WRc

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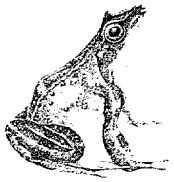

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PROVISIONAL ENVIRONMENTAL QUALITY STANDARDS FOR ENDOSULFAN IN WATER (DWE 9378)

DoE 2527-M

JULY 1990

PROVISIONAL ENVIRONMENTAL QUALITY STANDARDS FOR ENDOSULFAN IN WATER

Report No: DoE 2527-M

July 1990

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Contract No: DWE 9378

DoE reference no: PECD 7/7/220

Contract duration: January 1987 - March 1991

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SUMMARY

I OBJECTIVES

To propose provisional environmental quality standards (PEQSs) for endosulfan for the protection of aquatic life based on readily available information on environmental fate and ecotoxicity.

II REASONS

The UK Government has proposed, in the Ministerial Declaration in response to the second Ministerial Conference on the Protection of the North Sea, tighter controls over the most dangerous substances entering the aquatic environment (DoE 1987). In response to this declaration the DoE have published an agreed 'Red List' of 23 substances (DoE 1989a). This report is one of a series proposing PEQSs for 'Red List' substances for which no environmental quality standards have yet been set.

III CONCLUSIONS

Endosulfan is a broad-spectrum, non-systemic contact and stomach acting insecticide which is very toxic to fish. Endosulfan is an organochlorine compound and the technical product consists of two isomers of similar toxicity to most aquatic organisms. Endosulfan may be oxidised in water and organisms to endosulfan sulphate which is also toxic. Entry into the aquatic environment may occur from diffuse inputs via spray drift and land run-off, or by point discharges. Chemical and biological degradation result in half-lives of about 4 days in waters of pH >7 or greater than 1 week in water of pH <7 with degradation to the comparatively non-toxic endosulfan diol.

For the protection of freshwater life a PEQS of 10 ng/l is proposed based on applying an arbitrary safety factor of 30 to the acute LC50 of 300 ng/l for rainbow trout (Nebeker et al 1983), Table 1. A smaller safety factor of 30 compared to the more usual 100 has been applied as

tests have shown that, for fathead minnow, juvenile fish (7 day LC50 of 0.86 µg/l) and early life stages (NOEC of 0.2 µg/l for full lifecycle tests) have similar sensitivities to endosulfan, Macek et al (1976). The standard of 10 ng/l is expressed as annual average concentration and as "total dissolved endosulfan", which is defined as the sum of the concentrations of the two isomers plus the degradation product endosulfan sulphate and is measured after allowing the sample to settle for one hour before analysis of the supernatant. The standard is based on dissolved endosulfan because environmental data and field trials suggest that endosulfan tends to become adsorbed to suspended solids and that in this form it is not readily bioavailable to aquatic organisms and in particular to fish.

In addition to protect against episodic pollution a PEQS of 1 µg/l for "total dissolved endosulfan" expressed as maximum concentration is also proposed. This is based on applying an arbitrary safety factor of 30 to the short-term LC50 of 31.9 µg/l obtained by Kleiner et al (1984) for fathead minnow. A safety factor of 30 has been selected by applying a factor of 10 to protect against acute effects and an additional factor of 3 to take into account that other species are more sensitive.

Insufficient data are available to set a standard for total (dissolved and adsorbed) endosulfan.

For the protection of marine life a PEQS of 5 ng/l for "total dissolved endosulfan" expressed as annual average concentration is proposed based on the application of a safety factor of about 10 to the acute LC50 of 40 ng/l for the pink shrimp (Schimmel et al 1977). Only a relatively small safety factor has been applied as the chronic and acute toxicities appear to be similar. No maximum PEQS value is proposed for total or "total dissolved endosulfan" for the protection of marine life.

The analytical limits of detection for endosulfan currently achievable within the water industry (~10 ng/l in river waters, Standing Committee of Analysts 1988) are inadequate for monitoring the proposed PEQSs in natural waters.

Allowing that 1% of the acceptable daily intake (ADI) (0.008 mg/kg body weight, WHO 1984) may be derived from drinking water, the resulting maximum acceptable concentration (MAC) in drinking water would be 2.4 µg/l for a 60 kg adult drinking 2 l per day. This value is much greater than the MAC of 0.1 µg/l laid down in the EC Drinking Water Directive for individual pesticides. No "advisory value" is included for endosulfan in the Guidance on Safeguarding the Public Water Supplies (DoE 1989b).

IV RECOMMENDATIONS

The PEQS values proposed are based on a wide variety of laboratory toxicity data and evidence from field applications and environmental concentrations. However, insufficient information is available on the fate and bioavailability of endosulfan adsorbed on sediment. The PEQSs should therefore be regarded as guideline values which might need revision when additional data become available.

V RESUME OF CONTENTS

This report uses available information on the ecotoxicity and environmental fate of endosulfan to derive PEQSs for the protection of freshwater and marine life.

CONTENTS

CONTENTS - continued

SECTION 1 - INTRODUCTION

Following the Second Ministerial Conference on the Protection of the North Sea the UK announced the adoption of a more precautionary approach to the control of the most dangerous substances discharged to the aquatic environment by applying limit values and environmental quality standards (EQSs) (DoE 1987) to discharges. After the announcement and following consultations, the Department of the Environment issued a 'Red List' consisting of 23 substances (DoE 1989a). Recently endosulfan has also been proposed to be assigned List I status under Directive 76/464/EEC (COM 1990). This report is one of a series of reports proposing provisional environmental quality standards (PEQSs) for those 'Red List' substances for which no EQSs have previously been derived. It reviews the available information on the ecotoxicity and environmental fate of endosulfan and proposes PEQSs for the protection of aquatic life, Table 1.

Table 1 - PEQS values recommended by WRc for endosulfan

Water Use	PEQS value*
Protection of fresh waters	10 ng/l AA/D 1 µg/l M/D
Protection of marine waters	5 ng/l AA/D

Notes

M - maximum concentration
AA - annual average concentration
D - dissolved concentration (after 1 hour settlement and analysis of the supernatant)
* - values expressed as the sum of α endosulfan, β endosulfan and endosulfan sulfate

SECTION 2 - ENDOSULFAN IN THE ENVIRONMENT

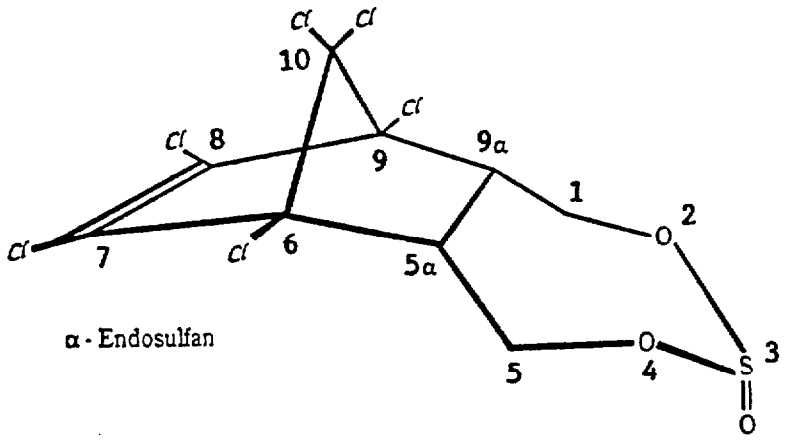
2.1 PHYSICO-CHEMICAL PROPERTIES

The technical endosulfan product (typically 96% active ingredient (ai)) is a mixture of two isomers, known as α (or A or I) and β (or B or II), in the ratio of 70-80% α to 30-20% β. Most of the data in Table 2 refer to this mixture.

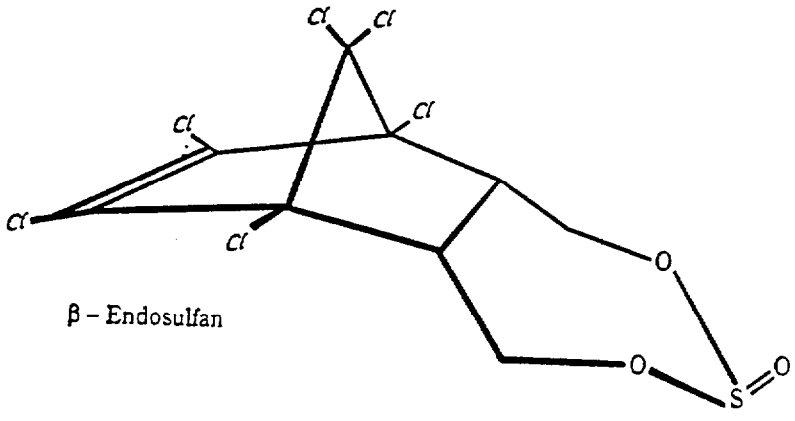
Table 2 - Physico-chemical properties of endosulfan

Chemical structure:		(See Figure 1)
Chemical name:		6,7,8,9,10,10-hexachloro-1,5,5a,6,9,9a-hexahydro-6,9-methano-2,4,3-benzodioxathiepin-3-oxide
CAS Registry Number:		115-29-7
Trade names:		Thiodan (also other than in the UK: Beosit, Chlorthiepin, Cyclodan, Insectophene, Kop-Thiodan, Malix, Thifor, Thimul, Thiotox, Thiodon, Thioden, Thionex and Hildan).
Physical state:		yellow-brown crystals (colourless when pure)
Molecular weight:		406.9
Melting point:		technical 70-100 °C
	α	108-110 °C
	β	207-209 °C
Boiling point:		106 °C at 0.0009 atm (partially decomposes)
Water solubility:		60-150 µg/l
		325 µg/l at 22 °C
	α	530 µg/l, 164 µg/l, 150 µg/l, 260 µg/l, 600 µg/l
	β	280 µg/l, 70 µg/l, 60 µg/l, 100 µg/l
Vapour pressure:		1.3 mPa at 25 °C
		1.2 Pa at 80 °C (reported "not determinable" at room temperature)
Henry's Law constant:		6.7×10^{-6} atm.m³/mol (α) (Cotham and Bidleman 1989)
		6.2×10^{-7} atm.m³/mol (β)
Octanol-water partition coefficient, Log Kow:		3.60, (α3.55), (β 3.62) (Ali 1978)

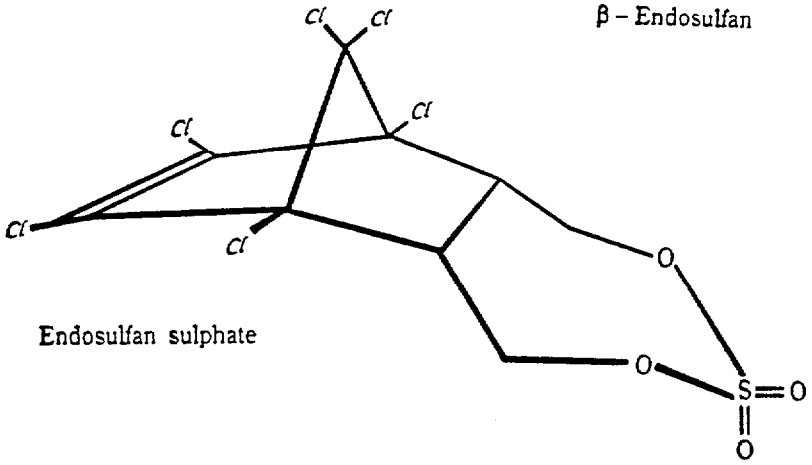
The data in Table 2 were collected from the literature studied, especially the review-type papers. The range of values for the water solubility requires some comment. From one of the reviews by Callahan



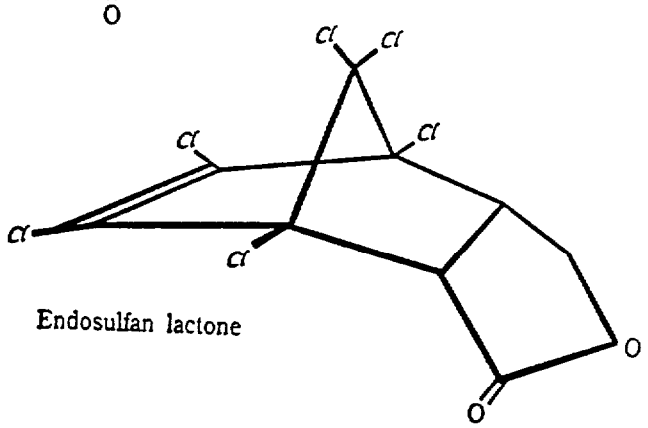
α - Endosulfan



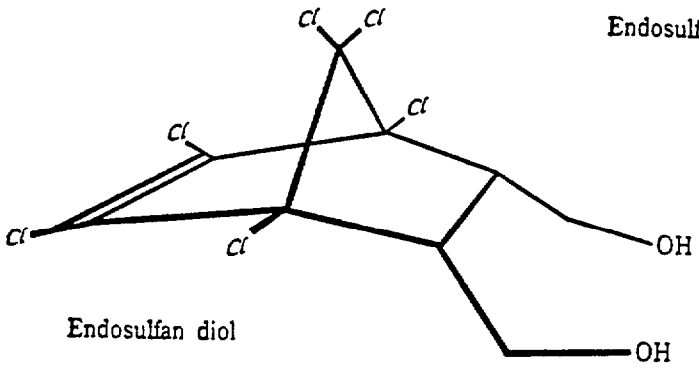
β – Endosulfan



Endosulfan sulphate



Endosulfan lactone



Endosulfan diol

Figure 1. Structure of Endosulfan Isomers and some Metabolites.

et al (1979) it seems that the solubility of both isomers is affected by the pH of the solution, with solubility increasing in acid solutions. If this is a real effect then pH will also affect the rate of volatilisation from aqueous solution and the octanol-water partition coefficient.

The Henry's Law constants were calculated from solubility and vapour pressure data assuming endosulfan was a liquid at 25 °C. This condition is more appropriate for calculating volatility from solution. The values used by Cotham and Bidleman (1989) were:

	α	β
solubility, mg/l	3.7	21.2
vapour pressure, Pa	0.0062	0.0032

2.2 MANUFACTURE AND USES

Endosulfan was introduced in the mid 1950s. Technical endosulfan is obtained through the Diels-Alder addition of hexachlorocyclopentadiene and cis-butene-1,4-diol to form a bicyclic dialcohol, followed by esterification and cyclisation with thionyl chloride (National Research Council Canada, NRCC 1975). The process gives a mixture of two stereo-isomers with different geometry at the sulphite group (see Figure 1).

The estimated EC production capacity is 6700 tonne/year (t/y) (Dequinze et al 1984). Actual production within the EC is estimated to be <5000 t/y with Hoechst in West Germany being the only manufacturer in the EC. World production has been estimated at approximately 10 000 t/y (WHO 1984). Dequinze et al (1984) also reported that some 1500 t/y are imported into the EC from Israel but that usage within the EC is about 375 t/y and only 5 t/y is formulated in the UK.

Endosulfan is a broad spectrum, non-systemic, contact and stomach acting insecticide and acaricide. It is sometimes seen as a replacement for other more persistent organochlorine insecticides (eg DDT, drins). It

is applied against mites, aphids, capsids, midges, beetles and weevils. It is available in many formulations including emulsifiable liquid concentrates, wettable powders, dustable powders and granules. Depending on the type of crop and where it is grown, application rates can range from 0.45 to 1.4 kg ai/ha. Minimum time intervals between last application and harvesting are laid down in most countries and vary between 0 and 42 days, depending on the crop, type of formulation used and agronomic needs.

In addition to its agricultural uses, endosulfan is also applied in some countries as a wood preservative and to control garden pests (WHO 1984). In Africa it has been used to control tsetse fly (Fox and Matthiessen 1982, Koeman et al 1978) at either high, single dose application rates of around 1 kg/ha or at low rates of about 10 g/ha but repeated up to three times at two- to three-weekly intervals.

In the USA the possibility of using endosulfan to control "trash" fish in, for example, fish farms and sport fisheries, has been investigated (Schoettger 1970a and Mulla et al 1967) and indeed one of the early patents covered this usage.

In the UK it is limited to professional use with permitted ("on-label") uses (The UK Pesticide Guide 1990) against pollen beetles, pod midge, cabbage seed weevil on rape and mustard, blackberry mites on blackberries, tarsonemid mites on strawberries, damson-hop aphid on hops and bulb-scale mite on narcissi. There exist "off-label" approvals for use on non-edible glasshouse crops until February 1991, against Colorado beetle on potatoes until November 1991 and on pot plants, bedding plants and plants for flower production until January 1992. Harvesting after last application is restricted for 24 hours for ornamentals and three to six weeks for food crops. Livestock should be kept off treated areas for at least three weeks and, because it is harmful to bees, it should not be used during flowering (including when flowering weeds are present). Among other restrictions and warnings given are that it is flammable, dangerous to fish, should not contaminate ponds, ditches and waterways, toxic if swallowed and harmful by skin contact. It is

subject to the Poisons Rules and Poisons Act and to the restrictions applied to Part II substances under the Poisonous Substances in Agriculture Regulations 1984.

