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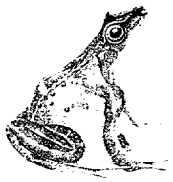

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PROVISIONAL ENVIRONMENTAL QUALITY STANDARDS FOR AZINPHOS-METHYL IN WATER

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SUMMARY

I OBJECTIVES

To propose provisional environmental quality standards (PEQSs) for azinphos-methyl for the protection of the different uses of water based on readily available information on its environmental fate and ecotoxicity.

II REASONS

The UK has adopted the dual approach for the control of particularly dangerous substances entering the aquatic environment ('The Red List') by applying limit values and environmental quality standards (EQSs). This report is one of a series aimed at proposing provisional environmental quality standards (PEQSs) for those 'Red List' substances for which no EQSs have so far been derived.

III CONCLUSIONS

Azinphos-methyl is a broad spectrum organophosphorus insecticide. Entry into the aquatic environment is likely to be mainly from diffuse inputs. Azinphos-methyl is not very persistent in natural waters, with hydrolysis and photolysis the main degradation processes.

For the protection of freshwater life a PEQS of 10 ng/l is proposed based on applying a safety factor of 10 to the "no effect" concentration of 0.1 µg/l for Daphnia magna (Dortland 1980). The safety factor takes into account that in acute tests other species were more sensitive than Daphnia. The same PEQS is proposed for the protection of marine life as insufficient data are available to derive a separate standard and the available data indicate that fresh and marine species have the same sensitivity to azinphos-methyl. The PEQSs should be expressed as annual average concentrations, because they are based on chronic data, and as "dissolved" azinphos-methyl. As the highest azinphos-methyl levels in the environment are likely to be associated with run-off from treated

land, a PEQS of 100 ng/l is also proposed as maximum "dissolved" concentration to protect against these episodic events. This PEQS is based on the 96-hour LC50 to the amphipod, Gammarus lacustris, taking into account the relatively low persistence of azinphos-methyl. Insufficient environmental data are available to verify the proposed standards for the protection of aquatic life.

Using the ADI of 0.0025 mg/kg body weight for azinphos-methyl (WHO/FAO 1974) and allowing that 1% of the ADI may be derived from drinking water, the resulting acceptable concentration in drinking water is 0.75 µg/l for an adult drinking 2 l water per day. This value is greater than the MAC of 0.1 µg/l laid down for individual pesticides in the EC Drinking Water Directive.

The analytical limits of detection for azinphos-methyl which can currently be achieved by the water industry (approximately 50 ng/l in river waters, Standing Committee of Analysts 1988) are inadequate for monitoring the proposed PEQSs in natural waters. It is recommended that for the determination of "dissolved" azinphos-methyl the sample is allowed to stand for at least one hour before analysis and the supernatant is analysed without filtration.

IV RECOMMENDATIONS

The PEQS values proposed should only be regarded as tentative values because, owing to time constraints, some of the papers quoted could not be fully assessed for the preparation of this report. The standards should therefore be reassessed when all information has been examined in detail.

V RESUME OF CONTENTS

This report uses available information on the ecotoxicity and environmental fate of azinphos-methyl to derive PEQSs for the protection of freshwater and marine life and considers likely safe levels for waters used for abstraction to potable supply. Insufficient data were available to consider other water uses.

CONTENTS

CONTENTS - Cont

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 ('The Red List') discharged to the aquatic environment by applying limit values and environmental quality standards (EQSs) (DoE 1987). After the announcement and following consultations, the Department of the Environment issued a 'Red List' consisting of 23 substances (DoE 1989a). This report is one of a series proposing provisional environmental quality standards (PEQSs) for those 'Red List' substances for which no EQSs have previously been derived. It briefly reviews the available information on the ecotoxicology and environmental fate of azinphos-methyl and proposes provisional environmental quality standards (PEQSs) for the protection of aquatic life.

SECTION 2 - AZINPHOS-METHYL IN THE ENVIRONMENT

2.1 Physico-chemical properties

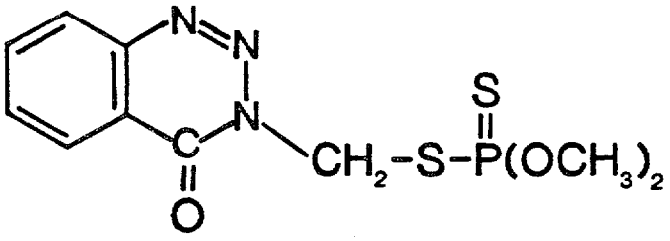
The physico-chemical properties of azinphos-methyl relevant to its environmental behaviour and fate are summarised in Table 1. It should be noted that the properties of the formulated product may differ considerably from those of the pure compound.

Azinphos-methyl is only sparingly soluble in water (14 mg/l at 15 °C) and the octanol/water partition coefficient is moderate (log K_{ow} = 2.99 to 3.77). Based on the soil organic carbon sorption coefficient (log K_{oc} = 3.56) sorption on suspended solids and surfaces is likely.

Anderson et al (1974) state that technical azinphos-methyl is moderately stable at room temperature, losing about 10% of its active ingredient during 12 months' storage. Dilute liquid formulations may be more stable although release of nitrogen gas may necessitate the use of vented containers.

Table 1 - Physico-chemical properties of azinphos-methyl

Chemical structure:



CAS name:	O,O-dimethyl S-[(4-oxo-1,2,3-benzotriazin-3(4H)-yl)methyl] phosphorodithioate	
IUPAC:	S-3,4-dihydro-4-oxo-1,2,3-benzotriazin-3-ylmethyl O,O-dimethyl phosphordithioate	
or	S-3,4-dihydro-4-oxobenzo[d][1,2,3]triazin-3-ylmethyl O,O-dimethyl phosphordithioate	
Other names:	Guthion, Gusathion M, Bay 17147, Carfene, Cotnion-methyl, Metiltriazotin	
CAS registry no.	86-50-0	
Physical state:	colourless crystals	
Molecular formula:	$C_{10}H_{12}N_3O_3PS_2$	
Molecular weight:	317.3	(a)
Melting point:	73-74 °C	(a)
Vapour pressure:	< 1 mPa @ 20 °C	(b)
	10×10^{-6} Pa @ 25 °C	(c)
Water solubility:	47 mg/l @ 35 °C	(d)
	29 mg/l @ 25 °C	(b)
	33 mg/l @ 20 °C	(e)
	14 mg/l @ 15 °C	(d)
Log K_{ow}:	2.99	
	3.77	(c)
Log K_{oc}:	3.56	(c)

Notes:
(a) Merck Index 1983
(b) The Agrochemicals Handbook 1988. 2nd ed, Royal Society of Chemistry
(c) Ghetti et al 1987 (draft EC Report)
(d) ECDIN*
(e) Verschueren K 1983. Handbook of environmental data on organic chemicals. 2nd ed Van Nostrand Reinhold Company Publ.

2.2 MANUFACTURE AND USES

Azinphos-methyl may be synthesised by the reaction of 3-chloromethyl-3,4-dihydrobenzo[d][1,2,3]triazin-4-one with dimethyl sodium phosphorodithioate in the presence of a proton acceptor at room temperature (Anderson et al 1974).

Azinphos-methyl is a broad spectrum, non-systemic, organophosphorus insecticide and acaricide with contact and stomach action. It is an inhibitor of acetylcholinesterase (AChE). It is used for the control of chewing and sucking insects of the orders Coleoptera, Diptera, Homoptera, Hemiptera and Lepidoptera and spider mites on fruit trees (including citrus), vines, strawberries, nuts, vegetables, potatoes, cereals, maize, cotton, ornamentals, beet, soya beans, tobacco, rice, sugar, coffee, sugar cane, forestry and other crops.

Crops are sprayed when pest populations are prevalent at application levels of 0.1 to 0.4 kg ai/ha. Azinphos-methyl products are available as wettable powders (200, 250, 400 or 500 g ai/kg), emulsifiable concentrates (200 g ai/l) and dustable powders (50 g ai/kg). MAFF/HSE (1988) list Alpha GB Ltd (London) and Bayer UK Ltd (Bury St Edmunds) as marketing companies for azinphos-methyl products in the UK. Ivens (1988) suggests that in the UK azinphos-methyl is only available in a mixture with demeton-S-methyl sulphone ('Gusathion MS', a wettable powder). However, contrary to Ivens (1988) Alpha GB Ltd products are sold under the names Alpha Azinphos-methyl 22EC and MCW Azinphos Methyl whereas 'Gusathion MS' is only marketed by Bayer.

SRI (1988) lists the Bayer AG plant at Leverkusen as the sole producer of azinphos-methyl in the EC with an estimated production capacity of 5000 to 10 000 tonnes. Other, non-European, manufacturers include Makhteshim-Agan and Mobay.

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

A tentative method for the analysis of organophosphorus pesticides in river and drinking water has been published (DoE 1983). The method gives a limit of detection of <1 µg/l and involves solvent extraction followed by gas chromatography (GC) using a phosphorus-sensitive detector.

The Standing Committee of Analysts (1988) have reviewed the detection limits for azinphos-methyl which can be achieved by the water industry. In 'clean' (drinking) water a limit of 10 ng/l is achievable whereas in 'dirty' samples (river water, industrial and sewage effluents and agricultural run-off) a detection limit of only 50 ng/l is likely. Interference from other compounds present may pose problems and the use

of mass spectrometry may be required for verification of identity. The analytical techniques available are inadequate for monitoring compliance with the proposed standards for "dissolved" azinphos-methyl.

