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Proposed EQS for Water Framework Directive Annex VIII substances: cypermethrin

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The UK Technical Advisory Group (UKTAG) supporting the implementation of the Water Framework Directive (2000/60/EC) is a partnership of UK environmental and conservation agencies. It also includes partners from the Republic of Ireland. This report is the result of research commissioned and funded on behalf of UKTAG by the Scotland & Northern Ireland Forum for Environmental Research (SNIFFER) and the Environment Agency's Science Programme.

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Steve Killeen

Head of Science

Use of this report

The development of UK-wide classification methods and environmental standards that aim to meet the requirements of the Water Framework Directive (WFD) is being sponsored by the UK Technical Advisory Group (UKTAG) for WFD on behalf of its members and partners.

This technical document has been developed through a collaborative project, managed and facilitated by the Scotland & Northern Ireland Forum for Environmental Research (SNIFFER), the Environment Agency and the Scottish Environment Protection Agency (SEPA) and has involved the members and partners of UKTAG. It provides background information to support the ongoing development of the standards and classification methods.

Whilst this report is considered to represent the best available scientific information and expert opinion available at the stage of completion of the report, it does not necessarily represent the final or policy positions of UKTAG or any of its partner agencies.

Executive Summary

The UK Technical Advisory Group (UKTAG) has commissioned a programme of work to derive Environmental Quality Standards (EQSs) for substances falling under Annex VIII of the Water Framework Directive (WFD). This report proposes predicted no-effect concentrations (PNECs) for cypermethrin using the methodology described in Annex V of the Directive. There are existing EQSs for cypermethrin, but the method used to derive these is not considered to comply with the requirements of Annex V and so is unsuitable for deriving Annex VIII EQSs.

The PNECs described in this report are based on a technical assessment of the available ecotoxicity data for cypermethrin, along with any data that relate impacts under field conditions to exposure concentrations. The data have been subjected to rigorous quality assessment such that decisions are based only on scientifically sound data. Following consultation with an independent peer review group, critical data have been identified and assessment factors selected in accordance with the guidance given in Annex V.

Where possible, PNECs have been derived for freshwater and saltwater environments, and for long-term/continuous exposure and short-term/transient exposure. If they were to be adopted as EQSs, the long-term PNEC would normally be expressed as an annual average concentration and the short-term PNEC as a 95th percentile concentration.

The feasibility of implementing these PNECs as EQSs has not been considered at this stage. However, this would be an essential step before a regulatory EQS can be recommended.

Properties and fate in water

Cypermethrin is a non-systematic pyrethroid insecticide with a wide range of agricultural applications, including the control of ectoparasites. Cypermethrin rapidly degrades in soil and sediment, with hydrolysis and photolysis playing major roles in the degradation. Cypermethrin is highly hydrophobic as indicated by its very low water solubility. This and the related high lipoaffinity (reported log Kow values 3.76–5.54) indicate a strong tendency to sorb to sediment and accumulate in aquatic biota. This contributes strongly to losses of cypermethrin from the water column.

Availability of data

Long-term laboratory data are available for five different freshwater taxonomic groups including algae, amphibians, crustaceans, fish and molluscs. Freshwater short-term toxicity data are available for 11 taxonomic groups including algae, amphibians, arachnids, bacteria, crustaceans, fish, insects, macrophytes, molluscs, protozoans and rotifers.

Freshwater fish and arthropod species are sensitive to cypermethrin, and there is an indication that amphibians may also be sensitive. For marine organisms, single

species acute toxicity data are available for seven different taxonomic groups (bacteria, crustaceans, echinoderms, fish, molluscs, annelids and rotifers), while chronic toxicity data are available only for crustaceans (two species). Laboratory data are supplemented by freshwater and marine mesocosm data, which confirm the high sensitivity of crustaceans to cypermethrin.

The recent *in vitro* data on the endocrine disrupting properties of cypermethrin are equivocal, but limited *in vivo* data indicate effects by cypermethrin on olfaction and milt priming in Atlantic salmon (*Salmo salar*) at low environmental concentrations.

Derivation of PNECs

Long-term PNEC for freshwaters

The most sensitive and reliable long-term (lt) toxicity value is a no observed effect concentration (NOEC) of 0.1 ng l⁻¹ for expression of milt by male Atlantic salmon (*Salmo salar*). This is a significant endpoint because it could lead to reduced fertility. Since reliable data are also available for algae and invertebrates, and there are several mesocosm studies which suggest that effects on arthropod assemblages do not occur at or below 10 ng l⁻¹, an assessment factor of 1 is recommended resulting in a PNEC_{freshwater_lt} of 0.1 ng l⁻¹ cypermethrin.

This value is similar to the existing EQS of 0.2 ng l⁻¹, which is based on applying a safety factor of 5 to the lowest chronic effects concentration, i.e. a 28-day lowest observed effect concentration (LOEC) to *Mysidopsis* of 0.6 ng l⁻¹. Although based on saltwater chronic data, this was justified because of the large dataset available, evidence of a small effect to no-effects ratio, and because *Mysidopsis* was clearly the most sensitive species for which data were available at that time. The value of 0.2 ng l⁻¹ was also considered equivalent to applying an extrapolation factor of 10 to the short-term EQS.

Short-term PNEC for freshwaters

Because cypermethrin exposure is likely to be short, the short-term (st) PNEC may be particularly important.

Reliable short-term data are available for algal, invertebrate and fish species. The most sensitive and reliable short-term toxicity values are a 96-hour LC₅₀ of 4 ng l⁻¹ for the mayfly *Cloeon dipterum* and the amphipod *Gammarus pulex*. Since amphipods were identified as among the most sensitive organisms in mesocosm tests, with effects at <30 ng l⁻¹, a reduced assessment factor of 10 (instead of the default value of 100) applied to the LC₅₀ is proposed. This results in a PNEC_{freshwater_st} of 0.4 ng l⁻¹ cypermethrin.

This value is lower than the existing EQS of 2 ng l⁻¹, which is based on applying a factor of 5 to the lowest reliable 96-hour LC₅₀ of 9 ng l⁻¹ reported in a laboratory flow-through study for *Gammarus pulex*. The assessment factor was selected based on the large dataset available and evidence of a small effect to no-effects ratio.

Long-term PNEC for saltwaters

Given the absence of long-term data for both algae and fish, it is not appropriate to generate a $PNEC_{\text{saltwater_lt}}$ based on the saltwater data alone. But since the long-term data for saltwater crustaceans indicate similar sensitivities to freshwater crustaceans and given the specific mode of action of cypermethrin, it is proposed that the combined freshwater and saltwater dataset be used for PNEC generation.

The most sensitive and reliable long-term toxicity value in the combined dataset is a NOEC of 0.1 ng l^{-1} for expression of milt by male Atlantic salmon. Since data are also available for algae and invertebrates and there are several mesocosm studies which suggest that effects on arthropod assemblages do not occur at or below 10 ng l^{-1} , an assessment factor of 1 is recommended resulting in a $PNEC_{\text{saltwater_lt}}$ of 0.1 ng l^{-1} cypermethrin.

This value is similar to the existing EQS of 0.2 ng l^{-1} , which was 'read across' from the freshwater long-term value.

Short-term PNEC for saltwaters

Reliable short-term data are available for invertebrate and fish species. The lowest valid acute toxicity value is a 96-hour LOEC of 4.1 ng l^{-1} for lethality of nauplii of the copepod *Acartia tonsa*. The use of a reduced assessment factor of 10 (instead of the default value of 100), because of the availability of data for exclusively marine species, results in a $PNEC_{\text{saltwater_st}}$ of 0.41 ng l^{-1} cypermethrin.

This value is lower than the existing EQS of 2 ng l^{-1} which was 'read across' from the freshwater short-term value.

PNEC for secondary poisoning

Bioconcentration data [as bioconcentration factor (BCF) values] for cypermethrin for invertebrates and fish range from 31–38 and 84–1,200 respectively; hence, the trigger of $BCF > 100$ is met and the derivation of PNECs for secondary poisoning of predators is required. The calculated $PNEC_{\text{secpois_water}}$ of $2.78 \mu\text{g l}^{-1}$ cypermethrin is much higher than the proposed long-term PNECs for the protection of the pelagic communities in both inland and marine water bodies, and so does not influence the development of EQSs for cypermethrin.

PNEC for sediments

Since the log Kow of cypermethrin is > 3 , the derivation of PNECs for the protection of benthic organisms is required. The resulting $PNEC_{\text{sediment_freshwater}}$ of $0.2 \mu\text{g cypermethrin/kg dry weight (dw)}$ is higher than the other long-term and short-term PNEC values.

Summary of proposed PNECs

Receiving medium/exposure scenario	Proposed PNEC (ng l ⁻¹ cypermethrin)	Existing EQS (ng l ⁻¹)
Freshwater/long-term	0.1	0.2
Freshwater/short-term	0.4	2.0
Saltwater/long-term	0.1	0.2
Saltwater/short-term	0.41	2.0
Freshwater sediment	0.2 µg/kg dw	–
Secondary poisoning	2.78	–

Analysis

The data quality requirements are that, at a third of the EQS, the total error of measurement should not exceed 50 per cent. Using this criterion, it is evident that current analytical methodologies (non-standard) employing gas chromatography/mass spectrometry (GC-MS) capable of achieving detection limits as low as 15 pg l⁻¹ should offer adequate performance for analysis for cypermethrin.

Implementation issues

Before PNECs for cypermethrin can be adopted as EQSs, it will be necessary to address the following issues:

1. The relevance of standards for cypermethrin in the water column should be considered because the high lipophilicity of cypermethrin means it is more likely to occur in sediment and biota.
2. Further data from manufacturers may be forthcoming once these standards are released for consultation. These are unlikely to affect the freshwater long-term PNEC, but could influence other PNECs.
3. Given the short persistence of cypermethrin in the water column, consideration needs to be given to the usefulness of the long-term and short-term PNECs.

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1. Introduction

The UK Technical Advisory Group (UKTAG) supporting the implementation of the Water Framework Directive (2000/60/EC)¹ is a partnership of UK environmental and conservation agencies. It also includes partners from the Republic of Ireland. UKTAG has commissioned a programme of work to derive Environmental Quality Standards (EQSs) for substances falling under Annex VIII of the Water Framework Directive (WFD). This report proposes predicted no-effect concentrations (PNECs) for cypermethrin using the methodology described in Annex V of the Directive. There are existing EQSs for cypermethrin, but the method used to derive these is not considered to comply with the requirements of Annex V and so is unsuitable for deriving Annex VIII EQSs.

The PNECs described in this report are based on a technical assessment of the available ecotoxicity data for cypermethrin, along with any data that relate impacts under field conditions to exposure concentrations. The data have been subjected to rigorous quality assessment such that decisions are based only on scientifically sound data.² Following consultation with an independent peer review group, critical data have been identified and assessment factors selected in accordance with the guidance given in Annex V. The feasibility of implementing these PNECs as EQSs has not been considered at this stage. However, this would be an essential step before a regulatory EQS can be recommended.

This report provides a data sheet for cypermethrin.

1.1 Properties and fate in water

Cypermethrin is a non-systematic pyrethroid insecticide with a wide range of agricultural applications, including the control of ectoparasites. Cypermethrin rapidly degrades in soil and sediment, with hydrolysis and photolysis playing major roles in the degradation. Cypermethrin is highly hydrophobic as indicated by its very low water solubility. This and the related high lipoaffinity (reported log Kow values 3.76–5.54) indicate a strong tendency to sorb to sediment and accumulate in aquatic biota. This contributes strongly to losses of cypermethrin from the water column.

¹ *Official Journal of the European Communities*, **L327**, 1–72 (22/12/2000). Can be downloaded from http://www.eu.int/comm/environment/water/water-framework/index_en.html

² Data quality assessment sheets are provided in Annex 1.

2. Results and observations

2.1 Identity of substance

Table 2.1 gives the chemical name and Chemical Abstracts Service (CAS) number for the substance of interest.

Table 2.1 Substance covered by this report

Name	CAS Number
Cypermethrin	52315-07-8

2.2 PNECs proposed for derivation of quality standards

Table 2.2 lists proposed PNECs obtained using the methodology described in the Technical Guidance Document (TGD), issued by the European Chemicals Bureau (ECB) on risk assessment of chemical substances [83], and existing EQSs obtained from the literature [9].

Section 2.6 summarises the effects data identified from the literature for cypermethrin. The use of these data to derive the values given in Table 2.2 is explained in Section 3.

Table 2.2 Proposed overall PNECs as basis for quality standard setting

PNEC	TGD deterministic approach (AFs)	TGD probabilistic approach (SSDs)	Existing EQS
Freshwater short-term	0.4 ng l ⁻¹	-	2.0 ng l ⁻¹ (MAC)
Freshwater long-term	0.1 ng l ⁻¹	Insufficient data	0.2 ng l ⁻¹ (AA – T)
Saltwater short-term	0.41 ng l ⁻¹	-	2.0 ng l ⁻¹ (MAC – T)
Saltwater long-term	0.1 ng l ⁻¹	Insufficient data	0.2 ng l ⁻¹ (AA – T)
Sediment	0.2 µg/kg dw	Insufficient data	-
Secondary poisoning	2.78 µg l ⁻¹	-	-

AA = annual average

AF = assessment factor

dw = dry weight

MAC = maximum allowable concentration

SSD = species sensitivity distribution

T = tentative

2.3 Hazard classification

Table 2.3 gives the R-phrases (Risk-phrases) and labelling for the substance of interest.

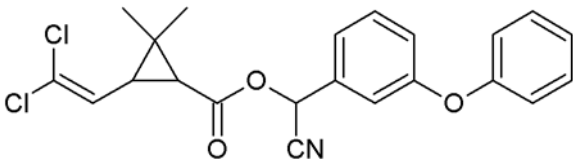
Table 2.3 Hazard classification

R-phrases and labelling	Reference
R10, 20/22, 36, 50/53, 65 S2, 13, 20/21, 23, 24/25, 36/37/39, 29/56, 62	[5]

2.4 Physical and chemical properties

Table 2.4 summarises the physical and chemical properties of the substance of interest.