In the UK it is available (Pesticides 1989) in three products, all of which are emulsifiable concentrates: Thiodan 20EC and 35EC (from Promark) and Endosulfan 35 (from Mandops Ltd). Estimates of usage during the early 1980s have been published (Sly 1985) and suggest yearly totals of less than 13 t ai/y with most being applied to soft fruit (8.9 t/y on 7500 hectare) and hops (3.3 t/y on 2700 hectare). This usage rate suggests that some 8 t/y is imported into the UK already formulated for use.

2.3 ANALYSIS

2.3.1 Analytical requirements for EQS monitoring

WRc recommends (Gardiner and Wilson 1976; Cheeseman and Wilson 1976) the following accuracy requirements for the selection of an analytical method to monitor a quality standard of X concentration units:

a) bias of analytical results should not exceed X/20 or 10% of the measured value, whichever is the greater;

b) the total standard deviation of individual analytical results should not exceed X/40 or 5% of the measured value, whichever is the greater.

In summary, these requirements imply a target limit of detection of X/10. For example, this would mean that for a proposed EQS of 10 ng/l the detection limit should not exceed 1 ng/l, the total standard deviation of individual results should not exceed 0.25 ng/l or 5% (whichever is the greater) and the bias should not exceed 0.5 ng/l or 10% (whichever is the greater).

2.3.2 Analytical techniques

The Standing Committee of Analysts (1978 and 1985) methods for organochlorine pesticides in water rely on solvent extraction by hexane (1978) or ethyl acetate (1985) followed by separation from PCBs using elution from a silica column and separation from other pesticides by gas chromatography with detection by an electron capture detector. A range of packed or capillary columns has been found suitable for the separation but capillary columns would be favoured now, especially when performing a general pesticide analysis. Other selective detectors have been used such as a microcoulometer for chlorine and flame photometer for sulphur (Greve and Wit 1971). The Standing Committee of Analysts (1988) has reviewed the limits of detection achievable by the water industry for the Red List substances. The Committee concluded that in 'clean' water samples (ie drinking waters) a detection limit of 0.5 ng/l was achievable for α-endosulfan but that in 'dirty' waters (ie river water, industrial and sewage effluents) a detection limit of only 10 ng/l could be expected but not guaranteed. Current experience at WRc indicates that these figures are of the correct order of magnitude for one litre samples but because of the more polar nature of β-endosulfan problems with recovery and separation can arise making identification and quantification more difficult. As in all such cases more confidence in peak identification is obtained if a substance can be identified on two different types of column or if mass spectrometric identification is possible. If available, negative-ion chemical ionisation mass spectrometry is preferred in order to achieve the best sensitivity for endosulfan.

Because both isomers are oxidisable to endosulfan-sulphate, which is reported to have a similar toxicity to the parent compounds, there is a need to analyse for the sulphate as well. Macek et al (1976) showed that the relative sensitivities of an electron capture detector to α-, β-endosulphan and endosulfan sulphate were 40:20:1.

2.4 ENTRY INTO THE AQUATIC ENVIRONMENT

In an answer to a question raised in the European Parliament the Commission (COM 1984) stated that, because the only production plant in the EEC was in Germany on the Main close to its discharge into the Rhine, the Convention on the Protection of the Rhine against Chemical Pollution (Rhine Commission) was the appropriate framework for providing rules to control emissions from production rather than setting Limit Values under the Dangerous Substances Directive (74/464/EEC).

As endosulfan is not manufactured in the UK point source pollution will be restricted to spillages and discharges from formulation plants and marketing outlets. Direct discharges may also result from the pesticide use ie disposal of unused chemical and cleaning of application and mixing equipment. However, the main route of entry into the aquatic environment is from diffuse sources associated with its use as a pesticide. The main diffuse sources are run-off from land and spray-drift as endosulfan is most frequently applied using air-blast equipment and boom sprayers.

2.5 LEVELS IN THE ENVIRONMENT

Up-to-date data on the levels of endosulfan in environmental samples appears to be lacking. Most of the available data refer to the late 1960s and early 1970s. The data indicate that, unlike some other organo-chlorine pesticides, endosulfan contamination of waters and biota is not widespread and most positive identifications can be related to known usage or spills.

2.5.1 Water

In a survey at 28 sites on major West German rivers during 1970 and 1971 (Herzel 1972) endosulfan was detected at two sites on the Rhine (Düsseldorf and Oestrich, which is just below the confluence with the Main), at one on the Main (Raunheim, downstream of Frankfurt) and at one on the Regnitz. Levels were in the range 0.01 to 0.1 µg/l for

individual isomers in the water and 0.01 to 0.024 µg/l on suspended solids. The positive suspended solid samples were from the sites on the Main and Regnitz. Industrial effluents were stated to be the source of endosulfan in these samples. Of the sites where endosulfan was detected repeat samples were taken only at Düsseldorf with five of the eleven samples analysed containing endosulfan.

A widespread fish-kill was observed in mid-1969 when approximately 30 kg of endosulfan was discharged into the Rhine in West Germany (Sievers et al 1972, Lüssem and Schlimme 1971). Concentrations of up to 5 µg/l endosulfan with 3.5 mg/l dissolved oxygen and a temperature of 19 °C were measured at the site of the fish kill. A second spill, when concentrations of 1 µg/l endosulfan with 1.5 mg/l dissolved oxygen and a temperature of 11.5 °C were found, did not result in fish kills, possibly because of the lower temperature. Endosulfan concentrations in the lower Rhine, in the Netherlands, resulting from the first spill were reported by Greve and Wit (1971) to range from 0.7 µg/l on the first day of the investigation to below 0.01 µg/l about a month later. These authors noted that most of the endosulfan was associated with the suspended solids in the samples. For the second endosulfan spill concentration peaked at 0.88 µg/l (Greve 1972) in the lower Rhine in November 1969. The presence of endosulfan coincided with elevated concentrations of cholinesterase inhibitors (probably organo-phosphorus insecticides). Subsequently from July 1970 to the end of the monitoring period, March 1972, endosulfan was generally below the detection limit of 0.01 µg/l. Wegman and Greve (1980) described the results of a sampling program on Dutch waters from 1969 to 1977 which included analyses for endosulfan. Both isomers of endosulfan were found in the Rhine at Lobith in 1969 (maximum level $\alpha+\beta$ 0.81 µg/l) and 1970 (maximum level $\alpha+\beta$ 0.4 µg/l) and at lower levels (α-endosulfan 0.02 to 0.25 µg/l) up to 1976 whereas the 1977 sample contained less than 0.01 µg/l. In the Meuse α-endosulfan was found at 0.09 to 0.01 µg/l in three of the five yearly samples in the period 1969 to 1973.

In only one stream out of 546 analysed in the western USA was endosulfan detected; the amount found was 0.02 µg/l. A National Research Council

Canada (NRCC) (1975) report provides information for Canadian waters taken from various sources, including data from unpublished reports. Endosulfan was found in five out of forty samples taken from Lake Erie (0.005 to 0.014 µg/l), six out of forty from Lake Ontario (0.005 to 0.051 µg/l) and a few samples from the St Lawrence River 0.02 to 0.06 µg/l. Over a six-year period samples collected quarterly from six rivers in Ontario and municipal supplies produced only one sample with endosulfan at a detectable level, 0.012 µg/l. Gummer (1980) reported that only one sample out of 1400 surface water samples collected during the period 1971 to 1977 in western Canada contained endosulfan. This sample was from the Souris River area of Manitoba and contained 0.011 µg/l.

The NRCC report (1975) gives details of two fish kills which occurred after nearby spraying with endosulfan. In the first incident, where concentrations of 0.096 and 0.26 µg/l were recorded, fish kills occurred but no kills were observed at concentrations of 0.022 and 0.026 µg/l. The second kill involved rainbow trout in a pond where endosulfan was at undetectable levels in the water, (<0.001 µg/l α-endosulfan) but residues of 0.47 mg/kg "total" endosulfan (ie α+β + sulphate) were found in the fish and up to 3 µg/kg dry weight in the sediment.

Fox and Matthiessen (1982) studied the levels of endosulfan in shallow waters in the Okavango Delta, Botswana, arising from aerial spraying. Six to nine hours after spraying at a nominal 9.5 g ai/hectare samples from marsh (<0.5 m deep), river (1 to 2 m deep) and pools (<0.5 m deep) contained 0.2 to 4.2 µg/l with no significant differences in concentrations for the three different waters. These values are comparable to the calculated concentrations of 0.95 and 9.5 µg/l assuming water depth of 1 m and 0.1 m. In practice analysis of targets within spraying areas demonstrated a mean application of 47% of the theoretical value but, even with the use of electronic navigation equipment and in ideal atmospheric conditions, considerable variations occurred, including some double-dosing. Residues disappeared from the water in weedy pools within five days but were detectable in clearer waters for up to 20 days. An experiment with tanks of clear water,

water plus uprooted vegetation and water plus undisturbed silt and vegetation confirmed that after aerial spraying with submerged material faster decline of endosulfan concentrations occurred in water. (The effects of the spraying programmes on aquatic life are discussed in Section 3.2.)

Studies of endosulfan in agricultural run-off in the USA by Epstein and Grant (1968) indicated that, if rain followed within 4 days of foliar application to potatoes at 0.35 kg ai/ha the concentration in the run-off averaged 18 µg/l. After nine run-off events totalling 45 mm of rain within a three month period 0.3% of the applied pesticide was lost in the run-off. In a later experiment Richardson and Epstein (1971) spiked 100 g samples of two different silt-loam soils with 1 mg of endosulfan and then wetted each sample with 400 ml water and determined the distribution of the pesticide between water and the various soil fractions. Recoveries of endosulfan in the water were 66% and 55% from the two soils. These values contrast to the recoveries of DDT and methoxychlor in the water which were in the ranges 1 to 2% and 7 to 30%, respectively. When readily oxidisable organic matter was removed by treating the soils with hydrogen peroxide retention of endosulfan decreased, with 83% and 92% being recovered from the water.

The company manufacturing the pesticide (Hoechst) investigated the distribution of endosulfan residues in waters from the River Brantas catchment in eastern Java during the wet season of 1969/1970 (Gorbach et al 1971a). About 800 t endosulfan was applied throughout the system to control rice stem borer, with half being used in the 1330 km² of the delta area at an application rate of 1.4 l emulsifiable concentrate/700 l water/ha over a four month period. Samples were taken along the length of the river, from the shallow coastal waters off the delta, and from irrigation/drainage canals and fish ponds within the delta. All samples were analysed for α- and β-endosulfan, and the sulphate with individual detection limits of 0.01 µg/l giving an overall detection limit of 0.03 µg/l for "total" endosulfan. Levels of total endosulfan varied between 0.07 and 7.0 µg/l at 18 sites along the river with only the site nearest the source of the river being below the detection limit. The highest value was assumed to be from a very recent

use because sulphate was not present in the sample. In most other samples the sulphate predominated. Of the coastal samples it was mainly the freshwater surface layer which was contaminated. Twelve out of 15 sites on the canals contained endosulfan, ranging from 0.07 to 8.6 µg/l. The site where the highest level of 8.6 µg/l was found was sampled two days later and the total endosulfan level had fallen to 1.0 µg/l and the distribution of the three components changed from 5.8 µg/l alpha: 2.4 beta: 0.4 sulphate to 0.23: 0.24: 0.55, respectively. However, at another moderately contaminated site, with 1.0 µg/l total endosulfan, the distribution of the three components did not change over a two day interval. Only four out of 21 fish ponds, which were recharged with canal water at infrequent intervals, were contaminated with levels ranging from 0.16 to 0.77 µg/l with the sulphate predominating. Gorbach et al (1971b) also investigated the rates of loss of endosulfan from sprayed rice fields in the same area. The fields were sprayed with 1.4 l Thiodan 35EC made up in 750 l water per hectare and at the time of the experiment daily rainfall was 15 to 30 mm. Field A, which was flooded, had no inlet or outlet, field B was fed from an irrigation canal at 1.5 l/sec and field C was mud, half of which was covered to protect it from rain (C-dry) and half (C-wet) was unprotected. There was a further sampling point (point-9) about 1000 m downstream in the canal receiving the water from field B. The concentrations (µg/l) in the water in fields A and B and at pt-9 during the period after spraying are given in Table 3.

Table 3 - Decay of endosulfan concentrations (µg/l) in rice fields (Gorbach et al 1971b)

Time	Field A			Field B			Point 9		
	α	β	sulphate	α	β	sulphate	α	β	sulphate
End of spray	110/ 250	70/ 300		28	40		3.2	2.0	0.2
After 6 hr	1.9	1.4		0.4	0.4				
1 d	4.7	3.5		0.35	0.45	0.1	0.08	0.09	0.3
3 d	0.66	0.68	0.13	0.08	0.15	0.2	0.05	0.05	0.19
8 d	0.20	0.19	0.18	0.02	0.05	0.16	0.03	0.14	0.27

The levels of endosulfan in the water in field B after one day were comparable with those in the inlet water, which derived from more general spraying in the project area (see above). Some residues were found in the mud of fields A and B. (The paper does not state whether the reported concentrations are on a wet or dry weight basis and confuses units between text, tables and a graphical representation of the decline in concentrations. The paper records a shift towards the sulphate in the mud.) The concentrations in the mud of field C started at around 1 mg/l and slowly declined in the dry portion but oscillated in the wet portion.

Daily sampling over a two week period of a river system in Ontario, receiving the run-off from treated orchards, detected endosulfan on only one day with concentrations ranging from 0.047 to 0.083 µg/l (NRCC 1975).

No endosulfan was detected (quoted detection limit 10 µg/l) in well water abstracted near fields in Wisconsin and Florida 100 and 282 days, respectively, after the last application (WHO 1984 and NRCC 1975 citing the US manufacturer's, FMC, unpublished data). Application rates amounted to 0.56 kg ai/ha over four years and 1.12 kg/ha over five years. NRCC (1975) gives other examples of run-off studies which indicate that initial levels of endosulfan in run-off fall quickly but sediments in drainage ditches may well contain up to about 100 µg/kg "total" endosulfan.

2.5.2 Biota

Some field data are available on the accumulation of endosulfan in aquatic species. Ourisson and Koch (1980) have summarised the concentrations measured by Eichner (1973) in different fish species in Germany, Table 4, with values ranging from non-detectable levels to 210 µg/kg.

Table 4 - Concentrations of endosulfan in freshwater fish in 1971 Eichner (1973) (Cited from Ourisson and Koch 1980)

Species	Location	Concentration (µg/kg)*
Alburnus lucidus (bleak)	Bodensee (lake) FRG	70-150
	Bodensee (flow) FRG	20-100
	R.Rhine, Mannheim FRG	40-80
Perca fluviatilis (perch)	Bodensee (lake) FRG	40-140
	Bodensee (flow) FRG	30-110
	R.Rhine, Mannheim FRG	30-80
Anguilla sp. (eel)	Bodensee (lake) FRG	50-210
	Bodensee (flow) FRG	50-180
Esox lucius (northern pike)	R.Rhine, Mannheim FRG	40-70
Leuciscus rutilis (roach)	R.Rhine, Mannheim FRG	30-200
Oncorhynchus mykiss (rainbow trout)	Blackforest lakes FRG	ND-60
	Fish farm	ND-70

Notes

ND not detectable
* assumed wet weight

Amodio-Cocchieri and Arnese (1988) detected endosulfan in six fish species from two out of four rivers in southern Italy: 24% of samples (carp and tench) from the River Calore and 22% of samples (bleak) from the River Sele contained up to 5 and 8 µg endosulfan/kg muscle wet weight, respectively. Despite the fact that lindane and endosulfan are the only organo-chlorine pesticides currently permitted for agricultural use in Italy, in this study endosulfan was seen less often and at lower concentrations than several banned organo-chlorines. The significance of these results in terms of the relative stabilities of the organo-chlorines, historical use patterns and current usage is not clear.