2.4 SOURCES OF CONTAMINATION

Azinphos-methyl is not manufactured in the UK and thus, the only point source releases into the aquatic environment will originate from formulating plants, marketing outlets and accidental spillages during transport, storage, use or bad practice. Diffuse pollution sources include spray-drift during application, agricultural run-off from treated land and the waste disposal of azinphos-methyl products.

2.5 LEVELS IN THE ENVIRONMENT

Data on the levels of azinphos-methyl in the environment are scarce. Coppage et al (1976*) analysed the effluent of, and the river water downstream from, an organophosphorus pesticide manufacturing plant. Concentrations as high as 2 to 4 mg/l were detected in the undiluted plant effluent, but maximum concentrations after 1:650 dilution in the receiving water were below the detection limit (50 µg/l). A previous report by Lawless et al (1972*) indicated that about 3.2 kg of azinphos-methyl entered the river every day to give a concentration of 0.16 µg/l at low flow. This would suggest a more typical concentration in the effluent in the region of 0.1 mg/l assuming 1:650 dilution.

A survey of waters bordering frequently sprayed blueberry fields was carried out by Bushway et al (1982) in Maine, USA. The blueberries were grown on "barrens", which are glacially-deposited sand and gravel located near the coast. Azinphos-methyl was detected in a well located

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* Some references quoted in this report (marked with an asterisk) were obtained from a draft EC ecotox report prepared by Ghetti et al (1987) which provided incomplete details for the references. Copies of these papers have not yet been obtained.

in a blueberry field which had been sprayed twice. Four days after the initial application 1.9 µg/l azinphos-methyl was detected in the water. Two weeks later, during which time it rained heavily and three days after a second application, the level had increased to 24 µg/l. However, after a further two weeks the pesticide level in the water had declined to below the detection limit (230 ng/l) which indicates either that azinphos-methyl degrades rapidly or, more likely, that it was diluted with fresh ground water moving through the open-textured, low-organic-content soil. Recycled washwater from a blueberry processing plant nearby was the only other water which contained detectable azinphos-methyl levels. The pesticide was present at 12.7 µg/l. Although no pesticide was detected in the waters over clam beds in the river estuaries draining the "barrens", the possibility that the delayed spawning of clams reported at these sites was caused by the presence of azinphos-methyl (or its degradation product, azinphos-methyl oxon) accumulated in the sediment of the beds could not be ruled out.

Bushway et al (1982) also investigated the amount of azinphos-methyl present in blueberries from three locations. The concentrations ranged from none detected (detection limit 50 µg/kg) to 120 µg/kg. These values are well below the US Environmental Protection Agency (EPA) tolerance level of 5 mg/kg for azinphos-methyl on blueberries.

Smith et al (1983) investigated the loss of azinphos-methyl in field run-off from trial plots. The insecticide was applied to the plots four times a year at a rate of 0.84 kg ai/ha and run-off samples (water and sediment) were collected within 8 hours of each storm event and analysed by GC. The highest azinphos-methyl concentration, 417.5 ± 136.4 µg/l, occurred in a run-off event one day after the application of the pesticide and another high concentration of 109.4 ± 26.8 µg/l occurred four days after a later application. The losses from these two events represented about 40% of the total seasonal loss of azinphos-methyl or 0.2% of the amount applied annually. Two heavier rainfall events, which occurred 5 and 16 days after separate pesticide applications, had lower pesticide concentrations in the run-off because of the large run-off volume and accounted for an additional 50% of the azinphos-methyl seasonal loss or 0.3% of the amount applied annually.

The application of azinphos-methyl to pine seedling plantations containing two watersheds that drained into a nearby recreational lake was studied by Bush et al (1986). The insecticide was sprayed from a helicopter at a rate of 3.37 kg ai/ha. Fish were collected monthly or bimonthly from the lake 25 to 50 m off-shore for four years and analysed by GC to ascertain if the insecticide was present in the flesh. No azinphos-methyl was detected in fish at a detection limit of 300 µg/kg. Drift of azinphos-methyl during spraying was quantified using glass fibre disks located around the edge of the lake. From measurements of the amounts collected on the disks it was calculated that drift of azinphos-methyl would have amounted to a concentration of <0.4 µg/l, assuming a water column depth of 0.3 m. Run-off from one watershed 10 days after application contained 1540 µg/l azinphos-methyl. The concentration of the insecticide in run-off decreased rapidly with subsequent storm events.

Zabik et al (1987*) suggest that airborne drift during and for several days after spraying can be a significant non-point source of contamination of surrounding waters.

2.6 FATE IN THE ENVIRONMENT

Ghetti et al (1987) calculated the expected concentrations of azinphos-methyl in the different environmental compartments using the model of Mackay and Paterson (1982*). A single input of 100 Mole to an environment consisting of 7×10^6 m^3 water, 4.5×10^4 m^3 soil and 2.1×10^4 m^3 sediment resulted in 29% of available azinphos-methyl being associated with water, 36% with soil and 34% with sediment.

2.6.1 Water

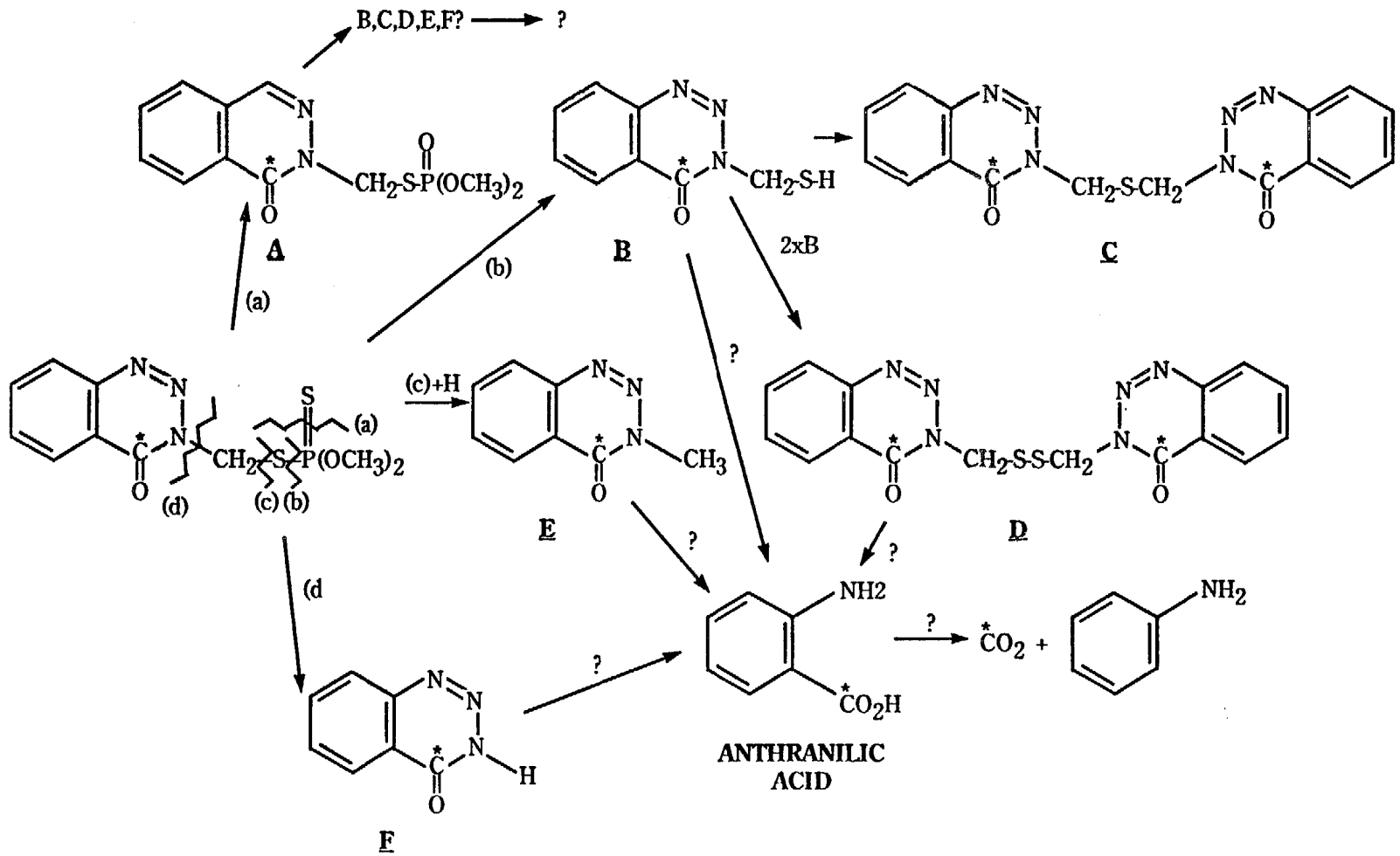
(a) Chemical degradation

Atwood et al (1987) investigated the stability of azinphos-methyl (50% WP) in aqueous media. Stirred suspensions of azinphos-methyl at concentrations of 0.6 g/l (the recommended field dose for use in

orchards) and 12 g/l in water at pH 4.5, 7 and 9 were kept in glass beakers in the light for 48 hours. The only significant loss was 9% from the 0.6 g/l suspension at pH 9.