Table 2.4 Physical and chemical properties of cypermethrin

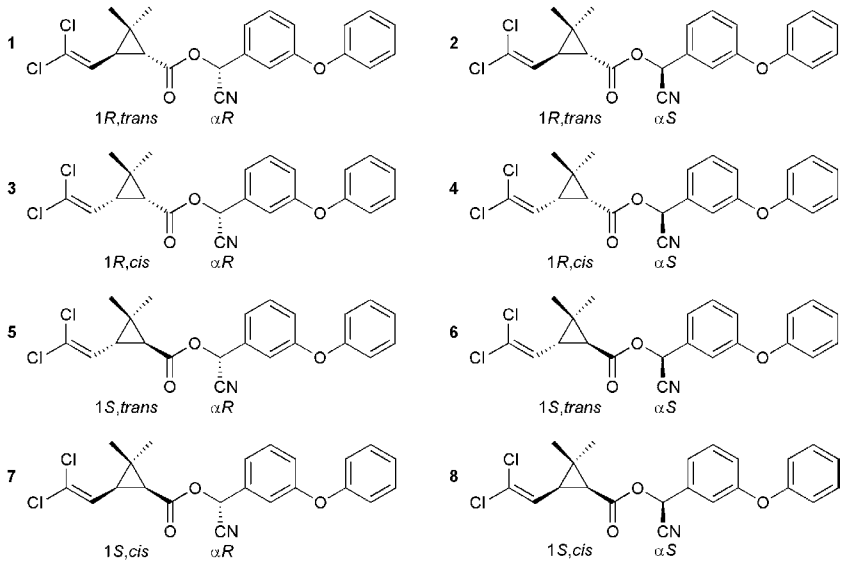
Property	Value	Reference
CAS number	52315-07-8	[15]
Substance name	α -cyano-3-phenoxybenzyl 3-(2,2-dichlorovinyl)-2,2-dimethylcyclopropanecarboxylate	[15]
Molecular formula	C ₂₂ H ₁₉ Cl ₂ NO ₃	[15]
Molecular structure		
Molecular weight	416.30	[38]
Colour/form	Viscous yellow-brown semisolid	[38]
Odour	Odourless	[38]
Melting point (°C)	80.5	[39]
Boiling point (°C)	200	[39]
Vapour pressure	3.07×10^{-9} mmHg at 20°C	[38]
Density/specific gravity	1.25 g cm ⁻³ at 20°C	[38]
Henry's Law constant	4.2×10^{-7} atm·m ³ /mole (estimated value)	[38]
Solubility	0.005–0.01 mg l ⁻¹ water 620 g l ⁻¹ acetone 515 g l ⁻¹ cyclohexanone 7 g kg ⁻¹ hexane 351 g l ⁻¹ xylene	[39]

The water solubility of alpha-cypermethrin (98.0 per cent), calculated as the sum of the *cis*-1 [(*S*)- α -cyano-3-phenoxybenzyl (*1R*)-*cis*-3-(2,2-dichlorovinyl)-2,2-dimethylcyclopropanecarboxylate] and the *cis*-2 [(*R*)- α -cyano-3-phenoxybenzyl (*1S*)-*cis*-3-(2,2-dichlorovinyl)-2,2-dimethylcyclopropanecarboxylate] isomers (ratio 2.6:97.4) concentrations range from 4.59 to 7.87 $\mu\text{g l}^{-1}$. In distilled water alone, its solubility is slightly less, i.e. 2.06 $\mu\text{g l}^{-1}$. The solubility is not strongly dependent on pH values within the range of 4 to 9. It is likely that ionic strength differences account for differences in solubility between values in pure water and in the buffer solutions [78].

2.5 Environmental fate and partitioning

Table 2.5 summarises the information obtained from the literature on the environmental fate and partitioning of cypermethrin.

Table 2.5 Environmental fate and partitioning of cypermethrin

Property	Value	Reference
Abiotic fate	The rate constant for the vapour-phase reaction with photochemically produced hydroxyl radicals has been estimated as 3.70×10^{-11} cm ³ /molecule/second at 25°C. This corresponds to an atmospheric half-life of approximately 18 hours at an atmospheric concentration of 5×10^5 hydroxyl radicals per cm ³ .	[60]
Speciation	<p>The cypermethrin molecule contains three chiral centres (two in the cyclopropane ring and one at the α-cyano carbon), resulting in a number of stereoisomers. These isomers are commonly grouped into four <i>cis</i>- and four <i>trans</i>-isomers; the <i>cis</i>-isomers have the greatest insecticidal properties. Cypermethrin is the equimolar mixture of all eight isomers:</p>  <p>The four main isomeric mixtures of cypermethrin are:</p> <ol style="list-style-type: none"> Alpha-cypermethrin (CAS No. 67375-30-8) is a racemic mixture of: <ul style="list-style-type: none"> (<i>S</i>)-α-cyano-3-phenoxybenzyl (1<i>R</i>)-<i>cis</i>-3-(2,2-dichlorovinyl)-2,2-dimethylcyclopropanecarboxylate (isomer 4) and (<i>R</i>)-α-cyano-3-phenoxybenzyl (1<i>S</i>)-<i>cis</i>-3-(2,2-dichlorovinyl)-2,2-dimethylcyclopropanecarboxylate (isomer 7) Beta-cypermethrin (CAS No. 65731-84-2) comprises two enantiomeric pairs of isomers in a 2:3 ratio: <ul style="list-style-type: none"> (<i>S</i>)-α-cyano-3-phenoxybenzyl (1<i>R</i>)-<i>cis</i>-3-(2,2-dichlorovinyl)-2,2- 	[39]

Property	Value	Reference
	<p>dimethylcyclopropanecarboxylate (isomer 4) and (<i>R</i>)-α-cyano-3-phenoxybenzyl (1<i>S</i>)-<i>cis</i>-3-(2,2-dichlorovinyl)-2,2-dimethylcyclopropanecarboxylate (isomer 7) with (<i>S</i>)-α-cyano-3-phenoxybenzyl (1<i>R</i>)-<i>trans</i>-3-(2,2-dichlorovinyl)-2,2-dimethylcyclopropanecarboxylate (isomer 2) and (<i>R</i>)-α-cyano-3-phenoxybenzyl (1<i>S</i>)-<i>trans</i>-3-(2,2-dichlorovinyl)-2,2-dimethylcyclopropanecarboxylate (isomer 5).</p> <p>3. Theta-cypermethrin (CAS No. 71697-59-1) is a racemic mixture of:</p> <p>(<i>S</i>)-α-cyano-3-phenoxybenzyl (1<i>R</i>)-<i>trans</i>-3-(2,2-dichlorovinyl)-2,2-dimethylcyclopropanecarboxylate (isomer 2) and (<i>R</i>)-α-cyano-3-phenoxybenzyl (1<i>S</i>)-<i>trans</i>-3-(2,2-dichlorovinyl)-2,2-dimethylcyclopropanecarboxylate (isomer 5)</p> <p>4. Zeta-cypermethrin (CAS No. 52315-07-8) is a mixture of the four α<i>S</i>-stereoisomers around the α-cyano carbon:</p> <p>(<i>S</i>)-α-cyano-3-phenoxybenzyl (1<i>R</i>)-<i>trans</i>-3-(2,2-dichlorovinyl)-2,2-dimethylcyclopropanecarboxylate (isomer 2), (<i>S</i>)-α-cyano-3-phenoxybenzyl (1<i>R</i>)-<i>cis</i>-3-(2,2-dichlorovinyl)-2,2-dimethylcyclopropanecarboxylate (isomer 4), (<i>S</i>)-α-cyano-3-phenoxybenzyl (1<i>S</i>)-<i>trans</i>-3-(2,2-dichlorovinyl)-2,2-dimethylcyclopropanecarboxylate (isomer 6) and (<i>S</i>)-α-cyano-3-phenoxybenzyl (1<i>S</i>)-<i>cis</i>-3-(2,2-dichlorovinyl)-2,2-dimethylcyclopropanecarboxylate (isomer 8). The ratio of the (<i>S</i>);(1<i>RS</i>,3<i>RS</i>) isomeric pair to the (<i>S</i>);(1<i>RS</i>,3<i>SR</i>) isomeric pair lies in the ratio range 45–55 to 55–45, respectively.</p> <p>Consequently, the isomers of cypermethrin are not likely to be found in isolation in the environment, but are most likely to occur as different mixtures of isomers present at ratios that relate to their parent formulations.</p>	
Hydrolytic stability	<p>Cypermethrin is stable under acidic or neutral conditions (pH 3–7), but hydrolyses in strongly alkaline media (pH 12–13). It decomposes above 220°C. Field data indicate that, in practice, it is stable to air and light.</p> <p>The abiotic hydrolysis half-life is 63 weeks at pH 7.</p>	<p>[39]</p> <p>[7]</p>
Photostability	<p>The photodegradation half-lives of <i>cis</i>- and <i>trans</i>-isomers in distilled water range from 2.6 to 3.6 days in sunlight and >10 days in dark controls. The photodegradation half-lives in river water and saltwater vary from 0.6 to 1 day.</p>	[38]
Volatilisation	<p>Volatilisation from water surfaces is not expected to be an important environmental fate process based upon the estimated Henry's Law constant (4.2×10^{-7} atm·m³/mol).</p>	[38]

Property	Value	Reference
Distribution in water/sediment systems (active substance)	If released into water, cypermethrin is expected to adsorb to suspended solids based upon the Koc values (3.76–5.20; 5.54) (see below). Approximately 99% is adsorbed (from water to sediment) within 24 hours.	[38]
Distribution in water and sediment systems (metabolites)	In an aquatic ecosystem experiment at a temperature of 15–19°C, the half-life ranged from 9.6 to 30.8 days depending on the concentration of cypermethrin in the water. In a pond experiment, surface applications of cypermethrin gradually partitioned to sediment with sediment concentrations exceeding water surface and subsurface concentrations after 13 days.	[51] [10]
Degradation in soil	The photodegradation of the <i>cis</i> - and <i>trans</i> -isomers in soil surfaces (when exposed to sunlight) range from 0.6 to 1.9 days; half-lives on dark soil are >7 days. Cypermethrin degrades rapidly in soil under aerobic conditions. The half-lives in soil were 4.1–17.6 days for <i>trans</i> -cypermethrin and 12.5–56.4 days for <i>cis</i> -cypermethrin under aerobic conditions in an incubated soil. Half-life in sandy soil of 2–4 weeks.	[38] [66] [6]
Biodegradation	The <i>trans</i> -isomer degrades more quickly in soil than <i>cis</i> -cypermethrin, being most rapid in sandy clay and sandy loam. The rate of degradation depends upon soil type, but generally 50% of <i>trans</i> - and <i>cis</i> -cypermethrin when applied to soils decomposed in 2 and 4 weeks, respectively.	[59]
Octanol–water coefficient (log Kow)	5.16 6.6	[38] [39]
Log Koc	3.76–5.20 5.54	[38] [53]
Bioaccumulation BCF	Bioconcentration factor (BCF) values of 420 and 430 for golden ide fish (<i>Leuciscus idus melanotus</i>) and rainbow trout (<i>Oncorhynchus mykiss</i>) suggest that bioconcentration in aquatic organisms is high. BCF of 3,280 for algae (<i>Chlorella fusca</i>)	[26, 32] [26]
BSAF (Biota to sediment accumulation factor)	0.31, 0.14 and 0.08 for <i>Daphnia magna</i> and 0.63, 0.19 and 0.08 for <i>Chironomus tentans</i> , in 1, 3 and 13% organic carbon sediments.	[53]

Cypermethrin is a pyrethroid insecticide which, in the aquatic environment, is subject to degradation and metabolic processes. The main route of pyrethroid insecticide decomposition comes through hydrolysis of the ester bond and oxidation [51].

The fate of a cypermethrin insecticide has been studied in replicated 25 m³ pond mesocosms: cypermethrin pesticide was sprayed to simulate spray drift deposition and, after treatment, it was found that cypermethrin residues in the water column declined rapidly [10, 22], presumably due to rapid degradation and adsorption onto particulate matter.

Based on Koc values (Table 2.5), it is expected that cypermethrin would be immobile in sediment/soil. However, it has been suggested that, although little of this pesticide would move through the sediment/soil profile, the degradation products are more mobile than the parent compound [44]. In addition, increased persistence of cypermethrin (or degradates) was observed in soil/sediment with high organic matter, high clay content, reduced microbial activity and anaerobic conditions [6]. Cypermethrin has a low Henry's Law constant and is not expected to be found in air, apart from some minor spray drift from the application of the pesticide to crops.

Cypermethrin degrades rapidly in soil and sediment [59], with hydrolysis and photolysis playing major roles in the degradation. Various degradation products are produced. When applied to soil, approximately 30–60 per cent of cypermethrin is converted into carbon dioxide. Hydrolysis of the *cis*-isomer is the primary pathway, producing carboxylic acid plus 3-phenoxybenzyl alcohol or 3-phenoxybenzaldehyde cyanohydrin. Both 3-phenoxybenzyl alcohol or 3-phenoxybenzaldehyde cyanohydrin are then converted into 3-phenoxybenzoic acid.

Biodegradation is most rapid in sandy clay and sandy loam sediment/soils with approximately 50 per cent of *trans*- and *cis*-cypermethrin being decomposed within 2 and 4 weeks, respectively. Six degradation products have been observed in soils [59]:

- 3-(4-hydroxyphenoxy)benzyl ester
- 3-(4-hydroxyphenoxy)benzoic acid
- 3-phenoxybenzoic acid
- *cis*- or *trans*-3-(2,2-dichlorovinyl)-2,2-dimethylcyclopropanecarboxylic acid
- carbon dioxide.

As indicated by its very low water solubility (see Section 2.4), cypermethrin is highly hydrophobic [62]. This and the related high lipoaffinity indicate a strong bioconcentration potential in aquatic organisms [62]. With such a low water solubility, the transport of cypermethrin from sediment/soil to water has been assumed to be negligible. In natural waters, cypermethrin may be quickly adsorbed by particulate matter [62].

2.6 Effects data

A summary of the mode of action for this substance can be found in Section 2.6.5.

Data collation followed a tiered approach.

First, critical freshwater and saltwater data were compiled from existing EQS documents. Further data published after derivation of the current UK EQS [9] were then retrieved from the US Environmental Protection Agency (US EPA) ECOTOX database.³

As data on sediment-dwelling organisms and mammalian or avian chronic oral toxicity were not available in ECOTOX, further data were sought from:

- ScienceDirect®;⁴
- Hazardous Substances Data Bank (HSDB®) database of the US National Library of Medicine;⁵
- US EPA Integrated Risk Information System (IRIS) database [40];
- World Health Organization (WHO) *Environmental Health Criteria 82: Cypermethrin* (EHC 82) [39];
- World Health Organization (WHO) *Environmental Health Criteria 142: Alpha-cypermethrin* (EHC 142) [78];
- European Commission's *Plant Health Technical Review Report: Alpha-cypermethrin* [14].

In addition, data were sought from the UK producers of cypermethrin. No additional data have been provided to date.

