

# ENVIRONMENTAL CHEMICAL REVIEW ASSESSMENT REPORT

Fenthion Food Uses Only

The chemical review of fenthion containing products that are used on crops and animals for human consumption.

This Report was prepared for the APVMA by

Department of the Environment

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#### Comments and enquiries:

The Manager, Public Affairs
Australian Pesticides and Veterinary Medicines Authority
PO Box 6182
KINGSTON ACT 2604 Australia

Telephone: +61 2 6210 4701

Email: communications@apvma.gov.au

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# Environmental Chemical Review Assessment Report

# **Fenthion**

# Food Uses Only

The chemical review of fenthion containing products that are used on crops and animals for human consumption.

CR366-1



# **Australian Government**

# **Department of the Environment**

**Environment Protection Branch** 

Date: 30 April 2014

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# 1 Introduction

The Australian Government Department of the Environment has undertaken this assessment for the Australian Pesticides and Veterinary Medicines Authority (APVMA).

Fenthion is an organophosphorus insecticide with widespread uses. Its major use is for the control of fruit flies, caterpillars, moths, bugs, thrips, and wingless grasshoppers mainly in orchards, with some use in vegetables. There is a minor veterinary use for lice on cattle. Non-food uses are for outdoors, subfloor and ceilings in and around dairies, stables, commercial, industrial and domestic buildings for control of flies, mosquitoes, cockroaches, ants and fleas and other household pests. The mosquito uses include applications to waterbodies where mosquitoes are breeding. It is also used as an avicide (bird control agent) for pigeons, starlings, Indian mynahs and sparrows in industrial and commercial premises.

# 1.1 Scope

This environmental risk assessment is limited to food uses of fenthion only. The environmental risk assessment for non-food uses was published in December 2005. These uses present broader environmental exposure to fenthion compared to non-food uses. This report focuses on the labelling of the products that are the subject of this review.

# 1.2 International reviews

In January 2001 the US EPA released for public comment its Interim Re-registration Eligibility Decision (IRED) dcoument for fenthion (US EPA, 2001). This document indicated that at the time only two uses remained in the US, which were both non-food uses. These uses were as an adult mosquiticide by ground and aerial application in Florida only, and for control of dragonfly larvae by direct application to contained ornamental fish production ponds in Arkansas, Florida and Missouri only.

In 2003 the US EPA announced that Bayer had requested cancellation of all its registered fenthion containing products and that the EPA had intended to grant the request with a cancellation date of 30 June 2004. The Canadian Pest Management Regulatory Agency had also announced that the registrant no longer supported continued use of fenthion containing products (all for external use on cattle) in Canada, with the last date of sale by the registrant set at 31 December 2004 and the last date of use at 31 December 2006.

In 2003, the European Commission announced that proposed use of fenthion baits in olive and citrus plantations had raised concerns with regard to the possible impact on birds (the very high acute risk to birds and the absence of "data on sublethal effects and other issues") and, as a result, fenthion containing products for plant protection were not expected to satisfy the Commission's requirements that allowed sale/use in Commission countries. On 11 February 2004 the Commission announced that all authorisations for plant protection products containing fenthion were to be withdrawn

by 11 August 2004, except for bait applications in citrus, olives and peaches, in which cases the authorisation is to be withdrawn by 30 June 2007 (European Commission, 2004). This was under 3 conditions:

- The remaining plant products are to be relabelled to match the restricted use conditions;
- To protect human and animal health and the environment all appropriate risk mitigation measures should be taken to reduce any possible risks; and
- To ensure that alternative products or methods for such uses are being seriously sought, in particular, by means of action plans.

# 1.3 Chemical Identity

Chemical name: O,O-Dimethyl O-(3-methyl-4-(methylthio)phenyl)

phosphorothioate

Common name: Fenthion CAS Registry number: 55-38-9 Molecular formula:  $C_{10}H_{15}O_3PS_2$ 

Structural formula:

Fenthion

Molecular weight: 278.3

# 1.4 Physico-Chemical Properties

The following physico-chemical properties are from Tomlin (1997, ed.). They refer to the pure chemical unless otherwise stated.

Appearance: colourless liquid

Odour: mercaptan-like

Melting Point: not applicable

Boiling Point: 90°C @ 1 Pa (calculated)

Specific Gravity/Density 1.25 @ 20°C

Vapour Pressure:  $4.7 \times 10^{-4} \text{ Pa } (2.20 \text{ °C})$ 

Solubility in Water 4.2 mg/L @ 20°C

Octanol-Water Coefficient. Log  $P_{ow} = 4.84$ 

Henry's Constant  $5 \times 10^{-2} \,\mathrm{Pa.m^3/mol} \,(4.93 \times 10^{-7} \,\mathrm{atm.m^3/mol}).$ 

Low volatility from water.

Dissociation Constant: no dissociable hydrogens.

Fenthion is slightly soluble in water and highly soluble in organic solvents. It has a high partition coefficient and moderate binding to sediment/soil is expected. It is slightly volatile but has low volatility from water.

# 2 Environmental Exposure

#### 2.1 Environmental Release

When the review commenced there were several food-use products registered. Subsequently, only two of these products are still available: an insecticide spray for fruit trees (product 32996) and a spot on treatment for cattle (33520). It's noted that home-use insecticide spray for fruit trees (61308) has been registered since the commencement of the review. Therefore it will not be assessed in this review although any advice or recommendations made in this report may also pertain to this product.

# 2.1.1 Application and use patterns

#### 2.1.1.1 Insect Control

Product 32996 is an emulsifiable concentrate (550 g/L fenthion) available for use on orchard crops, where it is used to control fruit flies, codling moth, oriental fruit moth, lightbrown apple moth, Rutherglen bugs, mealy bugs and wingless grasshoppers. The label indicates for vegetable crops (tomatoes, capsicums and eggplant) it is used to control fruit flies. However, currently only use on capsicums is permitted. Use on pasture for the control of wingless grasshoppers and armyworm was removed from the labels in 1999.

The maximum use rates stated on the label are: 150 mL/100 L (82.5 g ac/100 L) for Queensland and Mediterranean fruit flies in pome and citrus fruits with lower rates (50 - 100 mL/100 L) for grapes, stone fruit, deciduous fruit, tropical fruits etc. The permitted horticultural uses are summarised in Table 1.

Current usage is mainly for fruit fly as either field spray applications or to a much lesser extent post harvest dips. Other significant uses are for control of codling moth and Rutherglen bug.

It is normal practice in orchards situations to spray to runoff, normally requiring 1500 to 3 000 L/ha of spray solution for pome and stone trees but this could be as high as 4000 L/ha for larger pear trees and mangoes, while grapes require 1 000 - 1500 L/ha. Significant application rates are included in Table 1.

Citrus use is normally associated with very high application volumes (6 000 - 10 000 L/ha, corresponding to 4.95 to 8.25 kg ac/ha for 82.5 g ac/100 L, maximum rate for citrus). The company has stated that high application rates to citrus are rarely used and that in Western Australia 99% of citrus growers are said to use airblast sprayers applying 850-1 000 L/ha, with some going up to 2 000 L/ha. In Queensland fruit fly control is said to be commonly achieved by baiting. In other citrus growing areas such as South Australia and the MIA, fruit fly do not occur.

Table 1: Summary of the currently permitted horticultural uses.

Crops	Rates permitted (mL product/100 L water)	Maximum application rates (kg ac/ha)	Pests
Apples, Pears, citrus	75 - 150	2.47 (pome) 3.3 (large pear trees) 8.25 (normal citrus rate) 1.64 (citrus rate claimed by company)	Queensland fruit fly and Mediterranean fruit fly
Apples and pears	75 - 95	1.57 2.09 (large pear trees)	Codling moth and lightbrown apple moth Wingless grasshopper Rutherglen bug
Grapes	50 - 75 (lower rate WA only)	0.62	Fruit fly Mediterranean fruit fly
Stone fruit	75	1.24	Queensland and Mediterranean fruit fly
	75	1.24	lightbrown apple moth Oriental fruit moth Wingless grasshopper
Tropical and sub- tropical fruit	75	1.24	Fruit fly Yellow peach moth Wingless grasshopper
Persimmons	90	1.48	Greenhouse thrips
	75	1.24	Mediterranean fruit fly Queensland fruit fly and mealy bug
Capsicums	75 mL/100 L or 750 mL/ha	0.41	Fruit fly
Ornamentals	100 mL/100 L Soil drench	Spray: 0.55	Mealy bug
Tropical and sub- tropical fruit, Melons and watermelons, chillies	75 mL/100 L post- harvest dip	N/A dipping of fruit	Queensland fruitflies Mediterranean fruit fly

Prior to 2001, the registrant clarified that volumes of use of fenthion have been constant at around 10 tonnes per annum. Peaches accounted for  $\sim 6.5$  t, mangoes for  $\sim 1$  t, pome fruit for 0.7 t, tomatoes for 0.55 t, while citrus and grapes have accounted for < 0.5 t combined. It was confirmed use is primarily for control of fruit fly by spraying, with only around 1% (equivalent to about 100 kg/annum) used in post

harvest dips. Use for control of wingless grasshoppers in orchard situations appears to be very minor according to Pike (2001).

The use pattern, as stated on the permits, commences with full cover sprays when the pest is present with further applications every 1-3 weeks (7-21 days) until about 1-4 weeks before harvest. The maximum frequency is 5 applications at a minimum 7 days interval. for tropical and sub-tropical fruits and persimmons (inedible peel) (all at  $75-90\,$  mL/100 L). For capsicums the permit states application should be when the first fruit changes colour from dark to light green and then repeated every 14 days. For ornamentals the soil around the plants should be thoroughly drenched, and the plants sprayed if mealy bugs are seen, with a repeat spray 14 days later.

The company clarified that all fenthion used for fruit fly control is applied by orchard sprayers or ground rigs with no aerial application. However, aerial application might have previously been used for tomatoes, which was the main non-fruit use prior to the suspension of fenthion in October 2012.

The label contains instructions for both dilute and concentrate spraying which should be done at the same label rate. There is no information on the label regarding types of spray equipment used or on minimising spray drift—size of spray droplets etc.

According to the label post harvest treatment is for tropical and sub-tropical fruits as well as fruiting vegetables at a concentration of 75 mL/100 L (41.25 g ac/100 L = 0.413 ppm). Instructions indicate complete submergence in baths for 1 minute followed by draining and air drying, or by flood spraying for a minimum of 10 seconds and allowing to remain wet for at least one minute. Hollow fruited capsicums or chillies are only to be treated by the latter method.

#### 2.1.1.2 Cattle Pest Control

Product 33520 is a topical solution (spot on treatment) used for the control of lice on cattle by spotting the dose onto the rump or loin. The rate used is between 22-55 kg live weight per mL for the formulated product (200 g/L), with ~2 tonnes of fenthion used per year according to Pike (2001).

# 2.1.2 Packaging and Container Disposal

#### **2.1.2.1** Emulsifiable Concentrate (insect control)

Product 32996 (550 g ac/L) is supplied in 1 L and 5 L containers.

The label statement for disposal of agricultural chemical containers has been revised in light of the fact that burial of emptied containers is illegal in some states. Therefore the current disposal label statement should be amended to the following recommended statement:

Triple or preferably pressure rinse containers before disposal. Add rinsings to spray tank. Do not dispose of undiluted chemicals on site. If recycling, replace cap and return clean containers to recycler or designated collection point.

If not recycling, break, crush, or puncture and deliver empty container to an approved waste management facility. If an approved waste management facility is not available, bury the container below 500 mm in a disposal pit specifically marked and set up for this purpose clear of waterways, desirable vegetation and tree roots, in compliance with relevant local, state or territory government regulations. Do not burn empty containers or product.

# **2.1.2.2** Topical Solution (spot-on lice control for cattle)

Product 33520 is supplied in 500 mL, 2.5 L and 10 L containers. The disposal statement for products > 1 L should be amended to:

Triple rinse container before disposal. Dispose of rinsate or any undiluted chemical according to state or territory legislative requirements. If not recycling, break, crush or puncture and deliver empty packaging to an approved waste management facility. DO NOT burn empty containers or product.

The 500 mL container may either use the above statement or that for small containers from the APVMA's Veterinary Labelling Code (APVMA, 2008b):

Dispose of empty container by wrapping with paper and putting in garbage.

# 3 Environmental Fate

# 3.1 Chemical Degradation

All of the following reports for chemical fate and degradation were submitted by the registrant in response to the ECRP data call-in, unless otherwise stated.

# 3.1.1 Hydrolysis as a function of pH

# Jensen-Korte, 1983a

The hydrolysis of fenthion (99.9%) was determined at pH 4, 7 and 9 (in duplicate) in sterile solutions according to OECD Guidelines. The buffered solutions were kept at 50, 60 and 70°C and sampled at various time intervals from time 0. Sampling continued until the concentration of active was <30% of applied. There were between 7 and 9 samples taken per solution. The solutions were analysed by gas chromatography (GC).

From the first order rate constant and the Arrhenius equation, the half-lives at 22°C (average of two determinations) were calculated to be 222.8 days (pH 4), 199.6 days (pH 7) and 142.7 days (pH 9). The fit to first order kinetics equation was >0.99 in all cases, showing that hydrolysis could be adequately described as first order.

There was a hydrolysis product noted in the GC, 3-methyl-4-methylthiophenol (MMTP), but the method of identification used was not given. This is in contrast to the results of Simmons and Thornton (1976), where a number of hydrolysis products were identified.

It is noted by the Department of the Environment that the half-lives in this study are considerably longer than for the Simmons and Thornton (1976) and Flint and Shaw (1972) studies below. A clear explanation is not readily identifiable from these reports.

# Simmons and Thornton, 1976

The hydrolysis of radiolabelled fenthion (<sup>14</sup>C in ring) was determined at pH 5, 7 and 9 at a concentration of approximately 10 mg/L in sterile aqueous solutions. The study was not conducted according to current Guidelines.

The sterile buffered solutions at pH 5, 7 and 9 were kept at either 5, 25 or 40°C in the dark and sampled at weeks 2, 3, 7 and 23. The solutions were analysed by liquid scintillation counting (LSC) and metabolites quantified by TLC and a radio-chromatogram scanner. Sterile handling techniques were used during sample preparations and sampling of the hydrolysis flasks.

From the first order rate constant, the half-lives were calculated as given in Table 2 together with the fit to first order kinetics equation, showing that hydrolysis could be adequately be described as first order for temperatures 25 and 40°C.

Table 2: The half-life of hydrolysis and fit to first order equation at different pH and temperatures.

	5°	°C	25	°C	40°C		
pН	t½, weeks R <sup>2</sup>		$R^2$ $t^{1/2}$ , weeks $R^2$		t½, weeks	$R^2$	
5	198.0 0.6563		7.8	0.9854	3.4	0.9974	
7	85.6	0.3777	5.8	0.9939	2.8	0.9893	
9	128.4 0.9081		4.4	0.9879	2.4	0.9900	

The hydrolysis products were identified by comparison with known  $R_f$  values. There was a total of 8 metabolites noted, with fenthion sulfoxide, fenthoxon, phenol sulfoxide and phenol sulfone the principal metabolites reaching up to 37% of applied radioactivity (see Appendix 1 for structures). The authors note that under more basic conditions, the metabolites tended to be of higher oxidation states.

# Flint and Shaw, 1972

The persistence of fenthion was determined in phosphate buffer solutions at pH 5, 7 and 9. The study was performed according to an in-house protocol. The buffered solutions were dosed with fenthion at approximately 10 mg ac/L using an SC formulation and then incubated at temperatures of either 30 or 50°C for 16 days. The solutions were analysed by GC.

The half-lives were calculated by first order analyses and for 30°C were 31.3, 25.5 and 23.5 days for pHs 5, 7 and 9 respectively. At 50°C the half-lives were 6.4, 3.7 and 2.1 days respectively. There was no information on the sampling frequency presented and therefore it is unclear as to the reliability of these results.

# 3.2 Photodegradation

# 3.2.1 Aqueous Photolysis

# Christopher and Lane, 1987a

The aqueous photolysis of <sup>14</sup>C-fenthion (labelled at C1 in phenyl ring) was performed according to US EPA Guideline 161-2.

The study was conducted at pH 5 in phosphate buffer at  $25^{\circ}$ C under sterile conditions (in duplicate) and at a final concentration of 7 µg/mL. These solutions were irradiated for a period of 4.0 hours of continuous exposure under fluorescent lights (FS-20 Sunlamps and F20T12-BL 'black light). It was stated that the spectral distribution of the lights approximated that of natural sunlight, based on previous literature reports.

The half-life was determined to be 29 minutes of continuous exposure, based on HPLC analysis of the parent compound (average from duplicates). The dark control did not show any significant degradation, with 94% average recovery of fenthion after 4 hours. There was some degradation due to oxidation with 3% of fenthion sulfoxide (see Appendix 1 for structure) present in the dark control at the end of the study.

There were three principal metabolites detected in the HPLC analysis and confirmed by TLC using authentic samples, these were 3-methyl-4-methylthiophenol (MMTP), fenthion sulfoxide and MMTP sulfoxide. Four other minor metabolites were identified which did not exceed 10% of applied radioactivity. The photolytic route proposed involves initial hydrolysis, as indicated by its rapid formation of MMTP (23% after 0.5 hours), together with oxidation as evidenced by the formation of oxidative products.

#### Fredrickson and Nichols, 1976

The photolysis of radiolabelled fenthion (label in phenyl ring) was performed but did not follow any protocols.

A solution of the radiolabelled fenthion in distilled water was irradiated for 2 hours (2.6 hours for low temperature conditions) at 25 or 5°C using the same fluorescent light as above. The intensity was given as 1000 to 1200 µwatts/cm², less than natural sunlight. The report states that previous studies using DDT and mesurol showed degradation rates similar to reported values for natural light. In addition, samples containing 2% acetone were irradiated at 25 °C to mimic the photo-sensitising effect of natural water containing dissolved organic material. Dark controls were set up under identical conditions.

The irradiated solutions were sampled every 10 minutes and then analysed by TLC. Radioactive zones were quantified by scraping followed by radioanalysis of the scrapings.

There was rapid degradation of fenthion at 25°C with a half-life stated to be 15 minutes, but the Department of the Environment determined the half-life as 31 minutes with r² of 0.9661, determined from first order analysis of the TLC results given. There were 4 major degradation products identified, these were fenoxon (oxygen analogue of fenthion), fenthion sulfoxide, MMTP and MMTP sulfoxide. In addition three other metabolites were noted but not positively identified. Polar degradation products that remained at the origin accounted for the majority of radioactivity, 39% after 120 minutes of irradiation.

At 5°C the half-life was slower, as expected, and was calculated as 75 minutes ( $r^2 = 0.97$ ). The degradates were the same as previous, except that the concentration of MMTP was higher. For the photo-sensitised (acetone) solutions the degradation was fastest, half-life of 15 minutes ( $r^2 = 0.98$ ) for the first 70 minutes, with the major degradation product the fenthion sulfoxide. Other degradation products were similar to previous except fenoxon sulfoxide was detected and no MMTP.

The pattern of degradates was interpreted as two competing reactions, photo-induced hydrolysis and photo-oxidation. The rate of the two reactions are similar at 25°C, at 5°C oxidation is slower than hydrolysis and in the photo-sensitised solutions the rate of oxidation is increased.

#### Jensen-Korte, 1983b

In a standard irradiation test, an aqueous solution of fenthion was irradiated for 10 minutes with a mercury vapour lamp. The half-life of 4.5 minutes was obtained using first order kinetics ( $r^2$  0.994). The test was repeated using natural sunlight (central Europe), with a half-life of 4 hours obtained (summer, clear sky). A large number of photodegradation products were formed, with fenthion sulfoxide and MMTP identified by comparison with reference products.

The UV spectrum of fenthion was examined and showed to extend into the sunlight emission on the earth's surface. The absorbance of fenthion at 290 nm was 1190.

In addition, fenthion on silica-gel plates was irradiated using sunlight simulating fluorescent lights for 3 days. The half-life was determined as 22 hours, assuming first order reaction. Dark controls showed 78% degradation after 3 days. The report did not include any information about metabolites formed.

# **Wilmes**, 1988

The half-life of fenthion in water under natural sunlight was given based on the experimental determination of the quantum yield and subsequent calculations. Full details of the method were given but only as a general outline for obtaining the half-life of photolysis, specific details for fenthion were not given.

The quantum yield of fenthion was 0.8 using polychromatic light and the half-life was calculated as 7.2, 15.4, 31.4 and 9.8 hours for summer, autumn, winter and spring respectively at 30° latitude.

# 3.2.2 Photolysis on Soil

# **Christopher and Lane 1987b**

The photolysis of <sup>14</sup>C-fenthion (labelled at C1) on soil was conducted according to US EPA Guideline 161-3.

A layer (1 mm thick) of an air dried sandy loam soil (2.4% organic matter, 66.0% sand, 32% silt and 2% clay, pH  $5.1[CaCl_2]$ ) was dosed at approximately 53 µg/g (nominal) with  $^{14}C$ -fenthion. The dosed soil was exposed to sunlight (Latitude 39°) for 30 hours (day/night cycle). Air was passed through the test chamber and then through gas traps.

Soils were sampled at 0, 2, 8, 24 and 30 hours after dosing together with dark controls in duplicate. The soil samples were extracted and then analysed by HPLC and the identification of metabolites confirmed by TLC with reference standards. First order kinetics were used to determine the half-life.

The degradation of fenthion was rapid, from 98% of AR at time 0 to 34% of AR after 30 hours. The principal metabolite was fenthion sulfoxide, which reached 57.6% of AR after 30 hours, and small amounts of 3 other photo-products, fenthion sulfone, fenoxon sulfoxide and MMTP. The half-life was calculated as 6.6 hours of sunlight. There was <0.1% of AR in the volatile traps at any sample. The dark controls showed limited degradation of fenthion, with 93.7% of AR recovered as fenthion after 30 hours. The only degradate in the dark controls was the fenthion sulfoxide.

#### 3.2.3 Literature

# Chen, Zabik and Leavitt, 1984

The photodegradation rates of a number of pesticides was determined as thin films on glass using an artificial light. The artificial light source used had a peak energy output at 300 nm. The half-life for fenthion under the test conditions was 57 hours (film thickness  $0.67~\mu g/cm^2$ ) and this increased with increasing thickness of the pesticide film but the half-life is not directly comparable with natural conditions. The absorbance of fenthion over the range 295-305 nm, the highest energy of natural light, was  $\epsilon = 5200$  indicating that direct photolysis is possible.

#### Gohre and Miller, 1986

The photo-oxidation of fenthion on 4 sterile soils (autoclaved) was examined using natural sunlight. The soils used were a loam (0.79% om, pH 7.5), sandy loam (1.97% om, pH 7.2), a loam (5.19% om, pH 4.5) and another sandy loam (6.31% om, pH 6.5). The rate of degradation was fastest on the soils with the lowest organic matter and the major product was the sulfoxide on all soils tested. The degradation in the dark control and bare flasks (without soil) was significantly slower. The paper gives the results as graphs only and half-lives were not determined.

# 4 Degradation

# 4.1 Soil and Aquatic Metabolism

#### 4.1.1 Aerobic Soil Metabolism

# Honig-Bathelt, 1989

The degradation of <sup>14</sup>C-fenthion was studied in a silt loam soil under aerobic conditions according to the German BBA IV/4-1 Guideline (Honig-Bathelt, 1989).

A silt loam soil (sand 10%; silt 72%; clay 18%; oc 3%; pH 5.9) was dosed with <sup>14</sup>C-labelled fenthion (labelled at C1) at 1 mg/kg. The soil was moistened to 75% of field capacity then incubated for a total of 120 days (the temperature of incubation was not given). Volatile products were trapped. The soil was sampled as indicated in Table 3.

Table 3. Residues of <sup>14</sup>C-fenthion during an aerobic soil metabolism study. Results as percentage of recovered dose.

				Days A	After Trea	atment			
	0	1	3	7	14	30	59	90	120
Fenthion	95.2	42.1	11.4	5.1	3.0	1.9	0.7	0.4	0.4
fenthion sulfoxide	2.4	32.9	25.3	10.7	3.9	1.9	1.6	0.9	0.7
MMTP sulfoxide		6.1	17.8	17.0	7.5	2.3	1.1	0.4	0.4
MMTP sulfone		2.6	16.9	29.7	28.2	14.2	4.0	1.6	1.1
Other metabolites	0.4	5.6	8.3	2.6	4.8	7.2	7.2	5.4	5.0
$CO_2$	0.0	0.5	1.9	5.9	13.9	27.5	42.6	50.4	50.1
Non-Extractable	0.2	4.7	11.9	24.5	37.1	40.9	42.2	39.8	41.5

The principal metabolite, fenthion sulfoxide (see Appendix 1) formed rapidly and amounted to 33% of recovered radioactivity after the first day and then declined to 4% after 14 days, with increasing formation of hydrolysis products. During the course of the study  $CO_2$  was slowly evolved and reached 50% of recovered radioactivity by the end of the study period. There were no other significant metabolites detected. Total recovered radioactivity was good, being between 90 and 107% of AR for all samples. The degradation of fenthion was second order, with the first half-life <1 day and the  $DT_{90}$  about 5 days under aerobic soil metabolism conditions.

The study is acceptable to the Department of the Environment.

#### da Silva 1994a

The mineralisation of fenthion in two Brazilian soils was studied according to IBAMA protocols (Instituto Brasileiro de Meio Ambiente, Brazil).

The two soils used, a clay (om 2.7%, sand 9%, silt 11%, clay 80%; pH 4.7) and a loamy sand (om 1.5%, sand 84%, silt 6%, clay 10%; pH 3.7) were dosed with fenthion to nominal doses of 1 and 10 mg/kg, then incubated for 28 days (60% field moisture). Samples were taken weekly but only evolved CO<sub>2</sub> was analysed. The microbial activity of the soils (evaluated by radio-respirometry) was determined at the start and finish of the incubation period.

After 28 days there was 15.3% and 13.2% of AR evolved as  $CO_2$  in the clay soil for doses of 1 and 10  $\mu$ g/g respectively and 28.4% and 20.5% of AR for the loamy sand respectively. According to IBAMA classification, fenthion can be rated as reduced-persistent in the clay soil and not persistent in the loamy sand soil. The microbial activity of the soil decreased during the incubation with some 50% reduced respiration of the soil after incubation.

The Department of the Environment concludes that apart from showing that fenthion is readily mineralised, the study is of limited value.

# Takase and Yoshimoto, 1975

The degradation of fenthion and fenthion sulfoxide was studied in two Japanese soils under two conditions, flooded and at 60% of maximum water capacity. The two soils used, a volcanic ash (om 11.3%, pH 5.9, texture silt loam) and an alluvial loam (om 2.0%, pH 5.7, texture loam) were dosed with fenthion to nominal doses of 6 mg/kg, then flooded with distilled water to 2 cm depth before being incubated in the dark at 28°C for 63 days open to the air. In addition, the same soils were incubated under identical conditions but moistened to 60% capacity. The major product, fenthion sulfoxide was also incubated using the volcanic soil under flooded conditions as above. Samples were taken at 0, 3, 7, 14, 28, 49 and 63 days for all systems. The soil was extracted and then the extracts analysed by GC.

The results show that fenthion is readily oxidised to the sulfoxide in the moistened soils, with <20% of applied parent remaining after 14 days for both soils, but under flooded conditions the oxidation is significantly slower, >50% left after 14 days and 15% at the end of the incubation period. In all cases the sulfoxide was the major metabolite identified, it appears that the analytical method used may not have detected the hydrolysis products. Half-lives of fenthion were not determined and as all results were presented graphically, these could not be determined by the Department of the Environment, but the report stated that the half-lives of fenthion and metabolites that exhibit insecticidal activity (total insecticidal active) was about 25-30 days under flooded conditions and 15-20 days for the moistened soils.