Swackhamer and Hites (1988) found α-endosulfan (at 1.5 µg/kg lipid) only in the sample of medium-sized lake trout, Salvelinus namaycush, from Siskiwit Lake. Samples of three other size ranges of trout and of

whitefish, Coregonus culpeaformis, did not contain endosulfan (detection limit about 1 µg/kg). This finding suggests the possibility of long-range aerial transport of endosulfan as Siskiwit Lake is on an island which is a National Park in Lake Superior and it is therefore unlikely that endosulfan has ever been used on the island.

Gorbach and Knauf (1971) reported levels of endosulfan in living and dead whitefish taken from the Rhine at the time of the mid-1969 fish kill referred to in Section 2.5.1 above. Dead fish were found with "total endosulfan" residues of between 30 and 400 µg/kg but living fish had similar residues of 260 to 590 µg/kg. The authors also reported "contradictory" levels in living and dead fish from field trials in Java and up to 2500 µg/kg in living goldfish exposed for four days to 2 µg/l. Therefore, although conceding that the presence of endosulfan in the Rhine probably arose from aerial emissions from the production process, the authors state that endosulfan was not necessarily the cause of the fish kill. (These data are summarised in WHO (1984) as "a mean residue level in fish living in endosulfan-contaminated waters of 400 µg/kg".)

WHO (1984) quote a study by Koeman et al (1974) who measured residues in animal species in Java following several years of endosulfan use to control the paddy-stem borer. No residues were found (detection limit 30 µg/kg) in fish, molluscs, crabs or shrimps.

Aerial spraying in Botswana to control tsetse fly resulted in some accumulation in fish (Matthiessen et al 1982), with most residues being stored in fatty tissues. For example levels of between 100 and 300 µg/kg wet weight were found in the viscera of Clarias spp. After one year traces of only α-endosulfan were detected in these species. The maximum concentration found was 2800 µg/kg in the viscera of a pooled sample of Hepsetus odoë collected two weeks after the first spraying cycle in a year. In the same sample the level in the caudal muscle was 2 µg/kg. Levels in fish predators (birds and crocodiles) were similar to those in their prey and thus the authors estimated that the risk to predators was low. However, this conclusion is perhaps difficult to reconcile with findings of "total endosulfan" accumulations

of 780 µg/kg wet weight in the viscera of crocodiles, 200 µg/kg in the brains of pied kingfishers and 120 µg/kg in the liver of a fish eagle in specimens collected within three weeks of spraying.

Residues in food result from the use of endosulfan on a wide variety of food and non-food crops. Sittig (1980) quotes the dietary intake of endosulfan in the US (from 1965 to 1970) to be up to 0.001 mg/day using average market basket samples.

2.6 FATE IN THE ENVIRONMENT

The information available suggests that removal of endosulfan from the aqueous environment may occur by photolysis, hydrolysis, oxidation, volatilisation, biodegradation and sorption under certain conditions, but the relative importance of the different processes is likely to be difficult to predict for a particular circumstance. Callahan et al (1979) reviewed much of the available information.

As an example of the complexity of the situation Ali (1978) reported the results of a microcosm experiment with a mixture of endosulfan isomers. The β-isomer was reported to be rapidly lost to non-detectable levels after 26 d whereas, after 33 d, the α-isomer comprised 16% of the endosulfan material present, with the remainder being endosulfan sulphate. Endosulfan sulphate appeared to be the only degradation product in water and organisms (algae, snails, mosquito larvae and fish). The author concluded that the β-isomer was first converted to the α-isomer before oxidation to endosulfan sulphate. On separately exposing both endosulfan isomers and the sulphate to artificial light in microcosm water for 33 d less than 20% was lost; therefore hydrolysis and photolysis did not appear to be important fate processes compared to biological degradation.

The interaction of chemical, biochemical and physical processes has made the assignment of the discussion to the relevant sections of this report somewhat arbitrary and there is some overlap. The importance of the subject of environmental fate is illustrated by the observation by Greve

(1972) of the persistence of endosulfan for several hundred kilometres in the River Rhine following a spill.

2.6.1 Photolysis

The WHO report (1984) concluded that both the endosulfan isomers are 'fairly resistant' to photodegradation but the metabolites, including endosulfan diol and sulphate, are susceptible to photolysis. However, the conclusions of the review by Callahan et al (1979) do not really support WHO's conclusion. This review considered the results of experiments carried out under a variety of conditions. Gas-phase irradiation of β-endosulfan produced the ether, diol, lactone and sulphate derivatives as well as α-endosulfan and an ether which had lost some chlorine. Dechlorinated derivatives were also found among the products of irradiation at a wavelength >300 nm in various organic solvents and mixtures of water and organic solvents. The photolytic conversion of β- to α-endosulfan has also been observed in hexane and in aqueous suspension. However, endosulfan sulphate has not been found as a product of any liquid-phase photolysis experiment. Endosulfan sulphate has been detected when endosulfan on leaves was exposed to sunlight but was not detected when endosulfan adsorbed on glass was irradiated with >300 nm light; under these conditions the sulphate itself was stable.

Knowledge of the photolytic degradation of endosulfan would be of interest in assessing the risk of run-off from vegetation to any nearby water.

2.6.2 Oxidation

Greve and Wit (1971) measured the oxidation rate of each isomer of endosulfan in water by determining the difference in its rate of disappearance in air-saturated water and under anaerobic conditions at 20 °C. The rate constant under anaerobic conditions was ascribed to "pure" hydrolysis (see Section 2.6.3) and subtracted from the rate constant obtained in air-saturated water to give the oxidation rate

constant. The rate constants were similar for both isomers and were not very sensitive to a change in pH from 5.5 to 7.0. The constants were in the range 8.3 to 10.4×10^{-3} d^{-1}, which gives a half-life of about 70 days. At pH 7 hydrolysis was faster but at pH 5.5 the oxidation was faster.

Hoffman and Eichelsdoerfer (1971) reported that ozonisation of endosulfan was slower than for heptachlor or aldrin with 2% of α-endosulfan and 52% of β-endosulfan reacting within 45 minutes in hexane solution. The corresponding amounts reacting in water/acetone solution were 0 and 12%. Callahan et al (1979) found these results surprising, apparently on the basis that ozone is a well-known powerful oxidant, whereas the results indicate that ozone reacted more slowly with endosulfan than molecular oxygen. [The logic behind these conclusions is not clear, given a half-life in air saturated water of 70 days compared with measurable reactions in under an hour with ozone although the percentage reacted was low particularly for α-endosulfan. However, ozone generally reacts with carbon-carbon double bonds and this bond in endosulfan is "sterically hindered" by the proximity of the other parts of the molecule. The slower rate of reaction of the α-isomer, where the sulphite group is closer to the double bond than in the β-isomer, tends to support this argument. In any case there is no reason to suppose that the products of the two reactions should be the same.]

2.6.3 Hydrolysis

The hydrolysis of endosulfan to endosulfan diol has been investigated by a number of groups. The general conclusion is that the rate of hydrolysis increases with increasing pH. The problems of estimating rates of hydrolysis for endosulfan are the difficulties of isolating the effects of hydrolysis from those of biodegradation, volatilisation and adsorption. Of more theoretical interest is the question of whether endosulfan is oxidised to the sulphate before hydrolysis.

The data of Martens (1976) gives the best indication of the pH dependence of the rate of reaction. The amounts of endosulfan diol formed after incubation for ten days at 27 °C were:

pH	4.3	5.5	6.3	7.0	>8
% diol	<1	2	8	28	>90

Callahan et al (1979) calculated half-lives (Table 5) for endosulfan hydrolysis from the data of Martens and from the data of Greve and Wit (1971) obtained in the experiment described in the preceding section. Using these data they also calculated a half-life of 3.5 d for hydrolysis at pH 8 and 20 °C. This value compares well with the values 3.1 d (alpha) and 2.0 d (beta) found by Cotham and Bidleman (1989) for the hydrolysis of the two isomers in sterile seawater.

Table 5 - Calculated hydrolysis half-lives (days) for endosulfan

	Greve and Wit (1971) at 20 °C	Martens (1976) at 27 °C
pH 5.5	150 (alpha), 187 (beta)	343
pH 7.0	34 (alpha), 37 (beta)	21

Greve and Wit (1971) also showed evidence that the hydrolysis was catalysed by the presence of the iron(III) ion with an approximately threefold increase in the rate constant at 14 mg Fe(III)/l.

Eichelberger and Lichtenberg (1971) found that 10 µg/l of endosulfan in raw river water (pH 7.3 - 8) was reduced by 70% within one week (half-life ~4 days) confirming that removal of endosulfan by hydrolysis can be rapid although biodegradation may have contributed to the degradation of endosulfan.

The only direct information about the hydrolytic stability of endosulfan sulphate comes from the work of Ali (1978) who reported 88% recovery

after 33 days in the water used for the microcosm experiment discussed earlier. Field data (see Sections 2.5.1 and 3.2 of this report) suggest that endosulfan sulphate persists in river waters. This in turn, together with the observation of hydrolysis of endosulfan under anaerobic conditions by Greve and Wit (1971), suggests that direct hydrolysis of endosulfan without participation of the sulphate is possible and responsible for at least some of the diol found in hydrolysis experiments.

2.6.4 Volatilisation

Callahan et al (1979) calculated a theoretical half-life of 11 days for volatilisation of endosulfan from a still water body using the equations of Mackay and Leinonen (1975); the half-life would be less in turbulent water bodies. No distinction was made between the two isomers for this calculation although the differing values of the Henry's Law constants of the two isomers indicate that the volatisation rates should be different. Cotham and Bidleman (1989) calculated a tenfold difference in the Henry's Law constants for the two isomers and demonstrated the greater volatility of the α-isomer in a microcosm experiment (see Section 2.6.6).

Only 11% of the endosulfan present in an aerated aquaria was lost over 67 hours (Ernst 1977). The aeration rate was 2.5 l/h applied to 4 l of seawater in 10 l aquaria at 10 °C. Martens (1976) found that sorption on biota reduced the amount of endosulfan volatilised in biodegradation studies. During 10 days at 20 °C <1% endosulfan was volatilised in the presence of fungi, 2% and 20% volatilisation losses were reported in the presence of bacteria and actinomycetes, respectively. Under the same conditions but without any organisms present 30% was lost and the greater volatility of α-endosulfan was confirmed. Some experiments reported by Herzel and Lüdemann (1971) also demonstrated that aeration of solutions increased the rate of loss of endosulfan, but in this case there was no clear indication of which isomer was the more volatile. Aeration at 30 l/hr of 10-l solutions in 12-l aquaria at 20 °C increased

the rate of loss in 24 hours from around 10% (for non-aerated solutions) to about 60%.

Half-lives for volatilisation from the solid-state (on glass plates) with ultra-violet lamp irradiation could be as low as 7 days (Archer et al 1972).

2.6.5 Sorption

Sorption is an important fate for endosulfan in aquatic systems. Greve and Wit (1971) found that more than 75% of the endosulfan in the River Rhine was associated with the particulate matter (mud or silt). They also determined Freundlich adsorption isotherms for four different adsorbents. At 10 g/l both silt from the bank of the Rhine and silt from a polder adsorbed about 90% of both endosulfan isomers. A similar distribution was obtained with activated carbon at a dose of 10 mg/l. About 6:10 distribution between water and iron(III) hydroxide gel at 14 mg Fe/l was obtained. On the basis of these results the authors suggested that river water contaminated with endosulfan would be easy to treat for the preparation of drinking water. They also noted that, unless glassware was rigorously cleaned in laboratory work, substantial losses of endosulfan occurred from aqueous solution.

On a weight for weight basis retention of endosulfan was found to be highest on the colloidal and 0.08 to 0.5 µm fractions of the silt and clay from two different soils (Richardson and Epstein 1971). The authors found that removal of the oxidisable organic matter (by hydrogen peroxide) reduced the amount of endosulfan retained on the soil.

2.6.6 Biodegradation

At pH 7 and with air-saturated water Greve and Wit (1971) reported that the presence of Pseudomonas at 10^5 cells/l reduced the half-life of endosulfan at 20 °C to one week which represented a 3.5-fold increase on the rate of disappearance under abiotic conditions.

The degradation of endosulfan by cultures of various soil microorganisms was investigated by Martens (1976) in order to find organisms that could, perhaps, be used to detoxify production wastes. The 28 species of fungi used were isolated from three soils. (At least two of these soils, one from Herefordshire and one from Thailand, may have had a history of endosulfan treatment from use on hops and rice.) Also used were 49 species of bacteria and 10 actinomycetes. The organisms were grown in culture media in the presence of carbon-14 labelled endosulfan for six weeks in the case of the fungi and ten days for the bacteria and actinomycetes. The endosulfan was labelled at positions 1 and 5, which are the carbon atoms next to the sulphite group (see Figure 1). [Martens used a nomenclature system which results in these atoms being numbered 8 and 9 in his paper.] Any endosulfan and metabolites present were extracted from the organisms and culture media and then separated by thin layer chromatography for identification and for measuring radioactivity. The radioactivities of the biomass and media were also counted to estimate the amount of non-extractable carbon-14 and the carbon dioxide given off during the incubations was also trapped.

The fungal mycelia contained more than 60% of the radioactivity and sixteen species produced metabolites accounting for over 30% of the applied activity. Of these 16 species 13 produced endosulfan sulphate and three endosulfan diol as the major product. Small quantities of endosulfan hydroxyether and two other relatively non-polar unidentified metabolites were usually found. Fifteen species of bacteria were judged to have a high metabolic capability, and of these, ten produced the diol and five the sulphate as the major product. Three species of actinomycetes achieved more than 30% degradation and, in addition to the diol and sulphate, significant quantities of the hydroxyether metabolite were produced. In all cases less than 1% of the radioactivity introduced was recovered as carbon dioxide indicating that only the early stages of mineralisation had been achieved and that endosulfan would leave resistant chlorinated residues in soil. The relative importance of the two possible degradation pathways, prior oxidation to the sulphate before hydrolysis to the diol or direct hydrolysis of the sulphite, was not clear from the results of these experiments. Neither

was the relative importance of chemical versus enzymatic hydrolysis identified, although low pH in the culture medium was thought to favour the enzymatic route.

Gorbach and Knauf (1971) found that endosulfan was degraded to the diol in a simulated sewage treatment test (Husmann unit?) and that within seven days the daily conversion rate reached 50%. The growth of the alga Chlorella was not inhibited by 10 mg/l endosulfan and the insecticide was itself metabolised to the diol which was released into the culture medium. They also found that 500 mg/l endosulfan produced a 50% reduction of methane production in a test with anaerobic bacteria. However, in a respiration test 350 mg/l endosulfan did not significantly reduce oxygen uptake of bacteria degrading an organic substrate.

The degradation of endosulfan in marine microcosms was investigated by Cotham and Bidleman (1989). In filtered (0.45 µm) and filtered/autoclaved seawater the half-lives of α- and β-endosulfan, adjusted to pH 8, were 4.9 and 3.1 d, respectively, for the α-isomer and 2.2 and 2.0 d for the β-isomer. These results would seem to indicate virtually no biodegradation under the non-sterile conditions. [Comment: the odd result for the α-isomer may be a reflection of its volatility and faster loss from the sterilised medium and better adsorption on the solids in the non-autoclaved medium, assuming that there were equal amounts of solids in the non-autoclaved and autoclaved samples.] Degradation in unsterilised sediment-water mixtures was also studied. The sediment was taken from a creek on the South Carolina coast where a number of fish kills had occurred. The half-lives of the two isomers were 22 d for the alpha and 8.3 d for the beta forms. The system was spiked by adding the pesticide to the overlying water and it was not until day 4 that the majority of it was found adsorbed in the sediment layer. Again the greater volatility of the α-isomer was demonstrated with most of the remaining α-endosulfan being found in the polyurethane plug used to seal the flasks by day 20 of the experiment. Endosulfan diol was the only metabolite identified in these studies. [Note: the paper depicts the wrong stereochemistry for β-endosulfan, showing a compound which would, if it existed, be called "exosulfan".]

SECTION 3 - TOXICITY AND BIOACCUMULATION IN FRESHWATER ORGANISMS

3.1 TOXICITY

Studies on the toxicity of endosulfan to freshwater organisms are summarised in Table 7. Some data of Knauf and Schulze (1973) are given in Table 6 which compares the toxicities to both freshwater and saltwater organisms of each endosulfan isomer, technical mixture, endosulfan sulphate and four non-sulphur-containing metabolites or degradation products. The general conclusions are that:

- α-endosulfan is more toxic than β-endosulfan (see also 3.1.6) except to the guppy, brine shrimp, Tubifex tubifex and, in a very odd set of results, Chironomus thumini

- endosulfan sulphate is of a similar toxicity to most aquatic organisms as endosulfan

- the non-sulphur-containing metabolites are very much less toxic than endosulphan particularly to fish.