Liang and Lichtenstein (1972) studied the effects of light of different wavelengths, pH and temperature on the decomposition of azinphos-methyl in aqueous solution. They used azinphos-methyl ^{14}C-labelled at the carbonyl carbon in the heterocyclic ring, ie position 4. Solutions at 23 °C and, presumably, neutral pH kept in the dark or irradiated with red or yellow light for twelve hours showed little evidence of decomposition. However, solutions irradiated with ultra-violet light resulted in breakdown of azinphos-methyl by a variety of photochemical pathways (see Figure 1). Samples taken at various times during the experiment were separated into water-soluble and chloroform-soluble fractions. The radioactivity in the chloroform-soluble fraction, representing undegraded azinphos-methyl and degradation products A, B, C (or D), E, F and anthranilic acid (Figure 1), decreased to 10% of the initial value over the 12 hours of the test. The radioactivity of the water-soluble fraction, representing unidentified polar products, increased to 30% of the initial radioactivity within 4 hours and then remained constant to the end of the experiment. The loss of 50 to 60% of the initial radioactivity can, presumably, be attributed to the conversion of the carbonyl group of azinphos-methyl to volatile products including carbon dioxide by the decarboxylation of anthranilic acid. Similar results were obtained when azinphos-methyl adsorbed on silica gel was irradiated. In the experiments where the effect of temperature was investigated, azinphos-methyl dissolved in water or adsorbed on glass was kept at five different temperatures from 5 to 65 °C for seven days. Only small amounts were degraded in water and on glass at temperatures up to 37 °C but at 50 °C decomposition increased to 73% in water and 28% on glass. After seven days at 65 °C nearly all the starting material had disappeared from both phases. The effect of pH on the decomposition was studied at 25 °C for a period of seven days. At pHs 6, 7 and 8 decomposition was negligible but rose to 10% at pH 9, 20% at pH 10 and 95% at pH 11. The evidence suggested that anthranilic acid was the principal degradation product at pH 11.

Fig1: Photo-degradation of azinphos-methyl



$\overset{*}{C}$ = ^{14}C - label

Heuer et al (1974) determined the half-life of radiolabelled azinphos-methyl (labelled at the methylene carbon group) in buffered solutions at three different temperatures and pHs. The reported half-lives, which are given in Table 2, show that the degradation rate of azinphos-methyl increases with an increase in pH and temperature. The authors also investigated the degradation of azinphos-methyl on glass beads. When the beads were dry, half-lives ranged from 99 days (6 °C) to 66 days (25 °C) whereas when mixed to a 50% water paste (pH 9.6) half-lives decreased to 91 days at 6 °C and 10 days at 25 °C.

Table 2 - Azinphos-methyl half-lives in aqueous solution

Type of Water	Temperature (°C)	pH	Half-life (days)	References
Surface water	10	7.4	624 #	De Heer (1978*)
Surface water (outdoor tanks)	10-30	7.5-11	0.63-7.3	"
Buffer solution	20	8.7	6.1 #	"
Buffer solution	20	8.8	12.8 #	"
Buffer solution	6	8.6	36.4	Heuer et al (1974)
Buffer solution	25	8.6	27.9	"
Buffer solution	25	9.6	2.4	"
Buffer solution	25	10.7	2.0	"
Buffer solution	40	10.7	0.41	"

Notes:
stored in the dark

De Heer (1978*) found the conversion of azinphos-methyl in outdoor tanks to be much faster than in the dark in the laboratory and ascribed the difference to the effect of light. However, temperature and pH were also different and these differences may have affected the rates of hydrolysis.

Meyer (1965) applied azinphos-methyl WP directly to a farm pond containing algal, plant and fish life and calculated a half-life of approximately 2 days. The pH of the pond water varied from 7.2 to 8 and

the temperature from 25 to 35 °C. Following the application of 1 mg/l, the concentration in the water and plankton decreased from 0.8 mg/l at 4 hours to 0.4 mg/l at 48 hours post-application. After four days 0.1 mg/l remained and on day 14 azinphos-methyl could not be detected (detection limit not given).

Flint et al (1970, cited in EPA 1986) determined the half-life of Guthion at 30 °C in illuminated pond water and in phosphate buffer protected from light in the laboratory. The half-life in pond water was 1.2 days (pH 6.9) whereas that in the buffer solution (pH 7) was 10 days. The more rapid degradation in pond water was attributed to the effect of sunlight and microorganisms.

(b) Biological degradation

No specific study was found on the microbial degradation of azinphos-methyl in water but, as in soil, warm temperatures and the presence of organic matter will generally promote bacterial activity and consequently the degradation of the pesticide (Dortland 1980).

(c) Adsorption

No data have been found on the adsorption of azinphos-methyl to sediments and suspended solids. However, based on the soil organic carbon partition coefficient (Log K_{oc} = 3.56) adsorption is likely to be a significant removal process in most surface waters.

2.6.2 Soil

Azinphos-methyl has a reported average half-life in soil of about three months and on field crops of three to five days (Anderson et al 1974, Smith et al 1983).

The persistence of azinphos-methyl in soil has been investigated by Staiff et al (1975). Undiluted azinphos-methyl EC (1.89 l of 18.1% ai or 342 g ai) was poured onto a plot 0.3 x 0.3 m to simulate an

accidental spillage of commercially formulated insecticide. The levels of azinphos-methyl in the soil, initially very high (up to 71 g/kg in the topsoil and up to 52 g/kg below a depth of 25 mm), decreased to between one half and one third of their original values after one year. Appreciable quantities still remained at both levels after three years. From the fourth to eighth years concentrations in the lower (25 to 75 mm) level were consistently higher than in the top layer. Even after eight years azinphos-methyl had not leached below the 300 mm level. The highest concentrations, about 1 g/kg, was observed in the 75 to 150 mm layer. Azinphos-methyl sprayed at the recommended rate (0.045% ai WP and EC) to the same size plots disappeared almost completely in three months. The behaviour of EC and WP formulations showed no appreciable differences. After application at a concentration eight times greater than the recommended strength (0.36% ai WP and EC) most of the pesticide had disappeared within four years.

Schulz et al (1970) studied the persistence and degradation of azinphos-methyl in silt loam under field and laboratory conditions, Table 3. The insecticide was most persistent when the granular form was incorporated into the soil. In this case 28 days were required for the disappearance of 50% compared with 12 days when it was applied to the surface as an emulsion. Five months later all experimental plots still contained measurable azinphos-methyl residues (up to 10% of the dose when applied to the surface and 13% when it was incorporated into the soil).

A comparison of other data reported for the persistence of azinphos-methyl in soils is given in Table 4.

Table 3 - Persistence of azinphos-methyl in silt-loam (Schulz et al 1970)

Formulation	Site	Application method	Temperature °C	Time	Disappearance %
Analytical grade	Laboratory	Acetone soln	30	6 d	95
Emulsifiable concentrate	Laboratory	Acetone soln	30	22 d	95
Emulsion	Field	Surface	5 to 15	12 d 6 m	50 90
Granular	Field	Rototilled to 120 mm	5 to 15	28 d 5 m to 1 y	50 87

Table 4 - Persistence of azinphos-methyl in soils

Soil Type	Initial Conc (kg/ha)	% Degraded/ Dissipated	Time (days)	References
Sandy loam, planted with potatoes, 20-30 °C, 16-18% moisture content	10	50	5	Yaron et al (1974*)
Silty loam, 6 °C, 50% moisture content	75	45	56	"
Silty loam, 25 °C, 50% moisture content	75	50	13	"
	75	93	45	"
Silty loam, 40 °C, 50% moisture content	75	50	5	"
	75	99	21	"
Sandy loam	0.27	99	180	Staiff et al (1975)

SECTION 3 - TOXICITY AND BIOACCUMULATION IN FRESHWATER ORGANISMS

3.1 TOXICITY

Organophosphorus pesticides inhibit acetylcholinesterase (AChE), an enzyme which is essential to nerve impulse conduction and transmission. Results of toxicity tests for azinphos-methyl on freshwater organisms are summarised in Table 5 and those results relevant to the setting of a PEQS are discussed below.

3.1.1 Invertebrates

Acute LC50 values for freshwater invertebrates range from 0.1 to >3690 µg/l. The highest value (>3690 µg/l) was obtained for the snail Aplexa hypnorum in a flow-through test by Holcombe et al (1987). Sanders (1972) exposed the glass shrimp, Paleomonetes kadiakensis to azinphos-methyl in a flow-through bioassay for up to 20 days and obtained 5- and 20-day LC50 values of 1.2 µg/l and 0.16 µg/l respectively. The same author (1972) found for the amphipod, Gammarus fasciatus, the most sensitive aquatic organism tested, a 96-hour LC50 of 0.1 µg/l. Jensen and Gaufin (1966), also using a continuous flow system, exposed two species of stonefly naiads to azinphos-methyl. They calculated 4- and 30-day LC50 values for Acroneuria pacifica of 2.0 µg/l and 0.24 µg/l respectively, whereas for Pteronarcys californica the respective values were 4.6 µg/l and 1.3 µg/l.