For the fenthion sulfoxide, under the flooded conditions there was rapid loss of sulfoxide, to <7% of applied after 21 days with its reduction to fenthion a significant pathway, reaching about 50% of applied after 14 days. The fenthion formed degraded slowly over time to be <10% after 63 days. The reduction of fenthion sulfoxide indicates that with the flooded soils conditions were reducing and may have tended towards anaerobic.

This study is considered to be of limited value.

# **Wagner**, 1974

The degradation of fenthion was studied in two soils over 10 days. The two soils, Soil 1 (oc, 2.58%; pH 6.8) and Soil 2 (oc 0.57%, pH 5.2) were dosed with fenthion at 2  $\mu$ g/g then incubated at 22°C for 10 days. There was limited details on the soils given and no information on the conditions of the incubation except for temperature. The soils were sampled at 0, 0.2, 0.7, 0.9, 1.3, 3.0, 4.9, 6.8 and 9.8 days and analysed using a GC method.

There was rapid degradation on fenthion with  $DT_{50}s$  of 31 and 16 hours for soils 1 and 2 respectively, determined as square root time first order using the Timme-Frehse method for second order degradation curves (Timme, Frehse and Laska, 1986). The  $DT_{90}$  were 161 and 179 hours respectively. The main metabolite was the sulfoxide, identified by GC and TLC.

The study is acceptable (the original study was revised in 1993 with additional data and the Timme-Frehse analysis).

# Anonymous, 1974

The degradation of fenthion was studied in 4 Japanese soils under two conditions, flooded and at 60% of maximum water capacity (Anonymous, 1974). As part of this study, field studies were reported, which are addressed below.

The 4 soils used were, clay loam (om 2.1%, clay 23.1% pH 5.7), silty loam (om 15.2%, clay, 6.3%, pH 5.9), sandy loam (om 0.8%, clay 11%, pH 7.0) and a loam (om 13.9%, clay 13.6%, pH 5.5) were dosed with fenthion to nominal doses of 10 mg/kg. Then the clay loam and silty loam were flooded with distilled water to 1-2 cm depth while the other two soils were moistened to 60% capacity before all soils were incubated in the dark at 28°C open to the air. The flooded soils were incubated for 45 and 60 days for clay loam and silty loam respectively while both moistened soils were incubated for 30 days. Samples were taken at 0, 1, 3, 6 days then weekly for all systems. The soil was extracted then the extract analysed by GC.

There was rapid loss of fenthion with significant production of fenthion sulfoxide in the moist soils, with half-lives of total fenthion actives (fenthion + oxidative metabolites) given as 9 and 13 days for the sandy loam and loam soils respectively. The half-lives for fenthion alone are 5.6 and 4.9 days, calculated by the Department of the Environment. For the flooded soils, the degradation was slower, with half-lives for total fenthion actives about 18 and 25 days for clay loam and silty loam respectively, but formation of the sulfoxide was slower than in the moistened soils. The half-lives of fenthion alone was 14.6 days and 22.3 days respectively.

The results of this study strongly reflect those of Takase and Yoshimoto above and similar conclusions are drawn.

# Schäfer, 1996

Based on a metabolite degradation pathway proposed by Puhl and Hurley 1978 (report not presented to the Department of the Environment), involving the initial oxidation of fenthion to the sulfoxide and subsequent further oxidation or hydrolysis

to give MMTP sulfone, the mass balance equations for all reactions and products were derived. This was solved numerically and the half-lives of fenthion sulfoxide, MMTP sulfoxide and MMTP sulfone that were obtained are 1.1, 4.8 and 15 days respectively. While the modelled equations for MMTP sulfone reflect closely the concentrations observed by Puhl and Hurley (1978), the modelled results for fenthion sulfoxide and MMTP sulfoxide reflect the observations for approximately the first 14 days only. The calculations clearly indicate short half-lives for these metabolites.

# 4.1.2 Aerobic Aquatic Metabolism

#### Anderson and Wilmes, 1988

The degradation of fenthion was studied in two different aquatic/sediment systems under aerobic conditions according to US EPA Guidelines.

The aquatic/sediment systems consisted of natural water and sediment from ponds in the Netherlands and USA. Table 4 gives physical properties of the sediments used.

Table 4. Physical properties of sediment used in aquatic systems.

Sediment/soil	pН	organic carbon	sand	silt	clay	USDA classification
		Carbon				Classification
Lienden,	7.72	1.49	75.3	18.8	5.9	Loamy sand
Netherlands						
Stanley,	6.89	3.15	13.6	58.4	28.0	Silt loam
Kansas, USA						

The sediment was mixed with the corresponding natural water (approximately 10% sediment to 90% water), then 4 days later <sup>14</sup>C-C1-fenthion (in ethanol) was added to give a final concentration of 1.4 mg/L. Each trial was done in duplicate. The sediment/water systems were incubated at 25°C in the dark and stoppered with a gas tube containing oil soaked quartz wool and soda lime to trap volatiles and CO<sub>2</sub>. Samples of the sediment/aqueous phase for Lienden were collected at 0, 3, 7, 14, 31 and 66 DAT and for Stanley on 0, 31, 66 days only. Total radioactivity in the water and soil samples was determined then the samples extracted and the extracts analysed for fenthion and possible metabolites by HPLC and TLC. Evolved CO<sub>2</sub> in both the aquatic phase and adsorbed in the gas trap was determined by acidification and trapping the CO<sub>2</sub>. Table 5 gives the results for Lienden, average of duplicates and Table 6 gives the same for Stanley.

Table 5. Residues of fenthion in water and sediment together with metabolites from the aerobic aquatic metabolism study for Lienden. Results are the average from duplicates. MMTP = 3-methyl-4-methylthiophenol.

DAT		0	3	7	14	31	66
Fenthion	aquatic	62	13.0	13.0	2.1	0.5	nd
	sediment	6.1	44.9	29.3	7.4	1.6	0.45
MMTP	aquatic	11.9	13.4	7.2	14.3	5.3	0.6
sulfoxide	sediment	13.8	9.7	8.2	12.9	2.3	0.8
Desmethyl	aquatic	1.1	8.5	19.2	24.5	19.6	2.2
Fenoxon sulfone	sediment	0.7	2.8	6.0	5.6	3.6	0.8
Minor	aquatic	2.9	5.6	8.5	13.3	10.3	23.9
metabolites	sediment	0.2	0.8	2.5	4.3	5.1	5.7
Total CO <sub>2</sub>		nd	0.1	2.9	8.2	5.5	12.2
Non-extractable		0.4	1.3	3.4	12.4	42.2	55.6

Table 6. Residues of fenthion in water and sediment together with metabolites from the aerobic aquatic metabolism study for Stanley. Results are the average from duplicates.

Γ	DAT	Fenthion,		MMTP		Desmethyl		Minor	Total CO <sub>2</sub>	Non-
				sulfo	xide	fenthion sulfone		metabolites		extractable
Г		Aqu.	Sed.	Aqu.	Sed.	Aqu.	Sed.			
	0	70.0	10.1	7.3	5.3	0.4	0.7	5.1	nd	0.5
	31	0.1	0.9	0.2	0.9	5.6	2.7	13.4	8.2	70.3
	66	nd	0.3	< 0.1	0.5	0.25	0.35	8.5	15.0	74.6

The overall <sup>14</sup>C-mass accountability was good, with between 98.2% and 105.5% of applied radioactivity recovered in all samples before analysis.

There were two major metabolites identified, the phenol sulfoxide (3-methyl-4-(methylsulfoxide)phenol, MMTP sulfoxide) and a new product, the desmethylfenthion sulfone (see Attachment 1 for structure). The maximum amount of sulfoxide was approximately 13% in the aquatic and sediment at 14 DAT. The desmethylated product also peaked in concentration after 14 days but occurred mainly in the aquatic phase, which is expected given its polar nature. Thereafter the metabolites disappeared, with increasing amounts of sediment bound residues and CO<sub>2</sub> being the final products. There were a number of other minor metabolites produced, with the only ones of note being MMTP sulfoxide and the corresponding sulfone which occurred in the 66 DAT sample at about 12% each.

The 0 time samples both show significant adsorption and degradation having already occurred. The recoveries of applied radioactivity was good, implying that the samples were dosed correctly. It is not possible to determined precisely when these samples were taken but it could be some hours after the soil/water systems were dosed. This would then account for the adsorption and degradation that took place in the time 0 samples.

The study shows that disappearance and degradation of fenthion is fast, with halflives of 7 and 9 days for Lienden and Stanley systems respectively, calculated by the Department of the Environment (fit to first order kinetics was acceptable in both cases, 0.92). However, due to the limited data for Stanley, the calculated half-life for this system is not reliable. Using the data for the individual compartments for Lienden, the half lives (first order) are  $4.4 \ (r^2 = 0.982)$  and  $9.7 \ (r^2 = 0.900)$  days for aquatic and sediment respectively. Using the Timme-Frehse method (Timme, Frehse and Laska, 1986) for the aquatic compartment only the time 1.5 order gave the best fit  $(r^2 = 0.9844)$  with half-life of 0.94 days and  $DT_{90}$  of 4.9 days, which appears as a better fit to the raw data as it take into account the rapid loss for the first 3 days. The studies appear to be satisfactorily performed with very good overall recoveries and is acceptable for Lienden only.

It is noted that the US EPA rated this study as scientifically invalid due to the low level of fenthion in the time 0 sample and too few samples for the silt loam sediment.

# Scholz, Fritz, Anderson and Spiteller (1988)

The degradation of various pesticides in an aquatic model ecosystem was studied using a number of water/sediments systems. For fenthion the degradation was studied under aerobic and anaerobic conditions using the Stanley soil above. The only results were presented as a bar graphs and a half-life could not be determined. The authors note that under aerobic conditions  $CO_2$  was produced continuously but with anaerobic conditions only after a lag of 60-120 days, although larger amounts were produced. The metabolites also differed, with fenthion sulfoxide and desmethyl fenthion sulfone being the major metabolites under aerobic conditions and the phenols (MMTP and MMTP sulfoxide) being the major metabolites under anaerobic conditions.

# Fredrickson (1976).

To a water/sediment system (10 L water and 2000 g sediment, collected from a natural pond) was added <sup>14</sup>C-fenthion (labelled at C1) to give 10 mg/L. The system was incubated outside (open to the atmosphere) in a large tank of water (100 L) to buffer the system against temperature changes. Water and sediment samples were taken on 0, 1, 2, 5, 9, 16, 21, 28, 35, 42 and 49 DAT. Samples were extracted and analysed by TLC only and quantified by scraping the TLC zones and radiometric analysis of the scrapings. Table 7 gives the results for water and sediment.

Table 7. Concentration of fenthion and metabolites on aqueous and sediment. Results as percentage of total system activity (total applied).

DAT	0	1	2	5	9	16	21	28	35	42	49
Aqueous											
Fenthion	100	60	38	18	8	5	2	2	0	0	0
Phenol sulfoxide	0	8	15	14	15	12	12	7	6	5	6
Unidentified	0	3	7	9	12	20	22	17	18	20	25
				Sed	iment						
Fenthion	0	20	27	37	34	26	21	25	17	12	9
Phenol sulfoxide	0	1	1	2	4	3	2	2	3	3	3
Bound	0	5	8	14	19	28	34	39	47	49	46

Fenthion had a first order half-life of dissipation from the aqueous phase of 5.0 days  $(r^2 = 0.902)$  but the data appears to be second order with rapid initial dissipation. Using the Timme-Frehse method (Timme, Frehse and Laska, 1986) the square root

time  $1^{st}$  order gave the best fit ( $r^2 = 0.9825$ ) with half-life of 0.85 days and DT<sub>90</sub> of 9.4 days. The half-life of fenthion in the total system (aqueous + sediment) was 15.7 days (first order) and again the square root time  $1^{st}$  order gave the best fit ( $r^2 = 0.9695$ ) with half-life of 4.5 days and DT<sub>90</sub> of 50 days.

# Flint and Shaw, 1972

The degradation in a water sediment system was studied by adding fenthion to a mixture of water and sediment (ratio 10:1 volume of water:sediemnt). The system was incubated outside in full sun, buried up to the water level. The half-lives for water and sediment were estimated as 0.9 and 1.3 days respectively. The study does not present any results except for one graph and the estimated half-lives and is of limited value.

#### **4.1.2.1** Literature

#### Cripe, O'Neill, Woods, Gillman and Pritchard, 1989.

The degradation of fenthion in 3 salt-marsh environments in Florida was studied by taking samples of water and sediment from the salt marshes, at three sites designated as RP, A-10 and SA-79, then dosing the salt water-sediment systems with fenthion at 200  $\mu$ g/L before incubation at 25 °C in the dark. The amount of sediment used varied and is given in Table 8 below. For the sterile conditions, 20 mL/L of formalin was used to achieve sterility, although the paper does not indicate whether these systems were tested for sterility. Table 8 summarises these results for sediment water systems only.

The half-life in the natural salt marsh water was 22, >30 and 14 days for sites RP, A-10 and SA-79 respectively and for sterile water the half-lives were >30 days for both A-10 and SA-79 sites, there was no data for sterile water at RP. A radiolabelled study showed that there was <2% of applied radioactivity trapped as  $CO_2$  with the decreases in total fenthion corresponding with proportional increase in polar degradation products but these were not identified.

Table 8. Degradation of fenthion in water sediment from 3 salt-marshes in Florida under non-sterile and sterile conditions.

Site	Treatment	Sediment loading, mg/L	Half-life, days	$R^2$
RP	none	500	3.8	0.99
RP	sterile	500	14	0.80
A-10	none	500	7.4	0.98
A-10	sterile	500	>30	0.95
SA-79	none	500	10	0.94
SA-79	none	1000	4.5	0.98
SA-79	none	2500	2.1	0.98
SA-79	none	5000	1.8	1.0
SA-79	sterile	500	>30	0.73

In the paper, the authors showed that there was a positive correlation between sediment loading and the rate constant of dissipation. Also, the presence of plants or plants parts and sediment from round the root zone in the water systems increased the rate of disappearance, with Table 9 giving the results. Residue analysis showed no significant fenthion accumulation in any of the plants or plant parts.

Table 9. Degradation of fenthion in non-sterile water containing plants, plant parts or sediment from around the roots of plants (Spartina alterniflora).

	Non-sterile water	Whole plant	Roots	Outside leaves	Inside leaves	Sediment around roots
Half-life, days	>30	0.34, 0.74	0.54	2.6	21	14
$R^2$	0.80	0.99, 0.93	0.92	0.94	0.48	0.97

It is concluded that the paper clearly shows that fenthion would be expected to readily degrade in natural salt marshes, especially those with plants.

# O'Neill, Cripe, Mueller, Connolly and Pritchard, 1989.

In another study on the fate of fenthion in salt marshes, water and intact sediment cores with and without a salt marsh plant (*Juncus roemerianus*, black needlerush) were collected from salt marches then placed in microcosms. The microcosms were dosed with fenthion and samples (water and sediment) were taken 3, 6 hours after dosing, then daily. The samples were analysed by GC. The loss of fenthion conformed to first order kinetics with half-lives determined as 35.5, 33.2 and 105 hours for non-sterile without plants, with plant and sterile (sterilised using formalin) respectively. Fenthion was found at greater depths in the non-sterile system than for sterile, with bio-turbation given as a possible explanation. The distribution of fenthion in the sediment was not appreciably different between microcosms with and without plants.

# Walker, Cripe, Pritchard and Bourquin, 1988

The degradation rate of a number of pesticides, including fenthion, was determined in estuarine water with and without sediment. The sediment used was stated to be a silty clay. The treatment regimes were non-sterile water, non-sterile water plus sediment (500 mg per L of water) together with corresponding sterile system (sterilised using formaldehyde). These were incubated in the dark at 25 °C. The sampling schedule was not given but from the graphic data it appears that 6 samples taken over 260 hours. The rate constants are -0.00745, -0.00199 and -0.00129 per hour (half-lives of 3.9, 14.5 and 22 days) for non-sterile water/sediment, sterile water/sediment and non-sterile water respectively.

# Lacorte, Lartiges, Garrigues and Barcelo 1995

The degradation rate of a number of pesticides, including fenthion, was determined in estuarine water filtered to remove all sediment. The spiked water was exposed to ambient sunlight and temperature (Barcelona, daily temperature ranged from 7 to  $15^{\circ}$ C). The half-life for fenthion under these conditions was given as 4.5 days ( $r^2 = 0.95$ ).

# 4.1.3 Anaerobic Aquatic Metabolism

#### Fritz, Brauner and Bornatsch 1988.

The degradation of fenthion under anaerobic conditions was conducted to US EPA Guideline 162-3.

Natural water and sediment (approximately 9:1 water:sediment) was incubated for 30 days in a sealed system to give anaerobic conditions before the surface water was dosed with radio-labelled (ring-1-<sup>14</sup>C) fenthion at 1.5 mg/L and incubated for one year at 22°C in the dark. The sediment was a silt loam (sand 13.6%; silt 58.4%; clay 28%, pH 6.9, oc 3.15%) and the water was from the pond where the sediment was collected.

Due to the air tight seal breaking between 60 and 120 DAT, a follow up study was conducted as before and sampled on 120 and 190 DAT. Comparison of the follow up study and the original main study for 120 DAT shows that most of the evolved CO<sub>2</sub> was released and the dissolved CO<sub>2</sub> was also significantly reduced in the original study.

The water and sediment was sampled on 0, 3, 7, 14, 30, 60, 120, 252 and 360 DAT. Volatile metabolites were swept into the gas traps before sampling using nitrogen. The physical properties of the overlying water was then determined (redox, pH and dissolved oxygen). The dissolved CO<sub>2</sub> in the aqueous phase was liberated by acid and the evolved gases trapped for measurement. The remaining radioactivity was either directly analysed by HPLC (0-14 DAT) or extracted before subsequent analysis. Analysis was by HPLC or TLC. The structure of metabolites was confirmed by purification (separate incubation, conducted as before using non-labelled and labelled fenthion) followed by comparison with reference compounds using MS and <sup>1</sup>H-NMR.

Table 10 gives a summary of the principal metabolites.

The surface water was anaerobic when dosing occurred, with redox between -43 to -5 mV (4 replicates) and dissolved oxygen given as 0% of saturation. The system then became slightly more aerobic on day 7, with redox between 96 to 137 mV and approximately 1.0% dissolved  $O_2$ , but reverted to strongly anaerobic conditions on day 60 (-176 to -121 mV). Conditions remained strongly anaerobic until the last sample when the system became more aerobic again with redox of 10 to -24 mV and dissolved  $O_2$  increased to approximately 2% (3 replicates) and one replicate at 35% (experimental error).

			1						
Metabolite	phase	0	3	7	14	30	60	120	360
Fenthion	aqueous	72.1	38.8	20.1	17.8	6.7	nd	nd	nd
	sediment	20.1	43.5	40.2	59.5	32.3	1.9	0.9	0.2
Phenol	aqueous	nd	nd	3.5	4.2	23.7	18.1	0.4*	nd
sulfoxide	sediment	0.8	nd	0.9	1.4	2.4	6.4	0.4	< 0.1
Fenthion	aqueous	nd	4.1	4.7	2.8	9.3	30.1	1.3	nd
phenol	sediment	2.9	1.9	3.7	3.9	5.3	5.3	0.7	< 0.1
3-methyl-	aqueous	nd	nd	nd	nd	nd	8.8	0.2	nd
phenol	sediment	nd	nd	nd	nd	nd	0.9	nd	nd
Residue	aqueous	0.6	1.0	2.1	2.5	4.6	3.6	8.3	3.4
	sediment#	2.9	4.1	$18.9^{1}$	1.8	2.8	5.6	2.6	2.0
Total	Total <sup>14</sup> CO <sub>2</sub>		< 0.1	< 0.1	< 0.1	<1.0	1.0	51.6*	

Table 10. Summary of anaerobic metabolism study as percentage of applied radioactivity.

The half-lives for the system were 5.0, 12.4 and 10.7 days for aqueous, sediment and overall respectively (correlation coefficient, r<sup>2</sup> were 0.931, 0.841 and 0.904 respectively). At time 0 there was significant adsorption (20%) to the sediment but from the report it is unclear how long after dosing the samples were taken. The adsorption to sediment continued till day 14 where approximately 60% of applied fenthion is found with the sediment.

The study clearly shows that fenthion is readily degradable under anaerobic conditions and is acceptable.

# 5 Mobility

# 5.1 Soil Adsorption/Desorption

# **Daly, 1988**

A soil adsorption/desorption study was performed using the standard batch method according to US EPA Guidelines. Four soil types were used: a sand, sandy loam, silt loam and a clay loam, the characteristics are presented in Table 11.

Table 11. Soils characteristics used in Daly, 1988.

Soil Type	pН	% om	% Sand	% Silt	% Clay
Sand	4.3	1.0	88	7	5
Sandy loam	6.6	1.1	56	30	14
Silt loam	5.9	2.9	17	66	17
Clay loam	6.4	2.2	21	50	29

A preliminary study showed that after 6 hours of adsorption (1:10 soil:water) there was limited further adsorption (less than 5%) and after 24 hours HPLC analysis of the solutions showed that 55 to 76% of the applied radioactivity was fenthion. An equilibrium time of 6 hours was used in the definitive study. From the LSC data the

<sup>\*</sup> Figures from follow-up study, see text. \* Includes radioactivity loss due to processing. 1 17.2% of applied radioactivity was lost due to processing for this sample.

concentration of fenthion in the aqueous phase was determined and used to determine the adsorption and desorption coefficients for all the soils used. The results of the definitive study are given in Table 12.

Table 12. Adsorption/desorption results from Daly.

Soil Type	Adsorption			Desorption				
	K <sub>d</sub> ,	${ m K_{oc}}^{\#}$	$\mathbb{R}^2$	$K_d$ ,	$K_{oc}$	$\mathbb{R}^2$		
Sand	8.621	1638	0.9941	20.19	3836	0.9985		
Sandy loam	6.424	1110	0.9915	12.66	2186	0.9693		
Silt loam	15.81	1036	0.9931	33.04	2165	0.9907		
Clay loam	16.21	1400	0.9935	28.10	2427	0.9990		

<sup>#</sup> The equation %oc = %om/1.9 was used.

The adsorption phase was analysed by HPLC to determine the stability in the testing which showed that the fenthion was reasonably stable with 84.4 to 87.3% as fenthion at the end of the 6 hours equilibration. Recoveries of applied radioactivity were satisfactory for most samples except for the sand and sandy loam soils. These tests were repeated as the recoveries were <90% in the initial tests. In the repeated tests the recoveries were 96.9 and 104% of applied radioactivity for sand and sandy loam soils respectively which is acceptable.

In the desorption phase of the study, the desorbed material was not tested and the results are based on radioanalysis only. Given that fenthion readily degrades/oxidises and that another mobility study (Puhl and Hurley below) showed that there was significant amount of metabolites in the desorbed material. Therefore results for desorption in Table 12 could reflect a significant component from metabolites and need to be viewed with some caution.

The Koc shows low mobility in all soils tested.

# Puhl and Hurley, 1978

A soil adsorption/desorption study was performed using the standard batch method but was not performed to current Guidelines. Three soils were used in the study, Kansas, Hagerstown and Florida, the characteristics of which are presented in Table 13.

Air dried soils were mixed with aqueous solutions of radiolabelled fenthion (0.5 to 10.5 mg ac/L) then after shaking (1 hour) the liquid was separated by centrifuging and the liquid analysed by LSC. A preliminary study using Kansas soil had showed that after 1 hour, the amount of radioactivity in solution increased as the equilibrium time increased. Analysis of a sample that had been equilibrated for 16 hours showed that half of the radioactivity was associated with fenthion sulfoxide. Therefore an equilibration time of 1 hour was chosen for the adsorption study so that the adsorption data pertained to fenthion.

From the LSC data the concentration of fenthion in the aqueous phase was determined and used to determine the adsorption and desorption coefficients for all the soils used. The graphical data of the amount adsorbed against concentration showed good linear

fits and therefore use of the Freundlich equation is appropriate. These results are summarised in Table 14.

Table 13. Characteristics of test soils.

Origin	Soil Type	pН	% om	% Sand	% Silt	% Clay
Kansas	Loam	5.5	3.0	46	36	18
Hagerstown	Silty clay	6.7	2.1	4	53	43
Florida	Sand	6.9	3.7	92	7	1
No. 1	Loam	7.7	1.4	40	42	18
No. 2	Silty clay loam	6.3	2.0	8	54	38
No. 3	Silty clay loam	6.1	4.4	6	54	40

Table 14. The adsorption coefficients for the soils tested.

		Adsorption					
Origin	Soil Type	$K_d$ ,	$K_{oc}$	1/n			
Kansas	Loam	38.0	2222	0.968			
Hagerstown	Silty clay	19.8	1654	0.997			
Florida	Sand	36.2	1716	0.880			
No. 1	Loam	7.7	957	0.840			
No. 2	Silty clay loam	12.4	1078	0.980			
No. 3	Silty clay loam	67.3	2660	0.629			

Koc determined by the Department of the Environment. Organic matter (om) in Table 13 was converted to organic carbon (oc) using  $oc = om \times 0.575$ .

The results of the adsorption experiment for fenthion show that it is moderately absorbed to the three soils tested. Fenthion can be rated as having slight to low mobility in soil. The desorption experiments showed that Kdes increased with increasing concentration, eg for Kansas soil Kdes was 0.09 and 42.66 for initial concentrations of 0.46 and 10.4 mg/L respectively. After the final desorption analysis of the solution showed that 9-15% of radioactivity was fenthion sulfoxide.

# Flint and Shaw, 1972

As part of the investigation by Flint and Shaw on the mobility and persistence of fenthion in soil and water, the adsorption to three soils (soils 1, 2 and 3, details in Table 13) was determined. The method used was the shaking flask for 1 hours followed by GC analysis of solutions. The Kd are given in Table 14. There were strong correlations with the Freundlich equation for all soils. The result show that fenthion was moderately adsorbed.

# Hellpointner, 1995

The Koc for fenthion and its metabolites were determined using SAR (Structure Activity Relationship) methods using a published methodology (Meylan, Howard and Boethling, 1992 – not seen by the Department of the Environment). The Koc for fenthion was determined as 2346 and for the metabolites fenthion sulfoxide, MMTP sulfoxide and MMTP sulfone the Kocs are determined as 3703, 2188 and 320 respectively. The result for fenthion is comparable with those in Table 14.

# 5.2 Mobility Using Soil Columns

No studies on the mobility of fenthion itself in soil columns were presented.

# 5.2.1 Aged leaching

# Christopher and Lane, 1987c

An aged soil leaching study of fenthion in four soils was conducted according to US EPA Guidelines. The characteristics of the soils used are given in Table 15.

Table 15. Characteristics of test soils.

Origin	Soil Type	pН	% om	% Sand	% Silt	% Clay
Kansas	Sandy loam	5.1	2.4	66	32	2
Hagerstown	Silty clay	6.7	2.1	4	53	43
-	Sand	6.4	0.2	96	2	2
Stanley Kansas	Silt loam	6.4	2.74	13	63	24

Radiolabelled fenthion (<sup>14</sup>C at C1 in ring) was used to dose the sandy loam in Table 15 at approximately 1 ppm. After aging for 4 or 25 days under aerobic conditions at 75% of field moisture capacity in the dark, the soil was added to the top of untreated columns of soil. To minimise channelling, the soil columns were packed dry and saturated from the bottom up, then allowed to drain before the aged soil was added. The columns were then leached with 50.8 cm (20 inches) of 0.01 M CaCl<sub>2</sub>. The leaching was performed in duplicate for each soil column.