In many cases there are doubts as to the purity of the material used and whether the results are expressed as active ingredient or formulation or as nominal or analysed concentrations. Also the efficiencies of dosing and analytical procedures are not always easy to assess. Greve and Wit (1971) noted that rigorous cleaning of glassware was necessary in order to avoid adsorption of endosulfan. Thus, even though there is a large body of data, problems remain in interpreting the significance and comparability of the various test data, because the α- and β-isomers apparently have different toxicities and stabilities; a primary degradation product, endosulfan sulphate, is also toxic; but particularly as endosulfan can be toxic to some organisms at very low, sub-µg/l, concentrations and sometimes at levels which leave no measurable residues in the affected organisms.

Table 6 - Comparison of LC50s (48-hour) of endosulfan and its metabolites to various aquatic organisms (Knauf and Schulze 1973)

Species	Endosulfan (µg/l)	α-isomer (µg/l)	β-isomer (µg/l)	Endosulfan sulphate (µg/l)	Endosulfan lactone (µg/l)	Endosulfan diol (µg/l)	Endosulfan ether (µg/l)	Endosulfan α-hydroxy ether (µg/l)
Fish								
Idus melanotus	1.8	1.3	1.5	12.5	750	500	-	-
Lebistes reticulatus (Guppy)	1.4	1.4	0.8	1.6	25 000	7 500	2 500	900
Carassius auratus (Goldfish)	1.8	1.5	10	17.5	5 000	7 500	3 500	-
Crustaceans								
Daphnia magna (Water flea)	140	17.5	130	140	50 000	500	750	250
Artemia salina (Brine shrimp)	10 000	5 000	2 500	750	>100 000	10 000	20 000	-
Insects								
Aedes aegypti (Mosquito)	125	15	19	150	40 000	5 000	2 500	10 000
Chironomus thumini	25 000	500	12.5	500	-	2 500	5 000	-
Molluscs								
Planorbis corneus	1 000	2 500	5 000	4 000	100 000	100 000	100 000	10 000
Limnea stagnalis	1 200	3 000	7 500	6 000	50 000	10 000	3 000	-
Physa sp	500	2 500	7 500	750	70 000	-	6 000	-
Annelida								
Tubifex tubifex (Sludge worm)	3 500	7 500	1 000	2 500	-	40 000	90 000	-

Table 7 - Toxicity of endosulfan to freshwater organisms

Species	Exposure type	Temp °C	pH	Formulation	Exposure time	Effect	Concentration µg/l (a)	Ref
ALGAE:								
Chlamydomonas rheinhardtii	Static			94% Pure	2 hr	Various (see text): 45% loss of veg. cells, 45% loss of gametes, 20% loss of zygotes, 100% Delayed first meiosis.	10000	1
					2 hr	50% Delayed first meiosis.	4100	
Chlorella vulgaris (green alga)					5 d	Inhibited growth	>2000	2a
Chlorella vulgaris (green alga)						NOEC	10000	3
MOLLUSCS:								
Aplexa hypnorum (snail, adult)	Semi-static (24-hr) (b)	24.5	7.1	Thiodan-2 23.5% pure	96 hr	LC50, as grade used (calc as endosulfan	>1900 >450)	4
Lymnea stagnalis (freshwater snail)					48 hr	LC50	1200	2b
Planorbis corneus (ram's horn snail)					48 hr	LC50	1000	2b
Physa fontinalis (freshwater snail)					48 hr	LC50	500	2b
Lamellidens corrianus (bivalve mollusc)	Semi-static (12-hr)	28-31 Summer	<8.8	35 EC	96 hr	LC50 LC0 but sig. decrease in oxygen consumption	17 4	5
		25-27 Monsoon	<8.0	35 EC	96 hr	LC50 LC0 but sig. decrease in oxygen consumption	40 20	
		19-24 Winter	<7.6	35 EC	96 hr	LC50 LC0 but sig. decrease in oxygen consumption	44 24	
Lamellidens marginalis (bivalve mollusc)	Semi-static (12-hr)	28-31 Summer	<8.8	35 EC	96 hr	LC50 LC0 but sig. decrease in oxygen consumption	6 2	5
		25-27 Monsoon	<8.0	35 EC	96 hr	LC50 LC0 but sig. decrease in oxygen consumption	36 16	
		19-24 Winter	<7.6	35 EC	96 hr	LC50 LC0 but sig. decrease in oxygen consumption	40 22	

Table 7 - continued

Species	Exposure type	Temp °C	pH	Formulation	Exposure time	Effect	Concentration µg/l (a)	Ref
Dreissena polymorpha (zebra mussel)					24 hr	LC100	100000	3
ANNELIDS:								
Tubifex tubifex (oligochaete worm)					48 hr	LC50	3500	2b
Tubifex tubifex (oligochaete worm)					24 hr 96 hr	LC50 LC100	6000 10000	3
CRUSTACEANS:								
Daphnia carinata (water flea, adult)	Static	29-32	7.8-8.2	Technical	24 hr 48 hr	LC50 LC50	500 180	6
Daphnia magna (water flea)					48 hr	LC50	140	2b
Daphnia magna (water flea)					72 hr	LC50	200	7
Daphnia magna (water flea)	Static	10 10 19 19		96.4%	48 hr 96 hr 48 hr 96 hr	LC50 LC50 LC50 LC50	130 53 62 56	8
Daphnia magna (water flea)	Static	20		Technical	48 hr	EC50, two tests meas. "total" conc. (c)	270, 340	9
Daphnia magna (water flea)	Static	20	7.0-8.6		48 hr	EC50 mean of 6 labs (range) (12 results)	350 (160-740)	10
Daphnia magna (water flea)	Semi-static (3 times/wk)				21 d 21 d	EC50, parent survival, (Lab-1, 2 tests) Nos. of juv./female: NOEC/LOEC (d) Lab-1, 2 tests Lab-2, 2 tests Chronic Values: Lab-1 Lab-2	170, 130 35/73, 75/150 20/32, 32/48 51, 106 25, 39	11
Daphnia magna (water flea)	Static Flow	20	6.8-7.1	Technical (60% α + 40% β)	48 hr 64 d	LC50, measured conc(α + β) Reproduction NOEC/LOEC over 3 generations.	170 2.7 / 7.0	12

Table 7 - continued

Species	Exposure type	Temp °C	pH	Formulation	Exposure time	Effect	Concentration µg/l (a)	Ref
Daphnia magna (water flea)	Static	19			24 hr	LC50	240	13
					48 hr	LC50	60	13a
Daphnia magna (water flea)					48 hr	LC50	220	3
Daphnia pulex (water flea)					24 hr	LC50	300	3
Moina micrura (cladoceran, first or second instars)	Static	29-31		90% Thiodan	3 hr	LC50 as act. ingred.	130	14
					4 hr	LC50 as act. ingred.	52	
					24 hr	LC50 as act. ingred.	16	
(from 1st instar to 13th instar stage)	Semi-static (48-hr)				13 d	Reduced cumulative growth (32%) & egg production (21%)	4	
Cyclops stenuus (copepod)					24 hr	LC100	1000	3
Gammarus fasciatus (scud)	Static	21	7.1	Technical 96%	24 hr	LC50	10	15,16
					96 hr	LC50	6	
Gammarus lacustris (amphipod)	Static	21	7.1	Technical 96%	24 hr	LC50	9.2	16
					48 hr	LC50	6.4	17
					96 hr	LC50	5.8	16
Carinogammarus reoselii (amphipod)					24 hr	LC50	1	3
Asellus aquaticus (water hoglouse)					24 hr	LC50	10	3
Macrobrachium dayanum (prawn, carid decapod)	Static	26	7.6	Thiodan 35 EC	96 hr	LC50	4.1	18
Cambarus affinis (decapod)					24 hr	LC50	500	3
Procambarus clarkii (red crayfish)	Static	24±3	6.8	Thiodan	96 hr	LC50, juvenile, 1.1-1.5 g	24	19
					96 hr	LC50, adult, 25-32 g	420	
Oziotelphusa senex senex (field crab, 32 g, stage 4)	Static			Technical 99%	96 hr	LC50	19000	20
						"sub-lethal"	6200	
Oziotelphusa senex senex (field crab, 28 g)	Static			Technical 99%	96 hr	LC50	15000	21
						"sub-lethal"	3800	

Table 7 – continued

Species	Exposure type	Temp °C	pH	Formulation	Exposure time	Effect	Concentration µg/l (a)	Ref
Oziotelphusa senex senex (field crab, juvenile)	Static	28		Technical 99%	96 hr	LC50 (5-day-old)	570	22
					96 hr	LC50 (15-day-old)	950	
					96 hr	LC50 (30-day-old)	1500	
ARACHNIDS:								
Hydrachna trilobata (freshwater mite)	Static	25-31	7.9	Technical	48 hr	EC50 (immobilisation)	2.8	23
INSECTS:								
Pteronarcys californica (stonefly, 2nd year class)	Static	15	7.1	Technical 96%	24 hr	LC50	24	24,16
					96 hr	LC50	2.3	
Ischnura sp. (damselfly, naiads)		8		96.4%	96 hr	LC50	72	8
		19			96 hr	LC50	110	
Chironomus plumosus (midge, larva)				Technical	24 hr	LC50	53	3
Corethra plumicornis (phantom midge, larva)					24 hr	LC50	200	3
Aedes aegypti (mosquito, larva)					24 hr	LC50	1000	3
AMPHIBIA								
Bufo bufo (common toad, larva)					24 hr	LC100	15	3
FISH:								
Oncorhynchus mykiss 25	Static	1.6	7.1	Technical	24 hr	LC50	13	
(rainbow trout, 0.6-1.5 g)					96 hr	LC50	2.6	
		7.2			24 hr	LC50	6.1	
					96 hr	LC50	1.7	
		12.7			24 hr	LC50	3.2	
					96 hr	LC50	1.5	
Oncorhynchus mykiss (rainbow trout, 1.3 g)	Static	12		Technical	96 hr	LC50, 2 tests, measured concs.	1.7 & 1.6	9
0.6 g fish	Flow	12		Technical	96 hr	LC50, measured concentrations	0.3	
0.8 g fish	Flow	13		Technical	96 hr	LC50, measured concentrations	0.4	
Oncorhynchus mykiss (rainbow trout)	Static				"acute"	LC50, meas. conc., 12-lab "round-robin" mean (range)	1.2 (0.49-2.4)	10
	Flow					mean (range)	0.37 (0.17-0.75)	

Table 7 – continued

Species	Exposure type	Temp °C	pH	Formulation	Exposure time	Effect	Concentration µg/l (a)	Ref
Oncorhynchus mykiss	Static	10		Thiodan	96 hr	LC50	0.3	8
(rainbow trout)		1.5			96 hr	LC50	0.8	
Oncorhynchus mykiss	Static	2	7.1	Technical 96%	96 hr	LC50	2.9	16
(rainbow trout, 1.3 g)		7			96 hr	LC50	1.7	
		13			96 hr	LC50	1.4	
		18			96 hr	LC50	1.1	
Salmo irideus	Static	18-21	7.1-7.8		24 hr	NOEC	5	26
(rainbow trout fry)					24 hr	"significant effects"	8	
					24 hr	LC100	10	
Esox lucius	Static	18-21	7.1-7.8		24 hr	NOEC	0.5	26
(pike, juvenile)					24 hr	"significant effects"	1	
					24 hr	LC100	5	
Pimephales promelas	Static	18	7.1	Technical 96%	96 hr	LC50	1.5	16
(fathead minnow, 0.7 g)								
Pimephales promelas	Flow	25			7 d	Incipient LC50	0.86	12
(fathead minnow)								
20-d-old	Flow	20		Technical	240 d	NOEC parental survival, growth & spawning; egg hatchability; larval survival & growth to 60 d	0.2	12
Pimephales promelas	Static	20		Technical	96 hr	LC50, 3 tests, measured concs	1.3, 1.3, 0.8	9
(fathead minnow, 0.1 g)								
0.2 g fish	Flow	21			96 hr	LC50, measured cocncentration	1.7	
0.1 g fish	Flow	20			96 hr	LC50, measured cocncentration	1.0	
Pimephales promelas	Flow	24	7.3-7.8	Thiodan	24 hr	LC50, measured cocncentration	1.8	27
(fathead minnow)					96 hr	LC50, measured cocncentration	1.3	
(juvenile, 30-40-d-old)								
Short-term exposure plus recovery period: to calculate expected exposure times giving 50% mortality within 14-d recovery								27
30-40-d-old juveniles	Flow				1.67 hr	ExpT 50	31.8	
					3.74 hr	ExpT 50	12.9	
					37.97 hr	ExpT 50	1.1	
<24-hr-old fry	Flow				1.74 hr	ExpT 50 (24-hr recovery period)	35	
Pimephales promelas					"acute"	LC50, meas. conc., 12-lab "round-robin"		10
(fathead minnow)	Static					mean (range)	2.1 (1.2-3.5)	
	Flow					mean (range)	1.0 (0.29-1.9)	

Table 7 - continued

Species	Exposure type	Temp °C	pH	Formulation	Exposure time	Effect	Concentration µg/l (a)	Ref
Lepomis macrochirus (bluegill):								
Short-term exposure plus recovery period: to calculate expected exposure times giving 50% mortality within 14-d recovery								27
80-90-d-old	Flow				1.84 hr	ExpT 50	21.7	
					4.64 hr	ExpT 50	9.4	
					20.51 hr	ExpT 50	2.2	
Lepomis macrochirus (bluegill)	Static	18	7.1	96% TECH	24 hr	LC50	3.3	16
					96 hr	LC50	1.2	
Channa gachua (snakehead, 130-150 mm)	Static	24±2	7.2-7.8	Thiodon 35EC	96 hr	LC50	11	28
Channa gachua (snakehead)	Semi-static (24-hr)				30 d	Inhibition of the activity of various ATP-ases in liver, kidney and muscle tissue.	2.2	29
Channa punctata (snakehead)	Semi-static (24-hr)		7.2		120 d	Inhibition of oocyte development & ovarian steroidogenesis	0.24	30
Channa punctata (snakehead; 60g, 190 mm adult fish)	Semi-static (24-hr)	18±2	7.2	Technical	24 hr	LC50	11	31
					96 hr	LC50	6	
				Thiodan 35 EC	24 hr	LC50	8	
					96 hr	LC50	3	
Channa punctata (snakehead; 60 to 90 mm fish)	Flow	30±2	8.4	Technical 96%	96 hr	LC50, nominal concentrations,	4.8	32
				Thiodan 35 EC	96 hr	LC50 active ingredients	2.5	
				alpha-isomer	96 hr	LC50	0.16	
				beta-isomer	96 hr	LC50	6.6	
				4% dust	96 hr	LC50	16	
Channa striatus (140 ± 20 mm fish)	Static			Thiodan 35 EC	30 d	LC50	1.6	33
					2 d	Start of liver damage	0.75	
					15 d	Disruption of liver structure	0.75	
Colisa fasciatus (adult female fish in pre-spawning phase)	Semi-static (48-hr)			Thiodan 35 EC	30 d	Increased mucous secretion & air-gulping; retarded oocyte development.	1000 ? (e)	34
Catastomus commersoni (Western white sucker)	Static	19		Thiodan	48 hr	LC50	4.3	8
		19			96 hr	LC50	3.0	
		10			48 hr	LC50	6.4	
		10			96 hr	LC50	3.5	
Anguilla anguilla (eel)	Static	15	7.9		96 hr	LC50	38	35
		22			96 hr	LC50	42	
		29			96 hr	LC50	20	

