 560 ug/l (72 hours NOEC).
This indicates that endosulfan fulfils the T-criterion of the PBT criteria.

Overall assessment

With the available information, the rapporteur can not established if Endosulfan fulfils the PBT-criteria due to the potential persistence of metabolites with the same chemical structure and possibly the same mechanisms of action.

B.8.7 References relied on

Annex IIA or Annex IIIA point	Author(s) Year Title Reference	GLP GEP Y / N	Published Y / N	Owner	Data Protection
	Schnöder, F 2002 [^{14}C]AE F051327: soil Metabolism and degradation Aventis CropScience USA LP. Doc. No.: C019647; Report No. 1651-1490-019	Y	N	Aventis	Y
	Balluff, M 2001 Field Soil Dissipation of AE F002671 (endosulfan) following a single application to bare (preemergence) cotton plots at 1 location in Greece, 2000 Aventis CropScience USA LP. Doc. No.: C018180; Report No. 20003033/GR1-FS	Y	N	Aventis	Y
	Hardy, I.A.JH 2001 Endosulfan field soil dissipation study in Spain Aventis CropScience USA LP. Doc. No.: C015651; Report No. 26644	Y	N	Aventis	Y
	Winfried J. 2002 Degradation of [^{14}C] Endosulfan in two aerobic water/sediment systems Aventis CropScience Doc. No.:C022921	Y	N	Aventis	Y
	Winfried J. 2002 Degradation of [^{14}C] Endosulfan in two aerobic water/sediment systems (under acidic conditions) Bayer CropScience Doc. No.:C031060	Y	N	Bayer	Y
	Buerkle, Leo W. 2003 Endosulfan-fate in water sediment Comparision of different water-sediment studies conducted with pure ^{14}C-labelled test substance BayerCropScience Doc Nº: C032555	N/A	N	Bayer	Y
	Hammel, Klaus 2003 Kinetic evaluation of the dissipation of endosulfan and its metabolites endosulfan sulfate, endosulfan diol and endosulfan hydroxy carboxylic acid in aerobic water-sediment test systems BayerCropScience Doc Nº: C036633	N/A	N	Bayer	Y
	Neil Mackay 2002 Summary of pH conditions in surface waters in southern Europe	N/A	N	Aventis	Y

Annex IIA or Annex IIIA point	Author(s) Year Title Reference	GLP GEP Y / N	Published Y / N	Owner	Data Protection
	Aventis CropScience Doc. No.:C022977				
	Steve Kay and Chris Holmes 2000a Field observations of water bodies and agricultural practices volume I- Spain Study site Aventis CropScience Doc. No.:C019471	N/A	N	Bayer	Y
	Steve Kay and Chris Holmes 2000b Field observations of water bodies and agricultural practices volume II- Greece Study site Aventis CropScience Doc. No.:C019472	N/A	N	Bayer	Y
	Steve Kay 2001 Characterization and analysis of potential vulnerability of aquatic habits near agriculture Volume I: Sevilla, Spain Aventis CropScience Doc. No.:C019473	N/A	N	Bayer	Y
	Neil Mackay 2002d Aquatic ecological risk assessment for endosulfan uses on cotton in Spain Part 1: Characterising risks associated with spray drift BayerCropScience Doc Nº C021321	N/A	N	Bayer	Y
	Neil Mackay 2002b Estimations of run-off loadings and surface water exposure associated with representative endosulfan usage sites in Southern Europe BayerCropScience Doc Nº C021146	N/A	N	Bayer	Y
	Neil Mackay 2002c Aquatic ecological risk assessment for endosulfan uses on cotton in Spain Part 2: Characterizing risks associated with run-off BayerCropScience Doc Nº C021344	N/A	N	Bayer	Y
	Neil Mackay 2002a Site-Specific evaluation of realistic usage conditions for endosulfan in Greece, Spain and Portugal BayerCropScience Doc Nº C021352	N/A	N	Bayer	Y
	Buerkle, Leo W. 2002 Summary of the aquatic ecological risk assessment of endosulfan usage on cotton in Spain BayerCropScience Doc Nº C021461	N/A	N	Aventis	Y

Annex IIA or Annex IIIA point	Author(s) Year Title Reference	GLP GEP Y / N	Published Y / N	Owner	Data Protection
	Buerkle, Leo W. 2002 Aquatic ecological Risk Assessment of endosulfan usage on tomatoes in southern Europe BayerCropScience Doc Nº C02267	N/A	N	Aventis	Y
	Buerkle, Leo W. 2002 Aquatic ecological Risk Assessment of endosulfan usage on cotton in Greece BayerCropScience Doc Nº C023003	N/A	N	Aventis	Y
	Buerkle, Leo W. 2001 Endosulfan and its environmentally relevant metabolites- Assessment using the criteria for classification as persistent organic Pollutant Aventis CropScience Doc. No.:C013092	N/A	N	Aventis	Y
	D.Lerche *et al* 2002 Selecting chemical substances for UN_ECP POP protocol Chemosphere 47 (2002) 617-630 Bayer CropScience Doc. No.:C025221		Y		
	Buerkle, Leo W. 2003 Assessmentagainst PBT and vPvB criteria in the contex ofEuropean PBT strategy Bayer CropScience Doc. No.:C028892	N/A	N	Bayer	Y

TABLE OF CONTENTS