After leaching, the soil columns were segmented into 6 cm sections and the soil extracted. All extracts were analysed for radioactivity and extracts from 0-6, 12-18 and 24-30 cm from all soil columns were analysed by HPLC and TLC for metabolites. The residual radioactivity in the soils was determined by combustion. The leachates were analysed by LSC and HPLC. Results are given in Table 16.

The average recovered radioactivity from the soils columns using treated soil aged for 4 days was 108.6, 102.5, 100.5 and 87.2% of applied for the sandy loam, silty clay, silt loam and sand soils respectively. Apart from fenthion, fenthion sulfoxide and MMTP sulfoxide, given in Table 16, other metabolites detected in the soil columns including fenthion sulfone and MMTP sulfone, were <5.0% of AR in any given segment of the treated soil aged for 4 days. The exception was sandy loam soil in the 0-6 cm segment where the fenthion sulfone occurred at 5.7% of recovered radioactivity. Bound residues in the upper soil segment ranged from 4.5 to 10.2% of recovered radioactivity.

For the treated soil aged for 25 days the recovered radioactivity was 105.4, 107.3, 90.5 and 100.9% of applied respectively. There were 3 significant metabolites, fenthion sulfoxide, MMTP sulfoxide and MMTP sulfone, as given in Table 17. Again there were minor metabolites, all <3% of recovered radioactivity, which is less than for the 4 days aged soil, but on the other hand there was an increase in the bound residues in the upper layer of soil (0-6 cm) ranging from 13.6 to 20.6% of recovered radioactivity.

Table 16. The results of the analysis of leachates and soils from column sections as percentage of recovered dose for treated soil aged 4 days.

Soil Column		Leachate	Total		Co	olumn sec	tions*	
			soil	0-6	6-12	12-18	18-24	24-30
Sandy loam	TR	3.6	96.3	74.7	8.6	6.0	4.3	2.3
-	Fenthion	-	2.5	2.5	0.0	0.0	0.0	
	FN Sulfoxide	-	38.8	36.9	1.3	0.3	0.3	
	MMTP Sulfoxide	-	10.5	4.0	3.0	2.0	1.5	
Silty clay	TR	5.0	94.7	65.3	11.5	9.3	6.0	2.4
	Fenthion	-	2.2	1.9	0.0	0.2	0.1	
	FN Sulfoxide	-	44.8	35.1	4.7	3.1	1.9	
	MMTP Sulfoxide	-	5.7	3.1	1.2	0.8	0.6	
Silt loam	TR	5.0	94.3	73.8	9.3	5.7	3.0	2.3
	Fenthion		0.2	0.0	0.2	0.0		
	FN Sulfoxide	-	39.8	38.1	1.2	0.5		
	MMTP Sulfoxide	-	14.3	8.7	3.1	2.5		
Sand	TR	36.1	63.4	47.0	3.8	3.7	4.1	4.0
	Fenthion	0.0		0.0	0.1	0.0		
	FN Sulfoxide	11.0	32.4	29.0	1.7	1.7		
	MMTP Sulfoxide	8.8	4.1	3.2	0.4	0.5		

<sup>\*</sup>Average of duplicate soil columns. TR = total radioactivity. FN sulfoxide = fenthion sulfoxide, MMTP Sulfoxide = 3-methyl-4-(methylthio)phenol sulfoxide.

Table 17. The results of the analysis of leachates and soils from column sections as percentage of recovered dose for treated soil aged 25 days.

Soil Column		Leachate	Total		Col	umn secti	ons	
			soil	0-6	6-12	12-18	18-24	24-30
Sandy loam	TR	1.9	98.0	53.8	19.7	12.7	5.4	5.5
	FN Sulfoxide	-	16.3	10.8	5.5	0.0		
	MMTP Sulfoxide	-	17.0	5.9	3.7	4.8	2.6	
	MMTP Sulfone		24.7	11.7	5.3	5.8	1.9	
Silty clay	TR	5.0	95.0	59.4	12.6	9.3	7.4	5.7
	FN Sulfoxide	-	12.4	11.1	0.7	0.3	0.0	
	MMTP Sulfoxide		12.5	6.3	2.5	2.0	1.7	
	MMTP Sulfone	-	25.0	12.4	5.4	3.9	3.3	
Silt loam	TR	2.3	97.7	56.8	18.5	12.8	6.7	2.7
	FN Sulfoxide	-	9.9	9.8	0.0	0.0	0.1	
	MMTP Sulfoxide		20.5	7.4	5.0	4.8	3.3	
	MMTP Sulfone	-	25.1	9.8	9.0	4.9	1.4	
Sand	TR	45.7	54.0	46.1	1.8	1.7	1.8	1.8
	FN Sulfoxide	0.4		8.3				
	MMTP Sulfoxide	15.2		4.8				
	MMTP Sulfone	19.7	-	7.1				

Average of duplicate soil columns.  $TR = total\ radioactivity$ ,  $FN\ sulfoxide = fenthion\ sulfoxide$ ,  $MMTP\ sulfone = 3-methyl-4-(methylthio)phenol\ sulfone$ .

The study shows that while fenthion is almost immobile, with little evidence of leaching, the metabolites from soil degradation are more mobile and could leach, especially in soils prone to leaching.

# **Simmons**, 1975

An aged soil leaching study was performed using a loam soil (sand, 50%; silt, 34%; clay 16%; om 1.9% and pH 6.4) but not to current Guidelines. Air dried samples of the soil were dosed with <sup>14</sup>C-fenthion (labelled in the ring) at 10 mg/kg, then moistened to 50% of water holding capacity before aging for 30 days under aerobic conditions. The aged soil was then applied to the top of untreated soil columns containing the same soil. The soil columns were leached for 45 days with simulated rainfall corresponding to 12.7 mm per day. The leachate was collected daily and analysed by liquid scintillation counting. After the leaching, the soils were separated into layers (2 cm high) then the extractable and non-extractable radioactivity determined.

After leaching there was 16% of recovered radioactivity was in the leachate, 55% in the first 4 cm of the soil and remainder distributed throughout the column. The metabolites in the soil were not investigated.

Extraction of leachates followed by TLC showed that there was two principal products, MMTP sulfoxide and the corresponding sulfone at 4.48 and 2.75% of recovered radioactivity respectively. There were other minor metabolites, including the oxidation products for fenthion (fenthion sulfoxide and sulfone).

It was concluded that metabolites from soil metabolism could leach.

#### 5.3 Volatilisation

No studies on the volatilisation of fenthion were presented.

Based on the vapour pressure  $(4.7 \times 10^4 \, \text{Pa} \, @ \, 20^{\circ} \text{C})$ , given on page 2, Physico-Chemical P), fenthion is rated as very slightly volatile (Mensink, Montforts, Wijkhuizen-Maslankiecz, Tibosch and Linders (1995)). The low Henry's Law constant together with the rapid degradation in both water and soil will limit the volatility to minimal levels. Volatilisation is unlikely to be a significant route of dissipation in the environment.

# Hellpointner, 1994

The half life of fenthion in the troposphere was determined using a computer model Atmospheric Oxidation Program (AOP). The model is based on the reaction of hydroxyl radicals with the various chemical groups within fenthion. Using a radical concentration in the atmosphere as  $1.5 \times 10^6$  OH radicals/cm<sup>3</sup> over a 12 hour day, the half life of fenthion was calculated as 1.69 hours and the chemical lifetime in the air as 2.44 hours (average duration of fenthion molecules in the atmosphere).

It is concluded that vapours of fenthion will be rapidly degraded in the atmosphere.

# 6 Field Studies

There were no modern field studies presented, with the registrant indicating none are available.

There were 4 old studies on the persistence of fenthion in four soils from the USA (Anon. 1967 A-E). These studies were just one page summaries with limited information. Table 18 summarises the results. These results are of limited value and are not considered useable.

Table 18. Dissipation of fenthion in three soil types and 2 formulation types. The soil were treated then incorporated to 15 cm depth at 2 mg/kg. Half-lives were determined using Timme-Frehse.

Soil type	Formulation	Samp	Sampling DAT and results, mg/kg					
	type						DT <sub>90</sub> days	
Clay	S.C.	DAT	1	30	86			
		ppm	0.5	0.3	< 0.1			
	Granular	DAT	1	30	86	176	9.5	
		ppm	1.9	0.6	0.1	< 0.1	69	
Silt loam	S.C.	DAT	1	30	84			
		ppm	1.0	0.2	< 0.1			
	Granular	DAT	1	30	84	181	9.5	
		ppm	1.8	0.8	0.1	< 0.1	70	
Muck sand	S.C.	DAT	1	32	112	182	64	
		ppm	0.4	0.3	0.2	< 0.1	214	
	Granular	DAT	1	32	112			
		ppm	1.2	0.6	< 0.1			

# **Graney**, 1988

The document is a review of the results of field studies conducted with fenthion presented to the USEPA as part of Mobay response to a 1988 reregistration requirement from the US EPA. A summary table from this report is reproduced in ecotoxicology-field studies. While there are several comments on rapid dissipation, there are other comments on the slow dissipation leading to possible chronic effects and environmental impacts.

# 6.1 Modelling Study

#### Schäfer and Leicht, 1995.

The concentration of fenthion in groundwater was calculated using a model, PELMO (based on the US EPA PRZM-1) for application to cherry orchard in Germany and an olive grove. The application was assumed to be yearly with the rate of 800 g ac/ha for cherries and for olives 2 applications, 1 month apart, at 1.25 kg ac/ha. It was assumed that 50% of applied reached the soil. The results for 10 years of model data showed no fenthion below 110 cm of soil (the model's simulated soil profile). Note that for the olives the model used German weather data (from Hamburg in 1961) rather than that for a Mediterranean climate.

# Anonymous, 1987a

Groundwater samples were collected from 8 locations in Japan over a 2 year period and analysed for a number of pesticides by GC, including fenthion and its oxidation

metabolites. Recoveries were acceptable at 0.5  $\mu$ g/L, lowest limit tested, and detection limit given as 0.04  $\mu$ g/L for total fenthion (fenthion plus oxidation metabolites). Total fenthion was below the detection limit for all samples.

# Anonymous, 1987b

River water samples were collected from two rivers in Japan, the Shinano (on the west coast) and Kinu-Tone Rivers (north of Tokyo). The rivers were sampled on 8 and 9 dates respectively from spring to winter and analysed by GC for fenthion and its metabolites (edifenphos was also analysed). The rivers were sampled at several sites up and down stream on each sample date. The results were given as total fenthion (sum of fenthion plus oxidation metabolites). The detection limit was 0.2 µg/L.

For the Shinano River there were detections of total fenthion during summer in samples taken in June and July (June 17, July 7 and 29), with the highest detection of 0.4  $\mu$ g/L. On all other dates there were no detections, ie <0.2  $\mu$ g/L. For the Kinu-Tone River the detections were again in Summer (May 29, June 26, July 16 and 30) with the highest detections occurring in May and June of 1.4 and 0.6  $\mu$ g/L respectively. The detection in July were at the limit of detection (0.2  $\mu$ g/L). There was no comment on the pattern of detections although it is likely that they reflect usage in rice cultivation.

# 6.1.1 Literature

#### Iwakuma, Shiraishi, Nohara and Takamura, 1993.

Residues of pesticide in water and sediment were surveyed in the Koise river system during rice cultivation (May to September). Seven sampling sites were used including an up-stream site. A number of pesticides were noted with the maximum concentration of fenthion occurring after planting at 6.6  $\mu$ g/L at one sampling site. Other downstream sites had levels of 2.8  $\mu$ g/L at the same time. A small isolated peak of fenthion was noted in August but the authors indicate that this might be caused by aerial spraying that was conducted just before sampling. They did not indicate if fenthion was actually being aerially sprayed.

# Wang, Lenahan and Tucker, 1987

Fenthion was aerially applied above a salt marsh as a thermal fog at 32 g/ha. This was a typical application for Florida to control mosquitoes on the wing. The concentrations on filter paper, placed under the flight path, showed mean deposition of 18.6, 0.87, 1.25 and 0.39 ng/cm² for tests 1 through to 4. The peak concentrations in the ditch underneath the flight path was 1.69 to 0.16  $\mu$ g/L for tests 1, 3 and 4 and a trace in test 2. Note that the ditch was tidal which could have affected the measurements. The concentration of fenthion gradually decreased and after 24 hours was non-detectable (detection limit stated to be 0.01  $\mu$ g/L) in the ditch water. These results were presented graphically only.

In another paper tables of results from this study were presented (Wang, Lenahan, Tucker and Kadlac, 1987). While there was some additional information there was insufficient to determine a half-life in the ditch.

# 7 Bioaccumulation

# Ishikawa, Yoshimoto, Ueyama and Takase, 1979

The bioaccumulation of fenthion was studied in carp (*Cyprinus carpio*) and rainbow trout (*Salmo gairdneri*). The study was not performed to meet any Guidelines.

The fish were exposed to water containing fenthion at a concentration of 20 and 200  $\mu g/L$  (nominal) under flow-through conditions. The water was sampled before the study and during the bioaccumulation phase. The concentration of fenthion remained relatively constant before commencement and throughout the study with a range of 9 to 12  $\mu g/L$  and 100  $\mu g/L$  for the low and high doses respectively, as determined by GC analysis.

The accumulation phase lasted for 28 days for carp and 42 days for trout with the depuration phase lasting for 15 days for carp and 7 days for trout. The fish were sampled at 3 and 7 days then weekly during the uptake phases. For the depuration phase sampling occurred on days 3, 6 and 15 days for carp and 1, 4 and 7 days for trout. Whole fish were analysed by extraction, oxidation of extracts and GC analysis. Due to problems with interfering peaks in the GC, fenthion could not be analysed separately from the other peaks. The accumulation reached a plateau by day 14. Carp showed the maximum bioconcentration factors of 1956 (10  $\mu$ g/L) and 2312 (100  $\mu$ g/L) with maximum BCF for trout of 702. (Note that the BCF were calculated on fenthion in water and fenthion plus all oxidation metabolites in fish.)

The depuration was fast, with >95% reduction in the residues in the carp tissues by day 15 of the depuration phase and for trout 96% elimination occurred by day 4 of the depuration phase.

The study clearly shows that bioaccumulation of fenthion and its oxidation metabolites is species dependent, with BCF of 2300 and 700 for carp and rainbow trout respectively. Depuration of fenthion and metabolites is fast for both species. Bioaccumulation of fenthion or its metabolites is not expected. It should be noted that these results for carp would classify fenthion as a bioaccumulating but all other results indicate the fenthion is low to moderately bioaccumulating.

# Lamb, 1975

The bioaccumulation of fenthion was studied in bluegill sunfish (*Lepomis macrochirus*). The study was not performed to meet any Guidelines.

The fish were exposed to water containing  $^{14}C$ -fenthion at a concentration of 10 and 100  $\mu g/L$  (nominal) under flow-through conditions. The water was sampled before the study and during the bioaccumulation phase. The concentration of fenthion remained relatively constant before commencement and throughout the study with a range of 8 to 11  $\mu g/L$  and 108 to 115  $\mu g/L$  for the low and high doses respectively, as determined by radiometric analysis.

The accumulation phase lasted for 14 days and the depuration for 11 days. The fish were sampled at 0 (6 hours), 1, 4, 7, 10, 14, days during the uptake phase and on days 1, 4, 7, and 11 for the depuration phase. Whole fish were analysed by radiometric analysis. The accumulation reached a plateau of between BCF 400-500 by the fourth day and remained within this range for both concentrations. Extraction and TLC analysis of the fish tissues on day 11 showed that 28% of the radioactivity was due to parent and 8% due to fenthion sulfoxide with 62% of the radioactivity remaining in the water phase following chloroform extraction. None of the activity in the water was identified with known metabolites. The depuration was fast, with >99% reduction in the radioactivity in the fish tissues by day 7 of the depuration phase.

An additional study was conducted where fenthion was applied at 11.2 g ac/ha to the surface of an aquaria containing soil and water (one third of the surface area was soil and the rest water). The aquaria contained both bluegill and catfish. Samples of fish were collected at 15 minutes, 1, 2, 4, 8 hours, 1, 3, 6, 14 and 28 days after exposure. Radioactivity in the organic extracts was 4.2 ppb as fenthion and decreased to 3.0 ppb before increasing to 4.2 ppb after 3 days. The nature of the radioactivity was not determined. The maximum accumulation factors occurred after 8 hours of 118 and 144 for bluegill and catfish respectively.

The study clearly shows that bioaccumulation of fenthion is limited with rapid depuration of fenthion and metabolites. Bioaccumulation of fenthion or its metabolites is not expected.

#### 7.1 Literature

# Bruijn and Hermans, 1991

In a study on the uptake and elimination of a number of organophosphorous pesticides in the guppy (*Poecila reticulata*) and correlation with the octanol/water coefficient, the bioaccumulation factor for fenthion was determined as 16,600, based on extractable lipid. This is based on steady state concentration of active during exposure to flow-though conditions with GC analysis of the fish (3 fish per sample). The percentage lipid in the fish was not given but assuming approximately 3%, the results are similar to that of Lamb (1975) above.

#### Hall and Kolbe, 1980

As part of a study where tadpoles where exposed to fenthion under flow-through conditions before being fed to mallard ducks, the bioaccumulation factor for fenthion in tadpoles was determined as 62 from 96 hours exposure in water.

# Tsuda, Aoki, Kojima and Fujita, 1992

The paper reports on the accumulation and excretion of a number of organophosphorus pesticides by the willow shiner (*Gnathopogon caerulescens*). The fish were exposed to fenthion under flow-through conditions at an average concentration of 0.6 µg/L for 7 days. Three fish were sampled on days 1, 3, 5 and 7 following exposure. Analysis of water and fish used a GC method with satisfactory recoveries from both water and fish. The bioaccumulation factors for fenthion were 388, 654, 410 and 472 for days 1, 3, 5 and 7 respectively, with an average of 481. In the excretion experiment the half-life for fenthion was given as 9.9 hours.

# Tsuda, Kojima, Harada, Nakajima and Aoki, 1996

The accumulation and excretion of fenthion and two metabolites, fenthion sulfoxide and the sulfone, using killifish (*Oryias latipes*) was studied under flow through conditions. The accumulation phase lasted for 6 days and the excretion for 2 days. For fenthion the BCF were 154 after 48-144 hours (low dose, 1.1  $\mu$ g/L) and 170 after 72-144 hours exposure (high dose, 7.1  $\mu$ g/L). The BCF for the metabolites were determined as 1.7 for fenthion sulfoxide after 3-144 hours exposure and 3.2 for fenthion sulfone after 48-144 hours exposure. The excretion half-lives were 3.5, 2.9 and 4.3 hours for fenthion (both high and low dose), fenthion sulfoxide and the sulfone respectively.

# 8 Summary of Environmental Fate and Degradation

# 8.1 Hydrolysis

From three experiments, it may be concluded hydrolysis of fenthion is relatively slow at pH 5, 7 and 9 and is classified as slightly hydrolysing. At pH 9 the hydrolysis is slightly faster but still rated as slightly hydrolysing. Hydrolysis is unlikely to be a significant contributor to the overall degradation of fenthion in the environment.

# 8.2 Photolysis

# 8.2.1 Aquatic

Based on two laboratory studies using artificial sunlight lamps, the half-life for photodegradation in water is approximately 30 minutes with photo-oxidation and hydrolysis products the major degradates. Degradation in natural sunlight was slower with one study determining a half-life in sunlight in Europe of 4 hours. A study on photo-degradation, performed to German Guidelines and based on the experimental quantum yield of fenthion, calculated a half-life in summer and winter Europe of 7.2 and 31.4 hours respectively at 30° N.

The Department of the Environment concludes that photodegradation in water is likely to be a significant route of degradation under environmental conditions.

#### 8.2.2 Soil

A soil photolysis study using natural sunlight showed a half-life of photodegradation of fenthion using air dried soils of 6.6 hours. The major metabolite was identified as fenthion sulfoxide, with little photo-hydrolysis products, indicating that photo-oxidation was the major pathway in soil.

Photodegradation in soil could be a significant route of environmental degradation in Australia, given the high light levels during summer.

# 8.3 Metabolism

# 8.3.1 Aerobic Soil Metabolism

The degradation of fenthion under aerobic conditions was performed to German Guidelines using a silt loam soil, with a half-life of <1 day. The principle metabolite, fenthion sulfoxide formed rapidly after the first day and then declined to 4% after 14 days. Carbon dioxide slowly evolved during the course of the study and reached 50% of recovered radioactivity by the end (120 days). The  $DT_{90}$  was about 5 days under aerobic soil metabolism conditions.

The degradation of fenthion in two Japanese soils, a volcanic ash and alluvial loam, studied under moist and flooded conditions, showed half-lives for total insecticidal activity of between 15-30 days under moistened and flooded conditions. An older study that used 4 soils found there was rapid loss of fenthion in the moist soils, with half-lives of 5.6 and 4.9 days but slower in flooded soils with half-lives for fenthion of 14.6 and 22.3 days. In a study using two Brazilian soils, a clay and loamy sand, approximately 14 and 24% of applied radioactivity mineralised after a month respectively.

# 8.3.2 Aerobic Aquatic Metabolism

The degradation of fenthion in aerobic aqueous conditions is relatively fast, with a half-life of between 7 and 9 days in two water/soil systems. Two major metabolites were formed, desmethylfenthion sulfone and phenol sulfoxide, which were then mineralised to carbon dioxide and other degradates. The degradation pathway appears to be oxidation and/or hydrolysis followed by mineralisation of the hydrolysis products.

In another study the degradation of fenthion was studied under aerobic and anaerobic conditions. Under aerobic conditions  $CO_2$  was produced continuously but under anaerobic conditions  $CO_2$  was not produced until after a lag period of 60-120 days. The metabolites also differed, with oxidation products being the major metabolites under aerobic conditions and hydrolysis products the major metabolites under anaerobic conditions.

In a study using natural pond and sediment the half-life of fenthion was 0.85 days and  $DT_{90}$  of 9.4 days in the aqueous phase. For the total fenthion (sediment + water) the half-life was calculated as 4.5 days and  $DT_{90}$  of 50 days using  $2^{nd}$  order kinetics.

A literature study on the degradation of fenthion in marsh water/sediment systems found that half-lives were between 1.8-7.4 days for non-sterile systems and 14->30 days in the sterile systems. The presence of plants and plants parts increased the rate of degradation. In a similar study the degradation half-lives of fenthion were 3.9, 14.5 and 22 days for non-sterile water/sediment, sterile water/sediment and non-sterile water respectively. Another literature report on the fate of fenthion in salt marshes, the half-lives were 35.5, 33.2 and 105 hours for non-sterile without plants, with plants and sterile (sterilised using formalin) respectively in microcosms.

## 8.3.3 Anaerobic Aquatic Metabolism

The degradation of fenthion under anaerobic conditions was conducted to US EPA Guidelines. Water and sediment (silt loam sediment) from a pond was incubated to give anaerobic conditions then dosed with fenthion. The half-life for the system was 10.7 days and for the water and sediment half-lives were 5.0 and 12.4 days respectively. The major metabolite that was formed (phenol sulfoxide) further degraded quickly.

## 8.4 Mobility

### 8.4.1 Soil adsorption/desorption

The soil adsorption/desorption of fenthion was determined in six soils. The Kocs ranged from 957 to 2660 and show that fenthion is strongly to moderately adsorbed to the six soils tested. Fenthion can be rated as having slight to low mobility in soil (McCall classification). During the desorption the results were consistent with a significant amount of the desorbed material being degradation products.

The Koc for the fenthion and its major metabolites were calculated as 2346, 3703, 2188 and 320 and for fenthion, fenthion sulfoxide, MMTP sulfoxide and MMTP sulfone respectively using a SAR method.

### 8.4.2 Leaching

In 2 aged soil leaching studies using a total of 5 soils, it was shown that the metabolites from soil degradation are more mobile than fenthion itself and these could leach, in particular from soils prone to leaching. It is concluded that the ready degradation together with the strong to moderate adsorption of fenthion indicates that leaching is unlikely but that the metabolites could leach.

## 8.4.3 Volatility

No studies on the volatilisation of fenthion were presented. Based on the vapour pressure fenthion is rated as very slightly volatile and together with the rapid degradation in both water and soil, it was concluded that volatilisation is unlikely to be a significant route of dissipation in the environment.

The half life of fenthion in the troposphere was determined using a computer model Atmospheric Oxidation Program (AOP) as 1.69 hours based on a concentration of 1.5  $\times$  10<sup>6</sup> OH radicals/cm<sup>3</sup> over a 12 hour day. It is concluded that vapours of fenthion will be rapidly degraded in the atmosphere.

## **8.5** Field Dissipation Studies

No modern studies to internationally recognised guidelines were presented.

A paper reviewing older studies was provided. While the review is focused on ecotoxicological effects, there were comments on the rapid dissipation of fenthion in some of the studies reviewed but other comments noted that the dissipation was slow leading to possible chronic effects. The results from older studies where fenthion was applied as either an EC or granular formulation to 3 soils, a clay, silt loam and muck

sand, showed rapid loss of fenthion from the clay and silt loam but slower loss from the muck.

Computer modelling of the leachability of fenthion when used in orchards did not indicate the leaching was likely. A study examining groundwater collected from 8 locations in Japan did not find fenthion or its metabolites to be present above the level of detection of  $0.04~\mu g/L$ .

Literature reports for a river in an intensive rice growing region in Japan showed peak concentration in the river of 6.6  $\mu$ g/L at one monitoring site, with several other sites downstream having levels of 2.8  $\mu$ g/L at the same time. Another literature report showed that when fenthion is used to control adult mosquitoes in Florida by aerial fogging, the peak concentration in a tidal ditch underneath the flight path was 1.69  $\mu$ g/L. The concentration of fenthion decreased and after 24 hours was non-detectable (detection limit stated to be 0.01  $\mu$ g/L).

#### 8.6 Bioaccumulation

The bioaccumulation of fenthion and its oxidation metabolites was studied in carp and rainbow trout, with BCF of 2300 and 700 for carp and rainbow trout respectively for total fenthion plus oxidation metabolites. Depuration of fenthion and metabolites is fast for both species.

In another study steady state bioaccumulation factors were determined to be moderate from a bioaccumulation study using radiolabelled fenthion and bluegill sunfish, with the highest being 500 for the whole body. Elimination of residues was rapid, with >99% of the radioactivity eliminated after 3 days. Other literature studies report bioaccumulation factors of 154 to 480 for a number of fish species and elimination half-lives of <10 hours for fenthion, indicative of rapid depuration. A literature report on the accumulation of the metabolites, fenthion sulfoxide and sulfone, determined bioaccumulation factors of <5 for both metabolites.

Bioaccumulation of fenthion or its oxidation products in the aquatic environment is not expected.

#### 8.7 Conclusion

Fenthion is readily degraded in aquatic environments and readily degraded in soils. Bioaccumulation is not expected. Due to the moderate binding in soil and rapid degradation, leaching is not expected. However, as the principal metabolites are more stable and mobile in soils, these could leach in soils that are prone to leaching.

### 9 Environmental Effects

Most of the following reports were submitted by Bayer in response to the ECRP data call-in. Several of these studies are old and do not meet current requirements.

The regulatory type studies are rated by the Department of the Environment as being reliable, acceptable or for information only. The ratings can be described as:

- Reliable: There is a high level of confidence in the results. The study has been
  performed satisfactorily and while there are only minor problems, they do not
  affect the results.
- Acceptable: The results of the study are scientifically sound but there is a lower level of confidence in the results due to a significant problem or lack of critical information. Often the results are nominal only.
- For information: There are sufficient problems in the test that the results are not suitable for regulatory use.

## 9.1 Avian Toxicity

#### 9.1.1 Acute

The available studies for avian toxicity of fenthion assessed in this review are summarised in Table 19.