Table 7 - continued

Species	Exposure type	Temp °C	pH	Formulation	Exposure time	Effect	Concentration µg/l (a)	Ref
Gymnocorymbus ternetzi (widow tetra, 29-32 mm)	Static	28.5	7.4	Thiodan EC35	24 hr	LC50	2.3	36
					96 hr	LC50	1.6	
	Semi-static (24-hr)				90 d	Liver damage NOEC/LOEC	0.1 / 0.4	
Cirrhina mrigala (carp)					24 hr	LC50	2.9	37
					48 hr	LC50	1.8	
Cirrhina mrigala (carp, larvae)	Static	23±2	7.2-7.4	Thiotox 35EC	96 hr	LC50	2.5	38
					60 d	NOEC/LOEC, growth	0.09/0.12	
Idus melanotus					48 hr	LC50	1.8	2
Carassius auratus (goldfish)					48 hr	LC50	1.8	2
Heteropneustes fossilis (singhi catfish)	Static	20-25	7	Thiodan 35EC	168 hr	LC0	1.0	39
						LC50	1.6	
						LC100	2.5	
Heteropneustes fossilis (catfish, 140 mm, 21 g)	Flow	28±2	8.4	Endosulfan (technical)	96 hr	LC50, nom.conc. act. ingred. by analysis of stock soln.	1.1	40
Heteropneustes fossilis (catfish)	Static	30		Thiodan EC 35	96 hr	LC50, 100 mm, 11 g fish	7.7	41
					96 hr	LC50, 200 mm, 44 g fish	15	
		18			96 hr	LC50, 100 mm, 11 g fish	12	
					96 hr	LC50, 200 mm, 44 g fish	23	
		29±1			96 hr	LC50, 62 mm, 4.8 g fish	5.0	
					96 hr	LC50, 197 mm, 42 g fish	15	
Sarotherodon mossambicus (african cichlid, 1 mth old fry) (3 mth old adult)	Semi-static 24 hr renewal	28	8.2	Thiodan 35 EC	24 hr	LC50, based on measured conc in freshly changed solutions	0.5	42
					48 hr	LC50	0.2	
					96 hr	LC50	0.06	
					24 hr	LC50	10	
					48 hr	LC50	6.7	
					96 hr	LC50	4.3	
Sarotherodon mossambicus (african cichlid)	Flow	28	8.2	Thiodan 35 EC	4 wk	Delayed start of breeding behaviour (male and female), hypersensitivity and abnormal movements.	0.6	42
Tilapia mossambica (tilapia)	Static	20-25	7	Thiodan 35EC	168 hr	LC0	0.64	39
						LC50	1.4	
						LC100	3.2	

Table 7 - continued

Species	Exposure type	Temp °C	pH	Formulation	Exposure time	Effect	Concentration µg/l (a)	Ref
Cyprinus carpio (carp)	Static	20-25	7	Thiodan 35EC	168 hr	LC0	0.5	39
						LC50	0.92	
						LC100	2.5	
Cyprinus carpio (carp, larvae)	Semi-static	20-23	7.2	Thiotox	96 hr	LC50	0.3	43
					60 d	Standing crop, NOEC/LOEC (f)	0.009/0.013	
Cyprinus carpio (carp, 68 mm)	Static	17-19	7.2-7.8		48 hr	NOEC	5	44
					48 hr	LC50	11	
Lebistes reticulatus (guppy)					48 hr	LC50	1.4	2
Ictalurus punctatus (channel catfish, 1.7 g)	Static	18	7.1	96% TECH	24 hr	LC50	1.8	16
					96 hr	LC50	1.5	
Puntius sophore (exotic carp)					48 hr	LC50	1.4	45
Mystus vittatus (catfish, 6-10 g)	Static	26	7.5	Thiodan 35EC	24 hr	LC50	0.32	46
					96 hr	LC50	0.24	
Mystus vittatus (catfish, 6-10 g)	Static			Thiotox 35EC	96 hr	LC50	0.67	47
Mystus vittatus (catfish, 60 mm, 3.5 g)	Flow	28±2	8.4	Endosulfan (technical)	96 hr	LC50, nom.conc. act. ingred. by analysis of stock soln.	2.2	40
Mystus cavasius (catfish, 65 mm, 4.0 g)	Flow	28±2	8.4	Endosulfan (technical)	96 hr	LC50, nom.conc. act. ingred. by analysis of stock soln.	1.9	40
Ophiocephalus punctatus (catfish, 90-100 mm, 40-55 g)	Static	18.2	6.9-7.4	35% EC	96 hr	LC50	22	48
Gambusia affinis (mosquito fish)	Static	20±3	7.8	Thiodan 35 EC	96 hr	LC50	1.3	49
					96 hr	100% mortality	2.5	
Anabas testudineus (climbing perch, 55 mm)	Flow	32±2	8.4		96 hr	LC50, as active ingredient	1.2	50
Labeo rohita (Indian major carp, juv., 25 mm, 0.25 g)	Flow	28±2	8.4	Technical 96%	96 hr	LC50, nominal concentrations	1.1	51
				Thiodan 35 EC	96 hr	LC50 of active ingredient	1.0	
				alpha-isomer	96 hr	LC50	0.33	
				beta-isomer	96 hr	LC50	7.1	
				4% dust	96 hr	LC50	1.3	

Table 7 - continued

Species	Exposure type	Temp °C	pH	Formulation	Exposure time	Effect	Concentration µg/l (a)	Ref
Labeo rohita	Static		8.25	Hildan 35EC	24 hr	LC50 at 700 mg/l $CaCO_3$	4.3	52
(Indian major carp,					96 hr	LC50	2.7	
50-61 mm, 1.8-2.9 g)			7.9		24 hr	LC50 at 430 mg/l $CaCO_3$	2.7	
					96 hr	LC50	2.3	
			7.5		24 hr	LC50 at 250 mg/l $CaCO_3$	1.4	
					96 hr	LC50	0.36	
Ctenopharyngodon idella	Static		8.25	Hildan 35EC	24 hr	LC50 at 700 mg/l $CaCO_3$	5.7	52
(exotic carp,					96 hr	LC50	4.1	
63-71 mm, 2.7-3.1 g)			7.9		24 hr	LC50 at 430 mg/l $CaCO_3$	4.1	
					96 hr	LC50	3.7	
			7.5		24 hr	LC50 at 250 mg/l $CaCO_3$	2.8	
					96 hr	LC50	1.7	
Hypophthalmichthys molitrix	Static		8.25	Hildan 35EC	24 hr	LC50 at 700 mg/l $CaCO_3$	4.3	52
(exotic carp,					96 hr	LC50	2.5	
45-60 mm, 1.1-2.5 g)			7.9		24 hr	LC50 at 430 mg/l $CaCO_3$	2.7	
					96 hr	LC50	2.3	
			7.5		24 hr	LC50 at 250 mg/l $CaCO_3$	1.3	
					96 hr	LC50	0.26	
Puntius javanicus	Static		8.25	Hildan 35EC	24 hr	LC50 at 700 mg/l $CaCO_3$	10	52
(exotic carp,					96 hr	LC50	8.7	
51-55 mm, 1.4-2.1 g)			7.9		24 hr	LC50 at 430 mg/l $CaCO_3$	8.7	
					96 hr	LC50	8.3	
			7.5		24 hr	LC50 at 250 mg/l $CaCO_3$	7.4	
					96 hr	LC50	6.3	
Catla catla	Static		8.25	Hildan 35EC	24 hr	LC50 at 700 mg/l $CaCO_3$	4.9	52
(Indian major carp,					96 hr	LC50	3.2	
63-71 mm, 2.7-3.1 g)			7.9		24 hr	LC50 at 430 mg/l $CaCO_3$	3.2	
					96 hr	LC50	2.8	
			7.5		24 hr	LC50 at 250 mg/l $CaCO_3$	1.9	
					96 hr	LC50	0.9	
Schilbe mystus	Semi-static	11-20	8.2	Thiodan 35 EC	24 hr	LC50	5.1	53
(140 g)	(24-hr) (g)				48 hr	LC50	2.2	
Synodontis sp.	Semi-static	11-20	8.2	Thiodan 35 EC	24 hr	LC50	5.6	53
(lizard fish, 72 g)	(24-hr) (g)				48 hr	LC50	1.9	
Tilapia sparrmanii	Semi-static	11-20	8.2	Thiodan 35 EC	24 hr	LC50	7.3	53
(62 g)	(24-hr) (g)				48 hr	LC50	2.3	

Table 7 - continued

Species	Exposure type	Temp °C	pH	Formulation	Exposure time	Effect	Concentration µg/l (a)	Ref
Barbus sp. (cyprinid. 0.76 g)	Semi-static (24-hr) (g)	11-20	8.2	Thiodan 35 EC	24 hr 48 hr	LC50 LC50	1.2 0.5	53
Aplocheilichthys johnstonii (top minnow, 0.42 g)	Semi-static (24-hr) (g)	11-20	8.2	Thiodan 35 EC	24 hr 48 hr	LC50 LC50	2.6 1.1	53
Barilius bendelis (cyprinid)	Static	24-30	6.5 7.5 9.0	Thiodon 35 EC	96 hr 96 hr 96 hr	LC50 LC50 LC50	13 16 17	54
Catla catla (Indian major carp, 100-120 mm)	Static			Thiodan 35EC	96 hr	LC50 as formulated product	18	55
Rasbora daniconius	Static			Thiodan 35 EC	24 hr	LC50	0.75	56
Rasbora heteromorpha (harlequin fish)	Flow	20		Thiodan 20%	48 hr	LC50, as formulated product	0.014	57
Saccobranchus fossilis	Static	16-20	7.2	Thiotox Thiodon	96 hr 96 hr	LC50 LC50	6.6 11	58

Notes

Technical GRADE: a mixture of of two isomers that differ in their chemical, physical and toxicological properties. alpha-Endosulfan (70%) is more toxic than beta-Endosulfan.

(a) Concentration: results are given as reported in the papers but rounded to two significant figures. It is not alsways clear whether the reported results refer to formulation or active ingredient or whether the values are nominal concentrations or analysed stock or test solutions.

(b) Renewal frequency of test solutions

(c) "Total" = both isomers plus sulphate as analysed

(d) NOEC = "No observed effect concentration", ie the highest concentration at which there was no difference from the controls;
LOEC = "Lowest observed effect concentration", ie the lowest concentration at which there was a statistically significant difference from the controls.
Chronic Value = geometric mean of NOEC and LOEC

(e) Reference gives test concentration as "1000 ppm" and states this concentration to be sub-lethal. The other data in this table suggests that perhaps "ppm" was a misprint for ppb. The test species is an air-breather.

(f) Standing crop NOEC/LOEC compares average weight of survivors x number of survivors with values for controls.

(g) GRP tanks; loading rates varied from 0.06 g fish/l to 2.23 g fish/l for the larger fish.

References for Table 7

1 Netrawali et al 1986
2 Knauf and Schulze 1973 (2a cited in EPA 1980 & 2b in Ourisson and Koch 1980)
3 Lüdemann and Neumann 1962 and Gorbach and Knauf 1971
4 Holcombe et al 1983
5 Mane and Muley 1984 and Muley and Mane 1987
6 Santharam et al 1976
7 Krasowska and Proba 1979
8 Schoettger 1970a
9 Nebeker et al 1983
10 Lemke 1981 (results in table are calculated directly from paper and are not as quoted in EPA 1980)
11 Nebeker 1982
12 Macek et al 1976
13 Frear and Boyd 1967 (13a cited in Verschueren 1983)
14 Krishnan and Chockalingam 1989
15 Sanders 1972
16 Mayer and Ellersieck 1986 (review giving additional information on water quality etc to refs 15, 17 & 24)
17 Sanders 1969
18 Omkar and Murti 1985
19 Naqvi et al 1987
20 Rajeswari et al 1988
21 Vijayakumari et al 1987
22 Naidu et al 1987
23 Nair 1981
24 Sanders and Cope 1968
25 Macek et al 1969
26 Lüdemann and Neumann 1961
27 Kleiner et al 1984
28 Dalela et al 1978
29 Sharma 1988
30 Inbaraj and Haider 1988
31 Haider and Inbaraj 1986
32 Devi et al 1981
33 Kulshrestha and Jauhar 1984
34 Pandey 1988
35 Ferrando et al 1987
36 Amminikutty and Rege 1977
37 Arora et al 1972 (cited in Reddy and Gomathy 1977)
38 Verma et al 1984
39 Basak and Konar 1977
40 Rao and Murty 1982
41 Singh and Narain 1982
42 Matthiessen and Logan 1984
43 Verma et al 1981a
44 Lüdemann and Neumann 1960
45 Arora et al 1971 (cited in Ourisson and Koch 1980 and in Reddy and Gomathy 1977)
46 Reddy and Gomathy 1977
47 Verma et al 1980
48 Verma et al 1981b (cited in WHO 1984)
49 Naqvi and Hawkins 1988
50 Rao and Murty 1980
51 Rao et al 1980
52 Paul and Raut 1987
53 Fox and Matthiessen 1982
54 Deoray and Wagh 1987
55 Abidi 1983
56 Jawale 1985
57 Alabaster 1969
58 Verma et al 1982b

3.1.1 Algae

At least two species of green algae (Chlorella vulgaris and Chlamydomonas rheinhardtii) appear to be relatively tolerant to endosulfan. In the most detailed study available Netrawali et al (1986) exposed Chlamydomonas rheinhardtii at four growth stages (vegetative, gametes, during fusion and young zygotes) to 10.2 mg/l endosulfan. Exposed vegetative cells and gametes were reduced in number by 45% and 20% of zygotes were lost but no effect was seen when the alga was exposed during fusion. Development to first meiosis of zygotes formed after treatment of any of the four stages was inhibited by up to six days. However, from the data a no-effects level cannot be derived. For Chlorella vulgaris a no effects concentration of 10 µg/l has been estimated (Knauf and Schulze 1973).

3.1.2 Molluscs

The acute LC50s for endosulfan to three species of snails are in the range 0.5 to >1.9 mg/l (Knauf and Schulze 1973 and Holcombe et al 1983). However, some bivalve molluscs appear to be very much more sensitive (Mane and Muley 1984 and Muley and Mane 1987) with 96-hr LC50s in the range 6 to 44 µg/l and reduced oxygen consumption at concentrations as low as 2 µg/l. The exact values depended on which of the two species was under test and the temperature and pH of the test medium, with greater toxicities being recorded at the higher temperatures (28 to 31 °C) and pH (8.8). The results of a test (reported in various papers but perhaps originally by Lüdemann and Neumann 1962) on the bivalve, Dreissena polymorpha, give an LC100 of 100 mg/l but no results at lower concentrations were reported.

3.1.3 Annelids

The worm, Tubifex tubifex, appears to be less sensitive to the effects of endosulfan than many other types of aquatic organism with a 48-hour LC50 of 3.5 mg/l reported by Knauf and Schulze (1973) and a 96-hour LC100 of 10 mg/l reported by Lüdemann and Neumann (1962).

3.1.4 Crustaceans

The acute toxicity of endosulfan to various species of Daphnia have been found to lie in the range 50 to 750 µg/l. Results from 21-day chronic tests performed twice at two laboratories gave no-effect concentrations (NOEC) in the range 20 to 75 µg/l based on the numbers of juveniles produced per female (Nebeker 1982). In a multi-generation chronic test, reported by Macek et al (1976), it was noted that Daphnia began to be affected, in terms of numbers of the third generation, at 7 µg/l with a NOEC of 2.7 µg/l. Another cladoceran, Moina micrura, appears to be more sensitive than Daphnia with a 24-hour LC50 of 16 µg/l and reduced growth and egg production during 13-day exposure to 4 µg/l (Krishnan and Chockalingam 1989).

The amphipods, isopods and a small decapod, with acute LC50s in the range 1 to 10 µg/l, appear to be more sensitive than the cladocerans, copepods and larger decapods tested. Data generated by the US Fish and Wildlife Service on two species of Gammarus gave 96-hr LC50s of around 6 µg/l (Sanders 1972, Mayer and Ellersieck 1986). No experimental details are available on the test which produced a 24-hour LC50 of 1 µg/l for the amphipod Carinogammarus reoselii (Lüdemann and Neumann 1962). The same paper also reported LC50s of 10 µg/l for the isopod Asellus aquaticus (water hoglouse) and 500 µg/l for the decapod Cambarus affinis (crayfish) and an LC100 of 1 mg/l for the copepod Cyclops stenuus. The result for Cambarus affinus is in broad agreement with the LC50 of 420 µg/l obtained by Naqvi et al (1987) for adult crayfish, Procambarus clarkii but juveniles of this species were about twenty-times more sensitive with an LC50 of 24 µg/l which is more in agreement with the LC50 of 4.1 µg/l obtained by Omkar and Murti (1985) for the prawn Macrobrachium dayanum. The larger decapod, the field crab, Oziotelphusa senex senex (an inhabitant of Indian paddy fields) is much less sensitive with even the 96-hour LC50 for five-day-old juveniles being 570 µg/l (Naidu et al 1987). Rajeswari et al (1988) demonstrated a range of effects on the water contents and mineral balance of this species at both lethal (19 mg/l) and sub-lethal (6.2 mg/l) concentrations of endosulfan.

3.1.5 Arachnids and insects

The freshwater mite, Hydrachna trilobata, and nymphs of the stonefly, Pteronarcys californica, have similar sensitivities to endosulfan with reported acute LC50s of 2.8 µg/l (48-hour, Nair 1981) and 2.3 µg/l (96-hour, Sanders and Cope 1968) respectively. These values are lower than the corresponding values for the small crustaceans reported in the previous section and are also lower than values reported for the four other species of insect larvae given in Table 7. Stonefly nymphs are generally considered to be among the more sensitive species of insects in terms of exposure to "pollutants".