Dortland (1980) conducted bioassays with azinphos-methyl on a variety of invertebrates. In 48-hr acute tests Daphnia magna, with an EC50 of 1.6 µg/l, was found to be the most sensitive species tested. In 21-day tests Daphnia magna was again the most sensitive species with an EC50 and a 'no observed effect' concentration (NOEC) for immobilisation of 0.26 and 0.1 µg/l, respectively. The 21-day NOEC for the water hoglouse, Asellus aquaticus, was of the same order of magnitude at 0.25 µg/l but the 21-day LC50, at 2.4 µg/l, was higher than the corresponding value for Daphnia magna. Mayfly and phantom midge larvae, a leech and a flatworm were much less sensitive. Frear and Boyd (1967)

found Daphnia magna to be more acutely sensitive, with an EC50 of 0.18 µg/l (no exposure period quoted) compared to 1.6 µg/l obtained by Dortland.

3.1.2 Fish

Acute LC50 values for freshwater fish range from 0.36 µg/l to 17 000 µg/l. The highest values were obtained from static tests with goldfish, Carassius auratus, by Adelman et al (1976a), who reported an 8-hour LC50 of 17 000 µg/l and by Macek and McAllister (1970) who found a 96-hour LC50 of 4270 µg/l. The lowest 96-hour LC50 of 0.36 µg/l for the yolk-sac stage of the northern pike, Ecox lucius, was reported in the US Fish and Wildlife Servive data summary of Johnson and Finley (1980); however, the original source of the data and details of the test are not quoted. For three species Johnson and Finley also gave "time independent LC50" values of 0.32 µg/l (Yellow perch, Perca flavescens), 0.29 µg/l (Bluegill sunfish, Lepomis macrochirus) and 0.23 µg/l (Atlantic salmon, Salmo salar).

Toxicity tests for rainbow trout, Salmo gairdneri, have produced a range of 96-hour LC50s from 2.9 µg/l to 14 µg/l (Johnson and Finley 1980, Holcombe et al 1987, Macek and McAllister 1970, Katz 1961, Macek et al 1969, Marking and Mauck 1975, Mayer and Ellersieck 1986). The experiments were carried out under a range of temperatures, one under continuous flow conditions (Holcombe et al 1987, 96-hour LC50 9.1 µg/l) and all but Holcombe et al (1987) used technical or pure compound. The two lowest values of 2.9 and 3.2 µg/l were obtained at somewhat higher than usual test temperatures of 18 °C (reported in US Fish and Wildlife Service data summary of Mayer and Ellersieck) and 20 °C (Katz) respectively.

Ninety-six-hour LC50s for other salmonid species, coho salmon (Oncorhynchus kisutch), chinook salmon (Oncorhynchus tshawytscha), Atlantic salmon (Salmo salar) and brown trout (Salmo trutta), were all comparable to rainbow trout, ranging from 1.2 µg/l to 18 µg/l (Johnson and Finley 1980, Macek and McAllister 1970, Katz 1961, United Nations

Food and Agriculture Organisation (FAO) 1969, Nebeker and Gaufin 1964, Mayer and Ellersieck 1986). The lowest value of 1.2 µg/l for the brown trout was found in the summary report prepared by Mayer and Ellersieck. In the same data summary it is reported that Atlantic salmon yolk-sac fry and fingerlings are not much less sensitive but short-term tests indicated that the egg stage is not very sensitive.

The bluegill sunfish appears to have a similar sensitivity to the effects of azinphos-methyl as salmonid species with 96-hour LC50s ranging from 4.1 µg/l to 52 µg/l (Macek et al 1969, Macek and McAllister 1970, Holcombe et al 1987, Pickering et al 1962, Johnson and Finley 1980, Anderson et al 1974, Carter and Graves 1972, Mayer and Ellersieck 1986). The largemouth bass, Micropterus salmoides, which belongs to the same sub-order as the sunfish, has a similar 96-hour LC50 of 4.8 µg/l (Macek and McAllister 1970).

The effects of azinphos-methyl and other organophosphorus insecticides on the AChE activity in the brains of several species of fish have been investigated by Weiss and various co-workers. Azinphos-methyl at 500 µg/l (Weiss 1961) caused 50% mortality in both largemouth bass and fathead minnows, Pimephales promelas, within 40 minutes exposure. However, there were differences in the amounts of reduction in AChE activity recorded for surviving fish after one hour; in bass, the reduction averaged 94% and in minnows, 50%. Similar levels of reduction in activity were noted for the dead fish from these tests. In a second set of experiments bluegill sunfish and fathead minnows were exposed to 10 µg/l for 7 and 24 hours respectively and then allowed to recover for 30 days. AChE activity was monitored during both exposure and recovery phases. For both species the reduction in activity at the end of the exposure phase reached about 60% and activity returned to normal levels at the end of the recovery period but the shape of the recovery curves differed. After termination of the exposure phase the fathead minnows showed an immediate recovery to only 30% reduction in activity followed by a generally slow increase in activity, but with some "relapses". The bluegill sunfish showed a slow, steady recovery in activity which was considered to be consistent with continued inhibition or irreversible

inhibition of AChE and slow production of new enzyme. (Weiss differentiated five different types of exposure-recovery curves shown by different species of fish on exposure to various insecticides. He also suggested that the persistence of reduced AChE activity, evident for up to 30 days after exposure, would provide good evidence for contamination of natural waters, even when pesticide levels had declined to below their detection limits by chemical analysis.) In further experiments (Weiss and Gakstatter 1964) goldfish, Carassius auratus, and bluegill sunfish were exposed for 15 days to two or three concentrations of azinphos-methyl. At 10 µg/l all the bluegills had died within 48 hours, by which time AChE activity had declined by 90%. At 1 µg/l AChE activity in the bluegills fell steadily by 90% over the 15 days and in the goldfish activity fell by 50% over 10 days and then remained steady for the remaining exposure period. At 0.1 µg/l there was no effect on either species. In 30-day experiments slight downward trends in AChE activity in both species were observed at 0.05 µg/l.

The only chronic data available for fish were obtained by Adelman et al (1976b). Fathead minnows were exposed to Guthion for a complete life-cycle in flow-through tests. Exposure to 61.4 µg/l gave a 70% decrease in the hatching success of eggs but the dose-response relationship was complicated as the hatching success and survival of larvae in the early stages after hatching were reduced by the presence of a bacterial mat. At a higher dose hatching was a day earlier but more successful because the bacterial mat had not developed so much. Of the fry that successfully hatched from eggs exposed to 6.5 µg/l a significant number died within 22 days of hatching. After 57 days a significant number of fry exposed to 1.8 µg/l had died. The MATC for the survival of fry was calculated to lie between 0.51 and 1.8 µg/l. Fish which survived exposure to azinphos-methyl for 120 to 250 days spawned successfully but at exposure concentrations greater than 0.33 µg/l there were significant decreases in the number of eggs per spawning and in the number of eggs per female compared with controls. Therefore spawning appears to be the life-stage most sensitive to the effects of azinphos-methyl. In acute tests the fathead minnow appears to be less sensitive to azinphos-methyl (96-hour LC50s from 65 to

293 µg/l reported by Holcombe et al 1987, Mayer and Ellersieck 1986, Pickering et al 1962 and Macek and McAllister 1970), than the various salmonid species tested (96-hour LC50s of 1.2 to 17 µg/l). Thus it is possible that the early life stages of salmonid species will be more sensitive than those of the fathead minnow.

3.2 BIOACCUMULATION

There are no reliable data available to quantify the bioaccumulation potential of azinphos-methyl but based on the octanol/water partition coefficient (Log K_{ow} 2.99-3.77) this is likely to be only moderate. EPA (1986) calculated from the original data of Meyer (1965) that a bioaccumulation factor of no more than 20 is likely.

Johnson and Finley (1980) quote "cumulative toxicity indices" of 10.9 to 20.5 which they take to indicate a moderate to high degree of cumulative action for an organophosphate pesticide.

SECTION 4 - TOXICITY AND BIOACCUMULATION IN MARINE ORGANISMS

4.1 TOXICITY

Investigations into the toxicity of azinphos-methyl to marine organisms has centred on relatively few species. The relevant information is summarised in Table 6 and the tests on the more sensitive species are discussed below.

4.1.1 Invertebrates

From the limited data available it seems that shrimps are the most sensitive group of saltwater species. For the European species pink shrimp, Pandalus montagui, and brown shrimp, Crangon crangon, 48-hour LC50 values between 0.3 and 1 µg/l have been reported whereas the cockle, Cardium edule, was the least sensitive species tested with a

48-hour LC50 greater than 10 mg/l (Portmann and Wilson 1971). All these tests were conducted under static, continually aerated conditions at 15 °C.

The 48-hour LC50s for fertilised oyster, Crassostrea virginica, and clam, Mercenaria mercenaria, eggs were estimated to be 620 µg/l and 860 µg/l respectively (Davis and Hidu 1969).

Two US Government laboratories have reported similar results for crabs and shrimps. Butler (1963, cited in EPA 1986) gave 48-hour EC50s of 550 µg/l for the blue crab, Callinectes sapidus, and of 4.4 µg/l for the pink shrimp, Penaeus duorarum. Mayer (1987) reported 48-hour EC50s of 320 µg/l for the blue crab and of 2.4 µg/l for the brown shrimp, P. penaeus. Mayer also reported that juvenile oysters, Crassostrea virginica, were not very sensitive to azinphos-methyl with an EC50 of greater than 1 mg/l.

4.1.2 Fish

A number of acute LC50 values have been reported for fish species. For the threespine stickleback, Gasterosteus aculeatus, a 96-hour LC50 of 12.1 µg/l was obtained in slightly saline water (5 ppt) and of 4.8 µg/l in water with a salinity of 25 ppt (Katz 1961). Similar LC50s of 8 µg/l (96-hour; Lahav and Sarig 1969, cited in EPA 1986) and 3.2 µg/l (48-hour; Mayer 1987) have been reported for the striped mullet, Mugil cephalus. The 24-hour LC50 for the white mullet, Mugil curema, was found to be 5.5 µg/l (Butler 1963, cited in EPA 1986).