Study Type	Study	Species	Age	Results, LD50 or	Rating	Reference
	Guideline			LC50 as ac		
Acute,	US EPA	Bobwhite	21	7.2 (CI 5.2-9.9)	R	Stubblefield
single dose		quail	Weeks	mg/kg		1987a
Acute	US EPA	Bobwhite	10 days	60 (CI 44-82)	A	Stubblefield
dietary		quail		ppm		1987b
	US EPA	Mallard	9 days	1259 (CI 906-	A	Stubblefield

Table 19. Toxicity of fenthion (technical or active ingredient) to avian species.

Ratings used: R = result considered reliable, A = result considered acceptable, I = result for information only.

1985) ppm

1987c

There was only one acute test presented which was considered reliable. In this test 10 Bobwhite quails per treatment group (5 males and 5 female) were dosed with fenthion in corn oil by oral gavage. Dose levels were 0.75, 1.5, 3.0, 6.0, 12.0, 24.0, 48 and 96 mg ac/kg bw. The dosed oil solutions were not analysed. There was 100% mortality of birds dosed with 12 mg/kg or more of fenthion. Statistical analysis of body weights, growth and feed consumption showed statistically significant effects for all parameters in the 6.0 mg/kg treatment group and significant effects on feed consumption only for the 3.0 mg/kg group. The LD50 was determined by probit analysis and the No Observable Effect Concentration (NOEC) was set at 1.5 mg/kg.

#### **Acute Dietary**

The two acute dietary tests were performed to meet US EPA requirements. The birds (10 per treatment) were fed treated feed for five days, then observed for 3 days and the total number of mortalities recorded. Chemical analyses of the treated feed were within 96% of nominal for both the quail and mallard studies. Stability tests (samples of feed stored at room temperature for 6 days) showed <6% degradation had occurred for quail and for mallard feed there was <20% degradation.

Toxic effects (ataxia, wing drop, hyporeactive, tremors, etc) were observed at in all treatment groups for quail with 7 birds affected in the lowest treatment group (31 ppm). For mallards toxic effects were only noted at 489 ppm and all birds were affected. There was severe food avoidance noted in all treatment groups for both the quail chicks and mallard ducklings during the testing period with corresponding differences in body weights. However, all survivors from the treatment groups increased feed consumption when returned to fenthion-free feed at day 5 of the study.

The NOEC for quail was <31 ppm, based on gross observable clinical signs and reduced feed consumption and NOEC for mallards was <65 ppm based on feed consumption and reduced body weights.

These studies are considered acceptable.

## 9.1.2 Chronic Testing

No chronic tests available.

# 9.1.3 Literature Reports

### Keith, Ngondi, Bruggers, Kimball and Elliott, 1994

Fenthion (Queletox 60% ac) was applied to two bird roosts in Kenya at 2.88 and 12.0 kg ac/ha for Njoro dam and Gicheha farm dam respectively. Measured fenthion deposits reached 1.1 kg ac/ha. Following these applications, 61 birds of 14 species at the Njoro site and 22 birds of 8 species at the farm site were found dead or severely debilitated. The carcass searches at the Njoro site were limited to the edges of the dam as there was an impenetrable standing of cattails covering the roost site. Residues of fenthion on the carcasses (feathers) ranged from 12 to 750  $\mu$ g per carcass with a mean of 330  $\mu$ g. The authors note that a large raptor with bodyweight of approximately 1 kg was observed eating 4 dead birds, which could indicate that raptors may be exposed to lethal doses, based on the LD50 for American Kestrels of 1.3 mg/kg.

While this paper is of limited reference to Australia, as bird roosts are not expected to be treated, it does indicate that if birds were to be sprayed with fenthion at reasonably high rates significant bird mortalities and secondary effects could be expected.

### Hall and Kobe, 1980

Tadpoles were exposed to fenthion (and other OPs) in water before being fed to mallard ducklings (2 weeks old). In the first test, tadpoles were exposed to fenthion at 5 mg/L in flow-through conditions before being force fed to the ducklings (4 birds used). After 15 hours all ducklings died. In the second test, the tadpoles were

exposed to logarithmically spaced concentrations in water for 96 hours before being fed to the ducklings. The concentration of fenthion in the water exposures as well as concentration in tadpole tissues was determined by GC. Four out of 6 ducklings (67%) fed tadpoles exposed at 2.2 mg/L died. Measurements of the birds cholinesterase activity showed a strong dose response curve with relationship to the concentration of fenthion that the tadpoles were exposed to. The BCF for fenthion in tadpoles was determined as 62.

The authors note that a rough estimate for the LD50 of 4.9 mg/kg indicates that most of the toxicity was due to parent compound and that for 50% inhibition of the birds cholinesterase the level in water would be 0.78 mg/L.

## Other Avian End-points

A database from the Office of Pesticide Programs (OPP), US EPA (2008), contains the presently known ecotoxicity endpoints for registered pesticides used in the US. The toxicity data put into the database is compiled from actual studies reviewed by EPA in conjunction with pesticide registration or re-registration. These have been reviewed by Ecological Effects Branch biologists, judged to meet US EPA Guidelines, and therefore acceptable for use in the ecological risk assessment process. The studies are ranked as either core or supplemental (equivalent to reliable and acceptable used in this report). It should be noted, however, that some of these studies use nominal results and some care is needed in using these for the risk assessment.

Table 20. Summary of avian toxicity studies reviewed by the	e US EPA and found
acceptable by them.	

Species	Study	US EPA Test	Type, duration,	LD <sub>50</sub> or LC <sub>50</sub>
•	date	Guideline &	test material, %ac	50 50
		category*		
Mallard duck	1984	71-1a, S	Oral, 14 d, 90%	5.94 mg/kg
Japanese quail	1984	71-1, S	Oral, 14 d, 99%	10.6 mg/kg
Ring-necked pheasant	1984	71-1, S	Oral, 14 d, 99%	17.8 mg/kg
Chukar (Alectoris chukar)	1984	71-1, S	Oral, 14 d, 90%	25.9 mg/kg
Rock dove (Columba livia)	1984	71-1, S	Oral, 14 d, 99%	4.63 mg/kg
Canada goose	1984	71-1, S	Oral, 14 d, 99%	12 mg/kg
California quail	1984	71-1, S	Oral, 14 d, 99%	15 mg/kg
Mourning dove (Zenaida	1984	71-1, S	Oral, 14 d, 99%	2.5 mg/kg
macroura)				
House finch (Carpodacus	1984	71-1, S	Oral, 14 d, 99%	10 mg/kg
mexicanus)				
House sparrow	1984	71-1, S	Oral, 14 d, 99%	22.7 mg/kg
Bobwhite quail	1975	71-2a, C	Dietary, 8 d, Tech	30 ppm
Mallard duck	1975	71-2b, C	Dietary, 8 d, Tech	231 ppm
Japanese quail	1975	71-2a, S	Dietary, 8 d, Tech	86 ppm
Ring-necked pheasant	1975	71-2, C	Dietary, 8 d, Tech	202 ppm
Common grackle	1982	71-2, S	Dietary, 8 d, Tech	30 ppm
(Quiscalus quiscula)				

<sup>\*</sup> C = core, S = satisfactory.

As can be seen in Table 20 the acute oral toxicity to birds ranges from 2.5 mg/kg for the mourning dove to 25.9 mg/kg for the chukar and the acute dietary toxicity ranges

from 30 ppm for the common grackle to 231 ppm for mallard duck. These results are less than those in Table 19, indicating that over a large range of studies fenthion is more toxic. However, these studies have not be seen by the Department of the Environment but do give a broader indicating that the results for bobwhite quail in Table 19 represent a sensitive bird species, although not the most sensitive.

# 9.1.4 Reports of Australian Incidents

Fenthion was involved in a reported bird poisoning incident in Australia in Bowen area, Queensland (Bowen Independent, Wednesday 11 August 1999). The species affected and the numbers were not given in these reports. Follow up information provided to the Department of the Environment concerning this incident from Queensland Environmental Protection Agency indicates that birds of all description, including raptors, were affected and a local fruit grower was illegally using fenthion to prevent bird damage to his fruit.

### McKenzie, Lanham, Taylor, Gibson and Pierce, 1996.

Six incidents of poisoning of native birds over a 13 month period were investigated by the Queensland Department of Primary Industries in 1993-1994. In total 350 birds were found dead, with the major incident at a grain depot, 200 dead. Examination of the carcases showed fenthion present in the alimentary tract contents. It could not be determined if these deaths were from normal use but due to the number and occurrence in areas not associated with use of fenthion, it was considered that a significant number were due to malicious poisoning using fenthion.

### Schulz, 2001.

The South Australian State Government's primary industries department (PIRSA) acknowledged that birds were fatally poisoned from fenthion being sprayed to eradicate fruit fly around Clarence Park, Adelaide. The poisoned birds included native species, sparrows, starlings, pigeons and blackbirds. Many of them showed levels of fenthion in their tissue.

### Media reports, November 2004.

In November 2004, articles appearing in various newspapers suggested a potential risk of fenthion being carried to outdoor dining areas via the claws of poisoned birds. The Victorian "Herald Sun" also ran articles on the deaths of a pair of peregrine falcons and their chicks that had lived in the Melbourne Central Business District with the suggestion that the deaths were caused as a result of the falcons' eating pigeons that had been poisoned by the use of fenthion containing avicide products.

#### Animal Health Australia, 2009.

Eight Australian magpies, two crows and an Australian white ibis were found dead at a school in Wavell Heights, Brisbane in October. Significant levels of fenthion (3 mg/kg [bw]) and chlorpyrifos (26 mg/kg [bw]) were detected and quantified in two of the magpies.

### Australian Wildlife Health Network, 2012.

Between January and June 2012, there were four Western Australian events of confirmed or suspected organophosphate poisoning involving 33 little corellas. Presenting signs included weakness, neurological signs and death. In two events fenthion was detected in the gut contents.

## 9.1.5 Reports of Overseas Incidents

Most incident reports from overseas are from the USA and are available from the US EPA RED via the net (

http://www.epa.gov/pesticides/reregistration/REDs/0290ired.pdf)

As part of its re-registration process, the US EPA lists large number of reported incidents where 'Rid-A Bird Perches' had been used and subsequently raptors had died by feeding on the dead and dying target birds (normally starlings and pigeons in buildings). The addendum to the US EPA's Environmental Fate and Effects Assessment lists 15 separate confirmed (enough circumstantial evidence to link them with fenthion use) incidents where raptors (hawks, owls, eagles etc) were affected, and another 5 similar incidents where the use of the fenthion-impregnated perches were suspected. The only non-raptor (apart from the targets) species mentioned are 3 crows and some barn swallows. The former had eaten dead starlings which had been picked up and spread with a manure spreader on a field, whereas the latter are most likely to have been exposed through landing on a perch. Apart from this there is only one documented incident of an owl landing on a perch, with the majority attributed to secondary poisoning through the taking of sick birds or scavenging upon their carcases. Analysis of these clearly indicated the presence of fenthion in the intestines of these raptors at levels up to 55 ppm. More importantly in 2 cases residues on the starlings' feet upon which the birds had been feeding indicated these were 282 and 479.3 ppm respectively. Note that this product was cancelled in 1998.

Use to control adult mosquitoes has resulted in several incidents of avian mortalities in the USA, the most recent in the late nineties. The report states that:

The FWS (US Fish and Wildlife Service) investigator reported that dead and/or sick birds were found on at least 12 occasions between October, 1998, and August, 1999. The incidents occurred after aerial (helicopter) ULV application of Baytex at a rate of 2/3 ounce of Baytex (0.05 lb ai) per acre [56 g ai/ha], which conforms to the label application rate for aerial spraying. The FWS investigator observed dead and sick birds after several sprays, and others were reported by concerned citizens. According to the documentation, sprays were made over the beach early in the morning, and sick and dead birds were observed on the beach within 8-10 hours.

The US EPA also indicated several incidents in California also due to use as mosquito/midge control.

These reports highlight a concern with the use for fenthion, in particular due to the low rates used that resulted in these reported avian mortalities.

## 9.2 Aquatic Toxicity

# 9.2.1 Regulatory Studies for Fish

The following aquatic toxicity results for fenthion and an emulsifiable concentrate formulation of fenthion were presented by Bayer.

Table 21. Toxicity of Fenthion technical to fish.

Test	Test method	Species	Results LC50,	References
			mg ac/L	
96 hour acute static	US EPA 72-1	Rainbow trout	0.83* (0.49-3.3) <sup>a</sup>	Swigert, 1986
96 hour acute flow-through	US EPA 72-1	Bluegill	1.7* (0.95-3.6) <sup>a</sup>	Swigert, 1987
96 hour acute static	US EPA 72-1	Bluegill	1.6** (1.3-1.9) a	Carlisle and Roney, 1984
96 hour acute static	OECD	Golden Orfe	2.36** (2.32-2.44) a,c	Dorgerloh, 1994a
96 hour acute static	OECD	Rainbow trout	1.26** (0.71-6.9) a,c	Dorgerloh, 1994b
96 hour acute static		Golden Orfe	2.7** (2.6-2.9) a,c	Hermann, 1979
96 hour acute static		Rainbow trout	0.87** (0.74-1.00) <sup>a</sup>	Hermann, 1978
96 hour acute flow-through	US EPA	Sheepshead minnow	1.2 (0.87-1.4) <sup>a</sup>	Surprenant 1988a
Early life stage, embryos and larvae, 88 days	US EPA 72-4	Rainbow trout	MATC 0.013-0.027 Geometric mean 0.019	Surprenant, 1988b

<sup>\*</sup>Results calculated using nonlinear interpolation between confidence limits \*\* Results are nominal.

r Result considered reliable, a result considered acceptable, results converted from EUP to active ingredient.

The acute toxicity studies for bluegill (Swigert, 1987) and rainbow trout (Swigert, 1986) are acceptable. The results are based on mean measured concentrations with measurements taken at time 0, 48 and 96 hours after exposure. The highest concentrations tested, 8.0 and 5.0 mg/L nominal for bluegill and trout respectively, had an oily film present at all sampling, which was considered to have interfered with the 96 h sample for bluegill. This was not considered to affect the study as there was 100% mortality in both these treatments and the next lower treatment group. Measurements of temperature, dissolved oxygen and pH were all satisfactory during the tests. The data was not suitable for probit analysis and the results in Table 21 are from nonlinear interpolation. Using Trimmed-Spearman the LC50 is 1.76 (1.52-2.05) mg/L for bluegill and 0.81 (0.68-0.97) mg/L for rainbow trout.

The results for bluegill (Carlisle and Roney, 1984) were not conducted to any International Guidelines and the report is lacking some details on the conditions used and there is limited the raw data provided. However, the study was conducted under GLP and there are sufficient details on the methodology used to indicate that if additional data had been presented, the study could meet the 1984 US EPA Guidelines. The test solutions were not analysed and the LC50 was based on probit

analysis. Despite the lack of raw data and analysis of the test solutions, the LC50 was considered acceptable.

### Dorgerloh, 1994a

The report for golden orfe by Dorgerloh was a revised report from original study conducted in 1978/79, rewritten to meet OECD reporting requirements. The test substance used was Lebaycid 500 EC (550 g ac/L). The testing was conducted over a 4 month period with 6 concentrations tested, 3.4, 4.0, 4.2, 4.4, 4.6 and 4.8 mg/L of the test substance. The test solutions were not analysed for concentration of test material, although a stability control dosed at 1 mg/L of active ingredient was tested after 2, 48 and 96 hours with 67% of nominal after 2 hours increasing to 80% after 96 hours. This was taken as evidence that the solution was sufficiently stable during the testing.

Most of the tests were conducted on different dates, ranging from a week to 4 week between tests and only one test concentration tested at a time. For each test there was a control used with a total of 13 controls. In determining the LC50 all the data was pooled, with the same test concentrations considered as replicates, which is not statistically valid. However, while the study does not meet current requirements, the result is expected to be a true reflection of the actual LC50 for this species and is considered acceptable, noting that the result is nominal. The NOEC was <3.4 mg/L (1.87 mg ac/L), based on the irregular swimming behaviour of all fish at 3.4 mg/L.

### Dorgerloh, 1994b

The report is similar to that above in that it is a revised report from original study rewritten to met OECD reporting requirements and using the same test substance, Lebaycid 500 EC. The testing was conducted over a 2 month period, again with one test concentration tested at each date and 7 concentrations tested, 0.8, 1.0, 1.7, 2.0, 2.4, 2.8 and 4.0 mg/L of the test substance. The results in Table 21 are as given in the report using probit analysis of the results. The NOEC was given as <0.8 mg/L (0.44 mg ac/L) based on irregular behaviour of all fish at 0.8 mg/L.

### Hermann, 1978 and 1979

The two results from Hermann were conducted before Guidelines for testing were introduced and used pure active ingredient. The test solutions were not analysed and the results are nominal. The water temperature used for the trout study was higher than current Guidelines indicate, 16° C, but as there were no mortalities or effects noted in the control, this does to appear to affect the results. The results are considered as acceptable.

### Surprenant 1988a

The flow-through test using sheepshead minnow was performed using the TGAC and according to US EPA Guidelines. Analysis of the test solution showed that the test concentrations were 62-69% of nominal and were consistent throughout the 96 hour test. As there was only one partial response, the LC50 was determined by binomial probability and the NOEC is 0.61 mg ac/L, based on irregular swimming behaviour of the fish at 0.87 mg ac/L. Using Trimmed Spearman, the Department of the Environment calculated an LD50 of 1.23 (1.13-1.34) mg ac/L.

#### Surprenant, 1988b

As a substitute for a full life-cycle toxicity test, the toxicity of fenthion to the embryos and larvae of Sheepshead minnows was determined under flow through conditions according to US EPA Guideline 72-4. The rationale, as stated by the authors of this study, is based on the observation that these embryo/larvae studies are reasonably accurate short-term predictors of the chronic life cycle studies. The criteria used to determine the MATC (Maximum Acceptable Toxicant Concentration) was based on larval growth (length) at the termination of the test. Analysis of the test solutions showed that the mean test concentrations were 71-90% of nominal over the test period. While there was a significant deviation from the test protocol, in that 20 viable embryos were selected before hatching with surviving larvae released for the 60 day post-hatch exposures rather than 20 fry post-hatch as stated in the protocol, this is unlikely to affect the study and the deviation is acceptable. The study was well performed and it meets the current Guidelines. The results are considered reliable and would suggest a high acute to chronic ratio.

### **Acute Fish Toxicity for Metabolites**

#### Waggoner, 1989

The toxicity of the phenol metabolites MMTP sulfoxide and MMTP sulfone to rainbow trout and bluegill was determined under static conditions. Analysis of the highest test solution (100 mg/L) showed that all solutions were with 93% of nominal. There were no treatment related effects for either phenol in any of the tests at 100 mg/L. The two phenols are therefore rated as being practically non-toxic to fish.

# 9.2.2 Regulatory Studies for Invertebrates

The following studies on the toxicity of fenthion to aquatic invertebrates were presented by the registrants and have been summarised in Table 22.

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Results EC50, Species Test Test method References μg ac/L 48 h mortality US EPA Daphnia LC50 5.2 (4.6-6.0) r Forbis, 1987 flow-through magna 48 h **OECD** Daphnia EC50 5.7 (4.1-7.8)<sup>r</sup> Heimbach, 1985a static magna US EPA Forbis, 1988 21 day chronic Daphnia MATC 0.042-0.082 flow-through magna (Geometric mean  $(0.059)^{r}$ MATC\*\*\* 0.009-21 day chronic **OECD** Daphnia Adema, Dalsum 0.016 a,c and Bommel, 1989 static renewal magna Mysid shrimp 96 h mortality, US EPA LC50 0.22 (0.19-Surprenant, 1988c flow through  $0.27)^{a}$  $1.04^{**} (0.56-1.8)^{r}$ 28 day Proposed BBA Chironomus Heimbach, 1995 emergence Guideline riparius static US EPA 96 h, flow Eastern 370 (140-1000)<sup>r</sup> Surprenant, 1988d through Oysters

Table 22. Toxicity of fenthion to aquatic invertebrates.

ingredient.

The acute 48 hours daphnia test was conducted according to US EPA Guidelines under flow-through conditions. The mean measured test concentrations for 0 and 48 hours were similar and the overall mean concentrations used to determine the LC50. There were 10 daphnids, <24 hours old, used per replicate and 4 replicates per test concentration. The LC50 was determined using probit analysis. This was a well conducted study and the results are considered as reliable.

#### Heimbach, 1985a

The 48 hour mortality test was conducted according to OECD 202 Guidelines using the TGAC and nominal concentrations were 1.8, 3.2, 5.6, 10, 18, 32, 56 and 100  $\mu$ g/L. The test solutions were not analysed. A positive control gave satisfactory results and physical parameters (temperature, dissolved oxygen and pH) of the test solutions were satisfactory. The results are considered acceptable.

### **Forbis**, 1988

A 21 day reproduction study was performed according to US EPA Guideline 72-4 using <sup>14</sup>C-fenthion under flow-through conditions. The mean concentrations of the test solutions used were 0.013, 0.021, 0.042, 0.082, and 0.20 µg ac/L. Analysis was by extraction of the test water followed by radioanalyses of the extract. Spiked samples (4.19, 22.1 and 236 ng/L) showed a mean recovery of 95% with a range of 91-97%. The methodology is satisfactory.

There was 100% mortality in the highest concentration after 13 days and 12% mortality in the next lowest test concentration. Statistically significant effects on reproduction and mean adult length occurred at 0.082  $\mu g/L$ , with no statistically significant effect on reproduction or growth (body length) at the lower concentrations.

<sup>\*</sup> Results calculated using nonlinear interpolation between confidence limits \*\* Results are nominal.

The Result considered reliable, a result considered acceptable, results converted from EUP to active

Forbis, 1987

The MATC of 0.042- $0.082~\mu g/L$  was determined (geometric mean of  $0.059~\mu g/L$ ). The result is considered reliable.

#### Adema, Dalsum and Bommel, 1989

A 21 day reproduction study was performed according to OECD Guideline 202 under semi-static conditions using Lebaycid EC 50 containing fenthion at 50.3%. The test solutions used were 0.0056, 0.01, 0.018, 0.032, 0.056 and 0.1  $\mu$ g/L nominal of test material. Solutions were renewed on Monday, Wednesday and Friday. Analysis of the test solutions showed all were below the limit of detection of 1.0  $\mu$ g/L. There was only 20% mortality in the highest concentration 0.1  $\mu$ g/L after 21 days with statistically significant effects on reproduction at 0.032  $\mu$ g/L and approximately 50% reduction in repopulation at the highest test concentration. An EC50 was estimated to be 0.1  $\mu$ g/L, based on reproduction. The MATC of 0.018-0.032  $\mu$ g/L (0.009-0.0016  $\mu$ g ac/L) was determined for reproduction. Effects on subjective parameters were noted at 0.1 (size), 0.056 (swimming behaviour) and 0.032 (colour)  $\mu$ g/L. The results are considered acceptable.

### Surprenant, 1988c

The mysid shrimp study was performed according to US EPA Guidelines under flow through conditions using radiolabelled fenthion. The test concentrations were analysed at time 0, 48 and 96 hours by extraction and radioanalysis of the extracts. Preliminary studies showed that the method gave 93% recovery with a limit of reporting of 12 ng/L. The highest test concentration 500 ng/L was also analysed by HPLC, which gave consistent results but was at the reporting limit.

The concentration of all the test solutions decreased over the study period, with average measured concentrations of 89, 77 and 46% of nominal at time 0, 48 and 96 hours respectively. For 500 ng/L nominal, the mean measured concentrations were 435, 365 and 190 ng/L for 0, 48 and 96 hours respectively and the HPLC analysis showed similar results, 710, 560 (760 and 360) and 240 ng/L respectively. The quality assurance samples, prepared at each sampling interval, showed that the analysis gave results consistent with their nominal concentrations. The report indicates that the decrease in test concentrations was due to the behaviour of fenthion.

The LC50 was calculated by probit analyses as 220 (190-270) ng/L using mean measured concentrations over the 96 hours. Due to the difficulties encountered in maintaining the test concentrations during the test exposures, the results are considered as acceptable.

### Heimbach, 1995

The influence of fenthion on the development and emergence of larvae of *Chironomus riparius* was conducted according to a proposed BBA Guideline entitled "Effects of plant protection products in the development of sediment—dwelling larvae of *Chironomus riparius* in a water sediment system", dated June 1995.

Fenthion (technical 95.3% ac) was added to a sediment water system (2 cm sediment, 20 cm water, artificial sediment) containing larvae of the test organism. The test concentrations used were 0.1, 0.18, 0.32, 0.56, 1.0, 1.8, 3.2, 5.6 and 10  $\mu$ g/L. Three times during the study, on days 0, 7 and 28, the overlying water and pore water of the

sediment was analysed for fenthion in the treatments 0.32, 1.8 and 10  $\mu$ g/L only, the other treatments were not tested. The physical characteristics (temperature, pH, dissolved  $O_2$ ) of the test water for all concentrations remained relatively consistent during the testing period. The concentration of fenthion declined sharply from initial values of 9.43, 0.93 and 0.16  $\mu$ g/L for nominal concentration of 10, 1.8 and 0.32  $\mu$ g/L respectively to 0.2 and 0.88  $\mu$ g/L in pore water and overlaying water 7 days after treatment (DAT) for the highest concentration. The pore water was 3.8  $\mu$ g/L for 1.8  $\mu$ g/L but the overlaying water was below detection (<0.1  $\mu$ g/L). All samples were below detection for the 28 DAT analysis.

The time for emergence and the number of adult midges that emerged were reported. The EC50 was given as 1.04  $\mu$ g/L (probit) for emergence of midges but confidence limits could not be determined (only one partial result). The confidence limits of 0.56-1.8  $\mu$ g/L in Table 22 are the 0 and 100% effect levels.

### Surprenant, 1988d

The acute toxicity of fenthion (96.9%) to eastern oysters (*Crassostrea virginica*) was determined under flow-though conditions according to US EPA Guidelines. Analysis of the test solutions showed that at time 0 all were above nominal and averaged 144% of nominal. The 48- and 96-hour samples showed that concentration slowly decreased to be close to nominal after 96 hours. The mean concentration were averaged 119% of nominal and were used to determine the EC50 of 370 (140-1000) µg/L. The NOEC was 130 µg/L. The study is rated as reliable.

### **Acute Invertebrate Toxicity - Metabolites**

### Heimbach, 1996

The toxicity of the desmethylfenoxonsulfone (tetramethyl ammonium salt: 90.1% ac) to *Daphnia magna* was determined according to OECD Guideline 202. Ten first instar daphnia (<24 hours) were exposed to test concentrations of 0.1, 0.18, 0.32, 0.56, 1.0, 1.8, 3.2, and 5.6 mg ac/L for 48 hours. The acute exposure concentrations were determined at test initiation and determined to be between 100.0 and 114.4% of nominal. On day 2 only 3 test concentrations were analysed, 0.1, 1.0, and 10 mg/L, and these were 102.0, 104.8 and 98.1% of nominal respectively. The pH, dissolved O<sub>2</sub> and temperature were determined at the start and termination of the test and were satisfactory. The 48 hour EC50 was determined as 3.4 (confidence limits 2.3-5.1) mg/L. While this endpoint was determined using nominal results, the analysis that was conducted clearly shows that this is unlikely to significantly affect the results and therefore the study is rated as reliable.

## 9.2.3 Regulatory Studies for Algae

The following studies on the toxicity of fenthion to algae were presented by the registrants and have been summarised in Table 23.