3.1.6 Amphibians

Gorbach and Knauf (1971) reported a 24-hour LC100 of 15 µg/l to tadpoles of the common toad, Bufo bufo. It is not known whether any other concentrations were tested. In a field experiment Mulla (1963) found that a nominal concentration of 45 µg/l α-endosulfan killed 60% of tadpoles of the bullfrog, Rana catesbeiana within 24 hours but the same concentration of β-endosulfan killed only 10%.

3.1.7 Fish

The main conclusion from the many fish tests carried out with endosulfan is that fish are, as a group, the most sensitive organisms to the toxic effects of endosulfan. However, within that overall conclusion there are some subtleties. For example, the lowest recorded LC50 (48-hour) was 0.014 µg/l for the harlequin fish, Rasbora heteromorpha (Alabaster 1969) obtained during toxicity tests with 164 different organics, including many pesticides, with the same species. The relevance of the harlequin fish which originates in Malaysia and the East Indies, to UK waters has, however, not been established. It is reputed to be a difficult species to maintain in the laboratory and toxicity results may reflect some stress resulting from the test environment.

Rainbow trout, Oncorhynchus mykiss, is one of the species for which toxicity data are considered more relevant for British waters. Acute, mainly 96-hour, LC50s have been determined in a number of different tests with values ranging from 0.17 to 2.4 µg/l. These tests included an interlaboratory comparison exercise sponsored by the US Environmental Protection Agency (Lemke 1981). The LC50s were generally lower for tests performed under flow-through conditions and at higher, but not unreasonably high (10 to 18 °C), temperatures. Based on the results a best estimate of the 96-hour LC50 for juvenile rainbow trout would seem to be 0.3 µg/l for a technical (>95% pure) 70:30 mixture of α- and β-endosulfan, Nebeker et al (1983).

The results of tests on two other common test species, fathead minnow, Pimephales promelas, and bluegill sunfish, Lepomis macrochirus, show that these two species are slightly less sensitive to endosulfan than rainbow trout, especially in flow-through tests. The tests included an interlaboratory comparison using fathead minnow equivalent to the exercise with rainbow trout and gave a mean 96-hour LC50 of 1.0 µg/l while the mean value for trout was 0.37 µg/l (Lemke 1981). Kleiner et al (1984) performed some tests with sunfish and minnows to determine whether the effects of exposure to endosulfan persisted after the test organisms were removed from the test solutions. The results indicated, first, that the bluegill had a similar sensitivity to the fathead minnow, second, that both species could survive short-term exposure to levels of endosulfan much higher than the 96-hour LC50 (eg 20 µg/l for up to 1 hour) and, third, that the lethal effects of endosulfan did not persist after the fish had been placed in clean water. This last result is in contradiction with the results of Schoettger (1970a) who found that the mortality of rainbow trout continued to increase for some days after removal from solutions of endosulfan to clean water.

Schoettger (1970a) found no effect on the hatchability of rainbow trout eggs immersed 25 hours after fertilisation in 50 mg/l Thiodan solutions for two hours. He also reported some unpublished results of Berger that continuous exposure of eggs to 50 mg/l of the pesticide during the 25-day incubation period had no effect on hatchability but that fish

became more susceptible after hatching and as the yolk-sac was absorbed. These appear to be the only results available on the effects of endosulfan on the early life stages of rainbow trout. Macek et al (1976) conducted an early-life stage test with technical endosulfan using fathead minnows. The test was initiated with 20-day-old juveniles and continued for 240 days, until the second generation were about 60 days old. During the period 117 to 145 days, when the fish were undergoing rapid development before spawning, all fish exposed to 0.4 µg/l died. However at 0.2 µg/l no effects were seen on parental survival, spawning behaviour, hatchability and larval survival and growth.

Most of the other data on the toxicity of endosulfan to fish refers to effects on tropical species.

In laboratory tests Fox and Matthiessen (1982) estimated 24-hour LC50 values for four fish species resident in the Okavango Delta, Botswana. The LC50s ranged from 1.2 µg/l for the cyprinid fish Barbus sp (the test animals probably comprising of five different species) to 7.3 µg/l for Tilapia sparrmanii. Tests were conducted with Thiodan 35 EC in glass-reinforced plastic tanks and in the cases of the three heavier species at fish-loading rates of over 2 g/l. The toxicity of endosulfan to Sarotherodon mossambicus, an african cichlid, was studied by Matthiessen and Logan (1984). The 96-hour LC50 to three-month old adults was around 4.3 µg/l whereas the corresponding LC50 for one-month old fry was only 0.06 µg/l, although this result cannot be assumed reliable because it was based on the extrapolation of the regression curve. The 24-hour LC50 to fry was 0.5 µg/l. These results are based on the measured concentrations in freshly-prepared solutions. Breeding behaviour (male colouration and nest-site guarding and mouth-brooding by females) and steroid levels of five-month old adults were unaffected at 0.5 µg/l. However, three-month old fish exposed to 0.6 µg/l exhibited swimming abnormalities, increased sensitivity to external stimuli and delayed onset of breeding.

Acute LC50 values were determined for five species of Indian carp (Paul and Raut 1987). The experiments were conducted with different water hardnesses and pH values to ascertain if either of these parameters effected the LC50 values. Overall, the five fish species were more sensitive to the effects of endosulfan in softer water (250 mg/l $CaCO_3$) at a lower pH (7.5). [This may have resulted from more rapid hydrolysis of the toxicant at the higher pHs in these static tests.] Puntius javanicus, Ctenopharyngodon idella, Catla catla, Labeo rohita and Hypophthalmichthys molitrix showed 96-hour LC50s of 6.3, 1.7, 0.9, 0.36 and 0.26 µg/l respectively under these conditions.

The effects of the different isomers and formulations of endosulfan have been compared by the group led by Murty using two species of fish. Ninety-six-hour LC50s were measured in terms of nominal concentrations of active ingredients in flow-through tests. The results of the experiments on Channa punctata, a type of catfish, (Devi et al 1981) were that α-endosulfan, with an LC50 of 0.16 µg/l, was forty times more toxic than β-endosulfan (LC50 6.6 µg/l). On the basis of these results the LC50s of the technical mixture, with its greater proportion of α-endosulfan, of 4.8 µg/l and of the 35% emulsifiable concentrate of 2.5 µg/l are difficult to understand. Similar results for the two endosulfan isomers were obtained (Rao et al 1980) for Labeo rohita, a carp. In this case α-endosulfan, LC50 0.33 µg/l, was twenty times more toxic than β-endosulfan, LC50 7.1 µg/l and the values for the technical mixture and the 35EC formulated product (LC50s 1.1 and 1.0 µg/l, respectively) were more easily reconcilable to the toxicities of the individual isomers. One possible problem with these experiments was that the toxicant reservoir was linked to the test chambers by polythene tubing which may have adsorbed variable quantities of the toxicants.

Some of the more recent work on the toxicity of endosulfan to fish has investigated effects on the histopathology, histochemistry and metabolism on several species of Indian fish at sub-lethal exposure levels. However, the significance of these effects on the survival and development has not yet been fully established.

Jawale (1985) found that exposure for 12 hours to 0.4 to 0.75 µg/l 35% EC endosulfan resulted in increasing oxygen consumption rates for Rasbora daniconius but at 1 µg/l oxygen consumption decreased to about the level found at 0.4 µg/l. (The 24-hour LC50 was 0.75 µg/l.)

The effects of endosulfan on adenosine triphosphatase (ATPase) activity in liver, kidney and muscles of Channa gachua were investigated by Sharma (1988). Concentrations down to 2.2 µg/l inhibited several types of ATPase activity but particularly Na^+,K^+-ATPase in liver and kidney tissue.

Kulshrestha and Jauhar (1984) found 0.75 µg/l was a high enough concentration to initiate liver damage to Channa striatus (snakehead) within two days and lead to total disruption of the liver structure after 15 days. Liver damage was also found by Amminikutty and Rege (1977) in widow tetra, Gymnocorymbus ternetzi, exposed to 0.4 µg/l for 90 days. No damage was found at 0.1 µg/l.

Inbaraj and Haider (1988) exposed Channa punctatus oogonia to 0.24 µg/l endosulfan for 120 days and results show that development of the oogonia was significantly inhibited. Haider and Inbaraj (1988) also cultured oocytes from carp in endosulfan solutions and demonstrated effects on the rate of disappearance of germinal vesicles at a concentration of 0.01 ppb by volume.

In two papers Pandey recorded the effect of sub-lethal exposure of two species of fish to "1 ppm" endosulfan. This concentration must be assumed to be a misprint for "1 ppb" (ie 1 µg/l). In the 1986 paper (Pandey 1986) he reported that the activity of corticosteroidogenic cells of Ophiocephalus punctatus were affected and in the 1988 paper (Pandey 1988) he described histomorphological changes in the ovaries of pre-spawning Colisa fasciatus. Shukla and Pandey (1986) noted adverse histomorphological changes in the pituitary glands and ovaries of Sarotherodon mossambicus after treatment with 1 µg/l Thiodon 35EC for 20 days.

Elevated levels of lactate, pyruvate and glucose in the blood of Heteropneustes fossilis exposed to 1.5 µg/l endosulfan were found by Singh and Srivastava (1981). There were also initial decreases in muscle and liver glycogen levels at this concentration which was 75% of the 96-hour LC50. The results were taken as indications of stress and impairment of the homoeostatic survival mechanism. The effects of endosulfan on carbohydrate metabolism in fish were also investigated by Verma et al (1983). Blood glucose and lactate levels and liver and muscle glycogen levels were measured in Clarias batrachus, Saccobranchus fossilis and Mystus vittatus exposed for 30 days to endosulfan at concentrations corresponding to 1/4, 1/8 and 1/16th of each species' 96-hour LC50. Blood lactate levels were not significantly ($P<0.05$) elevated by any treatment but glucose levels were elevated at concentrations equivalent to 1/16th of the LC50 by 46% in C. batrachus (0.58 µg/l, $P<0.01$), by 38% in S. fossilis (0.39 µg/l, $P<0.05$) and by 42% in M. vittatus (0.042 µg/l, $P<0.01$). Liver glycogen levels were also sensitive to the same exposure concentrations whereas muscle glycogen levels were not affected. Verma et al (1982a) conducted a similar experiment on Mystus vittatus but assessed other blood chemistry variables and exposure concentrations equivalent to 1/5, 1/10 and 1/15th of the LC50. At 0.045 µg/l mean red blood cell volume, mean corpuscular haemoglobin and mean corpuscular haemoglobin concentration were significantly lower than the controls. At 0.067 µg/l clotting time, red blood corpuscles and packed cell volumes were affected. Haemoglobin concentration was affected at 0.13 µg/l but the white blood cell count, erythrocyte sedimentation rate and prothrombin time were unaffected.

3.2 FIELD STUDIES

Reports of field studies in Java, Nigeria, Botswana, South Africa and the USA are available. Some of the more detailed reports are discussed below. In most cases the results have to be assessed, not in terms of an LC50 or a no effect concentration, but whether the organisms survived an initially high level, how soon the levels declined to a survivable level and whether the population was likely to recover within a

reasonable period. The answers to these questions are not necessarily complete.

Gorbach et al (1971b) sprayed endosulfan on rice fields in Java. Cages containing Puntius javanicus, a carp native to the habitat and for which a laboratory 24-hour LC100 of 1 µg/l is quoted, were placed at various sites in the test area. Initially fish died within one hour when concentrations of endosulfan were around 200 to 600 µg/l and within two hours at about 70 µg/l. On the day following spraying and for up to 15 days fish in one field survived while endosulfan concentrations declined from 0.9 to 0.4 µg/l. In the other field with an initial concentration of 8 µg/l fish survived for three hours and, on the third day, for nearly a day at a concentration of 1.5 µg/l. From day 5, when the concentration had fallen to 0.87 µg/l, all the fish survived to day 15 when the concentration had decreased to 0.42 µg/l. Observations of the native invertebrate populations were also made. In both treated fields all Brachyura as well as most Coleoptera and Tipulidae larvae were killed but Tubificidae, Hydrocorisidae, Cyclopidae and Gastropoda survived. After five days the invertebrate population began to return to normal by immigration.

Aerial and back-pack spraying of endosulfan has been used for tsetse fly control in several parts of Africa. In some savannah areas of Nigeria (Koeman et al 1978) the side effects of single, high-dose spraying from helicopters has been studied. A 40 km strip of riverine "fringe-forest" along the Dinya River was sprayed at a nominal rate of 1 kg/hectare. Sufficient endosulfan penetrated the forest canopy to virtually eliminate fish from the treated stretch. Some juvenile fish were observed after six weeks and the area had been recolonised by immigrant fish when surveyed the following year. Observations of dead birds, reptiles and mammals in this and other study areas suggest that endosulfan affects insectivores only within a few days of an application thus suggesting a limited lifetime for the insecticide in prey organisms. This observation was in contrast to the more delayed, but longer, "lethal period" of dieldrin, although it was noted that the two

insecticides had similar persistence on leaves, taking about 14 days for a tenfold reduction in concentration.

In the Okavango Delta region of Botswana the effects of repeated aerial applications of very much lower doses, 6 to 12 g ai/hectare, of endosulfan have been investigated. Fox and Matthiessen (1982) described the type of spraying operations used and the levels and persistence of endosulfan likely to result from these operations (Section 2.5.1). Observations of dead fish were made up to 60 hours after spraying. Spraying of emergent grass-swamp areas rarely resulted in fish kills although localised kills were noted in shallow open pools. Numbers of dead fish varied from zero to over 3000 per hectare. Fish mortality in a sprayed riverine floodplain varied from zero to about 2400 per hectare representing 0 to 4.3% of the total population. It was noted that the highest mortalities were not usually in the smaller species, which had proved to be the most sensitive in laboratory tests, but this might be explained by predation of dying small fish by larger fish and birds. In one area, which received a triple dose, mortality of Serranochromis spp reached 60%. Tanks, with 0.2 m water, containing top minnows, Aplocheilichthys johnstonii, were placed in a 0.2 m deep pool in the spraying area. Some tanks also contained vegetation uprooted from the pool and some were covered as controls. Fish were also held in cages in the pool. The 24-hour mortalities in the clear water tanks and the tanks containing vegetation were 34 and 36% respectively but no fish died in the covered controls or in the cages.

Matthiessen and Logan (1984) cite a statement from an Overseas Development Administration report (Douthwaite et al 1981) that long-term effects of the spraying programme included a 75% reduction of Tilapia rendalli nests and a 25% reduction in recruitment of juveniles to the population. Russell-Smith and Ruckert (1981) examined the effects of the programme on aquatic invertebrate populations in lagoons in the spraying area. The two lagoons sampled for free-swimming zooplankton were about 2 m deep, contained dense growth of the under-water plant Najas pectinata and were surrounded by sedge. Periphytic invertebrates living on Najas pectinata were sampled in a number of lagoons over a

two-year period. The irregular variations in the zooplankton populations of rotifers, cladocerans and copepods could not be attributed to spraying. Similarly the variations in periphyton populations, except perhaps for some decreases in Oligochaetse and Trichoptera nymphs, did not correlate with endosulfan spraying.

In California endosulfan has been investigated as a control agent for mosquitoes. Mulla (1963) investigated the effects of endosulfan spraying on mosquito fish, Gambusia affinis, and tadpoles of the bullfrog, Rana catesbiana, which are predators of mosquito larvae. Shallow (about 0.25 m), outdoor ponds containing cages of the test animals were sprayed at the start of the experiment at four different application rates with either α- or β-endosulfan. The rates (0.01 to 1.0 lb/acre, ie 0.011 to 1.1 kg/ha) were approximately equivalent to initial, fully-mixed concentrations of 4.5, 45, 225 and 450 µg/l. Cages in which significant mortality of test organisms had occurred were replaced by cages of fresh organisms. In this way 24-hour or cumulative percentage mortalities were assessed as the endosulfan concentrations declined during the 15-day test. Gambusia all died on the first and second days at the nominal concentration of 450 µg/l of both α- and β-endosulfan. 24-hour mortalities on days 5, 7 and 14 were greater for α-endosulfan at 100, 80 and 40% than for β-endosulfan at 92, 30 and 2%. There was little difference between the toxicity of the two isomers at the lower application rates with 12% mortality or less on day 2 and no further mortality at the nominal concentration of 45 µg/l. For bullfrog tadpoles the α-isomer was again more toxic at the two concentrations tested with mortalities at days 1, 2, 5 and 6 of 100/100, 80/30, 0/0, 0/- % for α-/β-isomers at 225 µg/l and at days 1, 2 and 5 of 60/10, 20/0 and 0/0 % at 45 µg/l. Mulla et al (1967) conducted similar experiments with carp (of unspecified size) and fingerling largemouth bass, Micropterus salmoides, but with a mixture of the isomers, Endosulfan EC2. On the first day 100% 24-hour mortality was observed at both nominal initial concentrations of 50 and 100 µg/l. In the 100 µg/l pond the day 5 mortality was 20% but there were no subsequent deaths. For carp 100% 24-hour mortality persisted to day 3 at 100 µg/l and day 2 at

50 µg/l. At 25 µg/l 24-hour mortalities of 60, 30, 30 and 0% were observed on days 1, 2, 3 and 5.