Inhibition of acetylcholinesterase (AChE) activity and mortality caused by exposure to azinphos-methyl was investigated by Coppage (1972) in a static test in 4 ppt salinity using the sheepshead minnow, Cyprinodon variegatus, as test species. After 48 hours exposure greater than 80% AChE inhibition and 40 to 60% mortality were observed at 3.5 µg/l. After 120 hours exposure to 2 µg/l 78% AChE inhibition was observed but there were no mortalities.

Only one chronic toxicity test has been reported. Cripe et al (1984) exposed juvenile sheepshead minnows to azinphos-methyl for a partial life-cycle in a continuous flow apparatus. The test started with laboratory-reared juvenile fish and exposure continued through spawning for 219 days. Of the juveniles exposed to 1.9 µg/l 78% died within 7 days and those exposed to 0.83 µg/l developed sublethal abnormalities affecting the flexure of the backbone and muscular action and nearly all had died within 126 days, when the experiment was terminated at this exposure level. After 107 days exposure of minnows to 0.42 µg/l AChE activity was inhibited by 78%. Inhibitions of 76, 57 and 36% were recorded at nominal concentrations of 0.25, 0.12 and 0.06 µg/l but analysis of these exposure solutions, except for 20% of samples at 0.25 µg/l, failed to detect any azinphos-methyl. Fish that spawned after 28 days exposure to 0.42 µg/l showed a 66% reduction in the number of eggs laid per female per day. All the fry (newly-hatched from control embryos) exposed to 0.83 µg/l died within 28 days.

4.2 BIOACCUMULATION

No bioaccumulation data in marine species are available on azinphos-methyl.

SECTION 5 - RECOMMENDED PROVISIONAL ENVIRONMENTAL QUALITY STANDARDS

5.1 THE PROTECTION OF FRESHWATER LIFE

The available data on the toxicity of azinphos-methyl to freshwater life are summarised in Section 3. Azinphos-methyl is highly toxic to invertebrate species with Gammarus fasciatus having the lowest acute LC50 of 0.1 µg/l (Sanders 1972). Similar 96-hour LC50s of 0.13 µg/l have been reported for the glass shrimp, Palaemonetes kadiakensis, (Johnson and Finley 1980) and Gammarus lacustris (Nebeker and Gaufin 1964). However, there are indications that extending the exposure period increases the sensitivity to azinphos-methyl. For naiads of the stonefly Acroneuria pacifica a 30-day LC50 of 0.24 µg/l was determined

compared to the 96-hour LC50 of 2.0 µg/l (Jensen and Gaufin 1966). A similar ratio (1.6:0.26) between 48-hour and 21-day EC50s (immobilisation) was observed for Daphnia magna (Dortland 1980). In the same test the 21-day "no effect" concentrations (NOECs) for Daphnia magna for immobilisation and for reproduction by the surviving adults were of the same order of magnitude at 0.1 and 0.2 µg/l, respectively.

Of the fish species tested the northern pike, Ecox lucius, appears to be the most sensitive with a reported acute LC50 of 0.36 µg/l for the yolk-sac stage (Johnson and Finley 1980). Salmonid species have acute LC50s in the range 1.2 µg/l to 17 µg/l. Only one flow-through, life-cycle test on fish has been reported (Adelman et al 1976b); an MATC based on the growth of fathead minnow, Pimephales promelas, fry was estimated at between 0.51 and 1.8 µg/l whereas the "no observed effect concentration" (NOEC) for reproduction, based on the numbers of eggs produced, was found to be 0.33 and the corresponding "lowest observable effect concentration" (LOEC) was 0.51 µg/l. "Time-independent" LC50s of the same order of magnitude were reported by Johnson and Finley (1980) for three species of fish; yellow perch, Perca flavescens, (0.32 µg/l), bluegill sunfish, Lepomis macrochirus, (0.29 µg/l) and Atlantic salmon, Salmo salar, (0.23 µg/l).

Based on the available chronic toxicity data a provisional environmental quality standard (PEQS) of 10 ng/l is proposed for the protection of freshwater life. This is based on the 21-day NOEC of 0.1 µg/l obtained for the immobilisation of Daphnia magna (Dortland 1980) to which a safety factor of ten is applied to take into account that in acute tests other species were more sensitive than Daphnia magna. This PEQS should be adequate to protect freshwater fish as these appear to be less sensitive than some invertebrates. The PEQS should be expressed as annual average concentration, because it is based on chronic data, and as "dissolved" azinphos-methyl.

The available information indicates that the highest environmental concentrations of azinphos-methyl occur in run-off after rainfall from land treated with the insecticide. It is therefore desirable to set

also a maximum value to protect the aquatic environment from these episodic events. A PEQS of 100 ng/l expressed as "dissolved" azinphos-methyl is proposed as maximum concentration based on the 96-hour LC50 of 100 ng/l for Gammarus fasciatus and taking into account that azinphos-methyl is not very persistent in natural waters with reported half-lives for the dissolved pesticide of one to three days.

The standards are expressed as "dissolved" azinphos-methyl as they were derived from laboratory tests performed with dissolved material and test waters with negligible suspended solids concentrations. It is proposed that in environmental samples the "dissolved" fraction is measured in the aqueous supernatant phase after allowing the suspended solids to settle for at least an hour prior to analysis.

Because of the relatively high soil organic carbon sorption coefficient (Log K_{oc} = 3.56) it is likely that a significant fraction of the azinphos-methyl present in the aquatic environment and in run-off from treated land is adsorbed on sediments or suspended solids. But, based on experience with other pesticides, it is in this form probably less bioavailable to most aquatic organisms. As the adsorbed azinphos-methyl is much more persistent there is some concern that it may build up in sediments to levels which may be harmful to benthic organisms; but, at present, insufficient information is available to propose a separate standard for "total" azinphos-methyl.

5.2 THE PROTECTION OF MARINE LIFE

The available data on the toxicity of azinphos-methyl to marine life are summarised in Section 4. As for freshwater organisms, the most sensitive species appear to be invertebrates. For the brown shrimp, Crangon crangon, a 48-hour LC50 of 0.3 to 1 µg/l has been reported (Portmann and Wilson 1971). In a partial life-cycle toxicity test on the sheepshead minnow, Cyprinodon variegatus, (Cripe et al 1984) significant reductions in egg numbers from spawning adults were observed at 0.42 µg/l. These data indicate that marine species have a similar sensitivity to azinphos-methyl as freshwater species.

The same PEQSs of 10 ng/l as annual average and 100 ng/l as maximum concentrations expressed as "dissolved" azinphos-methyl proposed for the protection of freshwater life are therefore also proposed for the protection of marine life.

5.3 ABSTRACTION TO POTABLE SUPPLY

WHO/FAO (1974) derived an ADI for azinphos-methyl to man of 0.0025 mg/kg body weight. A suggested no adverse response level for long term exposure can be calculated by allowing 1% of the ADI from drinking water (DoE 1989b). Assuming a 60 kg adult drinking 2 l per day gives a value of 0.75 µg/l. This value is 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). Because of the uncertainties concerning the removal of azinphos-methyl in water treatment processes and during storage no PEQS is proposed for the protection of waters used for abstraction to potable supply.

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NOTE:

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Table 5 - Toxicity of azinphos-methyl to freshwater organisms

Species	Exposure type	Temp °C	pH	Formulation	Exposure time	Effect	Toxic concn µg/l	Ref
PROTOZOANS:								
Colpidium campylum		20			43 hr	minimal active dose	1000	1
INVERTEBRATES:								
Asellus brevicaudus (sowbug, mature)	STATIC	15/21	7.1	TECHNICAL(a)	24 hr	LC50	162/150	2/3
					96 hr	LC50	21	3
Asellus aquaticus (water hoglouse)	STATIC SEMISTATIC	18		>99% PURE	48 hr	LC50	4.8	5
					21 d	LC50	2.4	5
					21 d	NOEC (mortality)	0.5-1	5
					21 d	NOEC (no symptoms)	0.25	5
Gammarus pseudolimnaeus					30 d	NOEC	0.1	6
Gammarus fasciatus (scud, mature)	STATIC	15/21	7.4	TECHNICAL	24 hr	LC50	0.44	2/3
					48 hr	LC50	0.16	2
					96 hr	LC50	0.10	2/3
Gammarus fasciatus (scud, mature)	STATIC	21	7.1	TECHNICAL	24 hr	LC50	0.56	2
					48 hr	LC50	0.25	2
					96 hr	LC50	0.15	2/4
Gammarus lacustris	STATIC	15			96 hr	LC50	0.13	7
Gammarus lacustris					48 hr	LC50	0.3	8
Palaemonetes kadiakensis (glass shrimp)	STATIC	21		TECHNICAL	96 hr	LC50	0.13(b)	4