2.6.1 Toxicity to freshwater organisms

Long-term data are available for five taxonomic groups including algae, amphibians, crustaceans, fish and molluscs. Freshwater short-term toxicity data are available for 11 taxonomic groups, including algae, amphibians, arachnids, bacteria, crustaceans, fish, insects, macrophytes, molluscs, protozoans and rotifers. Fish and arthropod species are sensitive to cypermethrin and there is an indication that amphibians may also be sensitive.

Diagrammatic representations of the available freshwater data (cumulative distribution functions) for cypermethrin are presented in Figures 2.1 and 2.2. These diagrams include all data regardless of quality and provide an overview of the spread of the available data, but they are not species sensitivity distributions and have not been used to derive cypermethrin PNECs. The lowest critical freshwater data for cypermethrin are presented in Tables 2.6 and 2.7.

There was no evidence for a substantial difference in the sensitivity of organisms to different cypermethrin isomers when alpha-cypermethrin (the common racemic mixture in sheep dip formulations) was compared with cypermethrin containing a mixture of isomers [69, 71]. Data for different isomers and formulations have, therefore, not been separated in the figures or tables.

³ <http://www.epa.gov/ecotox/>

⁴ <http://www.sciencedirect.com/>

⁵ <http://toxnet.nlm.nih.gov/cgi-bin/sis/htmlgen?HSDB>

Figure 2.1 Cumulative distribution function of freshwater long-term data ($\mu\text{g l}^{-1}$) for cypermethrin

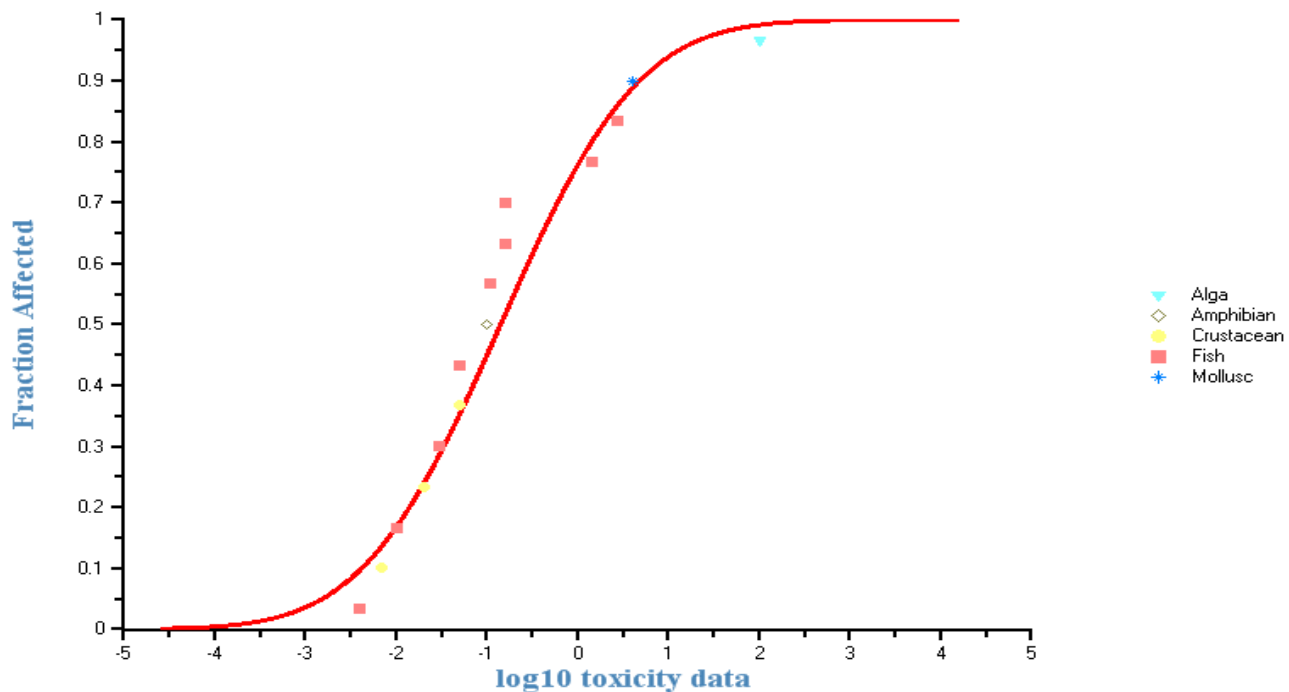


Figure 2.2 Cumulative distribution function of freshwater short-term data ($\mu\text{g l}^{-1}$) for cypermethrin

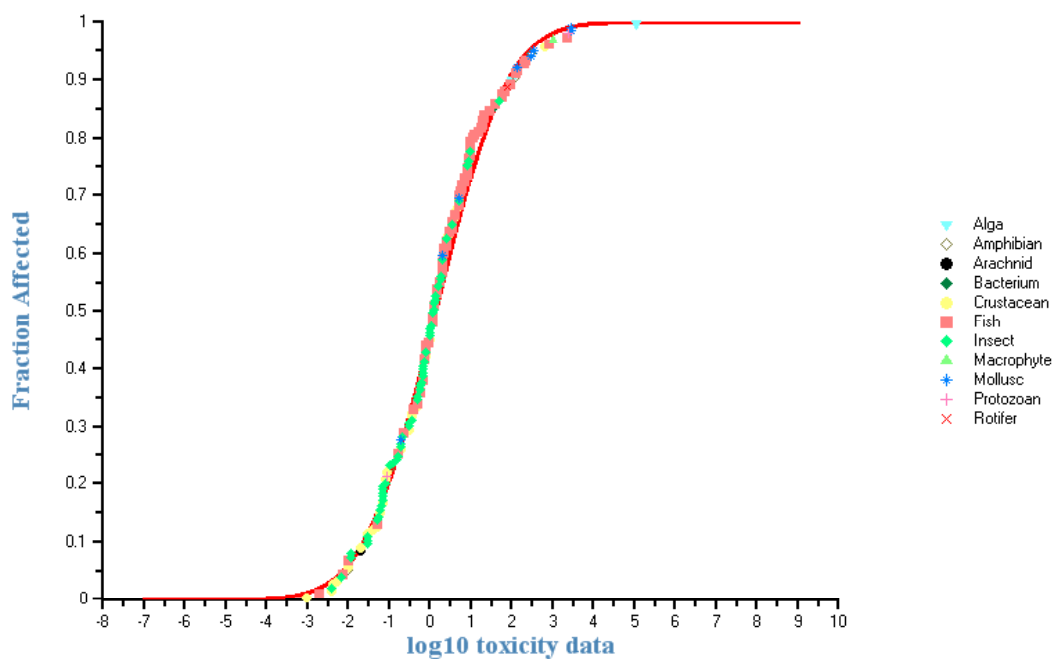


Table 2.6 Most sensitive long-term aquatic toxicity data for freshwater organisms exposed to cypermethrin

Scientific name	Common name	Taxonomic group	Endpoint	Effect	Test duration	Conc. ($\mu\text{g l}^{-1}$)	Exposure ¹	Toxicant analysis ²	Reliability index ³	Reference
Algae										
<i>Selenastrum capricornutum</i>	Green alga	Algae	NOEC	Population growth	96 hours	100	-	-	2	[69] (cited in EHC 82)
Invertebrates										
<i>Daphnia magna</i>	Water flea	Crustaceans	LOEC	Reproduction	21 days	0.007	-	-	2	[53]
<i>Daphnia magna</i>	Water flea	Crustaceans	NOEC	Reproduction	23 days	0.02	-	-	2	ICI unpublished data (cited in [86])
<i>Daphnia magna</i>	Water flea	Crustaceans	NOEC	Reproduction	21 days	0.05	ss	-	2	[85] (cited in EHC 82)
Vertebrates (fish and amphibians)										
<i>Salmo salar</i>	Atlantic salmon	Fish	NOEC	Olfaction response and milt priming	120 hours	0.0001	f	y	2	[61]
<i>Cyprinus carpio</i>	Common carp	Fish	NOEC	Early life stage test	Until two days after hatching completed	0.01	s	n	3	[12]
<i>Pimephales promelas</i>	Fathead minnow	Fish	NOEC	Early life stage test	34 days	0.03	-	-	2	[72]
<i>Salmo salar</i>	Atlantic salmon	Fish	Effect on fry emergence	Early life stage test	1200 degree days	0.05	s	n	3	[50]
<i>Rana arvalis</i>	Frog	Amphibians	NOEC	Early life stage	Until metamorphosis	0.1	s	n	3	[29]

¹ Exposure: s = static; ss = semi-static; f = flow-through.

² Toxicant analysis: y = measured; n = nominal.

³ See Annex 1.

LOEC = lowest observed effect concentration

NOEC = no observed effect concentration

Table 2.7 Most sensitive short-term aquatic toxicity data for freshwater organisms exposed to cypermethrin

Scientific name	Common name	Taxonomic group	Endpoint	Effect	Test duration	Conc. ($\mu\text{g l}^{-1}$)	Exposure ¹	Toxicant analysis ²	Reliability index ³	Reference
Algae										
<i>Selenastrum capricornutum</i>	Green alga	Algae	EC50	Population growth	96 hours	>100	-	-	2	[69] (cited in EHC 82)
<i>Ceratophyllum demersum</i>	Common hornwort	Macrophytes	NOEC	Biochemical	5 days	>1,000	s	n	3	[58]
Invertebrates										
<i>Daphnia magna</i>	Water flea	Crustaceans	Effect	Mortality	24 hours	0.001	s	n	3	[57]
<i>Cloeon dipterum</i>	Mayfly	Insects	EC50	Mortality	96 hours	0.004	f	y	1	[68]
<i>Gammarus pulex</i>	Shrimp	Crustaceans	EC50	Mortality	96 hours	0.004	f	y	1	[68]
Vertebrates (fish)										
<i>Lepidocephalichthys thermalis</i>	Loach	Fish	Decrease	Carbohydrate level	15 days	0.002	s	n	3	[42]
<i>Gambusia affinis</i>	Western mosquitofish	Fish	LC50	Mortality	96 hours	0.0073	s	n	3	[17]
<i>Cyprinus carpio</i>	Carp	Fish	Change	Glycogen and protein levels	96 hours	0.01	s	n	3	[64]
<i>Cyprinus carpio</i>	Carp	Fish	LC50	Mortality	96 hours	0.05	s	n	3	[64]
<i>Scardinius erythrothalmus</i>	Rudd	Fish	LC50	Mortality	96 hours	0.4	f	y	1	[70]

¹ Exposure: s = static; f = flow-through.

² Toxicant analysis: y = measured; n = nominal.

³ See Annex 1.

NOEC = no observed effect concentration

EC50 = concentration effective against 50% of the organisms tested

LC50 = concentration lethal to 50% of the organisms tested

2.6.2 Toxicity to saltwater organisms

Single species cypermethrin acute toxicity data for marine organisms are available for seven different taxonomic groups, i.e. bacteria, crustaceans, echinoderms, fish, molluscs, annelids and rotifers. Chronic toxicity data are available only for crustaceans (two species). No acute or chronic toxicity data for algae have been identified. Data from one higher tier mesocosm study with marine organisms are available. Chronic and acute toxicity data for marine species are summarised in Tables 2.8 and 2.9, respectively.

Diagrammatic representations of the available saltwater data (cumulative distribution functions) for cypermethrin are presented in Figures 2.3 and 2.4. These diagrams include all data regardless of quality and provide an overview of the spread of the available data. These diagrams are not species sensitivity distributions and have not been used to set the cypermethrin PNECs.

Figure 2.3 Cumulative distribution function of saltwater long-term data ($\mu\text{g l}^{-1}$) for cypermethrin

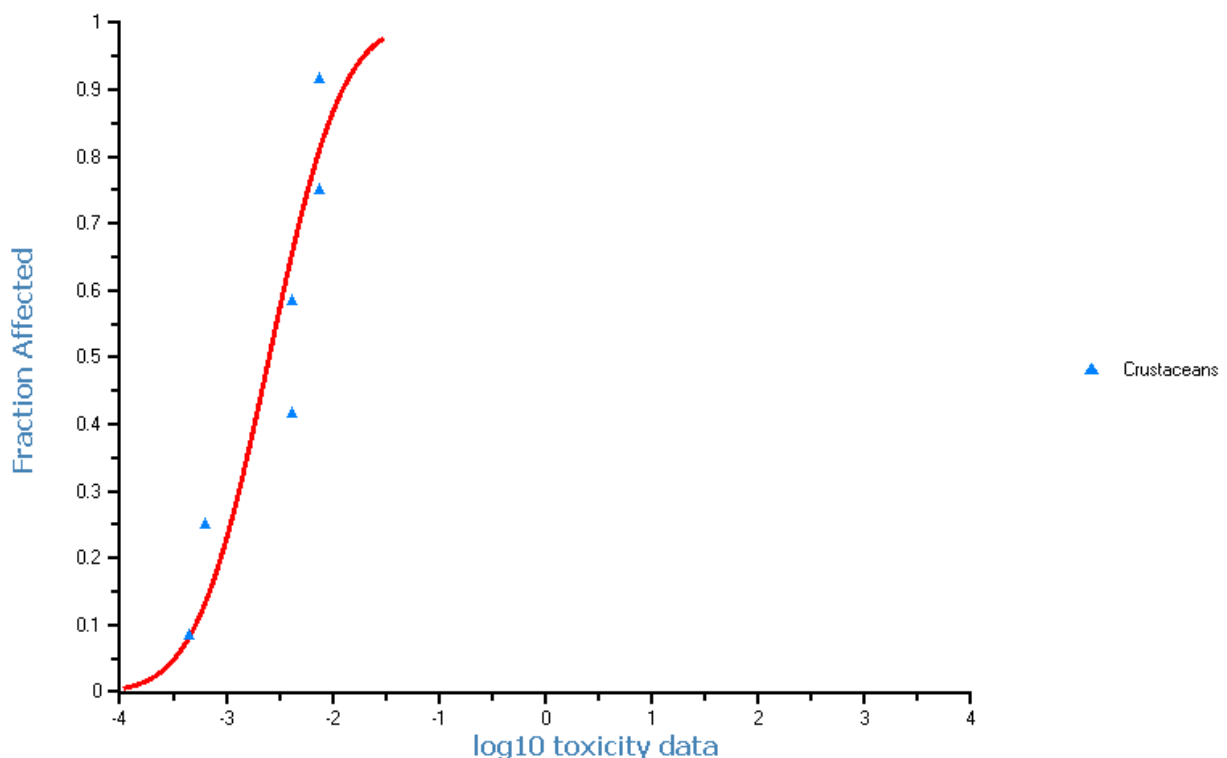


Figure 2.4 Cumulative distribution function of saltwater short-term data ($\mu\text{g l}^{-1}$) for cypermethrin