45

Test Test method Results EC50, References Species mg ac/L **OECD**  $E_bC50\ 0.55$ , Growth Inhibition, Scenedesmus Heimbach, 1985b 96 hours subspicatus E<sub>r</sub>C50 1.79 1.1 (0.87-1.3) Growth Inhibition. US EPA Selenastrum Forbis, 1986 96 hour capricornutum E<sub>b</sub>C50 0.75<sup>c</sup> ISO and OECD Growth Inhibition, Scenedesmus Heimbach, 1989a 96 hours subspicatus Growth Inhibition, US EPA  $10.7(3.2-72)^{1}$ Hughes, 1987a Anabaena flos-7 days aquae Growth Inhibition, US EPA Navicula 1.2 Hughes, 1986a  $(0.67-2.1)^{1, a}$ 7 days pelliculosa Growth inhibition, US EPA Skeletonema 0.33 Hughes, 1986b 7 days costatum

Table 23. Toxicity of fenthion to algae.

US EPA

Lemma gibba

NOEC\*>2.8

Hughes, 1987b

#### Heimbach, 1985b

Growth inhibition

14 days

The algae test was performed to meet OECD Guideline 201. The test solutions were not analysed and results are based on nominal concentrations. The physical measurements of the water quality showed that the pH rose from 8.5 at test initiation to 10.2 after 96 hours in controls and all test concentrations, except for the highest where pH remained relatively stable. Comments in the report indicate that this could be due to the high growth rates. For the reference standard (potassium dichromate) the EC50 values for biomass and growth both agree with known values, indicating that test conditions conform to standards for the test. The  $E_bC50$  was determined as 0.55 mg/L, the  $E_rC50$  as 1.79 mg/L using probit analysis and the 4 day NOECs were <0.10 and 0.56 mg/L for biomass and growth rates respectively. No confidence limits were given. The Department of the Environment recalculated the results (Toxcal, cell per field entered as  $10^6$  cells per mL) to give  $E_bC50$  as 0.98 (0.745-1.65) mg/L using probit analysis.

#### **Forbis**, 1986

This algae test was conducted according to US EPA Guideline 112-2. Analysis of the test solution at time 0 showed that concentrations varied from 88 to 105% of nominal but on termination of the tests (after 96 hours) the samples varied between 46 and 82% of nominal) probably due to degradation. The EC50 in Table 23 was based on mean measured concentrations and calculated using quadratic regressions. The data was not suitable for probit analysis and the EC50 was calculated by the Department of the Environment using trimmed Spearman-Karber as 1.06 (0.72-1.57) mg ac/L.

#### Heimbach, 1989a

The algae test was conducted according to ISO Guidelines and OECD Guideline 201 using Leybacid EC 50 as the test material. The analysis of the test solutions ranged from 78 to 99% of nominal at time 0. The solutions were not analysed again in the

<sup>\*</sup>The NOEC is for inhibition of duckweed. <sup>1</sup> Results recalculated by the Department of the Environment. <sup>r</sup> Result considered reliable, <sup>a</sup> result considered acceptable, <sup>c</sup> result converted from EUP to active ingredient, <sup>i</sup> results for information only.

test. The  $E_bC50$  was 1.5 mg/L (0.75 mg ac/L). A  $E_rC50$  could not be determined and was given as >2.0 mg/L.

### Hughes, 1987a

The algae test using the blue-green alga *Anabaena flos-aquae* was conducted to meet US EPA Guidelines using TGAC as the test substance. Analysis of the test solutions were 40 to 81% of nominal at initiation and at termination of the test were 17, 25 and 36% of nominal for test concentrations of 1.6, 3.2 and 6.4 mg/L nominal. The three lowest test concentrations were less than the detection limit of 0.014 mg/L. The authors note that after 7 days under the growing conditions degradation (mainly photolysis, study conducted under aseptic conditions) or adsorption of the active could have occurred, eg adsorption to alga cells, filters etc (note that the samples were filtered through a membrane to remove cells before extraction), resulting in the loss of active noted in the analysis. In addition, it is noted that the QA samples for day 7 were not acceptable, 0.11, 0.9 and 3.1 mg/L for nominal concentrations of 0.2, 1.5, and 5.0 mg/L, which could indicate a significant problem with the analysis. The mean measured concentration from day 0 and 7 were used to determine the end-points of the study.

There was 21 to 42% inhibition over the duration of the test. End-points were determined by inverse estimation linear regression with the EC25 as 0.19 (0.05-0.56) mg/L and the EC50 as 10.7 (3.2-72) mg/L. The EC50 is not considered acceptable as there were significant problems with the analysis and there was no test concentration with greater than 50% inhibition. The result is for information only.

### Hughes, 1986a

The test was conducted similarly to the above but using the freshwater diatom *Navicula pelliculosa*. The analysis at initiation showed a range from 96 to 100% of nominal concentrations but again after 7 days there was significant loss of active, with only the two highest concentrations (3.2 and 6.4 mg/L nominal) having detectable levels of active (0.50 and 1.5 mg/L respectively). The QA samples were acceptable for day 0 and 7. There was a response of 7 to 99% inhibition across the test concentrations with an EC50 of 0.98 mg/L but confidence limits could not be determined (the results were unsuitable for analysis by probit). When recalculated by the Department of the Environment, the EC50 was 1.2 (0.67-2.1) mg/L using Trimmed Spearman Karber.

### Hughes, 1986b

The test was conducted similarly to the above but using the saltwater algae *Skeletonema costatum*. The analysis at initiation showed a range from 45 to 53% of nominal for nominal concentrations 0.2 to 1.6 mg/L but was 66% and 97% for nominal concentrations of 3.2 and 6.4 mg/L. After 7 days there was significant loss of active, with only the two highest concentrations having detectable levels of active (0.38 and 1.4 mg/L respectively). The QA samples were only 56-64% for day 0 and 65-78% for day 7. There was a response of –9.5 to 99% inhibition across the test concentrations with an EC50 of 0.33 mg/L using inverse estimation least squares linear regression but confidence limits could not be determined. When recalculated by the Department of the Environment using ToxCalc 5.0, the EC50 was 0.30 (0.25-0.35) mg/L using probit.

### Hughes, 1987b

This test using duckweed, *Lemma gibba*, was conducted to US EPA requirements. The nominal concentrations used were 0.2, 0.4, 0.8, 1.6, 3.2 and 6.4 mg/L with initial (time 0) mean measured concentrations (HPLC analysis) of 0.092, 0.19, 0.51, 1.2, 2.5 and 5.4 mg/L. There were problems with the day 14 samples with all test replicates having 'less than' results, ie for 3.2 mg/L nominal the day 14 results were 0.32, <0.24 and <0.24 mg/L (the detection limit ranged from 0.012 for lowest test concentration to 0.60 for highest). This is possible due to adsorption/degradation during the study.

There was no inhibition in any test concentration, although there were problems of algae contamination of controls and some test replicates. While the test does have significant problems with regard to the analysis of the test solutions and contamination, it was clear that fenthion did not significantly affect the growth of duckweed at an overall mean concentration of 2.8 mg/L. As a limit test the result is acceptable.

## 9.2.4 Other Aquatic End-points

A database from the Office of Pesticide Programs (OPP), US EPA (2008), contains the presently known ecotoxicity endpoints for registered pesticides used in the US. The toxicity data put into the database is compiled from actual studies reviewed by EPA in conjunction with pesticide registration or re-registration. These have been reviewed by Ecological Effects Branch biologists, judged to meet US EPA Guidelines, and therefore acceptable for use in the ecological risk assessment process. The studies are ranked as either core or supplemental (equivalent to reliable and acceptable used in this report). It should be noted, however, that some of these studies use nominal results and some care is needed in using these for the risk assessment. The results from this database for fish are in Table 24, those for aquatic invertebrates are given in Table 25 and saltwater aquatic invertebrates in Table 26.

Table 24. Summary of fish studies reviewed by the US EPA and found acceptable by them.

Species	Study date	US EPA Test	Type, duration,	EC or LC	NOEL
Species		Guideline &	test material, %ac	50, μg/L	1,022
		category*	,	718	
Black bullhead	1980	72-1	Static, 96 h	1350	N.R.
Ictalurus melas		S	46		
Bluegill sunfish	1980	72-1	Static, 96 h	1380	N.R.
Lepomis macrochirus		S	47.5		
	1987	72-1a	Flow-though,	1700	410
		C	96 h 96.9		
Brown trout Salmo	1980	72-1	Static, 96 h	1330	N.R.
trutta		C	46		
Carp Cyprinus carpio	1980	72-1	Static, 96 h	1160	N.R.
		S	46		
Channel catfish	1980	72-1	Static, 96 h	1600	N.R.
Ictalurus punctatus		C	46		
	1986	72-1	Flow-through,	650	N.R.
		C	96 h 46		
Coho salmon	1980	72-1	Static, 96 h	1320	N.R.
Oncorhynchus kisutch		C	46		
Cutthroat trout	1980	72-1	Static, 96 h	1580	N.R.
Oncorhynchus clarki		C	97		
	1986	72-1	Flow-through,	1150	N.R.
		S	96 h, 97		
	1986	72-1	Static, 96 h	1020	N.R.
		C	97		
Fathead minnow	1968	72-1	Static, 96 h	3200	N.R.
Pimephales promelas		S	93		
	1986	72-1	Static, 96 h	1680	N.R.
		С	46		
Goldfish Carassius	1986	72-1	Static, 96 h	2780	N.R.
auratus		S	47.5		
Green sunfish Lepomis	1986	72-1	Static, 96 h	1880	N.R.
cyanellus		С	46		
Guppy Poecilia	1968	72-1	Static, 24 h	5810	N.R.
reticulata		S	N.R.		
Lake trout Salvelinus	1986	72-1	Static, 96 h	1450	N.R.
namaycush	1000	C	97	1710	
Largemouth bass	1980	72-1	Static, 96 h	1540	N.R.
Micropterus salmoides	1001	S	47.5	1.000	
	1986	72-1	Flow-through,	1220	N.R.
D 1 1	1077	C	96 h, 97	0.40	
Rainbow trout	1977	72-1	Static, 96 h	840	N.R.
Oncorhynchus mykiss	1000	S 72.1	93	020	NID
	1980	72-1	Static, 96 h	930	N.R.
	1006	C	46	550	NI D
	1986	72-1	Static, 96 h	550	N.R.
	1006	C 72.11	97	920	N D
	1986	72-1b	Flow-through,	830	N.R.
	1000	C	96 h, 96.9	LOEGIS	MD
	1988	72-4a	Flow-through,	LOEC 15	N.R
37.11. 1 P	1000	C 72.1	88 d, 96.9	1.550	NID
Yellow perch <i>Perca</i>	1980	72-1	Static, 96 h	1650	N.R.
flavescens	1	С	46		

Table 24. Continued

Species	Study date	US EPA Test Guideline &	Type, duration, test material, %ac	EC or LC 50, µg/L	NOEL
		category*	·		
Sheepshead minnow	1988	72-3	Flow-through,	1200	610
Cyprinodon variegatus		C	96 h, 97		
Sheepshead minnow	1986	72-3	Static, 48 h, 93	1900	N.R.
Cyprinodon variegatus		S			
Inland silverside	1986	72-3	Static, 48 h, 93	2200	N.R.
Menidia beryllina		S			
Spot Leiostomus	1986	72-3	Flow-through,	1200	N.R.
xanthurus		S	48 h, 93		
Striped mullet Mugil	1986	72-3	Flow-through,	1600	N.R.
cephalus		S	48 h, 93		
Striped bass Morone	1968	72-3	Static, 96 h, N.R.	453	N.R.
saxatilis		S			

<sup>\*</sup> C = core, S = satisfactory.

Table 25. Summary of freshwater aquatic invertebrate studies reviewed by the US EPA and found acceptable by them.

Species	Study date	US EPA Test Guideline & category *	Type, duration, test material, %ac	EC or LC 50, μg/L	NOEL
Water flea <i>Daphnia</i> magna	1986	72-2 S	Static, 48 h, 93	5.7	0.1
	1988	72-4b C	Flow-through, 21 d, 97.9	LOEC 0.021	
Water flea Daphnia pulex	1980	72-2 C	Static, 48 h, 97	0.8	N.R.
Daphnid Simocephalus serrulatus	1980	72-2 C	Static, 48 h, 97	0.62	N.R.
Scud Gammarus lacustris	1980	72-2 C	Static, 96 h, 97	8.4	N.R.
Scud Gammarus fasciatus	1986	72-2 C	Static, 96 h, 97	110	N.R.
Sowbug Asellus brevicaudus	1980	72-2 C	Static, 96 h, 97	1800	N.R.
Crayfish Orconectes nais	1980	72-2 S	Static, 5 d 97	50	N.R.
	1986	72-2 S	Static, 24 h, 97	350	N.R.
Stonefly Pteronarcys californica	1980	72-2 C	Static, 96 h, 97	4.5	N.R.
Stonefly Pteronarcella badia	1986	72-2 C	Static, 96 h, 97	10.7	N.R.
Glass shrimp Palaemonetes kadiakensis	1980	72-2 C	Static, 96 h, 46	10	N.R.

<sup>\*</sup> C = core, S = satisfactory

Table 26. Summary of saltwater aquatic invertebrate studies reviewed by the US EPA and found acceptable by them.

Species	Study date	US EPA Test Guideline & category *	Type, duration, test material, %ac	EC or LC 50, µg/L	NOEL
Mysid Mysidopsis bahia	1988	72-3 C	Flow-through, 96 h,	0.222	0.067
	1986	72-3 C	Flow-through, 96 h, 93	0.15	N.R.
	1985	72-4b S	Static, 14 D, N.R.	LOEC 0.079	0.037
Seed shrimp Cypridopsis vidua	1980	72-3 S	Static, 48 h, 46	18.0	N.R.
Brown shrimp Penaeus aztecus	1986	72-3 S	Flow-through, 48 h, 93	0.024	N.R.
Pink shrimp Penaeus duorarum	1986	72-3 C	Flow-through, 96 h, 93	0.11	N.R.
	1986	72-3 S	NR, 24 h, Tech	0.066	N.A.
Grass shrimp Palaemonetes pugio	1986	72-3 S	Static, 48 h, 93	4.7	N.R.
Blue crab Callinectes sapidus	1986	72-3 S	Flow-through, 48 h, 93.0	2.3	N.R.
Eastern oyster  Crassostrea virginica	1986	72-3b S	Flow-through, 96 h, 93	340	N.R.
Eastern oyster Crassostrea virginica	1988	72-3b C	Flow-through, 96 h, 96.9	321	130

<sup>\*</sup> C = core, S = satisfactory.

It is clear from Table 24, Table 25 and Table 26 that daphnia species are the most freshwater sensitive aquatic organisms with an acute EC50 of around 1  $\mu$ g/L and brown shrimp the most sensitive saltwater organisms with an EC50 of 0.024  $\mu$ g/L but Table 22, for which the Department of the Environment has reviewed the full reports, the most sensitive organism is the mysid shrimp with LC50 of 0.22  $\mu$ g/L. The results for fish range from an LC50 of 0.55 mg/L for rainbow trout to LC50 of 5.8 mg/L for guppy. The early life stage studies on fish and invertebrates clearly show that the early life stages are very sensitive and there is a very large acute to chronic ratio for the effects of fenthion on rainbow trout, with a ratio of 37, and for *D. magna* the ratio is 270. The high acute to chronic ratio is noted in Table 21 and Table 22.

#### 9.2.5 Field Studies

### Graney, 1988.

The principal registrant (Bayer) presented a review of the results of field studies conducted by the company, these are summarised in Table 27 below. While this was presented to the US EPA and, from the low application rates, relates mainly to mosquito applications, it shows that invertebrates are the most susceptible under field situations.

Table 27. Summary of a table in a Bayer report presented to the US EPA on field studies conducted using fenthion.

Application rate	Exposure	Max. Conc. μg/L	Field mortal	lity, % effect *	Comments	Study
g/ha and method	route	after each application	fish	Invertebrate		year
33; Aerial fog	Drift	1.19	-	0%	Rapid dissipation	1976
33; Aerial fog	Drift	4.27	-	0%	Rapid dissipation	1976
33; Aerial fog	Drift	1.69	-	no effect 1	Oil from thermal fog	1985
		< 0.01	no effect	59%	influences fenthion	
		0.16	no effect	no effect	fate	
		0.16	no effect	-		
Unknown;	Drift	0.49	No effect	-	Low DO caused	1986
ground ULV					mortality	
11.2; ground	Drift	0.28	0%	0%		1985
ULV		0.41	0%	0%		and
		0.31	0%	0%		1986
		0.37	0%	0%		
11.2; ground	Drift	0.68	-	No effect	Effects on	1985
ULV		0.38	-	No effect	invertebrates	
					community structure	
11.2; ground	Drift	0.48	-	33%	Sublethal effects,	1985
ULV					slow dissipation	
33; Aerial fog	Drift	1.5	0%	0%	Shrimp mortality	1986,
		0.29	0%	0%	occurred at sites	1987
		2.6	0%	100%	where limited mixing	
		0.51	0%	50%	occurred	
112, ULV	Drift	Not measured	-	No effect		1968
33; Aerial fog	Direct	Not measured	-	100%		1976
56, larvacidal	Direct	15-42	-	100%		1985
112,	Direct	27-32	0%	100%		1986
224, granular	Direct	Not measured	No effect	Effects	Affected fiddler crabs	1971,
					and amphipods, no	1973
					effect on fish and	
					molluses	
112	Direct	Not measured	No effect	Effects	Affected midges and	1964
					cladocerans but not	
					snails, clams or fish	

<sup>\*</sup> Percent effect relative to control. <sup>1</sup> Indicates that some mortality occurred but mortality at the reference site was greater or equal to test site.

### Nohara and Iwakuma, 1996

Residual pesticides and their toxicity to freshwater shrimp ( $Paratya\ compressa\ improvisa$ ) were studied in a river mouth in Lake Kasumigaura, Japan. The river is used for rice irrigation with water from the paddies returning to the river. Water samples were taken every ten days from April to July and analysed for several pesticides, including fenthion, as well as the toxicity to the local shrimp. The toxicity test was a 96 hour test in the river/lake water with 4 week old shrimps (8 per test) and total mortality determined. The maximum toxicity was 50% in mid to late May, corresponding with peak concentrations for the pesticides fenthion, diazinon and fenobucarb (1.9, 0.8 and 6.5  $\mu$ g/L respectively). Based on the toxicity of the pesticides to the shrimp, fenthion was considered to be the most likely toxicant.

# 9.3 Non-target Invertebrates

### 9.3.1 Bees

The contact toxicity of 12 pesticides as tested under standard conditions on worker honey bees was reported (Kudamatsu, 1977). This report is a summary of results and there is limited information. The contact LD50 for fenthion was given as  $0.16 \mu g/bee$ .

#### **US EPA Database**

The database from the Office of Pesticide Programs, US EPA (2008), has only one entry for bees, a contact test (1975) using AC with an LD50 of 0.31  $\mu$ g/bee and is rated as core (i.e. reliable).

#### 9.3.2 Other Invertebrates

## König, 1989

The effect of Lebaycid on *Trichogramma cacoeciae* was determined according to BBA Guidelines. The wasps (3 replicates, 241, 293 and 327 wasps per replicate) were exposed in a test chamber to glass plates that were sprayed with Lebaycid (535 g ac/L) using a 0.1% solution (1.6 mg/cm² wet residues applied, equivalent to 850 g ac/ha) 3 hours earlier and allowed to dry. After 24 hours no wasps survived. For the protected life stage study, parasitised eggs were kept for 7 days before dipping in a solution of Lebaycid (0.1% solution). The emerged wasps were then allowed to parasitise host eggs. No hatching occurred in treatment group, where as in controls there was an average of 22.8 parasitised eggs /wasp. Fenthion is rated as harmful to *Trichogramma cacoeciae*.

#### Kühner, 1992

The effect of Lebaycid on lace wing larvae (*Chrysoperla carnea*) was determined according to IOBC Guidelines. Glass plates were sprayed with Lebaycid (0.1% solution) at 1.16 mg/cm² (equivalent to 620 g ac/ha), air dried for 2-3 hours before the larvae (2-3 days old, 15 per replicate, 3 replicates) were exposed to the residues until pupation. The larvae were fed until pupation, then hatched. No larvae survived to pupation in treatments while 43 out of 45 larvae survived and hatched.in the control group

#### Mead-Briggs, 1992

The effect of Lebaycid on the hover fly *Episyrphus balteatus* was determined according to BBA Guidelines. Glass plates were sprayed with Lebaycid (1.5 L/ha equivalent to 800 g ac/ha) and allowed to dry (90 minutes) before 43 larvae of the fly were exposed to the residues. After 24 hours no larvae survived.

### 9.3.3 Earthworms

### Heimbach, 1989b

The toxicity of Lebaycid (50.3% fenthion) to earthworms (*Eisenia foetida*) was tested according to OECD Guideline 207 using artificial soil. Nominal concentrations of

Lebaycid used were 10, 100, 178, 316, 562 and 1000 mg/kg soil. There was 100% mortality in the highest test concentration and no mortalities in the next lowest concentration. The LD50 was determined as between 562 and 1000 mg/kg of soil. The LOEC was 178 mg/kg based on the reduction in weight of the surviving worms compared to control.

### Woodley, 1990

The toxicity of Baytex 550 (55% ac) to earthworms (*Eophila [Helodrilus] foetidus*) was determined in two tests. In the first test the worms were immersed for 1 minute in solutions at 0, 10, 100, 1000 or 5500 mg/L of Baytex 550, then placed onto a medium of manure sludge (from effluent tanks at Bahrs Hill Research Station). The number of live worms was recorded 0, 2, 3, 7, and 11 DAT. In the second test worms were placed on manure sludge before the sludge was covered with turf, which was sprayed with Baytex a day later at either the recommended rate 3 L/10 m<sup>2</sup> (1.65 g/m<sup>2</sup>, equivalent to 9 kg ac/ha) or 3 L/5 m<sup>2</sup> of Baytex.

Results for the first test show that there were no survivors at 5500 mg/L (recommended dilution rate) and at 1000 mg/L there was a slight increase in mortalities compared to controls and reduction in average weight of surviving worms. The author noted that due to the diurnal nature of earthworms they were unlikely to be directly exposed to the spray solution. In the second test there were no apparent dose related effects on mortality or bodyweight of the worms.

### 9.3.4 Soil micro-organisms

#### Anderson, 1989

The effect of Lebaycid on soil respiration was determined according to BBA Guidelines using two soils, a silty sand and a loamy silt, the details of these soils are given in Table 28.

Table 28. Characteristics for soils used in soil respiration and nitrification studies.

Soil	US	pН	% carbon	2000-63	63-2.0 μm	<2.0 μm
	Classification			μm		
Silty sand	Sandy loam	5.3	0.85	72.6	23.2	4.2
Loamy silt	Silt loam	5.7	1.75	4.3	82.5	12.1

Lebaycid was applied to the soils at 2 and 10  $\mu$ L/kg soil corresponding to 1 and 5 mg ac/kg soil, equivalent to 1.5 and 7.5 L/ha for 5 cm deep (assumes a soil density of 1.5 g/cm²) and incubated under aerobic conditions for 28 days. The amount of  $CO_2$  liberated in 12 hours following amendment by glucose was determined on 0, 14, and 28 DAT. Soil respiration was not significantly different to controls in the treatments at anytime. It was concluded that that fenthion has no adverse effect on soil respiration.

### Blumenstock, 1989

The effect of Lebaycid on nitrification in soil was determined according to BBA using the two soils given in Table 28 above.

For the nitrification studies the soils were amended with ammonium sulphate (1 g/kg soil) and dosed with Lebaycid at 0, 2 or 10  $\mu$ L/kg. All nitrification studies were aged for 28 days and sampled at 7 (or 8), 14, 21 and 28 days during the incubation period. Ammonium and nitrate (plus nitrite) were analysed.

The results show a slight decrease in concentration of nitrate in weeks 2 and 3 for the silty sand and a slight decrease for ammonium in the loamy silt. After 4 weeks there was no difference for all treatments compared to control.

It was concluded that use of Lebaycid is not expected to have any effect on nitrification in soil when applied at recommended rate of (1.5 L/ha).

### Minor and Parker, 1979

The effect of Baytex (active ingredient fenthion) on isolated soil micro-organisms was studied using standard disk methods. The 5 micro-organisms used, *Azotobacter chroococcum*, *Bacillus subtilis*, *Cellulomonas flavigena*, *Pseudomonas aeruginosa* and *Streptomyces* sp. were grown in nutrient before disks containing Baytex were placed on the surface. The disks were dipped once in solutions of Baytex at various concentrations. The zones of inhibition were measured after 24 and 48 hours. For the fungi tests the spores from 5 species, *Aspergillus niger*, *Penicillin daleae*, *Trichoderma viride* and *Phycomyces nitens*, were grown on nutrient gels before disks of the fungi were placed on agar gels that were prepared with Baytex at various concentrations.

Baytex did not inhibit the growth of any bacteria except for *Streptomyces* sp at 1000 and 10,000 mg/L. There was a significant effect on the fungi at the highest concentrations tested, 1000 and 10,000 mg/L, with minor effects at 10 mg/L for all species except for *P. nitens* where there was 22% inhibition and at 2 mg/L only *P. nitens* was affected, with 5% inhibition compared to controls. In the positive control (Captan) there was 17 to 42% inhibition for 2 ppm.

It is concluded that there is unlikely to be an effect on soil bacteria when used at 1.12 kg ac/ha (corresponds to 0.5 mg/kg soil 15 cm deep) but there could possibly be some effect on some fungal species.

### **9.3.5** *Mammals*

Fenthion is moderately toxic to mammals by the oral route, with LC50s for rats 566 mg/kg (females) and 405 mg/kg male and the multi-generation reproduction studies show a NOEC of 10 ppm and LOEC 14 ppm (US EPA 1998). In Australia it is scheduled as S6 for the emulsifiable concentrate (EC).

# 9.4 Phytotoxicity

No studies presented. Fenthion is non-phytotoxic when used as directed, although some varieties of apples and cotton may be injured (Tomlin, 1997).

The US EPA reregistration of fenthion includes results for the effect of fenthion on seed germination and seedling vegetative vigour when mixed with diesel oil (US

EPA, 1998). There were no major effects on germination or seedling vigour at 0.6 mg ac/L in diesel compared to control with diesel only.

## 9.5 Summary of Ecotoxicity

Fenthion is a highly toxic organophosphate insecticide. It is toxic to most organisms and in particular birds and aquatic invertebrates.

### 9.5.1 Avian

Fenthion can be rated as very highly toxic to quail by the acute oral route. The dietary route of exposure for birds is rated as highly toxic for quail and moderately toxic for mallards, based on reviewed studies. Results in a database of studies reviewed by the US EPA confirm the acute toxicity rating of very highly toxic (10 species) and the acute dietary as ranging from highly toxic to very highly toxic (5 species).

In a literature report, the effect of aerial application to bird roosts in Kenya was examined. Following these applications, 61 birds of 14 species at one site and 22 birds of 8 species at the other site were found dead or severely debilitated. The report is not considered applicable to Australia but it does highlight the high avian mortalities that can occur when used inappropriately.

Six incidents of poisoning of native birds over a 13 month period were investigated by the Queensland Department of Primary Industries, with a total of 350 bird deaths, with 200 dead in the major incident at a grain depot. It was considered that a significant number were due to malicious poisoning using fenthion.

Tadpoles were exposed to fenthion in water before being fed to mallard ducklings (2 weeks old). Tadpoles exposed to fenthion at 5 mg/L caused 100% mortality and at 2.2 mg/L 67% mortality. The BCF for fenthion in tadpoles was determined as 62.

The US EPA has reported that a number of adverse effects on non-target birds have been noted when fenthion is used to control pest birds and for mosquito control. In the former reports, fenthion was used to kill pest birds in buildings and then raptors were found dead after eating the dead or dying pest birds. In the latter reports where fenthion was used for mosquito control at low rates (56 g ac/ha), dead and sick birds were noticed after several sprays. These sprays were made over a beach early in the morning, and sick and dead birds were observed within 8-10 hours.