Table 5 - Continued

Species	Exposure type	Temp °C	pH	Formulation	Exposure time	Effect	Toxic concn µg/l	Ref
Palaemonetes kadiakensis (glass shrimp)	STATIC	24±3	7.4	TECHNICAL	24 hr	LC50	4.4-16.8(c)	9
Palaemonetes kadiakensis (glass shrimp)	FLOW	21		TECHNICAL	5 d	LC50	1.2	3
					20 d	LC50	0.16	3
Palaemonetes kadiakensis (glass shrimp, mature)	FLOW	21	7.4	TECHNICAL	24 hr	LC50	2.5	2
					96 hr	LC50	1.2	2
Pteronarcys californica (stonefly, 2nd year)	STATIC	15	7.1	TECHNICAL	24 hr	LC50	25.0	2
					48 hr	LC50	8.0	2
					96 hr	LC50	1.9	2/4
Pteronarcys californica (stonefly naiads)		15		TECHNICAL	24 hr	LC50	25	10
					48 hr	LC50	8	10
					96 hr	LC50	1.5	10
Pteronarcys californica (stonefly naiads)	STATIC			TECH. 89%	96 hr	LC50	22	11
	FLOW	13	~8	TECH. 89%	96 hr	LC50	4.6	11
					10 d	LC50	1.5	11
					20 d	LC50	1.4	11
					30 d	LC50	1.3	11
Pteronarcys dorsata (stonefly)					96 hr	LC50	12.1	6
					30 d	LC50	4.9	6
Acroneuria pacifica (stonefly naiads)	STATIC			TECH. 89%	96 hr	LC50	8.5	11
	FLOW	13	~8	TECHNICAL	96 hr	LC50	2.0	11

Table 5 - Continued

Species	Exposure type	Temp °C	pH	Formulation	Exposure time	Effect	Toxic concn µg/l	Ref
					10 d	LC50	0.55	11
					20 d	LC50	0.29	11
					30 d	LC50	0.24	11
Acroneuria lycorias (stonefly)					96 hr	LC50	1.5	6
Daphnia pulex/magna (water flea)						LC50	0.18	12
Daphnia magna (water flea)	STATIC SEMISTATIC	18		>99% PURE	48 hr	EC50	1.6	5
					21 d	EC50	0.26	5
					21 d	NOEC(immobilisation)	0.1	5
					21 d	NOEC(reproduction)	0.2	5
Hydropsyche bettoni (caddis fly)					96 hr	LC50	74	13
Ophiogomphus rupinsulensis (dragonfly)					96 hr	LC50	12	6
					30 d	LC50	2.2	6
Cloeon dipterum (mayfly)	STATIC SEMISTATIC	18		>99% PURE	48 hr	LC50	12.0	5
					21 d	LC50	3.4	5
					21 d	NOEC	2.0-4.0	5
Chaoborus crystallinus (phantom midge)	STATIC SEMISTATIC	18		>99% PURE	48 hr	LC50	33	5
					21 d	LC50	10.2	5
					21 d	NOEC	2.0-4.0	5

Table 5 - Continued

Species	Exposure type	Temp °C	pH	Formulation	Exposure time	Effect	Toxic concn µg/l	Ref
Anopheles quadrimaculatus					24 hr	LC50	82-89	14
(mosquito,4th instar larva)					24 hr	LC100	320	14
Ephemerella grandis					96 hr	LC50	14	15
(mayfly)								
Culex pipiens					24 hr	LC50	19	16
(mosquito,4th instar larva)					24 hr	LC90	26	16
Culex pipiens					24 hr	LC50	8	17
(mosquito,3rd & 4th instar)					24 hr	LC90	10 & 220	17
Aedes aegypti					24 hr	50% increase in mortality	25-50	18
(mosquito, 3-d old)								
Dugesia lugubris		18		>99% PURE	96 hr	LC50	>160	5
(flat worm)								
Herpobdella octoculata		18		>99% PURE	96 hr	LC50	>160	5
(leech)								
Procambarus sp.	STATIC	12	7.5	TECHNICAL	24 hr	LC50	>200	2
(crayfish)					96 hr	LC50	56	2/4
Procambarus clarkii	STATIC	21-26	8.4	GUTHION	48 hr	oral LD50	1.9 mg/kg	19
(red swamp crayfish)					8 month	20% reduction in life span	25 ug/kg	19
Procambarus clarkii					"short-term"	LC50	100	20
(red swamp crayfish)					"short-term"	LC50	2	21

Table 5 - Continued

Species	Exposure type	Temp °C	pH	Formulation	Exposure time	Effect	Toxic concn µg/l	Ref
White river crawfish	STATIC	26		GUTHION	96 hr	LC50	40	22
Aplexa hypnorum (snail)	FLOW	17	7.5	GUTHION	96 hr	LC50	>3690	23
FISH:								
Oncorhynchus kisutch (coho salmon, 0.7 g)	STATIC	12	7.5	TECHNICAL	24 hr	LC50	7.6	2
					96 hr	LC50	6.1	2/4
Oncorhynchus kisutch (coho salmon, 4.7 g)	STATIC	12	7.1	93% PURE	24 hr	LC50	23	2
					96 hr	LC50	3.2	2
Oncorhynchus kisutch (coho salmon, 9.5 g)	STATIC	12	7.1	93% PURE	24 hr	LC50	4	2
					96 hr	LC50	3.2	2
Oncorhynchus kisutch (coho salmon)	STATIC	13		100% PURE	96 hr	LC50	17	24
Oncorhynchus kisutch (coho salmon)	STATIC	20		93% PURE	24 hr	LC50	7	25
					48 hr	LC50	5	25
					72 hr	LC50	4.8	25
					96 hr	LC50	4.2	25
Oncorhynchus tshawytscha (chinook salmon)	STATIC	20		93% PURE	24 hr	LC50	6.8	25
					48 hr	LC50	6.2	25
					96 hr	LC50	4.3	25
Salmo gairdneri (rainbow trout, 1.0 g)	STATIC	12	7.1	TECHNICAL	24 hr	LC50	10	2
					96 hr	LC50	4.3	2/4

Table 5 - Continued

Species	Exposure type	Temp °C	pH	Formulation	Exposure time	Effect	Toxic concn µg/l	Ref
Salmo gairdneri (rainbow trout, 1.5 g)	STATIC	2	7.1	TECHNICAL	24 hr	LC50	26	2
					96 hr	LC50	7.1	2
Salmo gairdneri (rainbow trout, 1.5 g)	STATIC	7	7.1	TECHNICAL	24 hr	LC50	16	2
					96 hr	LC50	5.8	2
Salmo gairdneri (rainbow trout, 1.5 g)	STATIC	12	7.1	TECHNICAL	24 hr	LC50	13	2
					96 hr	LC50	6.3	2
Salmo gairdneri (rainbow trout, 1.5 g)	STATIC	18	7.1	TECHNICAL	24 hr	LC50	13	2
					96 hr	LC50	2.9	2
Salmo gairdneri (rainbow trout)	FLOW	17	7.5	GUTHION	96 hr	LC50	9.1	23
Salmo gairdneri (rainbow trout)	STATIC	13		100% PURE	96 hr	LC50	14	24
Salmo gairdneri (rainbow trout)	STATIC	20		93% PURE	24 hr	LC50	4.7	25
					48-72 hr	LC50	3.8	25
					96 hr	LC50	3.2	25
Salmo gairdneri (rainbow trout)	STATIC	1.6		TECHNICAL	24 hr	LC50	25	26
		1.6			96 hr	LC50	6.8	26
		7.2			24 hr	LC50	15	26
		7.2			96 hr	LC50	6.2	26
		12.7			24 hr	LC50	13	26
		12.7			96 hr	LC50	5.5	26

Table 5 - Continued

Species	Exposure type	Temp °C	pH	Formulation	Exposure time	Effect	Toxic concn µg/l	Ref
Salmo gairdneri (rainbow trout)		12			96 hr	LC50	7.1	27
Salmo salar (atlantic salmon)	STATIC	15		75% PURE	24 hr	a reduction of 4°C in the temperature preferred by the fish	2	28
Salmo salar (atlantic salmon, 0.5 g)	STATIC	12	7.5	TECHNICAL	24 hr	LC50	>9	2
					96 hr	LC50	2.1	2/4
					time-independent	LC50	0.23	4
Salmo salar (atlantic salmon, 0.8 g)	STATIC 4 TESTS	12	7.5	TECHNICAL	24 hr	LC50	7.5, 10, 9, >15	2
					96 hr	LC50	2.7, 3.2, 3.5, >15	2
Salmo salar (atlantic salmon, 0.5 g)	STATIC 2 TESTS	12	7.5	TECHNICAL	24 hr	LC50	7.6, -	2
					96 hr	LC50	3.6, 2.5	2
Salmo salar (atlantic salmon, fingerling)	FLOW	12	7.5	TECHNICAL	96 hr	LC50	2.5	2
Salmo salar (atlantic salmon, green egg)	STATIC 3 TESTS	7.0	6.6-7.8	TECHNICAL	24 hr	LC50	>50	2
					96 hr	LC50	>50	2
Salmo salar (atlantic salmon, yolk-sac fry)	STATIC 3 TESTS	7.0	6.6-7.8	TECHNICAL	24 hr	LC50	>15	2
					96 hr	LC50	>15, 18, 15	2
Salmo salar (atlantic salmon, yolk-sac fry)	STATIC 3 TESTS	12.0	6.6-7.8	TECHNICAL	24 hr	LC50	>15	2
					96 hr	LC50	1.8, 2.3, 3.5	2