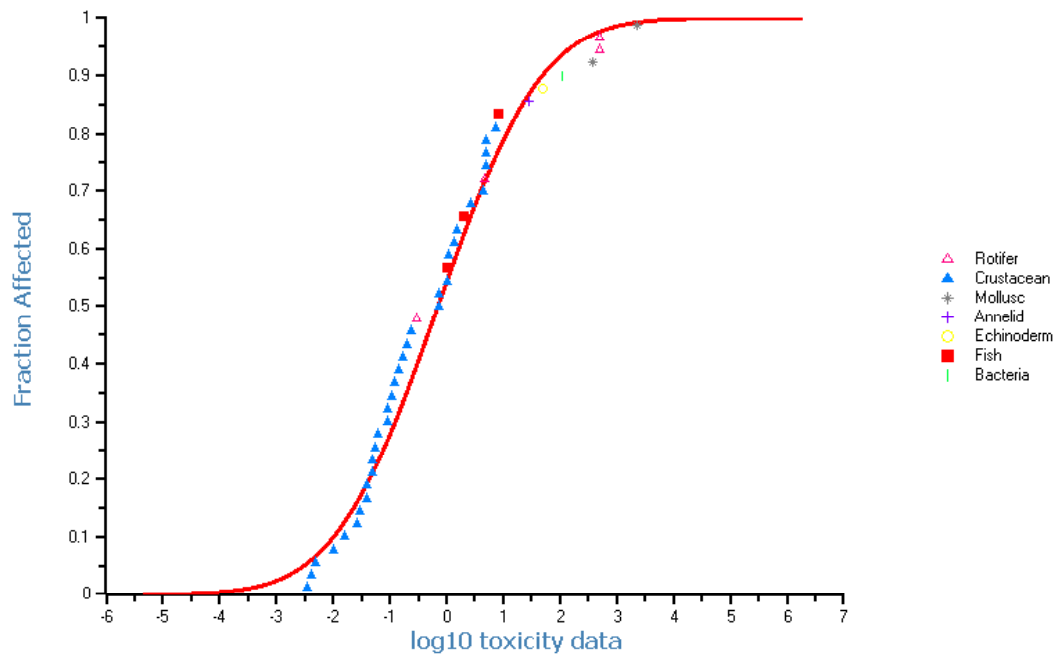


Table 2.8 Most sensitive long-term aquatic toxicity data for saltwater organisms exposed to cypermethrin

Scientific name	Common name	Taxonomic group	Endpoint	Effect	Test duration (days)	Conc. ($\mu\text{g l}^{-1}$)	Exposure ¹	Toxicant analysis ²	Comments	Reliability index ³	Reference
Invertebrates											
<i>Acartia tonsa</i>	Copepod	Crustaceans	NOEC	Fecundity	32	0.0041	ss	p	20°C; salinity 30‰	2	[2]
<i>Acartia tonsa</i>	Copepod	Crustaceans	NOEC	Population change	32	0.0041	ss	p	20 °C; salinity 30‰	2	[2]
<i>Mysidopsis bahia</i>	Mysid shrimp	Crustaceans	NOEC	Lethality	28	0.00044	ND (pf)	ND (pm)	-	4	ICI/AstraZeneca proprietary data cited in [53]

¹ Exposure: ss = semi-static; pf = presumably flow-through.

² Toxicant analysis: p = partial analysis of exposure concentrations where stock solutions were measured at beginning and end of the study; pm = presumably measured.

³ See Annex 1.

ND = no data

NOEC = no observed effect concentration

Table 2.9 Most sensitive short-term aquatic toxicity data for saltwater organisms exposed to cypermethrin

Scientific name	Common name	Taxonomic group	Endpoint	Effect	Test duration (hours)	Conc. ($\mu\text{g l}^{-1}$)	Exposure ¹	Toxicant analysis ²	Comments	Reliability index ³	Reference
Microbes											
<i>Vibrio fischeri</i>	Microbe	Bacteria	EC50	Bioluminescence inhibition	0.5	110	s	y	-	2	[23]
Invertebrates											
<i>Acartia tonsa</i> (nauplii)	Copepod	Crustaceans	LOEC	Lethality	96	0.0041	ss	p	20°C; salinity 30‰	2	[2]
<i>Homarus americanus</i>	Lobster	Crustaceans	LC50	Lethality	96	0.04	ss	y	10°C	2	[55]
<i>Mysidopsis bahia</i>	Mysid shrimp	Crustaceans	LC50	Lethality	96	0.005	f	ND	-	-	Cited in [86]
<i>Mysidopsis bahia</i> (<24h)	Mysid shrimp	Crustaceans	LC50	Lethality	96	0.027	s	n	25°C; salinity 25‰	-	[87]
<i>Palaemonetes africanus</i>	Shrimp	Crustaceans	LC50	Lethality	96	0.0035	ss	n	Salinity 17‰	3	[13]
<i>Palaemonetes pugio</i>	Grass shrimp	Crustaceans	LC50	Lethality	96	0.016	f	n	21–26°C	-	[88]
Fish											
<i>Salmo salar</i>	Atlantic salmon	Fish	LC50	Lethality	96	2.0	ss	y	10°C	2	[55]

¹ Exposure: s = static; ss = semi-static; f = flow-through.

² Toxicant analysis: y = measured; n = nominal; p = partial analysis of exposure concentrations where stock solutions were measured at beginning and end of the study.

³ See Annex 1.

EC50 = concentration effective against 50% of the organisms tested

LC50 = concentration lethal to 50% of the organisms tested

LOEC = lowest observed effect concentration

ND = no data

2.6.3 Toxicity to sediment-dwelling organisms

Toxicity data for cypermethrin in freshwater sediments are reported for the amphipod *Hyalella azteca* and the midge larva *Chironomus tentans* [53]. The 10-day LC50 values for *H. azteca* were 3.6, 18 and 32 µg/kg dry weight (dw) in sediments containing 1, 3 and 13 per cent organic carbon (growth NOECs: <1.8, 2.3 and 1.8 µg/kg dw). The corresponding LC50 values at similar organic concentrations for *C. tentans* were 13, 67 and 62 µg/kg dw (growth NOECs 3.8, 25 and 14 µg/kg dw). Equilibrium partitioning based predictions of aqueous concentrations at these LC50 and NOEC values are shown in Table 2.10, and are similar to the lowest concentrations causing effects on arthropods as reported in Tables 2.6 and 2.7.

Table 2.10 Effect concentrations (mortality and growth) for *Hyalella azteca* and *Chironomus tentans* normalised according to predicted concentrations in the water phase [53]

Sediment organic carbon content (%)	Koc	Predicted water phase concentration (ng l ⁻¹)			
		<i>Hyalella azteca</i>		<i>Chironomus tentans</i>	
		LC50	NOEC	LC50	NOEC
1	239,000 ¹	1.5	<0.76	5.5	1.6
	350,000 ²	1.0	<0.52	3.8	1.1
3	503,000 ¹	1.1	0.15	4.3	1.58
	350,000 ²	1.6	0.22	6.2	2.27
13	178,000 ¹	1.0	0.08	2.6	0.59
	350,000 ²	0.5	0.05	1.3	0.3

¹ Mean measured Koc for sediment in adsorption–desorption studies.

² Overall mean adsorption Koc.

In one study, the midge *Chironomus riparius* at different population densities (0.5, 1, 2 and 4 cm⁻²) was exposed to cypermethrin (0.015, 0.0225 and 0.3 µg l⁻¹) and population parameters monitored for 67 days [37]. Initial measured cypermethrin concentrations in the test sediment (10 per cent peat) were approximately 0.125, 0.175 and 0.21 mg/kg dw and had declined to 0.049, 0.073 and 0.086 mg/kg dw by the end of the study. All concentrations of cypermethrin led to effects on population parameters such as juvenile survival to emergence, time to emergence and reproduction, and population growth rate. However, reductions in the initial larval densities resulted in an increase in the available resources for the survivors. Exposed populations therefore emerged sooner and started producing offspring earlier than the controls. Cypermethrin had no effect on estimated fecundity and adult body weight (bw), but interacted with density to reduce the time to first emergence and first reproduction. As a result, population growth rate increased with cypermethrin concentration when populations were initiated at high densities.

In addition to these data, the EC plant protection product review for alpha-cypermethrin [14] identified a 28-day ‘sediment’ NOEC of 0.024 µg l⁻¹ for *Chironomus* larvae [33]. However, there were no further data with which to assess this study and the endpoint is reported as a water column concentration and not a sediment concentration.

2.6.4 Endocrine-disrupting effects

A report by consultants BKH for the European Commission [4] evaluated available data and considered that cypermethrin was a Category 2 endocrine-disrupting chemical under

the scheme proposed earlier by BKH [3]. This categorisation indicated that '*possible endocrine disrupting related effects have been observed but the working mechanism needs clarification*'.

Two recent *in vitro* studies of cypermethrin's endocrine-disrupting properties provide equivocal evidence. Data from the first study [43] suggest that cypermethrin has an oestrogenic (proliferative) effect on MCF7 cells,⁶ which can be further augmented by oestradiol itself. In contrast, a second study [45] failed to demonstrate MCF7 proliferation. As a result, it is not clear whether cypermethrin acts as an oestrogen mimic or whether it acts by some other mechanism.

Only limited *in vivo* data could be located on the effects of cypermethrin on the endocrine system of wildlife. Moore and Waring investigated the effects of cypermethrin on olfaction and milt priming in Atlantic salmon (*Salmo salar*) [61]. In the first experiment, mature male Atlantic salmon parr were exposed to a single concentration of 0.01 µg l⁻¹ cypermethrin for five days, with continuous insecticide dosing and renewal of stock solutions every 12 hours. Measured concentrations at the end of the exposure period were <0.004 µg l⁻¹. Fish were then removed to clean water, exposed to female salmon pheromone, and their olfactory response to this pheromone measured electrophysiologically over five days. The mean response of the exposed group was only 11 per cent of the control group.

In the second experiment, males were stripped of milt and left to recover for 96 hours, after which they were exposed to 0.0001, 0.001, 0.01, 0.05, 0.1 or 0.5 µg l⁻¹ cypermethrin for five days (measured concentrations from <0.004 to 0.33 µg l⁻¹), with continuous insecticide dosing and renewal of stock solutions every 12 hours. They were given either a five-hour exposure to female pheromone or to a control, after which they were anaesthetised and milt, blood and bile from gall bladders were sampled and analysed for steroids and weight of expressible milt. Cypermethrin concentrations of <0.004 µg l⁻¹ (nominal concentration 0.001 µg l⁻¹) removed the effect of exposure to the female pheromone on male milt expression, while slightly higher concentrations affected sex steroid concentrations.

2.6.5 Mode of action of cypermethrin

Arthropods

Initial symptoms of pyrethroid poisoning in crustaceans and insects include excitation, ataxia and convulsions. These symptoms have been correlated with electrical discharges of the nervous system [89]. Experiments have shown that pyrethroid insecticides affect sodium channels in nerve membranes, altering the kinetics of action potential [89]. This theory was investigated using the crayfish (*Astacus fluviatilis*) stretch receptor organ [89]. Since the nervous systems of crustaceans and insects are very similar, the crayfish stretch receptor organ provides a useful model system for investigating the intracellular effects of pyrethroids on arthropod sensory cells. A cypermethrin concentration of 4.2 ng l⁻¹ was found to cause depolarisation of the receptor neuron, while a concentration of 0.042 µg l⁻¹ led to complete inhibition of impulse conduction.

⁶ MCF7 is a breast cancer cell line.

In addition to the neurotoxic effects reported above, an osmotic imbalance may also contribute to toxicity, since pyrethroid insecticides have been shown to inhibit ATPase enzymes involved in the movement of ions against concentration gradients [90]. Similar effects have been reported in fish in which exposure to pyrethroids has been shown to disrupt respiratory surfaces and ion regulation [90].

Fish

Pyrethroid insecticides are thought to have their primary effect on the sodium gate in nerve axons. Cypermethrin causes a depolarisation of nerve membranes and blocks impulse conduction, due to an extremely prolonged sodium current [91]. Edwards *et al.* [92] reported that the initial symptoms of toxicity of rainbow trout (*Oncorhynchus mykiss*) exposed to a concentration of $10 \mu\text{g l}^{-1}$ were hyperactivity followed by loss of balance, indicating a mode of action on the central nervous system. Such neurotoxic effects were found to be dependent on the concentration of the parent compound in the target organ, the brain. A threshold concentration of $0.02 \mu\text{g/g}$ was required in the brain before toxic effects were observed.

It has also been reported that a disruption of osmotic balance at the gills may contribute to cypermethrin toxicity. Experiments with frog skin (the epithelial cells of which can be considered as the functional analogues of the chloride absorbing cells in gills of freshwater fishes) showed that cypermethrin inhibited sodium transport across the membrane. It was concluded that the disturbance in sodium transport may be an important factor in the pathogenesis of pyrethroid toxicity in fishes [93].

2.6.6 Mesocosm and field studies

Freshwaters mesocosm and field studies

There have been many studies on the biological effects of cypermethrin under field conditions. The majority report that the compound is not toxic to freshwater organisms in the field at concentrations that cause acute toxicity in the laboratory. This has mainly been attributed to the removal of cypermethrin from the aqueous phase by adsorption to suspended solids, thus reducing bioavailability. However, there is evidence to suggest that concentrations arising from agricultural spray drift may be acutely toxic to particularly sensitive crustaceans such as the freshwater shrimp, *Gammarus pulex*.

In a UK study, two experimental ponds were sprayed directly with a dose of 100 g ha^{-1} (i.e. much greater dosage than is likely to contaminate freshwaters under normal conditions of agricultural use) and the effects on fish and invertebrate populations were monitored over a 16-week period [10, 94]. In these experiments, no effects were observed on rudd (*Scardinius erythrophthalmus*) exposed to measured water concentrations of up to $2.3 \mu\text{g l}^{-1}$ during the period 0–96 hours after treatment compared with the 96-hour LC50 for rudd under laboratory conditions of $0.4 \mu\text{g l}^{-1}$. The survival of the fish in pond water containing apparently lethal concentrations was attributed to strong adsorption of cypermethrin to suspended solids. The importance of suspended particulate matter in reducing toxicity was confirmed in the laboratory when it was shown that rainbow trout (*Oncorhynchus mykiss*) survived 7 days exposure to $5.0 \mu\text{g l}^{-1}$ of cypermethrin in pond water containing 15 mg l^{-1} solids, whereas 100 per cent mortality was recorded within 24 hours for the same concentration in microfiltered mains water [46].