# 9.5.2 Aquatic

The toxicity to aquatic organisms, especially invertebrates, is very high. The acute toxicity to fish from submitted studies (9 species) ranges from an LD50 of 0.83 mg/L for rainbow trout to 2.7 mg/L for Golden orfe. Life cycle studies have not been performed but the embryonic and larvae life stages of rainbow trout have been tested and the maximum acceptable tolerated concentration was determined to be between 0.013 and 0.027 mg/L. The early life stages are considered to be normally the most sensitive. There is a high acute to chronic ratio of 43. In a database of regulatory-type studies that have been reviewed by USEPA, the toxicity to fish of fenthion ranges from LC50 of 0.55 mg/L for rainbow trout to LC50 of 5.8 mg/L for the guppy.

Fenthion is extremely toxic to invertebrates, which is typical for an organophosphate, with acute toxicity figures for *Daphnia magna* (EC50) of between 5.2-5.7  $\mu$ g/L and for mysid shrimp EC50 = 0.22  $\mu$ g/L (note that the mysid is normally a very sensitive test species.) The chronic toxicity to daphnia has been determined and the MATC found to be between 0.009 and 0.016  $\mu$ g/L. Again the acute to chronic ratio is high, with a value of 270. The USEPA database on reviewed regulatory studies gives the most sensitive freshwater species as a daphnid (*Simocephalus* sp.) EC50 = 0.62  $\mu$ g/L, and least sensitive invertebrate as the sowbug (*Asellus brevicaudus*) EC50 = 1800  $\mu$ g/L. For salt water species the most sensitive is brown shrimp (*Penaeus aztecus*), EC50 = 0.024  $\mu$ g/L and least sensitive is the Eastern oyster (*Crassostrea virginica*),  $EC50 = 321 - 340 \mu$ g/L

Fenthion is highly toxic to green algae, with EC50s of 0.55 and 1.1 mg/L for *Scenedesmus* and *Selenastrum* species respectively and to the saltwater algae *Skeletonema costatum*, EC50 of 0.33 mg/L. It is also moderately toxic to blue green algae (*Anabaena flos-aqua*) EC50 = 10.7 mg/L and the freshwater diatom *Navicula pelliculosa*, EC50 = 1.2 mg/L. The toxicity to the freshwater plant *Lemma gibba* was studied but the only information from the study is that the NOEC is > 2.8 mg/L.

No field studies were presented. A summary of field studies conducted presented to the US EPA clearly shows that under field conditions at rates associated with mosquito use the most sensitive aquatic organisms are invertebrates, with effects noted relative to control sites at 0.5  $\mu$ g/L and above, particularly where there was slow dissipation of fenthion.

A literature report on fenthion residues in a river mouth/lake associated with irrigated rice cultivation in Japan showed mortalities to local shrimp occurring at 1.9  $\mu$ g/L of fenthion. However, other organophosphate insecticides were present but not at concentrations considered to be significant.

# 9.5.3 Non-Target Invertebrates

There were no regulatory studies presented but an old report gives a contact LD50 of  $0.16 \mu g$ /bee and the US EPA database of studies that have been reviewed by them gives a contact LD50 of  $0.31 \mu g$ /bee.

In 3 laboratory studies on the effect of fenthion on parasitic wasps (*Trichogramma cacoeciae*), lace wings (*Chrysoperla carnea*) and hover fly larvae (*Episyrphus balteatus*), fenthion caused 100% mortality and can be rated as harmful according to the International Organisation of Biological Control (IOBC). It should be noted that some insects may be resistant to fenthion, which occurs in populations of predatory mites used in intergrated pest management (IPM).

The toxicity of fenthion to earthworms was tested according to OECD Guidelines. The LD50 was calculated as between 562 and 1000 mg/kg of soil. In a trial at rates used for turf, the spray solution was toxic to earthworms with direct contact for one minute but in simulated turf there were no adverse effects.

# 9.5.4 Soil micro-organisms

Fenthion has limited effects on micro-organisms. In tests using two different soil types, there was minimal effect on soil respiration and nitrification at 1 and 5 mg/kg soil, corresponding to the maximum field rate and 5 fold the rate. In studies using isolated cultures of soil bacteria and fungi, it was found that there is unlikely to be any effect on soil bacteria but there could be minor effects on some fungal species.

## 9.5.5 Phytotoxicity

No studies were presented. Fenthion is non-phytotoxic when used as directed, although some varieties of apples and cotton may be injured (Tomlin, 1997). The US EPA reregistration document of fenthion reports that when mixed with diesel at 0.6 mg ac/L there were no major effects on germination or seedling vigour compared to the control.

### 10 Prediction of Environmental Risk

## 10.1.1 Risk arising from agricultural and veterinary uses

In Australia fenthion is available for use in orchards (pome and stone fruit, citrus, tropical and subtropical fruits), grapes and vegetables, as well as for veterinary and domestic uses.

Currently fenthion is used mainly for the control of fruit flies, caterpillars, moths, bugs, thrips, and wingless grasshoppers in orchards, vine fruits and other fruit crops with some use in vegetables. Veterinary use is for lice on cattle.

Several years ago it was estimated that less than 25 tonnes were used per annum, mainly for fruit fly control, around buildings for control of various insects and lice on cattle. Wingless grasshopper use appears to be very minor.

The use rates stated on the labels and permits are: up to 150 mL/100 L (82.5 g ac/100 L) for Queensland and Mediterranean fruit flies in pome and citrus fruits, with lower rates (up to 75 mL/100 L) for grapes, stone fruits, deciduous fruit, tropical fruits etc. The currently permitted horticultural uses are summarised in Table 1, section 2.1.1.1. The application rates (L/ha) will vary considerably between orchards and crops depending upon planting density (low, medium or high density), growth stages (immature vs mature trees) and application target.

# **10.2** Application and Use Pattern

The following agricultural use pattern considers all the uses on the label of product 32996 but does not apply to all the permitted uses since suspension.

# 10.2.1 Orchards and other fruits

Traditionally application to orchards is by orchard air blasters using high volume equipment. However, many orchardists are now using low volume sprayers, and in some cases ultra low volume equipment, although the latter is not very common due

to its higher costs. The directions on the label for concentrate spraying instruct the user to apply the same amount of fenthion to the target crop as for the high volume rate. In addition, for citrus, oscillating horizontal booms may be used as well as high volume application equipment.

The labels do not prohibit aerial applications, however, this is not likely to be used for orchards due to the requirement to thoroughly wet the entire tree canopy and the increasing use of hail/bird netting in orchards to protect the fruit. The company has clarified that fenthion is not applied by air to fruit trees or vegetables for fruit fly control (the major use). However, it may have occurred for tomatoes, which was the main other use prior to the suspension of fenthion in October 2012.

Normal practice in orchards is to spray to the point of run-off, requiring 1500 - 3000 L/ha of spray solution for mature pome and stone fruit trees, but this could be as high as 4000 L/ha for large pear trees and mango trees. The maximum application rates range between 2.47 and 3.3 kg ac/ha for most pests at 82.5 g ac/100 L (Table 1). For stone fruit, deciduous fruit and tropical fruits the corresponding maximum rates are 1.57 to 2.09 kg ac/ha at 52.25 g ac/100 L. Citrus use, as previously noted, is normally associated with very high application volumes of 6000 - 10000 L/ha, corresponding to a maximum rate of 8.25 kg ac/ha. However, the company has clarified that they've found the application rates tend to be 850 - 2000 L/ha (a maximum rate of 1.64 kg ac/ha). Spraying grapes and other vine crops normally requires 1000 to 1500 L/ha and the maximum application rate is 0.62 kg ac/ha.

## 10.2.2 Vegetables (Tomatoes, Capsicums and Egg Fruit)

These crops are normally treated by boomsprayers at 1000 L/ha. The label rate is 75 mL/100 L or 750 mL/ha, both of which correspond to 412 g ac/ha at 1000 L/ha.

### 10.2.3 Veterinary use

The veterinary use is for control of cattle lice by spotting the dose onto the rump or loin (spot-on formulation) at a rate of 1 ml of formulated product (200 g/L) per 22 - 55 kg live weight of the animal.

### 11 Risk Characterisation

The following risk evaluation is from the Environmental Risk Assessment Guidance Manual for Agricultural and Veterinary Chemicals (EPHC, 2009) and follows the US EPA approach (Urban and Cook 1986) to establish a Q-value from the ratio of the Predicted Environmental Concentration (PEC) and lowest effect concentration, such as an  $LC_{50}$ ./ $EC_{50}$ .

The Department of the Environment normally assesses the environmental risk from acute exposure by calculating the Environmental Risk Quotient (Q = PEC/LC50 or EC50, based on Urban and Cook, 1986). For the aquatic risk this is evaluated using the predicted environmental concentration or PEC from spray reaching lentic water 15 cm deep is determined as a worst case situation in regard to water depth and acute toxicity data for the most sensitive species. The initial worst case situation of direct

overspray at the maximum label rate is considered, then a 10% spray drift situation if the risk from the direct overspray is unacceptable, and then modelling is used to aid in refining the risk.

The Department of the Environment generally considers the following as an appropriate guide for the estimation of risk:

- Q > 0.5: risk is unacceptable,
- $0.1 \le Q \le 0.5$ : risk may be able to be mitigated by some form of risk management, such as label restraints for a specific use and an identified risk arising from that use, and
- Q < 0.1: risk is considered acceptable (and may or may not require some form of risk management, such as general label restraints).

For chronic exposure (e.g. repeated sprays and/or relatively persistent substances), the Department of the Environment generally considers the risk acceptable if the NOEC for the species most sensitive to chronic exposure is greater than the PEC estimated for prolonged exposure.

The following risk characterisation considers all the agricultural uses on the label of product 32996 but does not apply to all the permitted uses since suspension.

Initially the risk to terrestrial organisms and aquatic organisms (agricultural uses) of fenthion will be considered.

# 11.1 Agricultural uses – terrestrial

#### 11.1.1 Avian

Birds feeding on sprayed fruit could be exposed to residues of fenthion. There are a number of bird species that are pests in orchards, grapevines etc. These species include silvereyes, parrots, lorikeets, rosellas, cockatoos, starlings, currawongs and Indian (common) mynas.

Incidents of fenthion poisoning of birds in Australia have been noted including in press reports but most appear to result from malicious use. In the US there have been reports of fenthion implicated in bird deaths associated with Rid-a-Bird perches and mosquito uses of fenthion but orchard use does not seem to have been registered.

Using the EPA food chain (Kenaga) nomogram (Fletcher; Nellessen, and Pfleeger, 1994), the concentration of residues on various food sources from applications at 2.47 kg ac/ha (maximum rate expected for pome fruit) is as follows (wet weight; Fletcher, Nellessen and Pfleeger, 1994):

- 33 mg ac/kg (fruit or large insects);
- 242 mg ac/kg (grain/long grass);
- 298 mg ac/kg (small insects or forage crops)

The risk quotients are then calculated for the mallard duck and the most sensitive species, bobwhite quail (Table 29), which are surrogate, standard species used in

place of Australian species, for which there are no data. It assumes that a mallard duck consumes 30% of its diet as grain (long grass) and 70% as large insects while a bobwhite quail consumes 30% small insects and 70% grain (long grass) (US EPA (1993)). Note that these quotients are derived from using endpoints only for which study reports are available and/or the endpoints which are considered core results (Table 20). The worst case scenario is that all of the birds' diet has been treated with fenthion: the risk is shown to be unacceptable for the bobwhite quail and a mitigatable for mallard ducks. If half of their diet has been treated with fenthion the risk is still unacceptable for the quail and further mitigation is still required for the duck.

Table 29. Acute risk to birds

Avian species	LC50 (ppm)*	Pome		
		Q (100% dietary intake	Q (50% dietary intake	
		treated)	treated)	
Mallard duck	231	0.42	0.21	
Bobwhite quail	30	8.6	4.3	

<sup>\*</sup> Refer to Table 20.

Some further considerations of the risk are needed:

- the orchard trees are expected to intercept the majority of the spray (up to 80%) and apart from ripening fruit, birds are unlikely to eat fruit tree leaves to any great extent;
- those that eat fruit are likely to be a very different suite of birds than those used in the estimates above but note from Table 20 that the common grackle (a blackbird) is also very sensitive to fenthion (LC50 = 30 ppm);
- while much higher rates are allowed than the 2.47 kg ac/ha assumed, spraying at the same application rate on denser vegetation (e.g. citrus and mangoes) yields the same level of deposit of insecticide on the fruit, leaves and any grasses (i.e. a 3-dimensional effect);
- while the risk is lower for those birds feeding on the orchard floor, if we assume 20% is not intercepted then the risk quotients are still unacceptable for the bobwhite quail and common grackle even assuming 50% of the diet is treated:
- however, food items are not the only route of exposure and other routes are potentially significant.

There have been reports of birds in Australia being poisoned by fenthion, the majority of situations have been by the illegal poisoning of pest birds and at least one report by non-targeted spraying. The assessment above indicates that there is a potential risk from a single treatment to birds frequenting and feeding on fenthion-treated orchards.

#### 11.1.1.1 Wingless grasshoppers

The use of fenthion to control wingless grasshoppers in orchards could lead to significant exposure to birds, especially small raptors. During locust plagues and when locusts are in hopper bands, birds may feed on the locusts, especially those dead or dying, until gorged. A similar situation will apply during heavy infestations of grasshoppers. A full cover spray is to be applied at 75 mL/100 L if hoppers infest fruit trees. Assuming maximum rates between 0.62 kg ac/ha (grapes) and 4.12

kg/ac/ha (citrus) (refer to Table 1), this will result in residues of 75 to 497 mg ac/ha fresh weight on small insects. Making the same assumptions as above the resulting PECs are 24 to 160 mg ac/ha and hence Qs of 0.1 to 0.7 for the mallard duck (100% dietary intake treated) while the PECs are 65 to 432 mg/ac/ha and hence Qs of 2.2 to 14.4 for the bobwhite quail (100% dietary intake treated). The Department of the Environment's concerns are with the risk of poisoning of predator birds such as raptors, as they tend to besensitive to organophosphates and are known to consume grasshoppers. While no direct data are available for fenthion, the use of fenthion for control of wingless grasshoppers is of concern, especially during periods of high insect pressure, which is when use is most likely. Although this use appears to be very minor it should be removed from the labels in view of the clear poisoning risk for birds.

### 11.1.2 Mammals

Terrestrial animals may be at risk from fenthion when applications of the chemical are made directly over them or from contact with sprayed surfaces, such as from orchard tree leaves or inter-row cover crops. It is expected that over-spray by tractor powered equipment is unlikely as larger animals will move some distance from the area where spray operations are occurring, while smaller mammals will be undercover, often underground. Most mammals are not expected to be directly over-sprayed.

It is difficult to assess the risk to terrestrial organisms, such as possums, that enter sprayed areas and are exposed to residues (dermal or dietary). Animals that enter recently sprayed areas are at some risk of exposure.

It is concluded that while there is unlikely to be significant effects on mammal populations from spraying, some individuals, especially those living and feeding in sprayed areas, could be affected.

#### 11.1.3 Bees

Fenthion is toxic to bees (Tomlin, 1997) and the bees are at risk if they're present when spraying occurs. Risk to honeybees from the use of product 32996 (Lebaycid) can be determined by converting the maximum application rate to each crop into an application rate per bee, assuming that the surface area of a bee is ~1 cm² (Davis and Williams, 1990). The risk quotients, based on comparison of the predicted amount of the active per bee with the contact LD50 value, are shown in Table 30. LD50 results were provided or found only for contact studies of fenthion on honeybees. The risk quotient values indicate an unacceptable risk to bees in a contact situation.

Table 30. Acute risk to honeybees.

Usage	Rate		Contact LD50 values (µg ac/bee)	Q values
	g ac/ha	μg ac/bee	Value	
Citrus fruit (lowest rate <sup>1</sup> - highest rate)	700 - 8250	7.0 - 82.5	0.31	22 – 266
Pome fruit (range of rates)	1240 - 3300	12.4 – 33.0	0.31	40 – 106
Tomatoes	410	4.1	0.31	13

<sup>&</sup>lt;sup>1</sup> = lowest rate according to the registrant.

Using the 'Environmental Risk Assessment Scheme For Plant Protection Products (Honeybees)' by the European and Mediterranean Plant Protection Organisation (2003), the risk to bees is categorised as a high (i.e. unacceptable) risk for citrus and pome fruit since the Q-value is > 25 and an intermediate to high risk for tomatoes since Q is between 0.5 and 25. Once again it's indicated that there's an unacceptable risk to bees in a contact situation.

If bees are over-sprayed it is expected 100% kill rates would occur and to limit the exposure of bees to the pesticide, the crop should not be sprayed when there are bees present, when the crop (or ground covers) are in flower or if likely to be in flower shortly afterwards.

Spray drift could also be toxic to bees. Spray drift modelling using the AgDRIFT model (AgDRIFT® Spray Drift Task Force Spray Software, Version 2.0.07) are representative of the diversity of conditions/practices undertaken in Australia (APVMA, 2008a). Therefore, AgDRIFT modelling will be applied to assess the risk to bees from spray drift originating from the sprayed area at certain distances from the bees. It should be noted that the AgDRIFT modelling program doesn't consider spray drift distances greater than 304 m. The concentration arising on a bee at various distances downwind of the sprayed area have been modelled. The modelling indicates that worst case application by orchard air blaster sprayers (early bud swell and an application rate of 8.25 kg ac/ha for citrus) results in an unacceptable risk to bees up to and beyond 300 m.

Therefore bees are at risk if spraying occurs when they are present in the crop or from spray drift. The label on product 32996 includes a precaution: "Dangerous to bees. Do not spray any plants in flower while bees are foraging". If any orchard uses are retained, this statement should be changed to:

Toxic to bees. Will kill bees foraging in the crop to be treated or in hives which are over-sprayed or reached by spray drift. Residues may remain toxic to bees for several days after application.

#### 11.1.4 Earthworms and other invertebrates

Earthworms and other soil dwelling invertebrates could be exposed to the pesticide, and at an application rate of 2.5 kg ac/ha, the top 5 cm of soil would contain fenthion

residues at 3.3 mg/kg of soil (assumes no crop cover, density of soil 1500 kg/m $^3$ ). This is significantly below the LD $_{50}$  and the NOEC for worms (see Earthworms, page 52) and acute effects are not expected. There are no data for chronic effects to earthworms but given the rapid degradation in the aerobic soil metabolism studies (page 11) and the fact that most of the fenthion is expected to be intercepted by the foliage on the trees, long term chronic effects are not expected.

Other soil arthropods may be significantly affected unless they can move away from contact with the sprayed areas or have become resistant to fenthion from past use. There are no toxicity data available for these organisms and the risk cannot be determined.

Soil micro-organisms may be affected if they come into contact with fenthion. The toxicity data available for these organisms indicate the risk is likely to be low as soil metabolism and nitrogen fixation was not affected at 5 mg/kg soil. Some growth inhibition of fungi (5-22%) was noted for soil fungi at 2 and 10 ppm on paper discs but it is unclear as to how this relates to soil concentrations.

The effects of the fenthion product on the hover fly larvae (*Episyrphus balteatus*), lace-wing larvae (*Chrysoperla carnea*) and wasp (*Trichogramma cacoeciae*) were studied. The results were determined by applying between 620 and 850 g ac/ha to the glass plates and testing chambers. The treatment was shown to be extremely toxic to the larvae and adult arthropods with no hover fly or lace-wing larvae surviving, no wasps surviving and none of the treated wasp eggs hatched.

In conclusion, fenthion applied at rates much lower than the label rates demonstrate that it's very toxic to other invertebrates (studies not rated). If orchard and vegetable uses are retained, a warning should be included on the label as follows:

Integrated Pest Management: Lebaycid may kill non-target beneficial invertebrates.IPM programs may be adversely affected.

## 11.1.5 Agricultural uses - terrestrial vegetation

Fenthion is stated to be non-phytotoxic with some varieties of apples and cotton could be injured (Tomlin, 1997). There were no phytoxicity studies presented. Effects on non-target plants are expected to be minimal.

# 11.2 Agricultural uses - aquatic

### 11.2.1 Direct over spray

Direct application of fenthion to a body of water 15 cm deep at the maximum proposed rates (3.3 kg ac/ha corresponding to 4 000 L/ha at 82.5 g ac/100 L for large pear trees and 8.25 kg ac/ha corresponding to 10 000 L/ha at 82.5 g ac/100 L for citrus) is calculated to give a concentration in the water of 2.20 and 5.50 mg/L, respectively. The resultant risk quotient values (Q) from acute exposure of the more sensitive aquatic organisms are shown in Table 31 (fish, fresh and saltwater invertebrates and algae; ecotoxicity data from Table 23, Table 24, Table 25 and Table

26). Even though the brown shrimp is more sensitive (has a lower endpoint) than the pink shrimp, the study for brown shrimp is considered to be less reliable than that for the pink shrimp. Although pink shrimp is not an Australian species, they are regarded as a suitable surrogate for the most sensitive Australian species. There were no data provided on the toxicity of fenthion to Australian freshwater or saltwater aquatic species. Note from Table 25 and Table 26 that a number of results are more sensitive than the reviewed daphnia result in Table 22.

Table 31. Acute risk quotients for the more sensitive aquatic species exposed to fenthion following a direct overspray based on the maximum proposed rates of 3.3 and 8.25 kg ac/ha, for large pears and citrus respectively, in a 15 cm water body.

<u> </u>		J /	
Aqueous species	$EC_{50}(\mu g/L)$	Risk quotients	
		Large pear trees	Citrus
Rainbow trout Oncorhynchus	550 <sup>C</sup> (US EPA)	4	10
mykiss			
Daphnia magna	5.2 <sup>R</sup> (reviewed)	423	1 058
Pink shrimp Penaeus duorarum	0.11 <sup>C</sup> (US EPA)	20 000	50 000
Scenedesmus subspicatus	$E_b C_{50} = 550^{OECD}$	4	10
	(reviewed)		

Key: Dark shading is Q > 0.5 (unacceptable risk). R = result considered reliable, C = Core study; OECD Guideline 201 test method.

The risk is unacceptable to all the aquatic organisms presented. Although direct overspray of shallow water is unlikely to occur using orchard air blasters or ground boom applicators, the likelihood of harm to sensitive aquatic organisms from such exposures is indicated and likely to be exacerbated given the possible use of aerial applications. (Aerial applications might lead to such direct over-spray and therefore it's of significant concern. Refer to Section 11.2.2.6 Aerial Application, below).

However, the Department of the Environment regards direct over-spray as being a rare occurrence and the following risk assessment for spray drift as being more realistic for Australian use patterns.

### 11.2.2 Spray Drift

#### 11.2.2.1 10% Spray Drift

A 10% spray drift event is the next refinement of the risk assessment. Spray drift is of major concern for aquatic organisms. Using the US EPA worst case assumption that 10% spray drift reaches water (Urban and Cook, 1986), this would result in a concentration of 220 and 550  $\mu$ g/L for a shallow pond, 15 cm deep (3.3 kg ac/ha corresponding to 4 000 L/ha at 82.5 g ac/100 L for large pear trees and 8.25 kg ac/ha corresponding to 10 000 L/ha at 82.5 g ac/100 L for citrus). The most sensitive aquatic endpoints for fish, aquatic invertebrates and algae have been used to calculate the risk quotients in Table 32.

Table 32. Acute risk quotients for the more sensitive aquatic species exposed to 10% spray drift of fenthion based on the maximum proposed rate of 3.3 and 8.25 kg ac/ha, for large pears and citrus respectively, in a 15 cm water body.

Aqueous species	EC <sub>50</sub> (μg/L)	Risk quotients	
		Large pear trees	Citrus
Rainbow trout Oncorhynchus	550 <sup>C</sup>	0.4	1
mykiss			
Daphnia magna	5.2 <sup>C</sup>	42.3	105.8
Pink shrimp Penaeus duorarum	0.11 <sup>C</sup>	2 000	5 000
Scenedesmus subspicatus	$E_bC_{50} = 550^{OECD}$	0.4	1

Key: Dark shading is Q > 0.5 (unacceptable risk); light shading =  $0.1 \le Q \le 0.5$  (risk may be mitigated).  $^R$  = result considered reliable,  $^C$  = Core study;  $^{OECD}$  = OECD Guideline 201 test method.

The risk quotients for the more sensitive fresh and saltwater organisms, *Daphnia magna* and the pink shrimp, indicate an unacceptable risk to these organisms. The results indicate the possibility of mitigating the risk for fish and algae for large pear trees only.

The risk to aquatic organisms from this crude calculation of 10% spray drift is therefore considered to be unacceptable, but the Department of the Environment accepts that 10% is an arbitrarily high figure for most spray drift situations and further refinements to more accurately determine the risk are required.

#### 11.2.2.2 AgDRIFT modelling

The Department of the Environment understands that the revised Ganzelmeier tables for spray drift were conducted under ideal conditions in Germany, with low wind speeds with well calibrated spray equipment delivering a coarse droplet spectrum. On this basis, they may be considered to represent a best case scenario for spray drift that is not representative of Australian weather and application conditions. As a result of this and recent information from the APVMA (2008a), a more conservative approach is taken with respect to spray drift modelling. APVMA and the Department of the Environment now consider that the data used in the AgDRIFT® model (AgDRIFT® Spray Drift Task Force Spray Software, Version 2.0.07) are more representative of the diversity of conditions/practices undertaken in Australia (APVMA, 2008a). Therefore, the spray deposition rates at various distances from the edge of field obtained from the AgDRIFT modelling will be applied to this risk assessment to protect aquatic organisms. Concentrations arising in a 3 m wide x 15 cm deep pond at various distances downwind of the sprayed area have been modelled. It should be noted that the AgDRIFT modelling program doesn't consider distances (distance of the water body from the edge of application area) greater than 304 m, as this is the limit of the model's capabilities and reliability.

For the five categories of major-use crops (citrus, large pear and mango trees, apple trees, grape vines and vegetables) the maximum rates for the trees will be used in the assessment of risk at various distances from the edge of the application area.

The aquatic invertebrates are the most sensitive aquatic organisms and therefore the endpoints used to determine the risk quotients and hence the assessments of risk

quotients at various distances will be based on *Daphnia magna* and pink shrimp (*Penaeus duorarum*).

### 11.2.2.3 Orchard/Air-Blast Spray Drift

The orchard/air blast model in AgDRIFT 2.0.07 is based on results from trials to measure the spray drift from orchard spraying in several orchard crops, including: grapes, apples (foliated and dormant), oranges, grapefruits, almonds and pecans. Due to the limited number of applications made to any given crop, the results for crop/situations giving similar levels of drift were pooled into five composite orchard scenarios grouped by orchard characteristics:

- *normal* [grapes (wrap-around sprayer), pome fruit and grapes with air blast; fully grown trees);
- *dense* [citrus (airblast and mister) and nut trees];
- *sparse* (small trees and dormant trees);
- vineyard [grapes]; and
- *orchard* [pome fruit, citrus, nuts and dormant pome fruit].

As well as composite orchard settings, the model can also be used for individual orchards (e.g. settings for *apple*, *orange*, *almonds*). However, the individual orchard settings won't be used due to the limited number of number of applications for each crop. Therefore for each type of crop/fruit the most appropriate composite orchard setting will be used. The model was not refined for equipment and nozzle types and is only considered as Tier 1. For risk assessment purposes the results that approximate the 95th percentile are used in the assessment of the risk quotients to be protective of most situations. It is noted that the APVMA Operational Notice (2010) advises against the use of the setting 'Normal Orchard' and instead to use 'Composite Orchard', 'Dense Orchard' or 'Sparse Orchard'. Although the following calculations have not been updated in line with the Operational Notice (2010) the Department of the Environment believes the various distances will not vary significantly and the final outcomes of acceptable or unacceptable risk are expected to remain unchanged.