Table 5 - Continued

Species	Exposure type	Temp °C	pH	Formulation	Exposure time	Effect	Toxic concn µg/l	Ref
Salmo salar (eggs)					11 d	LC50	>50000	4
Trout					48 hr	LC50	10	29
Salmo trutta (brown trout, 1.5 g)	STATIC	12	6.5	TECHNICAL	24 hr	LC50	7	2
					96 hr	LC50	4.3	2
Salmo trutta (brown trout, 1.5 g)	STATIC 4 TESTS	12	7.5	TECHNICAL	24 hr	LC50	7.0, 6.0, 8.0, 7.1	2
					96 hr	LC50	4.6, 5.1, 6.0, 6.6	2
Salmo trutta (brown trout, 1.5 g)	STATIC	12	9.5	TECHNICAL	24 hr	LC50	8	2
					96 hr	LC50	3.5	2
Salmo trutta (brown trout, 1.2 g)	STATIC	12	7.5	TECHNICAL	24 hr	LC50	2.3	2
					96 hr	LC50	1.2	2
Salmo trutta (brown trout)	STATIC	13		100% PURE	96 hr	LC50	4	24
Ecox lucius (northern pike, yolk-sac fry)	STATIC	12	7.5	TECHNICAL	24 hr	LC50	0.67	2
					96 hr	LC50	0.36	2/4
Carassius auratus (goldfish, 0.9 g)	STATIC	18	7.1	93% PURE	24 hr	LC50	7050	2
					96 hr	LC50	4270	2/24
Carassius auratus (goldfish)	STATIC	25	7		8 hr	LC50	17000	30
					11 d	LC50	800	30

Table 5 - Continued

Species	Exposure type	Temp °C	pH	Formulation	Exposure time	Effect	Toxic concn µg/l	Ref
Carassius auratus (goldfish)	FLOW	17	7.5	GUTHION	96 hr	LC50	1040	23
Carassius auratus (goldfish)	STATIC	25	7.5	90% PURE	24 hr	LC50	2400	31
					48 hr	LC50	2000	31
					96 hr	LC50	1400	31
				PURE(d)	96 hr	LC50	1300	31
Poecilla reticulata (guppy)	STATIC	25	7.5	90% PURE	24 hr	LC50	370	31
					48 hr	LC50	320	31
					96 hr	LC50	120	31
				PURE(d)	96 hr	LC50	110	31
Cyprinus carpio (carp, 0.6 g)	STATIC	18	7.1	100% PURE	24 hr	LC50	1240	2
					96 hr	LC50	695	2/24
Pimephales promelas (fathead minnow)	STATIC	20		PURE (d)	96 hr	LC50	93	31
Pimephales promelas (fathead minnow, 1.2 g)	STATIC	18	7.1	93% PURE	24 hr	LC50	255	2
					96 hr	LC50	235	2/24
Pimephales promelas (fathead minnow)	STATIC	25	7		4 hr	LC50	8500	30
					11 d	LC50	760	30
Pimephales promelas (fathead minnow)	FLOW	17	7.5	GUTHION	96 hr	LC50	65	23
Pimephales promelas (fathead minnow, 1.2 g)	STATIC	18	7.4	93% PURE	24 hr	LC50	524	2
					96 hr	LC50	293	2

Table 5 - Continued

Species	Exposure type	Temp °C	pH	Formulation	Exposure time	Effect	Toxic concn µg/l	Ref
Pimephales promelas (fathead minnow, 0.8 g)	STATIC	17	7.1	93% PURE	24 hr	LC50	160	2
					48 hr	LC50	160	2
					96 hr	LC50	148	2
Pimephales promelas (fathead minnow, egg-to-egg tests)	FLOW	25	7.5	GUTHION	22 d	sig. decrease in survival of fry	6.5	32
					57 d	NOEC/LOEC (e) survival of fry	0.51/1.8	32
					120-250 d	NOEC/LOEC (e) spawning (eggs/fem)	0.33/0.51	32
Ictalurus melas (black bullhead, 1.7 g)	STATIC	18	7.1	93% PURE	24 hr	LC50	5410	2
					96 hr	LC50	3500	2/24
Ictalurus melas (black bullhead, 1.2 g)	STATIC	18	7.4	93% PURE	24 hr	LC50	10000	2
					96 hr	LC50	4600	2
Ictalurus melas (black bullhead, 1.2 g)	STATIC	16	7.7	93% PURE	24 hr	LC50	7230	2
					48 hr	LC50	7130	2
					96 hr	LC50	4810	2
Ictalurus punctatus (channel catfish, 1.5 g)	STATIC	18	7.1	100% PURE	24 hr	LC50	4530	2
					96 hr	LC50	3290	24
Ictalurus punctatus (channel catfish)	FLOW	17	7.5	GUTHION	96 hr	LC50	3220	23
Ictalurus punctatus (channel catfish)	STATIC	25		25% WP	48 hr	LC50	9000	33
					48 hr	LC100	12000	33

Table 5 - Continued

Species	Exposure type	Temp °C	pH	Formulation	Exposure time	Effect	Toxic concn µg/l	Ref
Ictalurus punctatus (channel catfish)	STATIC	26		GUTHION	24 hr	LC50	3900	22
Lepomis cyanellus (green sunfish)	STATIC (prelim)	15-21	8	TECHNICAL	48 hr	total kill	1000	33
	STATIC	24		25% WP	48 hr	LC0	5	33
					48 hr	LC50	25	33
					48 hr	LC100	50	33
Lepomis cyanellus (green sunfish, 1.1 g)	STATIC	18	7.1	TECHNICAL	24 hr	LC50	130	2
					96 hr	LC50	52	2/4
Lepomis microlophus (redear sunfish)	STATIC	18		100% PURE	96 hr	LC50	52	24
Lepomis macrochirus (bluegill, 1.5 g)	STATIC	18	7.1	93% PURE	24 hr	LC50	26	2
					96 hr	LC50	22	2/4/24
					time-independent	LC50	0.29	4
Lepomis macrochirus (bluegill, 0.9 g)	STATIC	12	7.1	TECHNICAL	24 hr	LC50	14	2
					48 hr	LC50	11	2
					96 hr	LC50	8.2	2
Lepomis macrochirus (bluegill, 0.9 g)	STATIC	18	7.1	TECHNICAL	24 hr	LC50	16	2
					96 hr	LC50	8	2
Lepomis macrochirus (bluegill, 0.9 g)	STATIC	24	7.1	TECHNICAL	24 hr	LC50	17	2
					48 hr	LC50	9	2
					96 hr	LC50	4.1	2

Table 5 - Continued

Species	Exposure type	Temp °C	pH	Formulation	Exposure time	Effect	Toxic concn µg/l	Ref
Lepomis macrochirus (bluegill, 0.5 g)	STATIC	12	6.5	TECHNICAL	24 hr	LC50	42	2
					96 hr	LC50	17	2
Lepomis macrochirus (bluegill, 0.5 g)	STATIC	12	8.5	TECHNICAL	24 hr	LC50	52	2
					96 hr	LC50	34	2
Lepomis macrochirus (bluegill, 2.2 g)	FLOW	12	7.5	TECHNICAL	96 hr	LC50	4.8	2
Lepomis macrochirus (bluegill)	FLOW	17	7.5	GUTHION	96 hr	LC50	9.3	18
Lepomis macrochirus (bluegill)	STATIC	25		25% WP	48 hr	LC100	25	33
					24 hr	LC50	22	34
					48 hr	LC50	25	34
					96 hr	LC50	4	34
Lepomis macrochirus (bluegill)	STATIC	20		PURE (d)	96 hr	LC50	5.2	31
Lepomis macrochirus (bluegill)	STATIC	12.7		TECHNICAL	96 hr	LC50	6.9	26
		18.3			96 hr	LC50	7.4	26
		23.8			96 hr	LC50	4.2	26
Lepomis macrochirus (bluegill)	STATIC	23		GUTHION	96 hr	LC50	120	26
Lepomis macrochirus (bluegill)					15 d	AChE inhib	1	35
						No AChE inhib	0.1	35

Table 5 - Continued

Species	Exposure type	Temp °C	pH	Formulation	Exposure time	Effect	Toxic concn µg/l	Ref
Micropterus salmoides (largemouth bass)	STATIC	18		100% PURE	96 hr	LC50	5	24
Micropterus salmoides (largemouth bass)	STATIC	25		25% WP	48 hr	LC50	25	33
					48 hr	LC100	50	33
Micropterus salmoides (largemouth bass, 0.9 g)	STATIC	18	7.1	93% PURE	24 hr	LC50	23	2
					96 hr	LC50	4.8	2
Pomoxis nigromaculatus (black crappie, 1.0 g)	STATIC	18	7.1	TECHNICAL	24 hr	LC50	4.7	2
					96 hr	LC50	3	2/4
Perca flavescens (yellow perch)	STATIC	13		100% PURE	96 hr	LC50	13	24
Perca flavescens (yellow perch, 0.9 g)	STATIC	7	7.5	TECHNICAL	24 hr	LC50	100	2
					96 hr	LC50	40	2/4
Perca flavescens (yellow perch, 0.9 g)	STATIC	12	6.5	TECHNICAL	24 hr	LC50	54	2
					96 hr	LC50	17	2
Perca flavescens (yellow perch, 0.9 g)	STATIC	12	7.5	TECHNICAL	24 hr	LC50	>50	2
					96 hr	LC50	29	2
Perca flavescens (yellow perch, 0.9 g)	STATIC 4 TESTS	12	8.0	TECHNICAL	24 hr	LC50	>50	2
					96 hr	LC50	11, 18, 27, 36	2
Perca flavescens (yellow perch, 0.9 g)	STATIC	12	8.5	TECHNICAL	24 hr	LC50	70	2
					96 hr	LC50	8.5	2