In contrast to the lack of effects on field populations of fish, high invertebrate mortalities following a direct cypermethrin dose of 100 g ha^{-1} were reported [10, 94]. This dose led to measured concentrations of $0.69\text{--}1.4 \mu\text{g l}^{-1}$ in the aqueous phase, 0–48 hours following application. Laboratory tests indicate that many invertebrates would not be able to survive concentrations exceeding $0.5 \mu\text{g l}^{-1}$ over this time period. The observed mortality reported in the pond studies is therefore consistent with that seen in laboratory tests. Zooplankters were not found in samples taken from a treated pond until eight weeks after treatment. Populations of daphnids and copepods then increased exponentially to numbers far exceeding those in an untreated pond. Chironomid larvae and adult beetles of the genus *Helophorus* were found in pond samples only four weeks after treatment, while many other insect species were not found until 10–15 weeks after treatment [10, 94].

In both pond experiments, an increase in biomass of filamentous algae occurred. In the 16-week experiment, a dense algal mat developed that effectively inhibited penetration of light and photosynthesis in the water column, leading to a progressive depletion of dissolved oxygen. This increase in algal growth was attributed to the mortality of planktonic herbivores that normally graze on the algae [41]. It is conceivable that the consequent effects of the algal bloom may have contributed to the long recovery time of invertebrate populations, though there are no data to support this. Similar results were reported by Davies and Cook [95], who found that a bloom of filamentous algae occurred on a stream bed between 21 and 55 days following application of cypermethrin to a surrounding *Eucalyptus* plantation (water concentration $<1.0 \mu\text{g l}^{-1}$).

Invertebrate populations in a natural Canadian pool were found to be severely reduced following direct over-spray with cypermethrin, while caged fish populations were unaffected [96]. At a dose of 10 g ha^{-1} (approximately $8.0 \mu\text{g l}^{-1}$ based on the authors' estimation), 91–100 per cent mortality of mosquito larvae, *Aedes stimulans* and *Aedes euedes* (the target insects in this study) was reported, while populations of non-target invertebrates (i.e. crustaceans, Diptera and Coleoptera) were significantly reduced. Caged stickleback (*Culaea inconstans*) were unaffected at a dose of 20 g ha^{-1} (approximately $16.0 \mu\text{g l}^{-1}$ based on the authors' estimation).

Similar effects on invertebrate populations in experimental mesocosms were reported by Farmer *et al.* [22]. To simulate the quantity of cypermethrin residues that reach water bodies as a result of agricultural spray drift, the authors sprayed eight mesocosms at a rate of only 0.7 g ha^{-1} , equivalent to a drift rate of 2 per cent. This treatment was repeated on four separate occasions at intervals of two weeks. The highest residues reported in water were those following the third application, when the mean concentrations taken at the surface and a depth of 1 m after one hour were 0.035 and $0.031 \mu\text{g l}^{-1}$ respectively. At this concentration, numbers of copepods increased as a result of decreased competition for algal food sources from other adversely affected grazers. However, there were marked reductions in sensitive macroinvertebrate species. Amphipod and isopod crustaceans were particularly sensitive, with complete elimination of the freshwater shrimp (*Gammarus* sp.) and no evidence of recovery before the end of the study (19 weeks). However, there were no decreases in mayfly nymphs, a group of organisms normally very sensitive to cypermethrin exposure. The authors attributed this to the pattern of exposure following each application: the first organisms to be affected were semi-aquatic species at the water/air interface, followed by pelagic organisms, with

benthic invertebrates living on the bottom sediment (such as mayfly nymphs) the last organisms to be exposed to the compound.

No mortalities of rainbow trout (*O. mykiss*) held in steel enclosures within a mature experimental pond were reported following exposure to a direct over-spray dose of 50 g ha⁻¹ [97]. However, a dose of 100 g ha⁻¹ caused 100 per cent mortality. Since water concentrations were not measured, the authors concluded that the no-effect level (in terms of nominal application rate) lay between 50 and 100 g ha⁻¹, i.e. at levels much higher than those used under normal agricultural conditions and applied in such a way as to maximise water concentrations.

In the studies described above, the effect of cypermethrin following direct application was investigated. However, field studies have also been conducted that investigate the effect of cypermethrin on freshwater organisms exposed to spray drift resulting from its use on surrounding fields. One study involved sugar beet and potato fields in the UK being treated with a dose of 70 g ha⁻¹ using tractor-mounted sprayers [94]. Deposits of spray drift on the surface of three adjacent ponds were found to be very low (6.0–23.0 µg l⁻¹), while concentrations in subsurface water (0.01–0.07 µg l⁻¹) were near to or below the limit of detection, even though the site was chosen to maximise contamination of adjacent water bodies. At these concentrations, there were no detectable residues in fish and no effects on the aquatic fauna except on the surface of one corner of one of the ponds where immobility, but no mortality, was observed among a few individuals belonging to certain species of air breathing insects within the first few hours following treatment. However, all affected insects had recovered by the following day.

Shires and Bennet [98] investigated the effects of cypermethrin on the aquatic fauna of three drainage ditches contaminated as a result of application by aerial spray of 25 g ha⁻¹ to surrounding winter wheat fields. Very low (0.02 µg l⁻¹ maximum) concentrations of cypermethrin were measured in subsurface waters and these declined rapidly after spraying. Frequent sampling of the zooplankton and macroinvertebrate fauna of the ditches indicated that there were no marked effects resulting from exposure to cypermethrin. Only a few air breathing corixids and the highly susceptible water mites showed minor short-term reductions in abundance after spraying. The only visible effects were restricted to the ditch bordering the downwind edge of the treated field, where several corixids were immobilised and a few other individuals exhibited signs of hyperactivity. These effects were no longer apparent four hours after application. No effects were observed on either caged or indigenous fish stocks, and no significant levels were recorded in fish tissues [98].

However, the same authors also reported significant mortality (37–82 per cent) of the freshwater shrimp, *Gammarus pulex*, in 24-hour laboratory bioassays, conducted on contaminated ditch water containing 0.02 µg l⁻¹ cypermethrin, taken from two out of the five sampling stations at one hour to two days after application. In water taken four days after spraying, no mortality was observed [98]. The results of Farmer *et al.* [22] also provide evidence that some sensitive crustacean species may be affected in the field at concentrations that could arise from agricultural spray drift. These authors found that the freshwater shrimp (*Gammarus* sp.) was eliminated following exposure to 0.03 µg l⁻¹, arising from direct over-spray of mesocosms at a rate simulating agricultural spray drift (0.7 g ha⁻¹). However, this study is unlikely to reflect what will happen under true field

conditions, since the mesocosm was subjected to four applications over an eight-week period.

The effects of cypermethrin on the aquatic fauna of three streams adjacent to French vineyards treated with a dose of 30 or 45 g ha⁻¹ applied with mist blowers have also been investigated [94]. Deposits on the surface of these streams were found to range from 0.04–0.45 mg m⁻², while concentrations in the subsurface water were 0.4–0.7 µg l⁻¹ soon after spraying, decreasing to <0.1 µg l⁻¹ within a few hours. There was a marked increase in the numbers of live arthropods in the stream drift during the first few hours after spraying, but 24 hours later, their numbers were similar to those in pretreatment samples. Increased invertebrate drift had no detectable effect on population densities of benthic invertebrates [94].

However, the results of an Australian study [95] appear to contradict these findings, although the reasons for this are not clear. In this study, a *Eucalyptus* plantation in Northern Tasmania was sprayed aerially with an active ingredient concentration of 12.6 g ha⁻¹ and the resulting biological effects in three streams were recorded over a 16-month period. Analysis of samples immediately after spraying revealed that water concentrations did not exceed 1.0 µg l⁻¹. Due to an error in the analytical method, it was not possible to determine water concentrations below 1.0 µg l⁻¹, though the authors estimated that concentrations in the stream at the time of spraying would have been 0.1–0.5 µg l⁻¹. Immediately after spraying, invertebrate drift rates increased from 200–500 individuals to 123,000 individuals per 1,000 m³ at a distance of approximately 0.7 km from the edge of the plantation. Drift rates significantly higher than at the control sites were sustained for two days and returned to normal 20 days after application. Drift during the first eight days post-spraying was dominated by *Plecoptera* and *Ephemoptera* (89–92 per cent, decreasing to 60 per cent by day 8). Of the organisms caught in the drift nets on day 0, 68, 76 and 75 per cent mortality was observed for *Plecoptera*, *Ephemoptera* and *Amphipoda*, respectively. The proportion of dead *Plecoptera* and *Ephemoptera* fell to 4 and 8 per cent, respectively, by day 8 [95].

Davies and Cook [95] also reported the biological effects of spray drift on gravel riffle and lower gradient cobble habitats within the plantation. Overall abundance of invertebrates decreased markedly after spraying, with some recovery occurring by day 133. At both sites, baetids were eliminated and the abundance of leptophlebiids was greatly reduced. Simuliids, which were only present initially at the riffle site, were also eliminated, while other Diptera decreased after spraying but numbers were again high by day 55. Phreatoicids were eliminated and densities did not recover until day 337. Numerous dead phreatoicids were observed on the stream bed on day 0. No significant impact was detected on populations of larval *Trichoptera*, *Coleoptera* (adults or larvae) or *Oligochaeta*. The abundance of pupal *Trichoptera* increased significantly after spraying, although inspection revealed that over 80 per cent of pupae were dead late in development or during emergence. The authors attributed this increase to a delayed effect of cypermethrin exposure on pupal development. The authors stated that recovery of benthic fauna abundance after the spraying event took 6 months.

Giddings *et al.* [28] reviewed the available cypermethrin mesocosm studies, including some of those described above [8, 10, 22] and two further commercial studies by Getty *et al.* [99] and Palmeiri *et al.* [31]. Table 2.11 summarises the application rates and peak

water concentrations in these four studies and Table 2.12 summarises the observed effects.

Table 2.11 Reviewed cypermethrin mesocosm studies [28]

Application rate (g a.i. ha ⁻¹)	Number of applications	Total applied (g a.i. ha ⁻¹)	Nominal concentration (ng l ⁻¹)	Peak concentration (ng l ⁻¹)	Reference
100	1	100	10,000	1,000	[10]
3.15*	6	18.6	313	300	[31]
1.4	8	11.2	140	100	[99]
0.62	4	2.5	62	30	[22]

* Cypermethrin at 2.1 g a.i. ha⁻¹ applied as spray, followed 24 hours later by 1.05 g a.i. ha⁻¹ applied as slurry.

a.i. = active ingredient

Table 2.12 Summary of cypermethrin effects in mesocosm studies [28]

Concentration (ng l ⁻¹)	Cladocerans	Copepods	Rotifers	Chironomids	Ephemeropterans	Trichopterans	Odonates	Amphipods	Hydracarinids	Oligochaetes	Snails	Fish
30	+	+	+	+	+	=	=	-		+	+	
100	(-)	(-)	=	(-)	(-)	(-)	=	-	=	+	?	=
300	(-)	(-)	+	+(-)	(-)	(-)	+			+	+	=
1000	(-)	(-)		(-)	-		=	-	-	-	=	=

- reduction with no recovery

(-) reduction with recovery

= no effect

+

increase

+(-) some taxa increased, others reduced with recovery

? response uncertain

The lowest observed adverse effects concentrations (LOAECs) from these mesocosms are summarised and compared with laboratory LC50 data in Table 2.13.

There are some discrepancies between the laboratory and field results in Table 2.13, but amphipods and isopods are consistently among the most sensitive organisms. Based on the assumption that effects on amphipods and isopods would be mitigated in the field by immigration from unaffected areas, Giddings *et al.* [28] suggest that 100 ng l⁻¹ should be taken as the lowest concentration of cypermethrin that causes ecologically significant effects in mesocosms. However, this assumption remains untested.

Table 2.13 Comparison of lowest observed adverse effect concentrations (LOAECs) for taxonomic groups observed in cypermethrin mesocosm studies and geometric mean results from laboratory tests with the same or related taxa

Taxonomic group	Mesocosm LOAEC (ng l ⁻¹) [28]	Laboratory LC50 (ng l ⁻¹) [84]
Amphipods and isopods	30	21
Copepods	100	-
Cladocerans	100	1,300
Midges	100	120
Mayflies	100	10
Caddisflies	100	1,400
Odonates	>1,000	1,400
Mites	1,000	32
Fish	>1,000	2,700
Snails	>1,000	42,000
Oligochaetes	1,000	-
Rotifers	>300	-

Additional mesocosm studies with cypermethrin were reported subsequently [27, 76, 77]. PVC enclosures (0.65 m high, 0.4 m diameter) were placed in an artificial pond and triplicates dosed once with 50 ng l⁻¹ cypermethrin either alone or in combination with 1, 5 or 20 µg l⁻¹ of the herbicide metsulfuron methyl [77]. Copepod nauplii were reduced in numbers in the cypermethrin treatments on day 5 after exposure, but recovered to become significantly more abundant in these enclosures on days 10 and 14. Rotifers, phytoplankton, periphytic algae and the macrophytes, *Elodea canadensis* and *Myriophyllum spicatum*, were unaffected by the cypermethrin treatment and there were no observed additive, antagonistic or synergistic effects between cypermethrin and metsulfuron methyl.

In a separate study [27, 76], nine enclosures were constructed from 0.1 mm polyethylene (0.44 m wide, 1.5 m deep) and filled with 200 litres of lake water. Ten pooled plankton net hauls were added to these enclosures before they were anchored in the lake. Single enclosures were dosed with 0.01, 0.04, 0.13, 0.47, 1.7 and 6.1 µg l⁻¹ cypermethrin and zooplankton samples were taken for up to 11 days after dosing. The lowest overall no-effect concentration was 0.02 µg l⁻¹ measured after four days for cladocerans and after 12 hours for copepods. However, more detailed examination of the data produced lower no-effect concentration estimates of 0.01 µg l⁻¹ for the copepod *Eudiaptomus graciloides* on day 4 and copepod nauplii after 4 hours. There were no direct effects of cypermethrin on rotifers, protozoans, bacteria or algae in the enclosures, but the abundance of these organisms increased in those enclosures in which grazing zooplankton crustacean abundance was reduced.

Saltwater mesocosm data

The effects of cypermethrin on marine plankton communities were assessed in a simulated field study using mesocosms [56]. The marine mesocosms used consisted of cylindrical enclosures placed in natural systems, thus allowing large volumes of water to be manipulated in isolation from the environment. Each enclosure included a changeable bag (797 ml in volume), suspended from a triangular galvanized frame that floated with the aid of three buoys. The bags were made of 500-gauge polyethylene (125 mm thick),

which is biologically inert and has a good mechanical strength. Enclosures were located and moored beside a trout farm in Loch Etive, Scotland. In June 2001, six mesocosms were filled with local seawater filtered to 60 µm. Three mesocosms were set up as controls and three as treatments. To assure that all bags contained the same zooplankton community, the day after the enclosures were set up, equal volumes of a concentrated zooplankton sample were distributed to each enclosure. A single dose of cypermethrin (approximately 5 µg l⁻¹) was applied to the three treatment enclosures five days after the experiment was set up.