The multiple trials on fruit trees appear useful in comparison with equivalent Australian crops. Apart from Australian weather conditions, where air temperatures are likely to be higher and humidity lower, which may lead to greater spray drift, the results of the AgDRIFT model should be useful in estimating drift in orchard situations under typical usage.

As previously noted (section 2.1.1), citrus use is normally associated with very high application volumes (6 000 - 10 000 L/ha, corresponding to a maximum of 8.25 kg ac/ha for 82.5 g ac/100 L). The company has stated that high application rates to citrus are rarely used and that in Western Australia 99% of citrus growers are said to use airblast sprayers applying  $850-1\ 000\ L/ha$ , with some going up to 2 000 L/ha corresponding to a maximum rate of 1.64 kg ac/ha for 82 g ac/100 L. However, the label instructions for a full cover spray casts doubt on this.

The risk quotient values in Table 33 (*dense* setting used for citrus as recommended by the AgDRIFT program) were determined using application rates of 8.25 kg ac/ha (the

normal rate) and 1.64 kg ac/ha (registrant's claimed rate) in a body of water 15 cm deep and 3 m wide.

The resultant acute risk quotient values for citrus using application rates of 1.64 or 8.25 kg ac/ha (Table 33) indicate a very high risk to sensitive aquatic invertebrates with unacceptable risk for pink shrimp extending beyond 300 m from the area being sprayed. The risk is unacceptable to *Daphnia magna* up to 200 m even at the lower rate. (It should be noted that when determining the risk quotient for mango trees using the AgDRIFT program, the *dense* setting is also used and the same variables except the maximum application rate would be 2.09 kg ac/ha. Similarly when mango trees are sprayed, a very high risk to aquatic invertebrates is indicated with unacceptable risk to pink shrimp extending beyond 300 m from the area being sprayed and up to 250 m for daphnia.)

Table 33. Risk quotients for spray drift from airblast sprayers in citrus orchards (dense) using AgDRIFT at 1.64 and 8.25 kg ac/ha in water 15 cm deep and 3 m wide.

Dense (Citrus)						
Distance	Application rate		Application rate			
(m)	1.64 kg ac/ha		8.25 kg ac/ha			
	Q, Daphnia magna	Q, pink shrimp	Q, Daphnia magna	Q, pink shrimp		
	$EC_{50} = 5.2  (\mu g/L)$	$EC_{50} = 0.11  (\mu g/L)$	$EC_{50} = 5.2  (\mu g/L)$	$EC_{50} = 0.11  (\mu g/L)$		
10	13	651	69	3277		
20	6.5	305	32	1534		
60	1.7	78	8.3	392		
100	0.92	43	4.6	219		
200	0.45	21	2.3	106		
300	0.3	14	1.5	70		

Key: Dark shading is Q > 0.5; light shading =  $0.1 \le Q \le 0.5$ 

Large pear trees also require a high application rate of the fenthion product. The risk quotient values for large pear trees are given in Table 34. This modelling uses the maximum Australian rate for large fruit trees of 3.3 kg ac/ha (4 000 L/ha corresponding to 82.5 g ac/100 L), water dimensions as above and EC50s for daphnia of 5.2  $\mu$ g/L and pink shrimp of 0.11  $\mu$ g/L. The *normal* setting is used for pear trees (AgDRIFT program recommends this setting for stone and pome fruit). The risk is still unacceptable to pink shrimp up to and beyond 300 m.

Table 34. Risk quotients for spray drift from airblast sprayers in large pear tree orchards (normal orchards) using AgDRIFT at 3.3 kg ac/ha in water 15 cm deep and 3 m wide.

Normal (Large pear trees)					
Distance	Risk Quotients (Q)				
metres	Daphnia magna	pink shrimp			
	$EC_{50} = 5.2 \; (\mu g/L)$	$EC_{50} = 0.11  (\mu g/L)$			
10	2.1	96			
20	1.1	53			
60	0.37	17			
100	0.2	9.7			
200	0.09	4			
300	0.05	2.3			

Key: Dark shading is Q > 0.5; light shading =  $0.1 \le Q \le 0.5$ 

In order to determine the PEC values at certain distances for spraying apple orchards, the setting used is *normal* and the maximum rate is 2.47 kg ac/ha at 3000 L/ha (82.5 g ac/100 L). Other variables used for this modelling study are as above. The values indicate that the risk is unacceptable to the most sensitive aquatic invertebrates (Table 35) in this scenario.

Table 35. Risk quotients for spray drift from airblast sprayers in apple orchards (normal setting) using AgDRIFT at 2.47 kg ac/ha in water 15 cm deep and 3 m wide.

Normal (Apple trees)					
Distance	Risk Quotients (Q)				
metres	Daphnia magna	pink shrimp			
	$EC_{50} = 5.2  (\mu g/L)$	$EC_{50} = 0.11  (\mu g/L)$			
10	1.5	96			
20	0.85	39			
60	0.28	13			
100	0.15	7.2			
200	0.06	3			
300	0.04	1.8			

Key: Dark shading is Q > 0.5; light shading =  $0.1 \le Q \le 0.5$ 

Grapes are another crop that fenthion is sprayed on. The variables used in the AgDRIFT model include the *vineyard* setting, a maximum rate of 0.62 kg ac/ha (1500 L/ha corresponding to 41.25 g ac/100 L), a water depth of 15 cm and a water body width of 3 m. The risk to the most sensitive aquatic invertebrates is unacceptable up to ~250 m but may be mitigated beyond that zone (Table 36).

Table 36. Risk quotients for spray drift from airblast sprayers in vineyards (Vineyard setting) using AgDRIFT at 0.62 kg ac/ha in water 15 cm deep and 3 m wide.

Vineyard (Grapes)					
Distance	Risk Quotients (Q)				
metres	Daphnia magna pink shrimp				
	$EC_{50} = 5.2  (\mu g/L)$	$EC_{50} = 0.11  (\mu g/L)$			
10	0.67	31			
20	0.29	13			
60	0.07	3.4			
100	0.04	1.7			
200	0.01	0.65			
300	0.008	0.35			

Key: Dark shading is Q > 0.5; light shading =  $0.1 \le Q \le 0.5$ 

In refining the risk further the physical properties of fenthion are considered as well as a more realistic assumption concerning the environment where most orchards are found.

Photodegradation in water is a significant route of degradation of fenthion under environmental conditions (see section 3.2.1). It's estimated that after 1 day, the amount of fenthion in Australian water will be between 50 - 70% of the initial concentration (i.e. 30 - 50% of fenthion aquatically photodegraded) based on the following:

- the assumption that the ecotoxicity studies were performed under normal conditions with respect to day- and night-time;
- an aqueous photolysis study by Wilmes (1988) calculated the half-life of fenthion in water under natural sunlight based on experimental determination of the quantum yield and further calculations. The half-lives of fenthion were calculated as 9.8, 7.2 and 15.4 hours for spring, summer and autumn respectively at 30°N. The average half-life over these 3 seasons is ~11 hours;
- the higher concentration of fenthion (70%) assumes that photodegradation only occurs during sunlight hours and the average number of sunlight hours for Sydney (30° south) in one day is ~8 hours according to the Bureau of Meteorology (BoM) website (2014) (October to April when fenthion will be mainly used). Hence after 24 hours the number of hours of sunlight is 8 hours (i.e. ~ 2/3 of a half-life) during these seasons; and
- the lower concentration (40%) is based on the number of daylight hours in a day being ~12 hours (i.e. around one half-life).

It should be noted that the estimates of aquatic photodegradation made above may be overestimates since Australian waters can be quite turbid (i.e. the initial concentration of fenthion after 1 day would be expected to be higher than 50 - 70% as determined above).

The physical properties of fenthion clearly indicate moderate binding to soil, with Koc ranging from 957 to 2660 (see the Aerobic Aquatic Metabolism section, 4.1.2) and therefore moderate binding to sediment in Australia's turbid streams may be expected. The results from aquatic metabolism studies show significant adsorption to sediment, reaching 45% of applied active after 3 days (Anderson and Wilmes, 1988).

Another, although older study, showed 20% adsorption to sediment after 1 day (Fredrickson, 1976). From these two studies it appears that around 20% of the intial concentration of fenthion will be adsorbed to sediment after 1 day and hence the amount of fenthion (and metabolites) in solution will be ~80% of the initial concentration.

The values in Table 37 and Table 38 are generated for citrus (normal and lower rates), large pears, apples and stone fruit corresponding to application rates 8.25 and 1.64 kg ac/ha for citrus, 3.3 and 2.47 kg ac/ha for large pears and apples, and 1.57 kg ac/ha for stone fruit, allowing for aqueous photodegradation and sediment adsorption/desorption of fenthion. When considering the PECs for daphnia and pink shrimp, it's estimated the concentration of fenthion after one day will be 40-55% of initial due to aqueous photodegradation and soil adsorption. The EC50s are: daphnia 5.2  $\mu$ g/L and pink shrimp 0.11  $\mu$ g/L.

After allowing for the above mitigating factors and using the higher initial concentration of fenthion (55%) after one day, the risk quotient determinations based on the label rates indicate up to and beyond 300 m from the sprayed area the risk is still unacceptable to sensitive aquatic invertebrates (see Table 37) when fenthion is used on:

- citrus trees whether the normal rate or the lower rate (as claimed by the registrant) is applied;
- large pear trees;
- apple orchards (i.e. pome fruit orchards); and
- stone fruit orchards.

Table 37. Risk quotients for spray drift from airblast sprayers using the dense and normal settings in AgDRIFT applying the corresponding application rates for each crop in water 15 cm deep and 3 m wide and allowing for 1 day of aquatic photodegradation and sediment adsorption (i.e. 55% of initial concentration).

Distance		Dense					Nor	mal		
(m)	Citrus (1	normal	Citrus	s (low	Large	e pears	Apples (max		Stone fruit (max	
	rate	e)	ra	te)			rate)		rate)	
	$Q_{DM}$	Q <sub>PS</sub>	$Q_{DM}$	$Q_{PS}$	$Q_{DM}$	$Q_{PS}$	$Q_{DM}$	$Q_{PS}$	$Q_{DM}$	Q <sub>PS</sub>
10	38	1804	7.6	358	1.2	53	0.82	40	0.54	25
20	18	844	3.5	167	0.60	29	0.47	21	0.30	14
60	4.4	211	0.93	43	0.20	9.4	0.15	7.1	0.099	4.6
100	2.6	123	0.51	24	0.11	5.3	0.082	4.0	0.053	2.5
200	1.3	58	0.26	12	0.047	2.2	0.035	1.6	0.022	1.0
300	0.79	39	0.16	7.7	0.027	1.3	0.020	0.99	0.013	0.60

Key: Dark shading is Q > 0.5; light shading =  $0.1 \le Q \le 0.5$ ;  $Q_{DM} = risk$  quotient for *Daphnia magna*;  $Q_{PS} = risk$  quotient for pink shrimp (*Penaeus duorarum*)

Given the lower initial concentration of 40% after 1 day, the risk quotient determinations based on the label rates indicate up to and beyond 300 m from the sprayed area the risk is still unacceptable to sensitive aquatic invertebrates (see Table 38) when fenthion is used on:

- citrus trees whether the normal rate or the lower rate (as claimed by the registrant) is applied;
- large pear trees; and

• apple orchards (i.e. pome fruit orchards).

Since no further mitigation can be considered, the risk is also unacceptable to the most sensitive aquatic organisms for stone fruit.

Table 38. Risk quotients for spray drift from airblast sprayers using the dense and normal settings in AgDRIFT applying the corresponding application rates for each crop in water 15 cm deep and 3 m wide and allowing for 1 day of aquatic photodegradation and sediment adsorption (i.e. 40% of initial concentration).

Distance	Dense			Dense Normal						
(m)	Citrus (1	normal	Citrus	s (low	Large	e pears	Apples (max		Stone fruit (max	
	rate	e)	ra	te)			ra	te)	ra	ate)
	$Q_{DM}$	Q <sub>PS</sub>	$Q_{DM}$	Q <sub>PS</sub>	$Q_{DM}$	Q <sub>PS</sub>	$Q_{DM}$	Q <sub>PS</sub>	$Q_{DM}$	Q <sub>PS</sub>
10	27	1311	5.5	260	0.82	38	0.61	29	0.39	18
20	12	613	2.6	122	0.45	21	0.34	15	0.22	10
60	3.3	157	0.66	31	0.15	7	0.11	5.2	0.07	3.3
100	1.9	87	0.37	17	0.082	3.9	0.061	2.9	0.039	1.8
200	0.90	42	0.18	8.5	0.034	1.6	0.026	1.2	0.016	0.77
300	0.60	28	0.12	5.6	0.020	0.94	0.015	0.70	0.010	0.45

Key: Dark shading is Q > 0.5; light shading =  $0.1 \le Q \le 0.5$ ;  $Q_{DM} = risk$  quotient for *Daphnia magna*;  $Q_{PS} = risk$  quotient for pink shrimp (*Penaeus duorarum*)

Given the maximum application rates for deciduous trees (i.e. 1.65 kg ac/ha for large trees; Table 1) is between that for stone fruit and apples (1.57 and 2.47 kg ac/ha, respectively), and the *normal* setting would also be used when using the AgDRIFT modelling program, the risk will be unacceptable to sensitive aquatic invertebrates up to and beyond 300 m from the sprayed area. Similarly, the risk will be unacceptable to aquatic invertebrates when fenthion is used according to the label on mango trees given that the maximum application rate (2.09 kg ac/ha) is between that for citrus at the normal rate and the lower rate (8.25 and 1.64 kg ac/ha, respectively) and the setting used in AgDRIFT is also *dense*.

AgDRIFT (orchard air blast; Tier 1) is also capable of determing PEC values for grapes (*vineyard* setting). Using the same mitigating factors as those above and an application rate of 0.62 kg ac/ha, the results, as shown in Table 39, indicate the risk is unacceptable to sensitive aquatic invertebrates (mitigation of risk is not possible to be considered further).

Table 39. Risk quotients for spray drift risks from airblast applications for grapes (Vineyard setting) using AgDRIFT applying the corresponding application rates for each crop in water 15 cm deep and 3 m wide and allowing for 1 day of aquatic photodegradation and sediment adsorption (i.e. 40-55% initial concentration).

Distance (m)	Vineyard (Grapes)			
	$Q_{ m DM}$	Q <sub>PS</sub>		
10	0.27 - 0.37	12 - 17		
20	0.12 - 0.16	5.5 – 7.5		
60	0.029 - 0.040	1.4 – 1.9		
100	0.015 - 0.020	0.70 – 0.96		
200	0.006 - 0.008	0.26 - 0.36		
300	0.003 - 0.004	0.14 - 0.19		

Key: Dark shading is Q > 0.5; light shading =  $0.1 \le Q \le 0.5$ ;  $Q_{DM} = risk$  quotient for *Daphnia magna*;  $Q_{PS} = risk$  quotient for pink shrimp (*Penaeus duorarum*)

Even after taking aqueous photodegradation and sediment adsorption into consideration, the risk still remains unacceptable for all orchard and vineyard crops. Therefore the Department of the Environment can't support the retention of the use of fenthion for these crops.

#### 11.2.2.4 Applications by Boom Spray

Boom spraying is the normal method of spraying vegetables (including tomatoes). For ground application, the AgDRIFT model's options of a very fine to fine (ASAE, volume medium diameter 175  $\mu m$ ), taken to establish buffer distances for applications using fine spray quality nozzles, and a fine to medium/coarse spray (ASAE, volume medium diameter 341  $\mu m$ ), to establish buffer distances for use of medium quality spray nozzles and a high boom application (1.27 metres height [i.e. the height above the crop, not the ground]) have been considered. The decision to generate spray drift results from high boom (rather than low boom) is based on APVMA (2008a) directions that the higher risk conditions are assumed unless indicated otherwise on the label. This will be the case here. The drift values are based on 90th percentile values from the AgDRIFT program for all spray qualities other than coarse and very coarse where the 50th percentile data values from the medium/coarse spray setting are used (APVMA advice 2 September 2008) with 20 swaths. The AgDRIFT model for high boom application assumes a swath width of 13.7 m.

The label rate of 0.41 kg ac/ha and the water body depth of 15 cm and width of 3 m are used in the risk determination. For the risk assessment, the daphnia EC50 value of 5.2  $\mu$ g ac/L and pink shrimp EC50 value of 0.11  $\mu$ g ac/L are used. The distances assessed for fine, medium and course quality spray nozzles are shown in Table 40. The risk is unacceptable to pink shrimp regardless of which nozzle quality is used.

3.4

1.6

0.92

( 8	( ) ( ) ( ) ( ) ( ) ( ) ( ) ( ) ( ) ( )							
Distance		High Boom (Tomtaoes)						
(m)	Fine 1	Fine nozzle Medium nozzle Coarse nozzle				nozzle		
	$Q_{DM}$	Q <sub>PS</sub>	$Q_{DM}$	Q <sub>PS</sub>	$Q_{DM}$	Q <sub>PS</sub>		
10	3.5	166	0.78	37	0.57	27		
20	1.9	87	0.48	22	0.32	15		
60	0.62	20	0.21	0.8	0.12	5.7		

0.13

0.066

0.041

6.3

3.1

0.073

0.033

0.019

Table 40. Risk quotients for spray drift from high boom ground sprayers for tomatoes (high boom) using AgDRIFT at 0.41 kg ac/ha in water 15 cm deep and 3 m wide.

Key: Dark shading is Q > 0.5; light shading =  $0.1 \le Q \le 0.5$ ;  $Q_{DM} = risk$  quotient for *Daphnia magna*;  $Q_{PS} = risk$  quotient for pink shrimp (*Penaeus duorarum*)

16

6.6

3.5

Further mitigation, as detailed above, is considered. That is, allowing for 30 - 50% aquatic photodegradation and 20% sediment adsorption of fenthion after 1 day, the values in Table 41 are generated for tomatoes. The results indicate the risk is unacceptable to sensitive aquatic invertebrates (mitigation of risk will not be considered further) whether a fine, medium or coarse nozzle is used.

Table 41. Risk quotients for spray drift from high boom ground sprayers for tomatoes (high boom) using AgDRIFT and the application rate of 0.41 kg ac/ha in water 15 cm deep and 3 m wide and allowing for 1 day of aquatic photodegradation and sediment adsorption (i.e. 40-55%) initial concentration).

Distance	High Boom (Tomtaoes)					
(m)	Fine nozzle		Medium nozzle		Coarse nozzle	
	Q <sub>DM</sub>	Q PS Q DM Q PS		$Q_{DM}$	Q <sub>PS</sub>	
10	1.4 - 1.9	66 - 91	0.31 - 0.43	14 - 20	0.23 - 0.32	10 – 14
20	0.74 - 1.0	35 - 48	0.19 - 0.26	9.1 – 12	0.13 - 0.18	6 – 8.3
60	0.25 - 0.34	11 - 16	0.083 - 0.11	3.9 - 5.4	0.049 - 0.067	2.3 - 3.2
100	0.14 - 0.19	6.6 – 9.1	0.053 - 0.073	2.5 - 3.4	0.029 - 0.04	1.4 – 1.9
200	0.055 - 0.076	2.6 - 3.6	0.026 - 0.036	1.2 - 1.7	0.013 - 0.018	0.62 - 0.86
300	0.03 - 0.041	1.4 - 2.0	0.016 - 0.023	0.77 - 1.1	0.008 - 0.011	0.37 - 0.51

Key: Dark shading is Q > 0.5; light shading =  $0.1 \le Q \le 0.5$ ;  $Q_{DM} = risk$  quotient for *Daphnia magna*;  $Q_{PS} = risk$  quotient for pink shrimp (*Penaeus duorarum*).

Once again, with further mitigation taken into consideration as detailed above, the risk still remains unacceptable when vegetables are sprayed. Since ornamentals may also be sprayed (to control mealybug) using a label rate higher than that for tomatoes (i.e. 100 mL product/100 L and 75 mL/100 L, respectively), we can conclude that the risk to the most sensitive aquatic invertebrates will also be unacceptable when these plants are sprayed. Therefore the Department of the Environment can't support the retention of spraying fenthion on vegetables or ornamentals.

#### 11.2.2.5 Multiple applications

100

200

0.35

0.14

0.075

It should be noted that only single applications of fenthion will be considered since the persistence of the active constituent in an aquatic scenario should not be an issue. This is based on the results of the aquatic photodegradation studies, aquatic metabolism studies combined with the label instructions that the most frequent applications in a season will be 6, 4, 3, 2 and 1 weeks before harvest (i.e. at least 7 days between applications). With respect to the results from aquatic metabolism studies, they show significant adsorption to sediment of around 30% of applied active after 7 days and just 13% of the initial fenthion in solution and after 14 days ~7% of

the initial fenthion was adsorbed and 2% was in solution (Anderson and Wilmes, 1988). Therefore 7 days after application, it's expected less than 1% of the initial fenthion will be in the aquatic compartment. Therefore, there is unlikely to be a significant increase in concentration from multiple applications, even under worst case conditions with a high level of multiple applications.

However, the main problem is repeated effects on organisms and 7 days between sprays may not allow affected populations to recover.

For ground spraying and even taking mitigation into consideration, it's been shown that fenthion can no longer be used safely on orchard crops, vineyard crops, vegetables and ornamentals.

#### 11.2.2.6 Aerial Application

Aerial application is not regarded as the normal practice for applying pesticides to orchards and vegetables, and is likely to be used for tomatoes only. It's noted that aerial application is not precluded on the fenthion label. The fenthion application rate for tomatoes is 410 g/ha.

The spray drift risk assessment has been performed in accordance with the *APVMA Operating Principles in Relation to Spray Drift* (APVMA 2008a). Consequently, the model used is AgDISP (v 8.15). Three wind speeds have been modelled (8, 14 and 20 km/h) and the maximum downwind distance considered is 800 m (the reliable limit of the model). The model parameters used are in Table 42:

Table 42. Variables used in AgDISP

Aircraft: Air Tractor AT-502	Non-volatile fraction: 750 mL/ha in 20 L (set at
	0.0375)
Spray quality:	Active fraction: 410 g ac/ha in 20 L (set at 0.0205)
ASAE fine to medium (Dv0.5 254.7 µm) for	
application of a medium quality spray, and	
ASAE medium to coarse (Dv0.5 340.9 µm for	Minimum spray volume: 20 L/ha is used as
application of a coarse quality spray	specified by the APVMA.
Release (boom) height: 3 m	<b>Wind speeds:</b> 5.56 m/s (20 km/h), 3.89 m/s (14
	km/h) and 2.22 m/s (8 km/h)
No. of flight lines: 30	Wind direction: -90°
No. of nozzles: 34	Temperature: 30°C
Extent of nozzles: 70%	Relative humidity: 40%
Nozzle distribution: 70% of boom length	Atmospheric stability: Overcast
Swath width: 20 m;	Canopy: none
Swath displacement: 0	Surface roughness (m): 0.0075
Spray material: water	<b>Downwind water body dimensions:</b> 3 m width and
	0.15 m depth.

Model runs have been undertaken to account for differences in wind speed, differences in droplet size, and a spray volume of 20 L/ha. Following agreement with the APVMA, when modelling for a medium spray, the "fine to medium" spectrum is used, and when modelling for coarse spray, the "medium to coarse" spectrum is used. Therefore, median droplet sizes modelled were 255 and 341  $\mu$ m respectively. Based on these considerations and given the EC50 values of daphnia is 5.2  $\mu$ g ac/L and pink

shrimp is  $0.11~\mu g$  ac/L, the risk was unacceptable for both the medium and coarse spray nozzles at the various wind speeds (Table 43, Table 44 and Table 45) up to the limit of the model's capability. Therefore the Department of the Environment recommends aerial application of fenthion should be prohibited.

Table 43. Spray drift estimates from a single aerial application (wind speed 20 km/h) for tomatoes using AgDISP at 0.41 kg ac/ha in water 15 cm deep and 3 m wide.

Distance (m)	PEC (μg/L)	Risk quotient (Q)		
		Daphnia (Daphnia	Pink shrimp (Penaeus	
		magna)	duorarum)	
500	12.2	2.3	111	
600	10.6	2.0	96	
700	9.1	1.8	83	
800	7.9	1.5	72	

Key: Dark shading is Q > 0.5; light shading =  $0.1 \le Q \le 0.5$ .

Table 44. Spray drift estimates from a single aerial application (wind speed 14 km/h) for tomatoes using AgDISP at 0.41 kg ac/ha in water 15 cm deep and 3 m wide.

Distance (m)	PEC (µg/L)	Risk quotient (Q)		
		Daphnia (Daphnia	Pink shrimp (Penaeus	
		magna)	duorarum)	
500	1.1	0.22	10	
600	0.85	0.16	7.7	
700	0.65	0.12	5.9	
800	0.51	0.10	4.7	

Key: Dark shading is Q > 0.5; light shading =  $0.1 \le Q \le 0.5$ .

Table 45. Spray drift estimates from a single aerial application (wind speed 8 km/h) for tomatoes using AgDISP at 0.41 kg ac/ha in water 15 cm deep and 3 m wide.

Distance (m)	PEC (µg/L)	Risk quotient (Q)			
		Daphnia (Daphnia	Pink shrimp (Penaeus		
		magna)	duorarum)		
500	0.53	0.10	4.8		
600	0.38	0.074	3.5		
700	0.29	0.056	2.6		
800	0.23	0.044	2.1		

Key: Dark shading is Q > 0.5; light shading =  $0.1 \le Q \le 0.5$ .

#### 11.2.2.7 Run-off

There are large uncertainties involved in predicting runoff, and levels of chemical in run-off will be dependent on location specific and/or event specific parameters. The most important are rainfall and its intensity, infiltration of soil (in turn related to moisture content of soil), the slope, type of soil type of drainage, crop type, amount of trash on soil and cultivation (Mensink, de Greef and Linders, 1996). Other influences include mobility and persistence of the pesticide, formulation type and formulation placement (Environmental Chemistry of Herbicides 1989). In spite of this a reasonable estimation of the amount of chemical in run-off water may be made using

a sub-model of the REXTOX model proposed by the OECD (Probst et al., 2005). The model considers rainfall and run-off water, topography of the land (slope), degradation of the pesticide, mobility of the pesticide and buffer zones. In addition to the REXTOX model, CAS considers heterogeneity of fields, interception and retention of the pesticide by crops/weeds and sediment of transport of the pesticide.

For this assessment a tiered approach is carried out: initially water runoff is considered to the edge of the field and then if there's still an unacceptable risk to the sensitive aquatic organisms, consideration is given to dilution in a 1500 m<sup>3</sup> water body of environmental significance (adaptation of the US EPA model (US EPA, 2004)).

The first tier involves calculating the risk quotients to the edge of the field. The concentration of fenthion is based on a rainfall event of 100 mm with 20 mm run-off (the Department of the Environment currently considers this as the worst case scenario) containing 10% of the active constituent if sprayed directly to the ground (on a hectare basis the run-off will be 200 m<sup>3</sup> (200 000 L)). However, since fenthion is sprayed on crops with full foliage, it's expected that 80% of the active constituent will be intercepted by the crop (based on pome and stone fruit with full foliage, Linders et al., 2000). Assuming half of the fenthion on the crop is retained on the foliage after rain, it's therefore expected that 60% of the 10% AC is available for runoff (i.e. 6%). The Department of the Environment estimates that only 50% of the area effectively contributes to run-off in more realistic situations (Dunne and Black, 1970) and hence a worst case of 3% run-off is more likely. Assuming the maximum application rates for tomatoes, grapes, stone fruit, apples and citrus (i.e. corresponding to 0.41, 0.62, 1.57, 2.47 and 8.25 kg ac/ha, respectively) and the EC50 values of daphnia is 5.2 µg ac/L and pink shrimp is 0.11 µg ac/L, the risk quotients (Q) were determined and are presented in Table 46. The results indicate that the risk is unacceptable to these sensitive aquatic invertebrates.