Table 5 - Continued

Species	Exposure type	Temp °C	pH	Formulation	Exposure time	Effect	Toxic concn µg/l	Ref
Perca flavescens (yellow perch, 0.9 g)	STATIC	12	9.0	TECHNICAL	24 hr	LC50	77	2
					96 hr	LC50	29	2
Perca flavescens (yellow perch, 0.9 g)	STATIC	17	7.5	TECHNICAL	24 hr	LC50	51	2
					96 hr	LC50	5.6	2
Perca flavescens (yellow perch, 1.4 g)	STATIC	18	7.1	TECHNICAL	24 hr	LC50	52	2
					96 hr	LC50	15	2/4
Perca flavescens (yellow perch, 0.9 g)	STATIC	22	7.5	TECHNICAL	24 hr	LC50	>15	2
					96 hr	LC50	2.4	2/4
					time-independent	LC50	0.32	4
Perca flavescens (yellow perch, 15 g)	FLOW	12	7.5	TECHNICAL	24 hr	LC50	>4	2
					96 hr	LC50	6.5	2
Perca flavescens (yellow perch, 0.9 g)	0 DAY DEGRA.(f)	12	7.5	TECHNICAL	24 hr	LC50	>40	2
					96 hr	LC50	10	2
Perca flavescens (yellow perch, 0.9 g)	7 DAY DEGRA.	12	7.5	TECHNICAL	24 hr	LC50	>40	2
					96 hr	LC50	24	2
Perca flavescens (yellow perch, 0.9 g)	14 DAY DEGRA.	12	7.5	TECHNICAL	24 hr	LC50	>40	2
					96 hr	LC50	20	2
Perca flavescens (yellow perch, 0.9 g)	21 DAY DEGRA.	12	7.5	TECHNICAL	24 hr	LC50	>40	2
					96 hr	LC50	33	2

Table 5 - Continued

Species	Exposure type	Temp °C	pH	Formulation	Exposure time	Effect	Toxic concn µg/l	Ref
Notemigonus chryoleucas (golden shiner)	STATIC	25		25% WP	48 hr	LC50	100	33
					48 hr	LC100	200	33
Gambusia affinis (mosquito fish)	STATIC	24		GUTHION	96 hr	LC50	78	22
Gambusia affinis (mosquito fish)	STATIC			GUTHION EC	24 hr	100% mortality of fish added to Guthion soln on day 1, 2 & 3.	0.448 kg/ha (149-224 µg/l)	36
					24 hr	4% mortality of fish added to Guthion soln on day 7.	0.448 kg/ha (149-224 µg/l)	36
					24 hr	100% mortality of fish added to Guthion soln on day 1.	0.121 kg/ha (37-56 µg/l)	36
					24 hr	58% mortality of fish added on day 2. 54% mortality of fish added on day 3 & 4% mortality of fish added on day 7.	0.121 kg/ha (37-56 µg/l)	36
FIELD TRIALS:	STATIC	25-35	7.5	25% WP	48 hr	% survival		33
longnose gar						0	1000	
gizzard shad						0	1000	
carp						0	1000	
golden shiners						0	900	

Table 5 - Continued

Species	Exposure type	Temp °C	pH	Formulation	Exposure time	Effect	Toxic concn µg/l	Ref
fathead minnows						0	1000	
bigmouth buffalo						0	1000	
channel catfish						45	1300	
warmouth						0	900	
green sunfish						0	900	
orange-spotted sunfish						0	1000	
bluegill						0	900	
largemouth bass						0	1000	
white crappie						0	900	
freshwater drum						0	1000	
AMPHIBIANS:								
Rana catesbeiana (bullfrog, tadpole)	STATIC	23-26		GUTHION	96 hr	LC50	7600	22
Bufo woodhousei fowleri (Fowler's toad, tadpole)	STATIC	15	7.1	TECHNICAL	24 hr	LC50	710	2
					96 hr	LC50	109	2
Pseudacris triseriata (western chorus frog, tadpole)	STATIC	15	7.4	TECHNICAL	24 hr	LC50	>3200	2
					96 hr	LC50	3200	2

NOTES:
(a) Technical material, 93% in ref 2 and 88 - 100% in ref 4.
(b) Tested in hard water, 272 ppm CaCO3.
(c) Four different populations of shrimp were tested, LC50 varied between populations.
(d) PURE = result calculated from technical 90% product.
(e) NOEC = highest concentration at which no significant effect was observed,
LOEC = lowest concentration at which a significant effect was observed,
Implies that the maximum acceptable toxicant concentration (MATC) lies between the two concentrations.
(f) DEGRA = test with pesticide degraded for the specified period?

Table 5 - Continued

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36. Mulla et al 1963

Table 6 - Toxicity of azinphos-methyl to marine organisms

Species	Exposure type	Temp °C	Salinity g/l	Formulation	Exposure time	Effect	Toxic concn µg/l	Ref
INVERTEBRATES:								
Artemia salina (brine shrimp)					18 hr	100% inhibition of swimming	10	1
Pandalus montagui (pink shrimp)	STATIC	15			48 hr	LC50	0.3-1	2
Penaeus duorarum (pink shrimp)					48 hr	EC50	4.4	3a
Penaeus penaeus (brown shrimp, juvenile)	FLOW	31	25	96%	48 hr	EC50	2.4	4
Penaeus aztecus (shrimp, adult)					24 hr	50% increase in mortality & loss of equilibrium	25	3b
					48 hr	50% inc. mortality & loss of equilibrium	4.4	3b
Crangon crangon (brown shrimp)	STATIC	15			48 hr	LC50	0.3-1	2
Cardium edule (cockle)	STATIC	15			48 hr	LC50	>10000	2
Carcinus maenas (shore crab)	STATIC	15			48 hr	LC50	33-100	2
Callinectes sapidus (blue crab, juvenile)					24 hr	EC50	550	3a,b

Table 6 - Continued

Species	Exposure type	Temp °C	Salinity g/l	Formulation	Exposure time	Effect	Toxic concn µg/l	Ref
Callinectes sapidus (bluecrab, juvenile)	FLOW	27	27	96%	48 hr	EC50	320	4
Crassostrea virginica (oyster, eggs)					48 hr	LC50	620	5
Crassostrea virginica (oyster, juvenile)	FLOW	29	28	96%	96 hr	EC50	>1000	4
Mercenaria mercenaria (clam, eggs)					48 hr	LC50	860	5
Mercenaria mercenaria (clam, larvae)					12 d	LC50	860	5
FISH: Mugil curema (white mullet, juvenile)					24 & 48 hr	LC50	5.5	3a,b
Mugil cephalus (striped mullet)					96 hr	LC50	8	6
Mugil cephalus (striped mullet, juvenile)	FLOW	28	25	96%	48 hr	LC50	3.2	4
Limanda limanda (dab)	STATIC	15			48 hr	LC50	10-30	2
Lagodon rhomboides (pinfish)	STATIC	18-23	23-29	TECHNICAL	24 hr	80% inhibition of AChE activity	10	7

Table 6 - Continued

Species	Exposure type	Temp °C	Salinity g/l	Formulation	Exposure time	Effect	Toxic concn µg/l	Ref
Leiostomus xanthurus (spot)	STATIC	18-23	23-29	TECHNICAL	24 hr	96% inhibition of AChE activity	20	7
Leiostomus xanthurus (spot, juvenile)	FLOW	21	21		24 hr	EC50	55	8
					48 hr	EC50	50	8
Leiostomus xanthurus (spot, juvenile)	FLOW	21	21	96%	48 hr	LC50	28	4
Cyprinodon variegatus (sheepshead minnow, juvenile)	FLOW	30	25	96% PURE	7 d	78% mortality of juveniles	1.9	9
					7 d	abnormal flexure, tetany, lethargy, black tails and dark body areas	0.83	9
					126 d	virtual 100% mortality of parent generation	0.83	9
					107 d	78% inhibition of AChE activity	0.42	9
						36% inhibition of AChE activity	0.06[nom]	9
					28 d	100% mortality of newly hatched fry	0.83	9
(spawning adults)					>28 d	66% reduction in no. of eggs/female/day	0.42	9
Cyprinodon variegatus (sheepshead minnow)	STATIC	22	4	TECHNICAL	2 hr	40-60% mortality, 82% inhibition of AChE activity for all 2 hrs	50	10

Table 6 - Continued

Species	Exposure type	Temp °C	Salinity g/l	Formulation	Exposure time	Effect	Toxic concn µg/l	Ref
					24 hr	40-60% mortality, 82% inhibition of AChE activity for 18 hrs before death	7	10
					48 hr	40-60% mortality, 82% inhibition of AChE activity for 24 hrs before death	3.5	10
					120 hr	78% inhibition of AChE activity, no mortality	2	10
Gasterosteus aculeatus (threespine stickleback)	STATIC	20	5	93% PURE	24 hr	LC50	15.8	10
					72 hr	LC50	14.9	10
					96 hr	LC50	12.1	10
	STATIC	20	25	93% PURE	24 hr	LC50	6.9	10
					48 hr	LC50	5	10
					96 hr	LC50	4.8	10

References

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4. Mayer 1987
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9. Cripe et al 1984
10. Coppage 1972
11. Katz 1961