When cypermethrin was applied inside these mesocosms, its concentration decreased exponentially following a first-order kinetics model with an estimated half-life in the water column of 1.16 days. There were no significant differences between control and treated mesocosms in chlorophyll a and in total phytoplankton from 5 days before the application of cypermethrin to 2 days after its application. The pesticide reduced zooplankton density and biodiversity in the treated mesocosms immediately (compared with the controls) not only directly by killing copepods, but also indirectly by allowing an increase in the numbers of rotifers (probably as a result of the greater tolerance of this group to cypermethrin compared to the copepods). Zooplankton density recovered after treatment, but zooplankton biodiversity remained altered with reduced proportions of *Acartiidae* (33 per cent) and higher levels of *Temoridae* (67 per cent) compared with the controls (containing 55 per cent *Acartiidae* and 25 per cent *Temoridae*, with *Pseudocalanidae* and *Paracalanidae* accounting for the remaining 20 per cent).

3. Calculation of PNECs as a basis for the derivation of quality standards

3.1 PNECs for freshwaters

3.1.1 PNEC for deriving an annual average concentration

Table 2.6 summarises the most sensitive long-term (lt) freshwater toxicity data found for cypermethrin.

The lowest long-term result for algae is a 96-hour population increase NOEC of $100 \mu\text{g l}^{-1}$ for *Selenastrum capricornutum* [69]. This study is reported in a commercially confidential report and cited in EHC 82 [39]. The relative insensitivity of algae is supported by results from enclosure studies [27, 76, 77].

No long-term laboratory macrophyte data could be found. However, one of the enclosure studies [77] suggests that neither *Elodea canadensis* nor *Myriophyllum spicatum* would be affected by exposure to 50 ng l^{-1} of cypermethrin.

The lowest long-term result for invertebrates is reported in summary form as a 21-day *Daphnia magna* reproduction LOEC of 7 ng l^{-1} based on confidential company data. No further information on the study is available, though it is used as a reliable study in a subsequent published paper from the same group [53] based upon work undertaken by the industry Pyrethroid Working Group. It does not seem likely that such a group would use such a low value in risk assessments of cypermethrin if it was unreliable. This value is plausible, as other commercially confidential *Daphnia magna* reproduction studies report a 23-day NOEC of $0.02 \mu\text{g l}^{-1}$ [86] and a 21-day NOEC of $0.05 \mu\text{g l}^{-1}$ [85] (cited in EHC 82 [39]).

The lowest long-term results for fish are effects on olfaction and milt priming in Atlantic salmon (*Salmo salar*) are reported from a series of experiments in which measured cypermethrin concentrations at the end of each experiment mostly ranged between 38 and 66 per cent of nominal [61], although the limit of detection of $0.004 \mu\text{g l}^{-1}$ is higher than some of the nominal test concentrations used. In the first experiment, mature male Atlantic salmon parr were exposed to a single concentration of $0.01 \mu\text{g l}^{-1}$ cypermethrin for five days, with continuous insecticide dosing and renewal of stock solutions every 12 hours. Measured concentrations at the end of the exposure period were $<0.004 \mu\text{g l}^{-1}$. Fish were then removed to clean water, exposed to female salmon pheromone, and their olfactory response to this pheromone measured electrophysiologically over five days. The mean response of the exposed group was only 11 per cent of the control group. In the second experiment, males were stripped of milt and left to recover for 96 hours, after which they were exposed to $0.0001, 0.001, 0.01, 0.05, 0.1$ or $0.5 \mu\text{g l}^{-1}$ cypermethrin for five days (measured concentrations from <0.004 to $0.33 \mu\text{g l}^{-1}$), with continuous

insecticide dosing and renewal of stock solutions every 12 hours. They were given either a five-hour exposure to female pheromone or to a control, after which they were anaesthetised and milt, blood and bile from gall bladders were sampled and analysed for steroids and weight of expressible milt. Cypermethrin concentrations of $<0.004 \mu\text{g l}^{-1}$ (nominal concentration $0.001 \mu\text{g l}^{-1}$) removed the effect of exposure to the female pheromone on male milt expression, while slightly higher concentrations affected sex steroid concentrations. In the third experiment, unfertilised eggs and milt were exposed for ~30 seconds to 0.001, 0.01, 0.05, 0.1 and $0.5 \mu\text{g l}^{-1}$ cypermethrin to examine effects on egg fertilisation. Exposure to the two highest concentrations led to fertilisation rates that were 47 and 39 per cent of the control group, respectively.

Of these three studies, the second is most useful for deriving a PNEC. This is because the effect on expressible milt is of clear relevance to fish reproduction and, although the effect concentration is reported as $<0.004 \mu\text{g l}^{-1}$, the data show that there were no significant effects at the lowest nominal concentration of $0.0001 \mu\text{g l}^{-1}$, which can be taken as the NOEC for this study. This NOEC should be protective of effects on salmon olfaction that occurred at a nominal concentration 100 times higher (equivalent to a true exposure concentration at least 38 times higher if measurements at higher exposure concentrations are extrapolated to lower concentrations).

The most sensitive and reliable long-term toxicity value for deriving an annual average quality standard is therefore a NOEC of 0.1 ng l^{-1} for expression of milt by male Atlantic salmon. Since data are also available for algae and invertebrates, and there are several mesocosm studies which suggest that effects on arthropod assemblages do not occur at or below 10 ng l^{-1} , an assessment factor of 1 is recommended.

$\text{PNEC}_{\text{freshwater_lt}} = 0.1 \text{ ng l}^{-1} \text{ cypermethrin/AF (1)} = 0.1 \text{ ng l}^{-1} \text{ cypermethrin}$

3.1.2 PNEC for deriving a maximum allowable concentration

Table 2.7 summarises the most sensitive short-term (st) freshwater toxicity data found for cypermethrin.

The lowest short-term result for algae is a 96-hour population increase EC50 of $>100 \mu\text{g l}^{-1}$ for *Selenastrum capricornutum* [69]. This study is reported in a commercially confidential report and cited by EHC 82 [39]. The relative insensitivity of algae is supported by results from a number of enclosure studies [27, 76, 77].

The lowest short-term result for macrophytes is a 5-day NOEC of $>1,000 \mu\text{g l}^{-1}$ for biochemical parameters in *Ceratophyllum demersum* [58], though a lack of chemical analysis makes this result unreliable for deriving a PNEC. However, the enclosure study [77] suggests that neither *Elodea canadensis* nor *Myriophyllum spicatum*, two other macrophytes, would be affected by exposure to 50 ng l^{-1} of cypermethrin.

The lowest short-term result for invertebrates is a 24-hour reduction in the survival of *Daphnia magna* (9 per cent mortality at $0.001 \mu\text{g l}^{-1}$ compared with 2.7 per cent in controls), although a lack of chemical or statistical analyses makes this result unreliable for deriving a PNEC. The next most sensitive results are 96-hour LC50 values of $0.004 \mu\text{g l}^{-1}$ for the amphipod *Gammarus pulex* and the mayfly *Cloeon dipterum* [68]. These

results are suitable for deriving a PNEC because they are from flow-through tests with chemical analysis of cypermethrin concentrations.

The lowest reliable short-term result for fish is a 96-hour LC50 of 0.4 µg l⁻¹ for the rudd, *Scardinius erythrophthalmus* [70]. This test was performed in a flow-through system with chemical analysis of cypermethrin concentrations. More sensitive results are reported in Table 2.7 for the loach *Lepidocephalichthys thermalis*, the western mosquitofish *Gambusia affinis* and the carp *Cyprinus carpio*, but none of these studies was supported by chemical analysis of cypermethrin concentrations and hence they are unreliable for deriving a PNEC.

The most sensitive and reliable short-term toxicity values for deriving a maximum allowable concentration are 96-hour LC50s of 0.004 µg l⁻¹ (4 ng l⁻¹) for the insect *Cloeon dipterum* and the amphipod *Gammarus pulex*. Amphipods have been identified [28] as being among the organisms most sensitive to cypermethrin in mesocosm tests, with effects at <30 ng l⁻¹, so an assessment factor of 10 applied to the LC50 is justifiable.

$$\text{PNEC}_{\text{freshwater_st}} = 4 \text{ ng l}^{-1} \text{ cypermethrin/AF (10)} = 0.4 \text{ ng l}^{-1} \text{ cypermethrin}$$

3.2 PNECs for saltwaters

The effects database for marine species is considerably smaller than that for freshwater organisms. Acute (short-term) toxicity data are available for seven different taxonomic groups (bacteria, rotifers, crustaceans, molluscs, polychaetes, echinoderms and fish), while chronic (long-term) data are available only for crustaceans.

The toxicity data of the marine taxa do not markedly differ from the range of values obtained for their relatives dwelling in freshwater (see Tables 2.6–2.9). However, the marine database is too small to draw firm conclusions on possible differences, particularly with regard to chronic effects.

Since there are no obvious differences in the sensitivity of freshwater or saltwater species of the same taxonomic group, the TGD approach of using freshwater data within the marine effect assessment can be used where appropriate. Therefore, suggested freshwater PNECs for setting of quality standards should be considered in deriving corresponding values for marine water bodies.

3.2.1 PNEC for deriving an annual average concentration

Long-term single species toxicity data referring to marine organisms are only available for two crustacean species, the copepod *Acartia tonsa* and the mysid *Mysidopsis bahia*⁷ (Table 2.8).

The study on the copepod *Acartia tonsa* involved conducting a life table study in which the rate of change in population numbers was assessed over a 32-day exposure period [2]. The study was initiated with newborn nauplii hatched within the previous 24 hours. Groups of 50 nauplii were held in 1-litre borosilicate funnels filled with 500 ml of the appropriate test solution, but there was only one replicate per test concentration. In all

⁷ Now *Americamysis bahia*

treatments, animals were transferred to newly prepared solutions every other day. It was found that the age-specific fecundity curve (m_x) and intrinsic rate of population increase (r_m) were not affected up to exposure concentrations of 4.1 ng l^{-1} . Both endpoints were impaired at 7.1 ng l^{-1} while, at higher cypermethrin exposure concentrations, all the nauplii died before reaching adulthood and m_x and r_m could not be calculated.

The only NOEC relating to the long-term effects of cypermethrin on survival of the mysid shrimp is 0.44 ng l^{-1} . The study was conducted by ICI/AstraZeneca, but no detailed information is available on the experimental conditions.

Overall, the absence of long-term data for both algae and fish means that it is not appropriate to generate a $\text{PNEC}_{\text{saltwater_lt}}$ based on the saltwater data alone. However, since the long-term data for saltwater crustaceans are similar to those for freshwater crustaceans and given the specific mode of action of cypermethrin, it is proposed that the combined freshwater and saltwater dataset be used for the PNEC generation.

The most sensitive and reliable long-term toxicity value for deriving an annual average quality standard in the combined data set is a NOEC of 0.1 ng l^{-1} for expression of milt by male Atlantic salmon. Since data are also available for algae and invertebrates and there are several mesocosm studies which suggest that effects on arthropod assemblages do not occur at or below 10 ng l^{-1} , an assessment factor of 1 is recommended.

$\text{PNEC}_{\text{saltwater_lt}} = 0.1 \text{ ng l}^{-1}$ cypermethrin/AF (1) = 0.1 ng l^{-1} cypermethrin

3.2.2 PNEC for deriving a maximum allowable concentration

Single species acute toxicity data for marine organisms are available for seven different taxonomic groups (bacteria, crustaceans, echinoderms, fish, molluscs, polychaetes and rotifers), with crustaceans being the most sensitive group. Although no information is available for saltwater algae, the freshwater data indicate that this taxonomic group is considerably less sensitive to cypermethrin than invertebrates and fish.

Short-term toxicity test data are available for a range of marine crustacean species. The lowest recorded acute toxicity data for a crustacean is a 96-hour LC50 of $0.0035 \mu\text{g l}^{-1}$ for survival of juveniles of the shrimp *Palaemonetes africanus* [13]. In the study, a semi-static regime was adopted with replacement of test solutions every 24 hours. However, the cypermethrin exposure concentrations were not measured and the experimental design was not described in detail. There are also concerns regarding the prehistory of the organisms since they were obtained from Lagos lagoon immediately prior to the start of the study.

The lowest valid acute toxicity value is a 96-hour LOEC of 4.1 ng l^{-1} for lethality of nauplii of the copepod *Acartia tonsa* [2]. In the study, a semi-static regime was adopted in which test solutions were replaced every 48 hours. The cypermethrin exposure concentrations were not measured directly, but actual concentrations in test solutions were based on dilutions of the measured stock solution concentrations, which were determined as the interpolated midpoint value between initial and final concentration.

This value is supported by a 96-hour LC50 value of 5 ng l^{-1} for lethality of mysids (*Mysidopsis bahia*) (cited in [86]), though no details are available on the experimental

design of this study. A range of other studies have recorded 96-hour LC50 values for mysids and shrimps in the concentration range 0.01–0.1 µg l⁻¹.

Only limited short-term data are available for fish. The lowest value is a 96-hour LC50 of 1 µg l⁻¹ for survival of sheepshead minnow (cited in [86]). However, no details are available on the experimental design of this study and so its quality could not be assessed. The lowest reliable value for fish is a 96-hour LC50 of 2 µg l⁻¹ for Atlantic salmon [55]. This was a semi-static study with measured exposure concentrations and is valid for PNEC derivation.

In addition to the above fish and crustacean data, short-term EC/LC50 values are available for marine molluscs (*Crassostrea virginica*) and echinoderms (*Strongylocentrotus droebachiensis*) with 96-hour EC/LC50 values of 370 and >50 µg l⁻¹, respectively.

The TGD [83] does not provide specific guidance for assessment of acute effects of intermittent releases to marine water bodies. Therefore, it is recommended that the PNEC accounting for effects following short-term exposure to cypermethrin is calculated on the basis of the general guidance given in the TGD on the effects assessment for intermittent releases (Section 3.3.2 of Part II of the TGD). Based on the geometric mean 96-hour LOEC of 4.1 ng l⁻¹, a reduced assessment factor of 10 is recommended given the range of species for which data are available, including marine groups such as echinoderms and molluscs. This results in the following value:

$$\text{PNEC}_{\text{saltwater_st}} = 4.1 \text{ ng l}^{-1} \text{ cypermethrin/AF (10)} = 0.41 \text{ ng l}^{-1} \text{ cypermethrin}$$

3.3 Derivation of PNECs by the TGD probabilistic approach (SSD method)

There are insufficient data to construct an SSD based upon long-term exposure data. Indeed, it could be argued that such an SSD for water column organisms would be meaningless due to the rapid partitioning of cypermethrin onto solids [84].