Table 46. Risk quotients from run-off after mitigation for heterogeneity of field and interception by crops.

	Tomatoes	Grapes	Stone fruit	Apples	Citrus
PEC (µg/L)	61	93	235	370	1 237
Q <sub>DM</sub>	12	18	45	71	238
Q <sub>PS</sub>	554	845	2 141	3 368	11 250

Key: Dark shading is Q > 0.5; light shading =  $0.1 \le Q \le 0.5$ ;  $Q_{DM} = risk$  quotient for *Daphnia magna*;  $Q_{PS} = risk$  quotient for pink shrimp (*Penaeus duorarum*).

Further mitigation considers adsorption to the soil. A reasonable estimation of the amount of chemical in water may be made using a sub-model of the REXTOX model proposed by the OECD (Probst et al., 2005):

L\%\text{runoff} = (R/P) \times \text{Crsoil}\\_\text{surface} \times \text{f1slope} \times \text{f2bufferzone} \times 100.

(Where L% runoff is the percentage of application dose available in runoff water as dissolved substance, R is the quantity of runoff water (mm/day) and P daily precipitation (mm/day) and

Crsoil\_surface =  $e^{(-3 \ln 2 \div DTsoil)} \times (1 \div (1 + Kd))$  for three days of degradation)

Assuming that the run-off occurs 3 days after application and using the soil adsorption value (Kd) of 38 (most of the crops on the label are grown in sandy loam soil which corresponds to a Kd of  $\sim$ 38; refer to Puhl and Hurley, 1978; Section 5.1) and a DT50 of 5 days, then the Cr soil\_surface is 0.017. Since R is 20 mm, P is 100 mm and f1slope is 0.5 for a slope <12.5% and f2 buffer zone =  $0.83^{\text{buffer width}}$  (a default value for the buffer width is 1), then L% run-off is 0.14%. Further consideration of the heterogeneity of the field and interception of fenthion by the crops indicates a more likely run-off to be 0.042%. The risk quotients are in Table 47.

Table 47. Risk quotients from run-off after mitigation for soil adsorption/degradation

	Tomatoes	Grapes	Stone fruit	Apples	Citrus
PEC (µg/L)	0.86	1.3	3.3	5.2	17
Q <sub>DM</sub>	0.17	0.25	0.63	1.0	3.3
Q <sub>PS</sub>	7.8	12	30	47	158

Key: Dark shading is Q > 0.5; light shading =  $0.1 \le Q \le 0.5$ ;  $Q_{DM} = risk$  quotient for *Daphnia magna*;  $Q_{PS} = risk$  quotient for pink shrimp (*Penaeus duorarum*).

As indicated in Table 47, the risk is still unacceptable to the sensitive aquatic invertebrates pink shrimp to the edge of the field after mitigation for soil adsorption, heterogeneity of the field and interception of fenthion by the foliage.

Consideration is now given to run-off going into a 1500 m³ water body of environmental significance (e.g. a 1 ha pond that's 15 cm deep). In a worst case scenario the water body is considered to be fed entirely by the largest likely field which is 10 ha (USEPA, 2004). In most circumstances the amount of runoff from 10 ha will result in a water body larger than 1500 m³. The concentration in the water body may be calculated assuming that 200 m³ from each hectare for a total of 10 ha flows into the 1500 m³ water body resulting in a total water body of 3500 m³. The Q values taking this dilution into account are presented in Table 48. The risk is still unacceptable to pink shrimp for all crops although it is acceptable to daphnia when used on tomatoes.

Table 48. Risk quotients from run-off after mitigation for environmental receiving waters

	Tomatoes	Grapes	Stone fruit	Apples	Citrus
PEC (µg/L)	0.49	0.74	1.9	3.0	9.7
Q <sub>DM</sub>	0.094	0.14	0.36	0.57	1.9
Q <sub>PS</sub>	4.5	6.7	17	27	88

Key: Dark shading is Q > 0.5; light shading =  $0.1 \le Q \le 0.5$ ;  $Q_{DM} = risk$  quotient for *Daphnia magna*;  $Q_{PS} = risk$  quotient for pink shrimp (*Penaeus duorarum*).

Even with mitigation for soil adsorption, heterogeneity of the field, interception of fenthion by the foliage and dilution of the run-off into a body of water, the risk is still unacceptable to the sensitive aquatic invertebrate pink shrimp due to run-off effects and therefore fenthion cannot be used safely on orchard crops, vineyard crops and vegetables.

Thorough soil drenching is recommended to control mealybug on ornamentals (South Australia and Western Australia only). No further information was provided on the label with respect to the situation (e.g. nurseries, glass houses, etc). It's noted that the label dilution rate for ornamentals is 100 mL product/100 L (i.e. higher than the label rate for tomatoes at 75 mL/100 L). A vast area of soil will not be covered with fenthion when the soil is drenched but high concentrations of fenthion are expected around each plant. Therefore the overall concentration of run-off from such an application method is expected to be comparable to the concentrations calculated for those crops (i.e. tomatoes, grapes) investigated above when sprayed, which includes mitigation for soil adsorption, heterogeneity of the field and dilution of fenthion into environmental receiving waters. Therefore the Department of the Environment concludes fenthion cannot be used safely on ornamentals to control mealybug when the soil is drenched.

### 11.3 Risk assessment conclusion for agricultural uses

While there are no reports of avian toxicity when used according to label directions for orchard applications, based on available information application rates indicative of insect control on pome fruit (2.47 kg ac/ha) result in a potentially unacceptable risk from a single treatment to birds frequenting and feeding in fenthion-treated orchards. When fenthion is used for grasshopper control in orchards the risk is unacceptable to birds feeding off these insects. Therefore the use of fenthion for controlling grasshoppers should be prohibited.

The contact toxicity data for fenthion to bees indicates the risk is unacceptable, even at the lower application rates. There are no oral toxicity data. If any orchard uses are retained, the bee warning statement should be amended to:

Toxic to bees. Will kill bees foraging in the crop to be treated or in hives which are over-sprayed or reached by spray drift. Residues may remain toxic to bees for several days after application.

The acute risk to earthworms is acceptable. There are no data for chronic effects but considering the rapid degradation in the aerobic soil metablosim studies and most of the spray will be intercepted by the trees, it's expected the chronic risk will be acceptable. Fenthion applied at rates much lower than the label rates demonstrate that the risk is unacceptable to other terrestrial invertebrates. If orchard and vegetable uses are retained, a warning should be included on the label as follows:

Integrated Pest Management: Lebaycid may kill non-target beneficial invertebrates. IPM programmes may be adversely affected.

It's expected that the risk to terrestrial mammals will be acceptable since it's unlikely they will be exposed to direct overspray when fenthion is applied by ground based sprayers.

Using the AgDRIFT spray drift modelling (APVMA, 2008a), the risk to the most sensitive aquatic organisms is unacceptable when fenthion is applied by orchard air blast equipment to citrus, large pear trees, apples and grapes, even when the

calculations were refined to allow for aquatic photodegradation and adsorption of fenthion to sediment. Given the application rates for these crops, it also indicates that the risk would also be unacceptable when fenthion is applied to stone fruit, deciduous, tropical and sub tropical fruit. Therefore, fenthion cannot be used safely on orchard crops (citrus, pome and stone fruit, tropical and sub-tropical fruits) and vineyard crops by ground sprayers.

Through similar use of spray drift modelling, application by boom spray equipment to vegetable crops was determined to represent an unacceptable risk to the most sensitive aquatic invertebrates even when a coarse spray quality nozzle is used and aquatic photodegradation and adsorption to sediment were considered. Therefore fenthion cannot be used safely on vegetable crops using boom spray equipment.

There is currently little if any aerial application of fenthion, as this is not regarded as the normal practice for applying pesticides to orchards or vegetable crops, but it is not prohibited on the labels. Even though the risk assessment was carried out at various wind speeds and various quality spray nozzles, it showed an unacceptable risk to sensitive invertebrates. Therefore, aerial application of fenthion should be prohibited.

The risk was unacceptable to sensitive aquatic invertebrates when the run-off effects of fenthion applied to vegetables, vineyard crops and orchard crops were considered even when a number of factors were taken into consideration (i.e. interception of the spray by the crops, homogeneity of the field, soil adsorption and degradation and dilution in environmental water). Soil drenching is used to control mealybug on ornamentals. It's expected the risk will be unacceptable to sensitive aquatic organisms from the run-off generated from a rain event after the soil has been drenched. These outcomes further support the above conclusions that fenthion cannot be used safely on vegetables, ornamentals, vineyard crops and orchard crops.

The risk to terrestrial vegetation is expected to be minimal since fenthion was stated to be non-phytotoxic although some varieties of apples and cotton could be injured (Tomlin, 1997). There were no phytoxicity studies.

#### 11.4 Post-harvest treatment

There is use of fenthion for the post-harvest dipping and flood spraying of tropical and subtropical fruits and vegetables to control fruit flies as a quarantine treatment. As these applications occur in packing sheds using either dips or flood sprays (see Section 2.1.1.1) at a concentration of 75 mL/100 L (41.25 g ac/100 L = 0.413 ppm), the environmental exposure is limited to when the spent dips are disposed. Currently the directions on the labels refer to departmental guidelines for the disposal of the spent dips.

The NT Primary Industry and Fisheries Agnote (No 743, dated September 1998) entitled "Guidelines for disposal of fenthion/prochloraz dip or spray mixture" suggests the following options for disposal:

1. Used fenthion/prochloraz mixtures can be disposed of after treating with lime for two months in a tank used only for that purpose. To neutralise the chemical component, add 3 kg either of slaked, hydrated or quick lime per

100 litres of waste solution. Check the tank regularly to ensure the pH level remains above 11. Add more lime if the pH starts to fall.

At the end of the 60 day period, the inert mix can be poured into a trench or sprayed on fallow or unproductive ground or disposed of at least 100 metres away from any streams, drains, channels, wells, boreholes or water courses.

- 2. Alternatively used fenthion/prochloraz can be sprayed under the orchard trees at a maximum rate of 1000 litres per fortnight.
- 3. Used fenthion (not mixed with prochloraz) can be diluted and re-used in an approved spray program. The withholding period for foliar application to mangoes is 7 days.

None of these would appear to be the optimal solutions. The difficulty in raising the pH above 11 and ensuring complete degradation has already been raised in relation to disposal of other dips, e.g. diazinon sheep dips (APVMA, 2002). The need to store for 60 days and check the pH regularly also raises practicality problems. This option is not likely to be either practical or effective. Further through the RLC project which developed guidelines for the disposal of spent dipping solutions, it has been made clear that many States view disposal to land as non-sustainable. The concept of spraying such mixtures onto the orchard floor has in particular highlighted concerns about residues etc, even if the actives are registered for application to the trees.

Based on the work carried out on the disposal of spent dipping solutions, a set of criteria which should allow ground disposal of spent dipping solutions have been developed by the Department of the Environment and agreed by the APVMA and RLC, namely:

1. The active has a half-life in soil <10 days at the likely concentrations following dip disposal;

#### AND/OR

2. The active must be able to be denatured safely, quickly and completely (>98% in 2 hours) prior to disposal;

#### **AND**

- 3. If repeat applications are to be made to the same site, and denaturing is not possible, these should not occur until 4 half-lives have passed;
- 4. The spent dip should be evenly spread over flat land at a rate not exceeding 100 000 L/ha for spent sheep dips and 20 000 L/ha for spent fruit dips;
- 5. The disposal site must be dedicated and adequately bunded (soil at least 15 cm high).

With respect to fenthion, studies indicate that aerobic soil metabolism half-lives are in the range of <1 to ~6 days depending on the conditions (applied at 1-10 mg/kg). Examination of the data shows this is largely based on a single acceptable study at 1 mg/kg, with other studies performed at up to 10 mg/kg considered less reliable. Another aspect is that fenthion is mainly oxidised to its sulphoxide, which is expected

to be toxic. Therefore the Department of the Environment is unable to state uneqivocally that the half-lives of fenthion and its toxic residues in soil would be <10 days at the expected concentration range (up to 11 mg fenthion/kg soil) following disposal of spent dipping solutions to soil. However, direct disposal to dedicated land would be a better option than the current practice of neutralising with lime and storing for 60 days.

The disposal instructions for the spent dip on the labels, which refer the user to departmental guidelines for the disposal of the spent dips, are outdated. Pending a study, such as one performed according to OECD TG 307 (*Aerobic and Anaerobic Transformations in Soil*), or preferably a field study simulating expected conditions, can demonstrate that fenthion and its toxic residues have half-lives in soil <10 days at the likely concentrations following dip disposal (up to 11 mg fenthion/kg soil), the interim label statement should read:

Dispose of used dip solution and sludge at a rate not exceeding 20 000 L/ha over an area of dedicated and bunded flat land, away from watercourses and any drainage areas, etc, that could contaminate watercourses, and restrict access to humans and stock for a period of at least 3 months.

#### 11.5 Veterinary use

Veterinary usage is as a spot-on for cattle. Usage is declining due to the withdrawal of the claim for use in dairy cattle. As noted previously (Section 2.1.1.2) total usage is below 5 tonnes per annum. Fenthion is applied in one spot, to the rump or loins in cattle.

The method of application, a single spot on the backs of cattle using an applicator gun, is unlikely to result in significant environmental exposures to beneficial arthropods that breed in the excreta, eg dung beetles. Although cattle are treated dermally, there is potential for absorption as well as ingestion (and therefore excretion in the faeces) of fenthion as cows are known to lick themselves periodically. However, data supplied by the registrant indicates that fenthion is extensively metabolised in animals and largely excreted in the urine, with only a minor portion appearing in the faeces. As the metabolites are likely to be considerably less toxic than the parent compound, these are unlikely to create an adverse impact on beneficial arthropods in dung. The Department of the Environment is not aware of any reports where organophosphates have been implicated in toxicity to dung dwelling invertebrates.

#### 11.6 Risk assessment conclusion for veterinary use

The method of application as a spot-on formulation to backs of target animals is unlikely to result in significant environmental exposure. Once applied fenthion is expected to remain with the animal until it is degraded and active that is adsorbed is expected to be metabolised before excretion. Any residues in the application equipment is expected to be disposed of with domestic garbage and once in the landfill, fenthion should degrade. Therefore fenthion remains acceptable to be used as a spot-on product for cattle.

#### 11.7 Risk arising from formulation, handling and disposal

The risk from formulation of the fenthion in Australia is expected to be minimal. This is expected to be done in suitable facilities, with relevant environmental controls to limit environmental exposure. Wastewater is expected to be treated before discharge to the sewer and environment. With dilution and adsorption, the environmental hazards are expected to be minimal. Any spills are expected to be cleaned up and treated according to the MSDS.

#### 11.8 Controls/Labelling

Fenthion or its used containers must not be allowed to contaminate wetlands or watercourses (e.g. rivers, streams, ponds, waterways) or drains.

The material safety data sheet contains adequate information and instructions for containing and disposing of spills during transport.

With respect to storage, the labels on both the agricultural and veterinary products are satisfactory.

### **Agricultural product 32996**

Spray drift modelling (AgDRIFT and AgDISP) and risk determinations for run-off indicated that fenthion can no longer be used on the tree and vine crops and the non-tree/vine crops listed on the label. The only safe use remaining is for post-harvest treatment (dips and flood spraying). Therefore extensive label amendments (including deletions) will be required that pertain to the use of fenthion on tree and vine crops and the non-tree/vine crops (i.e. Directions for Use, General Instuctions pertaining to spraying of fenthion, Crop Safety, etc). The Directions for Use section on Post-harvest Treatment are satisfactory.

The label statement for disposal of agricultural chemical containers has been recently revised in light of the fact that burial of emptied containers is illegal in some states. Therefore the current disposal label statement should be amended to the following recommended statement:

Triple or preferably pressure rinse containers before disposal. Add rinsings to spray tank. Do not dispose of undiluted chemicals on site. If recycling, replace cap and return clean containers to recycler or designated collection point.

If not recycling, break, crush, or puncture and deliver empty container to an approved waste management facility. If an approved waste management facility is not available, bury the container below 500 mm in a disposal pit specifically marked and set up for this purpose clear of waterways, desirable vegetation and tree roots, in compliance with relevant local, state or territory government regulations. Do not burn empty containers or product.

The disposal instructions for the spent dip on the labels, which refer the user to departmental guidelines for the disposal of the spent dips, are outdated. Pending a

study, such as one performed according to OECD TG 307 (*Aerobic and Anaerobic Transformations in Soil*), or preferably a field study simulating expected conditions, can demonstrate that fenthion and its toxic residues have half-lives in soil <10 days at the likely concentrations following dip disposal (up to 11 mg fenthion/kg soil), the interim label statement should read:

Dispose of used dip solution and sludge at a rate not exceeding 20 000 L/ha over an area of dedicated and bunded flat land, away from watercourses and any drainage areas, etc, that could contaminate watercourses, and restrict access to humans and stock for a period of at least 3 months.

#### **Veterinary product 33520**

For the spot-on lice control for cattle product the disposal statement should be amended to:

Triple rinse container before disposal. Dispose of rinsate or any undiluted chemical according to State legislative requirements. If not recycling, break, crush or puncture and deliver empty packaging to an approved waste management facility. DO NOT burn empty containers or product.

The 500 mL container may either use the above statement or that for small containers from the APVMA's Veterinary Labelling Code (APVMA, 2008b):

Dispose of empty container by wrapping with paper and putting in garbage.

#### 12 Conclusions and Recommendations

Fenthion does not have a history of reported fish kills either in Australia or the USA. In the USA there are a number of incident reports related to non-target bird kills when used for mosquito control and to kill pest birds in buildings. There are also instances of bird poisonings in Australia. Fenthion has been withdrawn for use in horticulture in Europe, the USA and Canada.

Fenthion degrades in natural systems by abiotic and biotic pathways. It degrades in photolysis studies in natural sunlight with a half-life of 7 hours and in laboratory soil studies with a half-life between <1 and 22 days. Limited data from field studies show the rapid loss of fenthion. It is moderately to strongly bound to soil and together with the rapid degradation is not expected to leach. However, some of the metabolites could leach.

It is rated as very highly toxic to birds, mammals, fish and aquatic invertebrates. As noted above incident reports from the US involving fenthion as the known toxicant indicate that environmental effects from its use as a bird toxicant due to secondary poisonings are possible.

A comprehensive data package for fate and environmental toxicity has been submitted, and no specific additional studies are identified to complete the assessment, though the field data are poor.

#### **Agricultural product 32996**

The risk assessment for the agricultural uses for fenthion indicated fenthion cannot be used safely when sprayed on the tree and vine crops as well as non-tree/vine crops listed on the current label. All such uses should be removed from all labels. The Department of the Environment can only support post-harvest dips and flood sprays used under the following conditions.

The label statement for disposal of agricultural chemical containers has been recently revised in light of the fact that burial of emptied containers is illegal in some states. Therefore the current disposal label statement should be amended to the following recommended statement:

Triple or preferably pressure rinse containers before disposal. Add rinsings to spray tank. Do not dispose of undiluted chemicals on site. If recycling, replace cap and return clean containers to recycler or designated collection point.

If not recycling, break, crush, or puncture and deliver empty container to an approved waste management facility. If an approved waste management facility is not available, bury the container below 500 mm in a disposal pit specifically marked and set up for this purpose clear of waterways, desirable vegetation and tree roots, in compliance with relevant local, state or territory government regulations. Do not burn empty containers or product.

The disposal instructions for the spent dip on the labels, which refer the user to departmental guidelines for the disposal of the spent dips, are outdated. Pending a study, such as one performed according to OECD TG 307 (*Aerobic and Anaerobic Transformations in Soil*), or preferably a field study simulating expected conditions, can demonstrate that fenthion and its toxic residues have half-lives in soil <10 days at the likely concentrations following dip disposal (up to 11 mg fenthion/kg soil), the interim label statement should read:

Dispose of used dip solution and sludge at a rate not exceeding 20 000 L/ha over an area of dedicated and bunded flat land, away from watercourses and any drainage areas, etc, that could contaminate watercourses, and restrict access to humans and stock for a period of at least 3 months.

#### Veterinary product 33520

Fenthion remains acceptable to be used as a spot-on product for cattle since it's unlikely to result in significant environmental exposure and that adsorbed by the animal is expected to degrade and be metabolised before excretion.

For the spot-on lice control for cattle product in the 2.5 and 10 L containers, the disposal statement should be amended to:

Triple rinse container before disposal. Dispose of rinsate or any undiluted chemical according to State legislative requirements. If not recycling, break,

crush or puncture and deliver empty packaging to an approved waste management facility. DO NOT burn empty containers or product.

The 500 mL container may either use the above statement or that for small containers from the APVMA's Veterinary Labelling Code (APVMA, 2008b):

Dispose of empty container by wrapping with paper and putting in garbage.

# 13 Glossary

$ \begin{array}{c} ac \\ ac/L \\ ac/ha \\ Active constituent per litre \\ ac/ha \\ Active constituent per hectare \\ APVMA \\ Australian Pesticides and Veterinary Medicines \\ Authority \\ AR \\ Applied radioactivity \\ BBA guidelines \\ German guidelines for soil degradation and adsorption \\ BCF \\ Bioconcentration Factor \\ DAT analysis \\ Days after treatment \\ DO \\ Dissolved oxygen \\ DT_{50} \\ Time for 50\% of the substance to dissipate \\ EC \\ Emulsifiable concentrate formulation \\ EC_{50} \\ The concentration of a test substance resulting in an effect on 50% of the test species. \\ E_bC_{50} \\ The concentration of a test substance resulting in a 50% inhibition of biomass in an algal test \\ E_rC_{50} \\ The Existing Chemical Review Program of the \\ \\ ECRP \\ The Existing Chemical Review Program of the \\ \\ \\ ECRP \\ The Existing Chemical Review Program of the \\ \\ \\ ECRP \\ The Existing Chemical Review Program of the \\ \\ \\ ECRP \\ The Existing Chemical Review Program of the \\ \\ \\ ECRP \\ The Existing Chemical Review Program of the \\ \\ \\ ECRP \\ The Existing Chemical Review Program of the \\ \\ \\ ECRP \\ The Existing Chemical Review Program of the \\ \\ \\ ECRP \\ The Existing Chemical Review Program of the \\ \\ \\ ECRP \\ The Existing Chemical Review Program of the \\ \\ \\ ECRP \\ The Existing Chemical Review Program of the \\ \\ \\ ECRP \\ The Existing Chemical Review Program of the \\ \\ \\ ECRP \\ The Existing Chemical Review Program of the \\ \\ \\ ECRP \\ The Existing Chemical Review Program of the \\ \\ \\ ECRP \\ The Existing Chemical Review Program of the \\ \\ \\ \\ ECRP \\ The Existing Chemical Review Program of the \\ \\ \\ \\ ECRP \\ The Existing Chemical Review Program of the \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\$
ac/haActive constituent per hectareAPVMAAustralian Pesticides and Veterinary Medicines AuthorityARApplied radioactivityBBA guidelinesGerman guidelines for soil degradation and adsorptionBCFBioconcentration FactorDAT analysisDays after treatmentDODissolved oxygen $DT_{50}$ Time for 50% of the substance to dissipateECEmulsifiable concentrate formulation $EC_{50}$ The concentration of a test substance resulting in an effect on 50% of the test species. $E_bC_{50}$ The concentration of a test substance resulting in a 50% inhibition of biomass in an algal test $E_rC_{50}$ The concentration of a test substance resulting in a 50% inhibition of growth rate in an algal test
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$ \begin{array}{c} BBA \ guidelines & German \ guidelines \ for \ soil \ degradation \ and \ adsorption \\ BCF & Bioconcentration \ Factor \\ DAT \ analysis & Days \ after \ treatment \\ DO & Dissolved \ oxygen \\ DT_{50} & Time \ for \ 50\% \ of \ the \ substance \ to \ dissipate \\ EC & Emulsifiable \ concentrate \ formulation \\ EC_{50} & The \ concentration \ of \ a \ test \ substance \ resulting \ in \ an \ effect \ on \ 50\% \ of \ the \ test \ species. \\ E_bC_{50} & The \ concentration \ of \ a \ test \ substance \ resulting \ in \ a \ 50\% \ inhibition \ of \ growth \ rate \ in \ an \ algal \ test \\ E_rC_{50} & The \ concentration \ of \ a \ test \ substance \ resulting \ in \ a \ 50\% \ inhibition \ of \ growth \ rate \ in \ an \ algal \ test \\ \end{array}$
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APVMA
EPA or USEPA Environment Protection Authority of the USA
EUP End use product
GC Gas chromatography
<sup>1</sup> H-NMR Hydrogen-1 nuclear magnetic resonance
spectroscopy
HPLC High pressure liquid chromatography?
IOBC guidelines International Organisation of Biological Control
guidelines
IPM Integrated Pest Management
K <sub>d</sub> Soil sorption constant
K <sub>des</sub> Soil desorption constant
K <sub>oc</sub> Soil sorption/desorption coefficient, normalised
to organic carbon content
LC <sub>50</sub> Concentration (for example, in water, food or
soil) resulting in a 50% mortality of the test
organism.
LD50 Dose resulting in a 50% mortality of the test
organism
Lentic water Still or standing water such as in a lake, pond or
reservoir.
LOEC Lowest Observed Effect Concentration i.e. the
test concentration at which some effect occurs

LSC	Liquid scintillation counter
MATC	Maximum acceptable toxicant concentration
MS	Mass Spectrometry
mV	Millivolts: used as a measure of redox potential
NOEC	No observable effect concentration i.e. the test
	concentration at which no effect is observed
NOEL	No observable effect level i.e. the test dose at
	which no effect was observed
oc	Descriptor of soil - organic carbon
OECD	Organisation for Economic Co-operation and
	Development
om	Descriptor of soil - organic matter
PEC	Predicted environmental concentration
PELMO	Pesticide-Leaching-Model
Q or Q- value	The Environmental risk quotient. If <0.1 the risk
	is considered acceptable. If 0.1< Q< 0.5 possibly
	mitigatable. If $Q > 0.5$ the risk is considered
	unacceptable.
QA	Quality Assurance
SAR	Structure activity relationship
TGAC	Technical grade active constituent
TLC	Thin layer chromatography
ToxCal / ToxCal 5.0	Ecotoxicological software package used to
	calculate endpoints
TR	Total Radioactivity
Trimmed-Spearman -	Statistical tests
Trimmed-Spearman-	
Karber	
UV	Ultra violet light
US EPA	United States Environment Protection Authority

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# 15 Appendix I

## Fenthion

$$\begin{array}{c|c} CH_3O & & & & O\\ CH_3O & & & & & \\ CH_3O & & & & \\ \end{array}$$
 Fenthion sulfoxide 
$$\begin{array}{c} CH_3 \\ CH_3 \\ \end{array}$$

$$\begin{array}{c|c} CH_3O & & & & & \\ CH_3O & & & & & \\ CH_3O & & & & & \\ \end{array}$$
 Fenthion sulfone 
$$\begin{array}{c} CH_3 \\ CH_3 \\ \end{array}$$

$$CH_3O$$
 $P$ 
 $CH_3O$ 
 $CH_3O$ 
 $CH_3$ 
 $CH_3$ 
 $CH_3$ 

$$\begin{array}{c} O \\ O \\ CH_3O \end{array}$$
 CH<sub>3</sub>O 
$$\begin{array}{c} O \\ CH_3 \\ CH_3 \end{array}$$
 desmethylfenthion sulfone

$$HO$$
  $\longrightarrow$   $SCH_3$   $CH_3$ 

3-methyl-4-methylthiophenol MMTP

$$\begin{array}{c|c} & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ &$$

MMTP sulfoxide

$$\begin{array}{c|c} & O \\ & \parallel \\ & SCH_3 \\ & \parallel \\ & O \\ & CH_3 \end{array}$$

MMTP sulfone