3.3 BIOACCUMULATION AND METABOLISM

Because of the higher solubility of endosulfan in water compared to other organochlorine pesticides, it does not have the high affinity for lipids that most related compounds have (WHO 1984). Consequently, biomagnification and accumulation of endosulfan in food chains is not expected to occur. The typical response for most organisms exposed to endosulfan at sub-lethal levels is to accumulate the compound up to a plateau, but to clear the residues fairly rapidly once the source of endosulfan has been removed. The higher the exposure level the higher the plateau and the longer it takes to reach the plateau.

Schoettger (1970a) exposed western white suckers, Catastomus commersoni, to 20 µg/l ^{14}C-labelled endosulfan for up to 12 hours. Fish were removed as they died and then analysed for the distribution of the labelled substance in their various tissues. After a rapid take-up in the first few hours the concentration in most tissues levelled off. The highest concentrations were found in the liver and gut plus faeces. The concentration in muscle tissue was lower but, because of the relatively large amount of muscle, it formed the greatest reservoir of endosulfan. The bioaccumulation factors (BCFs) for muscle and liver were 55 and 695 after 9 hours and 65 and 550 after 12 hours exposure respectively, based on dry weight of tissue and nominal concentration of endosulfan in the water. Further evidence, using exposure of white suckers and northern creek chubs, Semotilus atromaculatus, to radio-labelled endosulfan, suggested that endosulfan is removed from the blood by the liver, metabolised and conjugated to glucouronic acid. The glucouronate is discharged with bile which accounts for the high activity found in the gut plus faeces.

Oeser and Knauf (1973) calculated the half-life for elimination of endosulfan from goldfish, Carassius auratus, to be 2 to 3 days following a 5-day exposure to 1 µg/l during which time tissue residues reached a

mean level of 0.35 mg/kg wet weight. Goldfish exposed to 1 µg/l in a flow-through test accumulated similar levels of 0.4 mg/kg, a BCF of 400. When the fish were transferred to clean water the accumulated endosulfan was totally eliminated in 14 days (Osadchuk et al 1971, cited in Ourisson and Koch 1980). In another experiment with goldfish (Gorbach and Knauf 1971) exposure to 100 µg/l endosulfan for four hours resulted in a residue of 4.7 mg/kg in dead fish. At 1 and 2 µg/l the fish were still alive after four days and contained 1.0 and 2.5 mg/kg "total endosulfan" corresponding to BCFs of 1000 and 1250. Oeser et al (1971) obtained a BCF of 2500 for a Chlorella alga based on whole cell weights.

In microcosm studies conducted by Ali (1978, cited in Callahan et al 1979), BCF values were found to depend on the starting material (α-, β- or endosulfan sulphate) and the organism used. Bioaccumulation was measured for all three compounds in algae, snails, mosquito larvae and fish. Snails showed the greatest accumulation of endosulfan with BCFs of up to 5763 (alpha), 39457 (beta) and 29430 (sulphate). For algae, mosquitoes and fish the highest BCFs were obtained for β-endosulfan (up to 3863, 1508 and 388, respectively). No details are given on the exposure concentrations nor on the calculation of BCFs (whether based on wet or dry weights). The octanol-water partition coefficients quoted in Section 2, Table 2(taken from this paper) indicate similar lipid solubilities of the three compounds. Endosulfan sulphate was the only metabolite of endosulfan found in the experiments and the results were interpreted to indicate that β-endosulfan has to be isomerised to α-endosulfan before oxidation to the sulphate can occur.

Qualitative studies of the metabolism of endosulfan have been made with several species of Indian fish - Labeo rohita (Rao et al 1980), Anabas testudineus (Rao and Murty 1980), Channa punctata (Devi et al 1981) and Heteropneustes fossilis, Mystus cavasius and M. vittatus (Rao and Murty 1982). In all cases the importance of the liver in metabolising endosulfan was established. There were few differences between the species but in some cases endosulfan sulphate was not found. In all cases the diol, lactone, ether and hydroxyether metabolites were found.

SECTION 4 - TOXICITY AND BIOACCUMULATION IN MARINE ORGANISMS

4.1 TOXICITY

Data on the toxicity of endosulfan to marine and estuarine organisms are detailed in Table 8. There are similar difficulties in comparing the data from the different tests as were discussed in the section on toxicity to freshwater organisms.

Trim (1987) notes that endosulfan and malathion were suspected of being responsible for the majority of the 72 pesticide-related fish kills in the coastal waters of South Carolina during the period 1977 to 1984.

4.1.1 Algae

Thursby et al (1985) conducted experiments to determine the effects of technical endosulfan on the growth and reproduction of the marine red macroalga (seaweed), Champia parvula. Growth of female and tetrasporophyte structures was significantly reduced after 14 days exposure to 47 µg/l (lowest concentration tested) and 130 µg/l, respectively. Growth of both females and tetrasporophytes and production of tetrasporangia were totally inhibited by 600 µg/l and at 360 µg/l females failed to produce cystocarps.

4.1.2 Molluscs

Effects of endosulfan at concentrations of less than 100 µg/l were only observed in the test on the inhibition of shell growth in the eastern oyster, Crassostrea virginica, reported by Butler (1964). However, this test was performed at 28 °C, which is above the recommended (EPA 1982) temperature range for the species. At 19 °C the EC50 for shell growth was six times larger at 380 µg/l. The effect was temporary with recovery periods in clean water of seven weeks at 19 °C and two weeks at 28 °C.

The toxicity of the α- and β-isomers of endosulfan to the common mussel, Mytilus edulis, was assessed by Roberts (1975) who measured the effects

Table 8 - Toxicity of endosulfan to marine organisms

Species	Exposure type	Temp °C	Salinity ppt (a)	Formulation	Exposure time	Effect	Concentration µg/l (b)	Ref
ALGAE:								
Champia parvula (red macroalga)	Semi-static (24-hr) (c)	23	30	Technical	14 d	LOEC (d) Growth reduction:		1
						female	47	
						tetrasporophyte	130	
Natural phytoplankton community					4 hr	87% reduction in productivity	1000	2
ROTIFERS:								
Brachionus plicatilis	Static	25	12		24 hr	LC50, strain-1	5600	3
						strain-2	6600	
						strain-3	7200	
MOLLUSCS:								
Cerastoderma edule (cockle)	Static	15			48 hr	LC50	>10000	4
Cardium edule (cockle)	Static	15			48 hr	LC50	>10000	5
Mytilus edulis (common mussel,	Static	20		alpha-isomer	48 hr	35% red. in byssal attachment	200	6
						67% red. in byssal attachment	500	
seed-stage, 0.25 g)		20+		beta-isomer	48 hr	95% red. in byssal attachment	100	
	Static	20		Thiodan 20EC	48 hr	EC50 byssal attachment	440	
	Static	15			96 hr	31% red. in byssal attachment	600	
Chlamys opercularis (queen scallops, 25 mm)	Static	15		Thiodan 20EC	24 hr	72% red. in byssal attachment	600	6
Crassostrea virginica (eastern oyster)	Flow	19		Thiodan	24 hr	Inhibition of shell growth	210	7
		19	21		96 hr	EC50 shell growth	380	8
		28			24 hr	Inhibition of shell growth	42	7
		28	22		96 hr	EC50 shell growth	65	2,8
Crassostrea virginica (eastern oyster)						LC50	160	9
Crassostrea virginica (eastern oyster, larva)	Static	20	20	Technical (e)	48 hr	EC50, nom. conc.	460	10
(juvenile)	Flow	28	22	Technical	96 hr	EC50, measured conc.	42	
ANNELIDS:								
Dinophilus gyrociliatus (archiannelid)				Endosulfan	96 hr	LC50	1000	11

Table 8 - continued

Species	Exposure type	Temp °C	Salinity ppt (a)	Formulation	Exposure time	Effect	Concentration µg/l (b)	Ref
Nereis virens (ragworm, a polychaete)	Semi-static (48-hr)	9	seawater		12 d	LC50	100	12
	Semi-static (96-hr)	9	sediment + seawater		12 d	LC50 sediment (av.conc. in water above sediment = 100 µg/l)	340 µg/kg	12
Neanthes arenaceodentata (polychaete worm)	Flow + sediment	20	30	Thiodan 94.4%	96 hr	LC50 mean of 6 labs (range)	195 (>134->243)	13
					96 hr	EC50 inability to burrow	180 (>134->243)	
					28 d	LC50	106 (80-145)	
					28 d	EC50	105 (77-145)	
Neanthes arenaceodentata (polychaete worm)					96 hr	LC50	730	14
CRUSTACEA:								
Acartia tonsa (copepod)	Static				"acute"	LC50 mean of 6 labs (range)	0.22 (0.032-0.45)	15
Artemia salina (brine shrimp)					48 hr	LC50	10000	16
Palaemonetes pugio (grass shrimp, 31 mm)	Flow	24	21	Technical	96 hr	LC50, measured conc.	1.3	17
Penaeus duorarum (pink shrimp, 62 mm)	Flow	25	16	Technical	96 hr	LC50, measured conc.	0.04	17
					96 hr	20% mort at <analyt. det. limit	0.01	
Penaeus aztecus (brown shrimp, adult)	Flow	18	seawater		96 hr	EC50	0.4	2
Penaeus aztecus (brown shrimp, juvenile)	Flow	30	24	Technical	48 hr	EC50, measured conc.	0.24	10
Palaemon macrodactylus (korean shrimp)	Static				96 hr	LC50	17	18
	Flow				96 hr	LC50	3.4	18
Mysidopsis bahia (mysid shrimp)	Static				"acute"	LC50 mean of 5 labs (range)	0.80 (0.24-1.5)	15
	Flow				"acute"	LC50 mean of 5 labs (range)	0.90 (0.38-1.3)	15
Mysidopsis bahia (mysid shrimp)						Chronic value, life-cycle test	0.48	14

Table 8 - continued

Species	Exposure type	Temp °C	Salinity ppt (a)	Formulation	Exposure time	Effect	Concentration µg/l (b)	Ref
Mysidopsis bahia (mysid shrimp, <48-hr old)	Flow	22±2, 25±2	25-30		96 hr	LC50 mean of 5 labs (range)	2.6 (1.0-5.0)	19
	Flow	22±2, 25±2	25-30		28 d	Chronic value, mortality, mean of 4 labs (range)	0.34 (0.21-0.48)	19
Crangon septemspinosa (shrimp, 2 g)	Semi-static (48-hr) (f)	20	seawater		96 hr	LC50 (g)	0.2	20
	Static (f)	10	sediment (h) + seawater		96 hr	LC50 (i)	6.9 µg/kg	
Crangon crangon (brown shrimp)	Static	15			48 hr	LC50	10	5
Callinectes sapidus (blue crab, juvenile)	Flow	30	24	Technical	48 hr	EC50, nominal conc.	19	10
Callinectes sapidus (blue crab, juvenile)	Flow	30	seawater		48 hr	EC50 death or equilibrium loss	35	2
4 Tests on miscellaneous zooplankton:								
Acartia sp (copepod)	Static		seawater	Technical	24 hr	LC50	240	21
Sagitta sp (arrow worm)	Static		seawater	Technical	24 hr	LC50	420	21
Eucalanus sp	Static		seawater	Technical	24 hr	LC50	180	21
Lucifer sp (decapod)	Static		seawater	Technical	24 hr	LC50	290	21
FISH:								
Cyprinodon variegatus (sheepshead minnow)	Static				"acute"	LC50 mean of 6 labs (range), nominal conc.	2.4 (1.2-3.5)	15
	Flow				"acute"	LC50 mean of 6 labs (range), analysed conc.	0.82 (0.34-1.2)	15
Cyprinodon variegatus (sheepshead minnow)						Chronic value	0.4	14
Cyprinodon variegatus (sheepshead minnow, 24-hr old embryo)	Flow	30	15-30	Technical (64% I + 36% II)	28 d	Embryo-larva chronic value based on growth or survival; 7 labs, mean of 10 results (range)	0.63 (0.27-1.77)	22
Mugil curema (white mullet)	Flow	29	seawater		48 hr	LC50	0.6	2

Table 8 - continued

Species	Exposure type	Temp °C	Salinity ppt (a)	Formulation	Exposure time	Effect	Concentration µg/l (b)	Ref
Mugil cephalus (striped mullet, 27 mm)	Flow	24	15	Technical	96 hr	LC50, measured conc.	0.38	17
Lagodon rhomboides (pinfish, 30 mm)	Flow	24	16	Technical	96 hr	LC50, measured conc.	0.3	17
Leistomus xanthurus (spot, 39 mm)	Flow	25	18	Technical	96 hr	LC50, measured conc.	0.09	17
Leistomus xanthurus (juvenile spot)	Flow	22	26	Thiodan	48 hr	LC50	0.6	8
Fundulus heteroclitus (mummichog)	Static	20	20	30EC	96 hr	LC50	1.2	23
Morone saxatilis (striped bass, 33 mm)	Flow	17	30		96 hr	LC50	0.1	24
Agonus cataphractus (armed bullhead)	Static	15			48 hr	LC50	33-100	5

Notes

(a) ppt = parts per thousand

(b) Concentration: results are given as reported in the papers but rounded to two significant figures. It is not always clear whether the reported results refer to formulation or active ingredient or whether the values are nominal concentrations or analysed stock or test solutions.

(c) Renewal frequency of test solutions

(d) NOEC = "No observed effect concentration", ie the highest concentration at which there was no difference from the controls;
LOEC = "Lowest observed effect concentration", ie the lowest concentration at which there was a statistically significant difference from the controls.
Chronic value = geometric mean of NOEC and LOEC

(e) For references 10 and 17 for work done at EPA Gulf Breeze Laboratory "Technical" endosulfan is reported as 96%.

(f) Test chambers prepared by evaporating a solvent solution of endosulfan in the empty chamber before adding water or water and sediment.

(g) Based on measured concentration by analysing for the alpha-isomer. Concentration reached a maximum in 2 hr and declined linearly to a sixth of the maximum at 48 hours. Results are based on time-averaged concentrations.

Notes to Table 8 continued

(h) Sediment = 97% sand, 30 mm deep overlain with 15 mm of water.

(i) Based on maximum concentration during exposure period but authors suggest that the water above the sediment also contained toxicant.

References

1 Thursby et al 1985
2 Butler 1963
3 Serrano et al 1986
4 Portmann 1970, cited in Roberts 1975
5 Portmann and Wilson 1971
6 Roberts 1975
7 Butler, personal communication cited in Roberts 1975
8 Butler 1964
9 Butler 1964, cited in EPA 1980 but not found in the original reference by the present author.
10 Mayer 1987
11 Carr et al 1986
12 McCleese et al 1982
13 Pesch and Hoffman 1983
14 Unpublished EPA results, cited in EPA 1980
15 Schimmel 1980, cited in EPA 1980
16 Knauf and Schulze 1973, cited in Ourisson and Koch 1980
17 Schimmel et al 1977
18 Schoettger 1970b, cited in EPA 1980
19 McKenny 1990
20 McCleese and Metcalfe 1980
21 Rajendran and Venugopalan 1988
22 Hansen and Cripe 1984
23 Trim 1987
24 Korn and Earnest 1974

of the chemicals on the development of the byssal threads used by bivalves to anchor themselves. The β-isomer was found to be more toxic than the α-isomer with reductions in byssal thread attachment after 48 hours exposure to 200 µg/l of 85% for β and 35% for α-. In experiments with an emulsifiable formulation of endosulfan the toxicity was greater for smaller mussels and at higher temperatures.