Short-term SSDs using LC50 and EC50 data have been derived [84]. A log-normal model was fitted and datasets in which test concentrations exceeded the water solubility were excluded from the analysis. Separate analyses were performed for all organisms, arthropods alone, and vertebrates alone. The resulting 10th percentiles for cypermethrin acute toxicity data were 10 ng l⁻¹ for all organisms, 6.4 ng l⁻¹ for arthropods and 380 ng l⁻¹ for vertebrates.

3.4 Derivation of existing EQSs

The derivation of EQSs for cypermethrin was started originally in 1993 and, although a number of draft reports were produced (the latest in 1996), the report published in July 2001 [9] represented the final view of the UK EQS Steering Group.

In freshwaters, the annual average was derived by applying a safety factor of 5 to the lowest chronic effects concentration (i.e. the 28-day LOEC to *Mysidopsis* of 0.6 ng l⁻¹)

resulting in an EQS of 0.2 ng l⁻¹ total cypermethrin to account for extrapolation to a no-effects concentration and possible interspecies differences in sensitivity. Although based on saltwater chronic data, this was justified because of the large dataset available, evidence of a small effect to no-effects ratio and because *Mysidopsis* was the most sensitive species for which data were available at that time. Therefore, the resulting standards were reported to be, if anything, over protective. It was proposed that the annual average be expressed as 'tentative', until chronic *Gammarus* data (most sensitive organism to acute exposures) became available and would thus reduce any additional uncertainty. The annual average was influenced by the MAC, since a value of 0.2 ng l⁻¹ was considered equivalent to applying an extrapolation factor of 10 to the MAC (see below).

The freshwater MAC for cypermethrin was based on the lowest reliable 96-hour LC50 of 9 ng l⁻¹ reported in a laboratory flow-through study for *Gammarus pulex*. Given the large dataset available and evidence of a small effect to no-effects ratio, a factor of 5 was applied to this value. This resulted in an EQS of 2.0 ng l⁻¹ total cypermethrin expressed as a MAC.

A more limited dataset was available at that time for saltwater organisms. However, their sensitivity to cypermethrin appeared to be similar to that of freshwater species. In addition, a saltwater organism had been used as the basis of the freshwater annual average concentration. Therefore, it was proposed that the EQSs expressed as 'total' MAC and annual average concentrations for freshwaters (i.e. 2.0 and 0.2 ng l⁻¹, respectively) were also adopted as tentative EQSs for the protection of saltwater life.

3.5 Derivation of PNECs for sediment

Since the log K_{ow} of cypermethrin is >3 (see Section 2.5), the derivation of PNECs for the protection of benthic organisms is required.

A number of studies have been conducted to evaluate the effects of sediment-bound cypermethrin on aquatic organisms (see Table 2.10).

Toxicity data are available for sediment-dwelling organisms, including amphipods. From both laboratory water column studies [68] and mesocosm studies [28], these appear to be among the most sensitive organisms to cypermethrin toxicity. Ten-day growth NOECs for the amphipod *Hyalella azteca* were reported as <1.8, 2.3 and 1.8 µg/kg dw in sediments containing 1, 3 and 13 per cent organic carbon [53]. The authors predicted water concentrations leading to these sediment concentrations as <0.52, 0.22 and 0.05 ng l⁻¹, assuming a K_{oc} of 350,000 for cypermethrin.

A value of ~2 µg/kg dw, therefore, appears to be a growth NOEC for sediments containing a moderate amount of organic carbon (the TGD 'standard sediment' contains 4 per cent organic matter). Data on the 10-day growth of the infaunal species *Chironomus tentans* are also available and show that it is approximately an order of magnitude less sensitive than *H. azteca* to sediment-bound cypermethrin [53]. Data are also available from other studies with chironomids [33, 37]. The TGD [83] recommends application of an AF of 50 when two long-term NOEC values are available for two sediment-dwelling species with different living and feeding conditions, as is the case here. However, mesocosm data are also available which suggest that amphipods such

as *H. azteca* are likely to be among the most sensitive sediment-dwelling organisms to cypermethrin toxicity. An AF of 10 applied to the *H. azteca* NOEC is, therefore, appropriate.

$$\text{PNEC}_{\text{sediment_freshwater}} = 2 \mu\text{g cypermethrin/kg dw/AF (10)} = 0.2 \mu\text{g cypermethrin/kg dw}$$

3.6 Derivation of PNECs for secondary poisoning of predators

3.6.1 Mammalian and avian toxicity data

Mammalian and avian toxicity data were obtained from:

- the plant protection product (PPP) review on alpha-cypermethrin produced by the European Commission [14];
- the WHO Food Additives Series 38 report [79];
- the toxicological profile on pyrethrins and pyrethroids produced by the Agency on Toxic Substances and Disease Registry (ATSDR) [1].

Additional literature searches were also performed to locate any lower effect data since 2003. However, no further data were found.

After oral administration, cypermethrin is readily absorbed, distributed and excreted in rats, chickens, sheep and cattle. Cypermethrin is primarily eliminated in urine and faeces in about equal proportions and less than 1 per cent is excreted in milk. When cypermethrin is applied dermally to sheep, 2.5 per cent is eliminated in urine and faeces within 6 days. After an oral dose, about 60 per cent is eliminated within 2 days.

The major metabolic route for both cypermethrin and individual isomers, including those of alpha-cypermethrin, is cleavage of the ester bond followed by hydroxylation and conjugation of the cyclopropyl and phenoxybenzyl portions of the molecule [11].

The acute oral toxicity of cypermethrin is moderate to high. In rats and mice, the oral LD50 ranges from 82 to 4,000 mg/kg body weight (bw) for cypermethrin, depending on the vehicle used. At lethal or near lethal doses, the signs are typical of type-II pyrethroids and include salivation, ataxia, gait abnormalities and convulsions [79].

Table 3.1 Most sensitive mammalian and bird oral toxicity data relevant for the assessment of secondary poisoning

Study and result	Details
Sub-chronic toxicity to mammals	
Pickering 1981 [63] Cited in WHO 1996 [79] Sub-chronic NOAEL = 5 mg/kg bw/day	Male and female Wistar rats (12 per sex per group) received cypermethrin orally via their diet at doses of 0, 25, 100, 400 or 1600 mg/kg diet for 90 days. The no observed adverse effect level (NOAEL) was based on: <ul style="list-style-type: none"> • decreased haemoglobin concentration, mean corpuscular volume and eosinophils, and increased prothrombin time,

Study and result	Details
	<p>plasma urea levels and relative liver and kidney weights in males at the top dose;</p> <ul style="list-style-type: none"> • decreased eosinophils and increased liver weights in males at the 400 mg/kg diet dose; • reduced food intake and increased liver weights in females at the top dose.
Chronic toxicity to mammals	
<p>McAusland <i>et al.</i> 1978 [54] Cited in WHO 1996 [79] Chronic NOAEL = 5 mg/kg bw/day</p>	<p>Male and female Wistar rats (48 per sex per group) received cypermethrin orally via their diet at 0, 1, 10, 100 or 1,000 mg/kg diet for 2 years. The NOAEL was based on reduced body weight and food consumption at the highest dose.</p>
<p>Primary reference unclear Cited in EC 2004 [14] Chronic NOAEL = 3 mg/kg bw/day</p>	<p>Mice (sex and strain unspecified) received cypermethrin orally (method unstated) for 78 weeks (doses unspecified). The NOAEL was based on decreased body weight gain and clinical signs of neurotoxicity. No signs of carcinogenic potential were observed. No further details provided.</p>
<p>Buckwell 1981 [5] Cited in WHO 1996 [79] Chronic NOAEL = 7.5 mg/kg bw/day</p>	<p>Male and female Beagle dogs (four per sex per group) received cypermethrin orally via their diet at 0, 3, 30, 300 or 1,000 mg/kg diet for 2 years. Due to severe signs of intoxication at the high dose, the dose was reduced to 750 mg/kg diet/day and was then further reduced to 600 mg/kg diet/day. No effects were observed on ophthalmoscopy, clinical chemistry, organ weights, macroscopy and microscopy. No abnormalities were found in the sciatic nerves, brain or spinal cord. No evidence of carcinogenicity was observed. The NOAEL was based on licking and chewing of the paws, a stiff high stepping gait, whole body tremors, head shaking, incoordination, ataxia and, in some cases, convulsions.</p>
Effects on reproduction of mammals	
<p>Hend <i>et al.</i> 1978 [34] Fish 1979 [25] Thorpe 1985 [75] Cited in WHO 1996 [79] NOAEL = 5 mg/kg bw/day</p>	<p>Male and female Wistar rats (30 per sex per group) received cypermethrin orally via their diet at 0, 10, 100 or 500 mg/kg diet for 5 weeks prior to mating and then throughout pregnancy and lactation for three successive generations. The NOAEL was based on reduced body weight gain and food consumption and a concomitant reduction in litter size in all generations and reduced weight in the F1a progeny only at the highest dose. This NOAEL is representative of maternal and reproductive toxicity.</p>
<p>Primary reference unclear Cited in EC 2004 [14] NOAEL = >20 mg/kg bw/day</p>	<p>Rats (sex and strain unspecified) received cypermethrin orally (method and exposure period unstated). No effects were observed on reproduction. No further details provided.</p>
<p>Office of Pesticide Programs 1992 [18] Cited in ATSDR 2003 [1] NOAEL = 45 mg/kg bw/day</p>	<p>CD rats (sex unspecified) received cypermethrin via their diets (method and exposure period unstated). No effects were observed on reproduction. No further details provided.</p>

Study and result	Details
<p>Abd El-Khalek <i>et al.</i> 1999 [16] Cited in ATSDR 2003 [1] LOAEL = 3.8 mg/kg bw/day</p>	<p>Rats (sex and strain unspecified) received cypermethrin orally (method unspecified) at doses of 3.8 or 7.7 mg/kg bw/day for 65 days. The lowest observed adverse effect level (LOAEL) was based on decreases in plasma testosterone levels, which lasted throughout the 30 days of post-treatment observation, reduced male reproductive organ weights and significantly altered sperm characteristics (unstated). No further details provided.</p>
Effects on development of mammals	
<p>Primary reference unclear Cited in EC 2004 [14] NOAEL = >9 mg/kg bw/day</p>	<p>Rats (sex and strain unspecified) received cypermethrin orally (method, doses and exposure period unstated). The NOAEL was based on reduced foetal weight at maternally toxic doses. No further details provided.</p>
<p>Malaviya <i>et al.</i> 1993 [52] Cited in ATSDR 2003 [1] LOAEL = 15 mg/kg bw/day</p>	<p>Female Wistar rats received cypermethrin via gavage in oil at doses of 15 mg/kg bw/day during gestation days 5–21 and lactation days 1–21. The LOAEL was based on increased levels of dopamine and muscarinic receptors in striatal membrane of foetuses. No further details provided.</p>
Embryotoxicity and teratogenicity	
<p>Gupta 1990 [30] Cited in ATSDR 2003 [1] NOAEL = 8 mg/kg bw/day</p>	<p>Female rats (strain unspecified) received cypermethrin orally (method unspecified) at doses of 2, 4 or 8 mg/kg bw/day during gestation days 6–15. The NOAEL was based on the absence of foetotoxicity, teratogenicity or maternal toxicity. No further details provided.</p>
<p>Tesh <i>et al.</i> 1978 [74] Cited in WHO 1996 [79] NOAEL = 70 mg/kg bw/day</p>	<p>Female pregnant Sprague–Dawley rats (25 per group) received cypermethrin orally in corn oil via gavage at doses of 0, 17.5, 35 or 70 mg/kg bw/day. Animals were sacrificed on gestation day 21. The NOAEL was based on no signs of embryotoxicity being observed. However, one death, neurological disturbances and reduced body weight gain were noted at this dose. Cypermethrin is reported to not cause embryotoxicity or teratogenicity in rats at doses of up to 70 mg/kg bw/day. The NOAEL for maternal toxicity was 17.5 mg/kg bw/day.</p>
<p>Tesh <i>et al.</i> 1984 [73] Cited in WHO (1996) [79] NOAEL = 120 mg/kg bw/day</p>	<p>Female pregnant New Zealand white rabbits (four per group) received cypermethrin orally in corn oil via gavage cypermethrin at doses of 0, 25, 50, 100 or 120 mg/kg bw during gestation days 6–18. Animals were sacrificed on gestation day 29. No adverse effects were seen in mothers or foetuses.</p>
Neurotoxicity to mammals	
<p>Primary reference unclear Cited in EC 2004 [14] Acute NOAEL = 4 mg/kg bw/day (in corn oil) Sub-chronic NOAEL = 10 mg/kg bw/day (in DMSO)</p>	<p>Rats (sex and strain unspecified) received cypermethrin orally (method and doses unspecified). Central nervous system and peripheral motor nerve toxicity were observed, but were reversible within 3 days following the single, acute dose No further details provided.</p>

Study and result	Details
Office of Pesticide Programs 1992 [18] Cited in ATSDR 2003 [1] LOAEL = 27 mg/kg bw/day	CD rats (sex unspecified) received cypermethrin orally via their diet for >120 days (doses unspecified). The LOAEL was based on hypersensitivity to sound.
IRIS 2003 [40] Cited in ATSDR 2003 [1] NOAEL = 5 mg/kg bw/day LOAEL = 15 mg/kg bw/day	Beagle dogs (sex unspecified) received cypermethrin orally (method and doses unspecified) for 52 weeks. The NOAEL and LOAEL were based on tremors, gait abnormalities, incoordination, disorientation and hypersensitivity to sound.
Endocrine disruption	
<p>A report for the European Commission, <i>Study on gathering information on 435 substances with insufficient data</i> [4], evaluated available data and considered that, with respect to wildlife, cypermethrin was a Category 2 endocrine-disrupting chemical under the scheme proposed in an earlier report [3]. This categorisation indicated that 'possible endocrine disrupting related effects have been observed but the working mechanism needs clarification'.</p> <p>One study [16] reported that oral exposure of rats (sex and strain unspecified) to cypermethrin at doses of 3.8 or 7.7 mg/kg bw/day for 65 days resulted on decreases in plasma testosterone levels, which lasted throughout the 30 days of post-treatment observation, reduced male reproductive organ weights and significantly altered sperm characteristics. A recent <i>in vivo</i> study in rabbits involving oral application of a sublethal dose of cypermethrin of 24 mg/kg bw every other day for 12 weeks found a significant impact on several reproductive parameters and on plasma testosterone concentrations [82].</p>	
Sub-chronic and chronic toxicity to birds	
No studies were available on the sub-chronic and chronic toxicity of cypermethrin to birds.	
Effects on reproduction to birds	
Primary reference unclear Cited in EC 2004 [14] NOEC = 130 mg/kg diet	Japanese quail (<i>Coturnix coturnix japonica</i>) received cypermethrin orally via the diet for 20 weeks. The basis of the NOEC was unstated and no further details were available.
No studies were available regarding the potential effects of cypermethrin on avian development or on potential carcinogenicity or other toxicity.	