4.1.3 Annelids

The results of a six-laboratory ring-test on the toxicity of technical endosulfan to the polychaete worm, Neanthes arenaceodentata, were reported by Pesch and Hoffman (1983). The worms were exposed in flow-through systems and sand was provided as a sediment in which they could burrow. After exposure for 96 hours, 10 days and 28 days LC50 values were 195 µg/l, 158 µg/l and 106 µg/l, respectively. Values for EC50s, based on the numbers of test animals which did not burrow, were almost identical to the corresponding LC50s. The results were based on mean measured concentrations which varied from 39 to 98% of the nominal values. Variations between individual samples indicated that concentrations were generally maintained to within ±30% of the mean values.

In another experiment with a polychaete worm McLeese et al (1982) investigated the toxicity of endosulfan to the ragworm, Nereis virens, with and without sediment in the test vessel. The preparation of the test solutions and dosed sediments was somewhat unusual in that solutions of the toxicant in a volatile solvent were evaporated in the test vessels before water or water and sediment were added. The exposure regime was semi-static with aqueous test solutions being changed every 48 hours and sediment-water mixtures every 96 hours. (This type of experimental procedure was also used by McLeese and Metcalfe (1980) in the tests on Crangon septemspinosa described in Section 4.1.4.) The sediment, consisting of silt and clay (83%) and sand (17%), was 30 mm deep and was covered with 15 mm of water. The 12-day LC50 values for worms exposed to seawater only and to seawater in the presence of sediment were 100 µg/l. Stressed worms in the test with

sediment emerged from the sediment and subsequently did not burrow, even after the sediment was changed. The LC50 in the sediment-water experiment expressed in terms of the concentration of endosulfan in the sediment was 340 µg/kg. Graphs presented in the earlier paper by McLeese and Metcalfe (1980) on Crangon septemspinosa show that the concentration of endosulfan in the water-only experiment increased to a maximum in about two hours and declined linearly by a factor of about six after 48 hours, but the temperature in this experiment was ten degrees higher than in the Nereis experiment and the test concentrations were very much lower. The build-up and decline in concentration in the sediment-water experiments followed a similar pattern but is assumed to be slower. The LC50 values are calculated on the basis of time-averaged exposure concentrations.

4.1.4 Crustacea

Short-term LC50s for a variety of species of shrimp vary between 0.04 and 17 µg/l.

The highest value of 17 µg/l was reported by Schoettger (1970b) in a static test on the Korean shrimp, Palaemon macrodactylus. There may have been some problem with maintaining the exposure concentration in this test because in the parallel flow-through test the LC50 was 3.4 µg/l. The low value of 0.04 µg/l (measured concentration) is the LC50 found by Schimmel et al (1977) in a flow-through test on the pink shrimp, Penaeus duorarum. In this test 20% mortality was recorded at a nominal concentration of 0.01 µg/l. This was also the detection limit of the analytical method used (summing α- and β-isomers and the sulphate) and analyses did not detect any endosulfan in the test vessel at the nominal concentration of 0.01 µg/l. A higher LC50 of 1.3 µg/l was reported in the same paper for the grass shrimp, Paleomonetes pugio, based on the same test procedures.

Two sets of ring-tests, both involving five different laboratories, measuring the acute toxicity of endosulfan to Mysidopsis bahia, a mysid shrimp, have been reported by Schimmel (1980) and McKenney (1990).

Although the mean LC50s of 0.9 and 2.6 µg/l for the two sets of tests are different the ranges of the results obtained in the two ring-tests, 0.38 to 1.3 µg/l and 1.0 to 5.0 µg/l, overlap. The ring-test discussed by McKenney also involved a 28-day mortality and reproduction test. Chronic values, based on mortality, in the range 0.21 to 0.48 µg/l were obtained by four of the laboratories. (The latter figure may be the Chronic Value for the species given in the 1980 EPA Ambient Water Quality Criteria Document.)

McLeese and Metcalfe (1980) used similar methods to those discussed for annelids in Section 4.1.3 to investigate the acute toxicity of endosulfan to a carid shrimp, Crangon septemspinosa, in water and in a sediment-water system. The main differences between the two sets of experiments were that for the Crangon experiments the sediment was 97% sand, rather than the more adsorbent 83% silt, and the exposure time was limited to 96 hours rather than 12 days so that in the sediment-water case the test vessels were not renewed. An LC50 of 0.2 µg/l was found in the water-only test. In the sediment-water test stressed shrimps left the sediment but no data were reported for the concentration of endosulfan in the water above the sediment and the "sediment LC50" value of 6.9 µg/kg may have little real meaning.

The blue crab, Callinectes sapidus, and the brine shrimp, Artemia salina, appear to be less sensitive to endosulfan than the other crustaceans tested.

4.1.5 Fish

From the available data the most sensitive species of fish appear to be the spot, Leistomus xanthurus, (Schimmel et al 1977) and striped bass, Morone saxatilis, (Korn and Earnest 1974) with 96-hour LC50s of 0.09 µg/l and 0.1 µg/l respectively. In the test with the spot there was 35% mortality (compared with 10% in the control) at the lowest test concentration of 0.05 µg/l. Acute LC50s have been reported for five other species ranging from 0.3 to 1.2 µg/l.

The most widely studied species is the sheepshead minnow, Cyprinodon variegatus. The values for acute LC50s under static and flow-through conditions obtained in a ring-test with five participating laboratories have been reported by Schimmel (1980). The mean values were 2.4 µg/l for the static tests (range 1.2 to 3.5 µg/l) and 0.82 for the flow-through tests (range 0.34 to 1.2 µg/l). The sheepshead minnow was also the subject of an embryo-larval ring-test reported by Hansen and Cripe (1984). The seven laboratories produced ten valid tests, giving an overall mean Chronic Value of 0.63 µg/l (range 0.27 to 1.77 µg/l). The most sensitive endpoint in each test was either larval growth or survival. At the concentrations used, up to 10 µg/l, there was little if any effect on hatching success.

4.2 BIOACCUMULATION

The bioaccumulation of endosulfan has been investigated in molluscs, polychaete worms, crustaceans and fish. Metabolism has also been studied in some marine organisms.

A maximum BCF of 22.5 was reported for mussels exposed to 100 µg/l endosulfan for 70 days; the BCF decreased to 17 by day 112 (Roberts 1972). Exposure to concentrations of 500 and 1000 µg/l resulted in greater tissue levels but bioaccumulation factors (BCFs) of only 11 and 8.1 after 112 days. Ernst (1977) also tested mussels but used α-endosulfan in a mixture of pesticides and worked at much lower concentrations. He reported a BCF of 600 for mussels at 10 °C in water initially containing 2.05 µg/l α-endosulfan. The BCF was calculated using the steady-state water concentration of 0.14 µg/l and tissue concentration of 84 µg/kg wet weight obtained within 50 hours. The paper reports a half-life of 34 hours for α-endosulfan in mussels based on a one-compartment model. However, on considering the data presented, it appears that more than 50% of the accumulated pesticide is lost after only 9 hours in clean water, suggesting that perhaps a two-compartment model might apply, although the concentration decay data are probably insufficient to draw a firm conclusion.

Haya and Burridge (1988) exposed the polychaete worm Nereis virens to solutions of endosulfan in aquaria containing seawater and sediments. The worms were exposed to concentrations of 60 µg/l under hypoxic (12% saturated) and normoxic (presumably close to air-saturation) conditions at 7 °C for four days, with the test solutions being renewed after two days. After four days the animals were transferred to clean water for the depuration phase. Uptake of endosulfan appeared to be linear under both hypoxic and normoxic conditions although the bioaccumulation rate was nearly three times faster in the oxygen-deficient conditions. The maximum concentrations in the worms under hypoxic and normoxic conditions were about 4.4 and 1.7 mg/g lipid, respectively, and were recorded at the end of the exposure period and in neither case was equilibrium reached. The half-life for elimination of the endosulfan was approximately 60 hours and conformed to a one-compartment accumulation model. No mention was made of the presence or absence of endosulfan sulphate or any other possible metabolites.

During their investigation of the toxicity of endosulfan to two species of shrimp and three species of fish Schimmel et al (1977) investigated the uptake of endosulfan by the test animals. In all cases where measurable (10 µg/kg wet tissue) residues were found after exposure for 96 hours to a technical mixture of α- and β-endosulfan the predominant form in the tissue was endosulfan sulphate. The pink shrimp, although extremely sensitive to the acute toxic effects of endosulfan, does not appear to accumulate the chemical. Even when exposed to the highest test concentration of 0.089 µg/l no residue was detected in the shrimp tissues. Bioaccumulation factors of 81 to 245 were calculated for the grass shrimp based on measured concentrations of 0.16 to 1.75 µg/l. The highest concentration in this test gave 65% mortality and residues of endosulfan of 78, 42 and 360 µg/kg (alpha, β and sulphate respectively). BCFs reported for pinfish (Lagodon rhomboides), spot and striped mullet (Mugil cephalus) after exposure for 96 hours reached 1299, 895 and 1344, respectively.

In the same paper the authors also reported that during the course of a 28-day experiment juvenile striped mullet exposed to an endosulfan

concentration of 0.035 µg/l reached a BCF of 1000 after 96 hours and 2755 after 28 days with tissue concentrations still increasing at the end of the test. The concentration of endosulfan sulphate in the fish was, at 80 µg/kg, nearly five times greater than that of β-endosulfan (17 µg/kg) whereas α-endosulfan was below the detection limit (10 µg/kg). The endosulfan was totally eliminated after only 48 hours in clean water. At the nominal concentration of 0.008 µg/l in the water, which could not be measured accurately, no residues were detectable in the fish.

SECTION 5 - RECOMMENDED PROVISIONAL ENVIRONMENTAL QUALITY STANDARDS

5.1 PROTECTION OF FRESHWATER LIFE

The data available on the toxic effects of endosulfan to freshwater organisms are summarised in Section 3 and Table 7. Indications are that fish are the most sensitive group of aquatic organisms and some of the more sensitive fish appear to be tropical species. For example, the harlequin fish, Rasbora heteromorpha, which, when tested in the UK under possibly stressful conditions, had a 48-hour LC50 of 0.014 µg/l expressed as the formulated product 20% Thiodan (Alabaster 1969). The Indian catfish, Mystus vittatus, (Reddy and Gomathy 1977) and fry of the african cichlid, Sarotherodon mossambicus, (Matthiessen and Logan 1984) also appear to be among the more sensitive species with acute toxic effects observed at around 0.2 µg/l. However, these results were obtained with species and under test conditions that cannot be considered relevant to British waters. The PEQS value for the protection of freshwater life is, therefore, proposed at 10 ng/l, derived by applying a safety factor of 30 to the 96-hour LC50 of 0.3 µg/l obtained for rainbow trout under flow-through conditions at 12 °C (Nebeker et al 1983). The reason for the application of a relatively small arbitrary safety factor compared to the factor of 100 usually applied to acute LC50s is threefold. First, there is evidence that whole populations are unlikely to be killed by continuous exposure to low levels of endosulfan because those fish with higher lipid

contents seem to be resistant (Fox and Matthiessen 1982). Second, early-life stages of fish and juvenile fish have similar sensitivities to endosulfan as indicated by the comparison of the 7-d LC50 of 0.86 µg/l for juvenile fathead minnows, Pimephales promelas, and the no effects concentration (NOEC) of 0.2 µg/l for a full life-cycle test (Macek et al 1976). Third, bioaccumulation of endosulfan and food-chain effects are small in comparison with the effects of other more persistent organochlorine insecticides such as dieldrin.

The PEQS should be considered as an annual average for "total dissolved endosulfan". "Total endosulfan" is defined as the sum of the concentrations of α-endosulfan, β-endosulfan and endosulfan sulphate. Endosulfan is readily adsorbed on sediments and data from field studies suggests that in this form it may not be readily bioavailable to aquatic organisms and in particular to fish. Therefore it is suggested that for the purpose of monitoring the standard the sample is allowed to stand for one hour before the supernatant is analysed for "total dissolved endosulfan". However, the currently used analytical methods for pesticides are not satisfactory for monitoring the proposed PEQS for endosulfan of 10 ng/l.

The available information indicates that, except for accidental spills, endosulfan is only likely to be present at elevated concentrations in the aquatic environment as a result of spray drift and run-off from treated land. To protect against these short-term episodic events a PEQ of 1 µg/l expressed as a maximum concentration of "total dissolved endosulfan" is proposed by applying an arbitrary safety factor of 30 to the short-term LC50 (1.67 hours) of 31.9 µg/l obtained by Kleiner et al (1984) for fathead minnow, Pimephales promelas. A safety factor of 30 has been selected by applying a factor of 10 to protect against acute effects and an additional factor of 3 to take into account that other species (eg rainbow trout, Oncorhynchus mykiss) are more sensitive.

There is little evidence on the ultimate fate of endosulfan and its metabolites or decomposition products in sediments and on any effects on

freshwater benthic organisms although, presumably, some sediment-dwelling crustaceans may be at risk.

5.2 PROTECTION OF SALTWATER LIFE

Data available on the toxic effects of endosulfan to marine organisms are summarised in Section 4 and Table 8. Marine crustaceans and fish appear to have similar sensitivities to endosulfan. The lowest 96-hour LC50 for a crustacean species is 0.04 µg/l for Penaeus duorarum (Schimmel et al 1977). Crangon septemspinosa had an LC50 value of 0.2 µg/l (McLeese and Metcalfe 1980) whereas the LC50s for all other crustaceans were greater than 0.4 µg/l. The lowest fish LC50s were 0.09 µg/l for Leistomus xanthurus (Schimmel et al 1977) and 0.1 µg/l for Morone saxatilis (Korn and Earnest 1974). The chronic values for the shrimp, Mysidopsis bahia, and the sheepshead minnow, Cyprinodon variegatus, are higher than the acute LC50s cited above.

A PEQS of 5 ng/l is proposed for the protection of marine life, derived by applying an arbitrary safety factor of approximately 10 to the acute LC50 of 0.04 µg/l for P. duorarum. The reason for such a low safety factor applied to an acute LC50 value is that the reported chronic toxicity values are similar to the acute values. For instance for the mysid shrimp, Mysidopsis bahia, a range of acute LC50 values of 0.24 to 1.5 µg/l has been reported (Schimmel 1980) compared to a chronic value for a life cycle test of 0.48 µg/l (EPA 1980). Similarly for the sheepshead minnow, Cyprinodon variegatus, mean acute LC50s of 0.34 to 1.2 µg/l were obtained in a ring-test of six laboratories (Schimmel 1980) which compares to a chronic value of 0.4 µg/l (EPA 1980). The PEQS should be expressed as annual average concentration and dissolved total (α, β and sulphate) endosulfan, (ie analysis to be performed on the supernatant after settlement for one hour). No maximum PEQS value is proposed for dissolved endosulfan as the input to marine waters is predominantly via rivers which undergo high dilutions in estuaries and coastal waters this making it unlikely that marine waters would be affected significantly by episodic events. However, it is likely that a significant amount of endosulfan present in the marine environment

will be adsorbed on sediments but insufficient data are available to propose a standard for total (dissolved and adsorbed) endosulfan.

The analytical techniques currently applied to marine waters are inadequate to monitor the proposed standard for the protection of saltwater life.

5.3 ABSTRACTION TO POTABLE WATER

Endosulfan was reported not to be mutagenic to Escherischia coli or Salmonella typhimurium (WHO 1984). Contradictory reports exist as to whether the compound induces reverse mutations, cross overs and mitotic gene conversions in Saccharomyces cerevisae. Endosulfan did not induce chromosomal aberrations in bone marrow cells or spermatogonia of male rats. Other reported results are also negative.

Technical grade endosulfan was found not to be carcinogenic to female Osborne-Mendel rats or female B6C3F1 mice in one study, although another study utilising two different strains of male and female hybrid mice was inconclusive.

The toxicity and residue data on endosulfan have been reviewed by the Joint Meetings on Pesticide Residues (JMPR) and an estimate of a temporary acceptable ADI for man of 0.008 mg/kg body weight (total of α- and β-endosulfan and endosulfan sulphate) has been made (WHO 1984). The suggested no adverse response level (SNARL) for chronic exposure from drinking water, assuming a 60 kg adult drinking 2 l water per day with 1% of the ADI derived from drinking water is 2.4 µg/l. This value is much higher than the maximum allowable concentration (MAC) of 0.1 µg/l laid down for individual pesticides in the EC Drinking Water Directive (CEC 1980). No advisory value is included for endosulfan in the Guidance on Safeguarding the Public Water Supplies (DoE 1989b). Because of the uncertainties concerning the removal of endosulfan in water treatment processes and during storage no PEQS is proposed for the protection of waters used for the abstraction to potable supply.

However, Greve and Wit (1971) demonstrated that endosulfan can be removed from water by adsorptive processes, especially using activated carbon.

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