The indirect effects of cypermethrin application on brown trout (*Salmo trutta*) due to heavy feeding on dead drift organisms have been reported [95]. On day 0, many fish with full or distended guts were observed feeding on drifting organisms. Indeed, observations on stomach fullness indicated a significant rise on day 0 from pre-spray means of 40–55 per cent to means of 140 per cent, with drift organisms comprising >90 per cent of the diet. Over an eight-day period, this gorging on contaminated food led to a loss of self-righting ability, lethargy, development of a striped colouration accompanied by hardening and haemolysis of muscular tissue (similar to tetany), anaemic appearance of blood and gills, pale liver colouration and dark green bile. In addition, transient physiological responses were observed in fish during the first three weeks after spraying which appeared to be related to dietary uptake of cypermethrin rather than exposure to concentrations in the water phase. The RNA/DNA ratios (an indication of instantaneous growth rate) in fish muscle at a site approximately 0.7 km downstream from the plantation, increased significantly (30 per cent) coincident with the marked increase in

stomach fullness, indicating a transient increase in instantaneous growth rate. By contrast, at a site within the plantation, the RNA/DNA ratio decreased by 25 per cent suggesting that the impact of spraying on invertebrates was more severe at this site and that loss of feed or secondary physiological effects had already affected instantaneous growth rate.

3.6.2 PNECs for secondary poisoning of predators

Bioconcentration data (as BCF values) for cypermethrin for invertebrates and fish range from 31–238 and 84–1200, respectively, with depuration half-lives of 8–27 days (see Section 2.5). Hence the trigger of BCF >100 is met and the derivation of PNECs for secondary poisoning (secpois) of predators is required.

The lowest reported reliable oral NOAELs are 5 mg/kg bw/day derived from a 90-day rat study, a 2-year rat study and a three-generation rat reproductive study which corresponded to 100 mg/kg feed (Table 3.1). Despite a lower oral NOAEL of 3 mg/kg bw/day being reported from a 78-week mouse study and LOAEC of 3.8 mg/kg bw/day being reported for rats from a 65-day study, these values have not been used for PNEC derivation because they were poorly reported.

The appropriate assessment factor to derive a PNEC based on a chronic NOEC_{food} of a mammalian study is 30 (Table 23 of TGD [83]).

$$\text{PNEC}_{\text{secpois_biota}} = \text{NOEC}_{\text{food}} (100 \text{ mg/kg}) / \text{AF } 30 = 3.33 \text{ mg/kg prey (wet weight)}$$

Reported BCF values for invertebrates and fish range from 31–1,200. Information on the biomagnification of cypermethrin is not available but, due to its rapid metabolism and elimination from the body within a short period of time, the occurrence of biomagnification is considered unlikely (see Section 2.5). Biomagnification is, therefore, not considered in the following calculations.

The corresponding safe concentration in water (preventing bioaccumulation in prey to levels >PNEC_{secpois_biota}) is calculated as follows:

$$\text{PNEC}_{\text{secpois_water}} = \text{PNEC}_{\text{secpois_biota}} / \text{BCF}$$

If the highest reported BCF of 1,200 is used for the calculation, this results in a (lowest) corresponding water concentration of:

$$\text{PNEC}_{\text{secpois_water}} = 3.33 / 1200 = 2.78 \text{ } \mu\text{g l}^{-1} \text{ cypermethrin}$$

This concentration is much higher than the proposed long-term PNECs for the protection of the pelagic communities in both freshwaters and saltwaters. Therefore, if quality standards are set on the basis of these PNECs, the protection of predators from secondary poisoning is included and the derivation of additional quality standards with particular reference to secondary poisoning is not considered necessary.

4. Analysis and monitoring

Analytical methods for the determination of cypermethrin published between 1990 and 2001 are discussed in Environment Agency R&D Technical Report P2-115/TR5 [9] (see Annex 2).

The main problem with analyses for cypermethrin is that it consists of four geometric isomers, each of which can occur in two enantiomeric forms. Therefore, depending on the analytical technique used, up to eight individual responses can be obtained. So although a low limit of detection (LOD) may be achieved for an individual component of cypermethrin, the overall LOD for 'total cypermethrin isomers' is considerably higher. With techniques utilising gas chromatography (GC), usually four peaks are detected for cypermethrin because the enantiomers (optical isomers) are not separated.

Many of the more recent publications concerning the analysis of cypermethrin refer to food-related matrices, such as vegetable oil [21], baby food [35] or olive oil [24, 48], or are related to human health investigations where urine [47] or blood [49, 65] were analysed for cypermethrin metabolites.

However, other publications relate to water and/or soil.

An analytical method involving solid-phase extraction (SPE) using Oasis HLB cartridges has been described [81]. Water samples (1 litre) were filtered prior to extraction. A methanol/acetonitrile mixture was used to elute the cartridges and, after reducing the extract to dryness, the residue was dissolved in acetone for analysis using GC. Initially samples were analysed using GC with electron capture detection (ECD). Some samples were also analysed using gas chromatography/mass spectrometry (GC-MS). It is not clear what the LOD of this method is for cypermethrin, as the paper describes a multiresidue method for 31 pesticides and merely states that the LODs for water were in the range from 5×10^{-4} to 1.5×10^{-2} ng l⁻¹. No supporting data are provided to assess these claimed LODs and the LOD for individual compounds is not given. Assuming that cypermethrin is one of the pesticides with the highest LOD, the suggestion is that its LOD is no worse than 15 pg l⁻¹. As the lowest concentration at which spiked samples were analysed was 50 ng l⁻¹, the claimed LODs should be regarded with some suspicion, especially as the analytical quality control (AQC) samples analysed were spiked at 100 ng l⁻¹. The highest reported concentration of cypermethrin in reservoir water samples was 1.89 ng l⁻¹. Sediment samples were also analysed (ultrasonication was used to extract the pesticides) and the highest reported concentration of cypermethrin was 8.77 ng kg⁻¹.

A microwave-assisted extraction procedure has been reported for the extraction of nine pyrethroids, including cypermethrin, from soil [20]. Analysis of the extracts was carried out using GC-ECD. The LOD is stated to be 3 µg kg⁻¹, but this is based on $3s_{\text{blank}}/b$, where s_{blank} is the standard deviation of five measurements of a 50 µg l⁻¹ (i.e. 50 pg µl⁻¹) standard solution and b is the slope of the calibration curve for the range 10–1,000 µg l⁻¹. Using negative ion chemical ionisation mass spectrometry as the detection technique, a LOD of 0.7 µg kg⁻¹ is reported.

The preferred extraction technique for the determination of cypermethrin in aqueous samples (based on publications that have appeared over the last 10 years) is SPE. Provided samples are filtered prior to extraction, relatively large sample volumes (≥ 1 litre) can be extracted rapidly and, provided suitable equipment is available, this process can be automated. Relatively small volumes of solvent (< 10 ml in total, typically 2×2 ml) are used to elute SPE cartridges, so concentration of extracts to a volume suitable for GC-MS analysis (typically 100 μ l) is relatively quick. As cypermethrin is a high-boiling compound (compared with the solvents used for the elution of the SPE cartridges), equipment such as Turbovap apparatus can be used, which allows many extracts to be concentrated simultaneously.

An assessment of those papers relating to non-aqueous matrices suggests that GC-MS with electron impact ionisation and selected ion monitoring (using the ions at m/z 181, 165 and 163) is usually the preferred detection/quantification technique for cypermethrin; it provides improved certainty of detection and better sensitivity compared with GC-ECD. One report [21] describes the use of GC-MS/MS, with transitions from a precursor ion at m/z 163.1 to product ions at 127.1 and 91.1 being monitored. It is not clear whether this latter technique merely provides greater specificity (compared with GC-MS or GC-ECD) or better sensitivity (in terms of signal-to-noise ratios) and hence a lower LOD.

For water, proposed PNECs derived for cypermethrin range from 0.1 to 0.41 ng l^{-1} . The data quality requirements are that, at a third of the EQS, total error of measurement should not exceed 50 per cent. Using this criterion, it is evident that current analytical methodologies (non-standard) employing GC-MS, which are capable of achieving detection limits as low as 15 pg l^{-1} , should offer adequate performance to analyse for cypermethrin.

5. Conclusions

5.1 Availability of data

Long-term laboratory data are available for five different freshwater taxonomic groups including algae, amphibians, crustaceans, fish and molluscs. Freshwater short-term toxicity data are available for 11 taxonomic groups including algae, amphibians, arachnids, bacteria, crustaceans, fish, insects, macrophytes, molluscs, protozoans and rotifers.

Freshwater fish and arthropod species are sensitive to cypermethrin, and there is an indication that amphibians may also be sensitive. For marine organisms, single species acute toxicity data are available for seven different taxonomic groups (bacteria, crustaceans, echinoderms, fish, molluscs, annelids and rotifers), while chronic toxicity data are available only for crustaceans (two species). Laboratory data are supplemented by freshwater and marine mesocosm data, which confirm the high sensitivity of crustaceans to cypermethrin.

The recent *in vitro* data on the endocrine disrupting properties of cypermethrin are equivocal, but limited *in vivo* data indicate effects by cypermethrin on olfaction and milt priming in Atlantic salmon (*Salmo salar*) at low environmental concentrations.

5.2 Derivation of PNECs

The proposed PNECs are described below and summarised in Table 5.1.

5.2.1 Long-term PNEC for freshwaters

The most sensitive and reliable long-term toxicity value is a NOEC of 0.1 ng l⁻¹ for expression of milt by male Atlantic salmon (*Salmo salar*). This is a significant endpoint because it could lead to reduced fertility. Since reliable data are also available for algae and invertebrates, and there are several mesocosm studies which suggest that effects on arthropod assemblages do not occur at or below 10 ng l⁻¹, an assessment factor of 1 is recommended resulting in a PNEC_{freshwater_lt} of 0.1 ng l⁻¹ cypermethrin.

This value is similar to the existing EQS of 0.2 ng l⁻¹, which is based on applying a safety factor of 5 to the lowest chronic effects concentration, i.e. a 28-day LOEC to *Mysidopsis* of 0.6 ng l⁻¹. Although based on saltwater chronic data, this was justified because of the large dataset available, evidence of a small effect to no-effects ratio, and because *Mysidopsis* was clearly the most sensitive species for which data were available at that time. The value of 0.2 ng l⁻¹ was also considered equivalent to applying an extrapolation factor of 10 to the short-term EQS.

5.2.2 Short-term PNEC for freshwaters

Because cypermethrin exposure is likely to be short, the short-term PNEC may be particularly important.

Reliable short-term data are available for algal, invertebrate and fish species. The most sensitive and reliable short-term toxicity values are a 96-hour LC50 of 4 ng l⁻¹ for the mayfly *Cloeon dipterum* and the amphipod *Gammarus pulex*. Since amphipods were identified as among the most sensitive organisms in mesocosm tests, with effects at <30 ng l⁻¹, a reduced assessment factor of 10 (instead of the default value of 100) applied to the LC50 is proposed. This results in a PNEC_{freshwater_st} of 0.4 ng l⁻¹ cypermethrin.

This value is lower than the existing EQS of 2 ng l⁻¹, which is based on applying a factor of 5 to the lowest reliable 96-hour LC₅₀ of 9 ng l⁻¹ reported in a laboratory flow-through study for *Gammarus pulex*. The assessment factor was selected based on the large dataset available and evidence of a small effect to no-effects ratio.

5.2.3 Long-term PNEC for saltwaters

Given the absence of long-term data for both algae and fish, it is not appropriate to generate a PNEC_{saltwater_lt} based on the saltwater data alone. But since the long-term data for saltwater crustaceans indicate similar sensitivities to freshwater crustaceans and given the specific mode of action of cypermethrin, it is proposed that the combined freshwater and saltwater dataset be used for PNEC generation.

The most sensitive and reliable long-term toxicity value in the combined dataset is a NOEC of 0.1 ng l⁻¹ for expression of milt by male Atlantic salmon. Since data are also available for algae and invertebrates and there are several mesocosm studies which suggest that effects on arthropod assemblages do not occur at or below 10 ng l⁻¹, an assessment factor of 1 is recommended resulting in a PNEC_{saltwater_lt} of 0.1 ng l⁻¹ cypermethrin.

This value is similar to the existing EQS of 0.2 ng l⁻¹, which was 'read across' from the freshwater long-term value.

5.2.4 Short-term PNEC for saltwaters

Reliable short-term data are available for invertebrate and fish species. The lowest valid acute toxicity value is a 96-hour LOEC of 4.1 ng l⁻¹ for lethality of nauplii of the copepod *Acartia tonsa*. The use of a reduced assessment factor of 10 (instead of the default value of 100), because of the availability of data for exclusively marine species, results in a PNEC_{saltwater_st} of 0.41 ng l⁻¹ cypermethrin.

This value is lower than the existing EQS of 2 ng l⁻¹ which was 'read across' from the freshwater short-term value.

5.2.5 PNEC for secondary poisoning

Bioconcentration data [as bioconcentration factor (BCF) values] for cypermethrin for invertebrates and fish range from 31–38 and 84–1,200 respectively; hence, the trigger of BCF >100 is met and the derivation of PNECs for secondary poisoning of predators is required. The calculated PNEC_{secpois_water} of 2.78 µg l⁻¹ cypermethrin is much higher than the proposed long-term PNECs for the protection of the pelagic communities in both inland and marine water bodies, and so does not influence the development of EQSs for cypermethrin.

5.2.6 PNEC for sediments

Since the log Kow of cypermethrin is >3, the derivation of PNECs for the protection of benthic organisms is required. The resulting PNEC_{sediment_freshwater} of 0.2 µg cypermethrin/kg dw is higher than the other long-term and short-term PNEC values.

Table 5.1 Summary of proposed PNECs

Receiving medium/exposure scenario	Proposed PNEC (ng l ⁻¹ cypermethrin)	Existing EQS (ng l ⁻¹)
Freshwater/long-term	0.1	0.2
Freshwater/short-term	0.4	2.0
Saltwater/long-term	0.1	0.2
Saltwater/short-term	0.41	2.0
Freshwater sediment	0.2 µg/kg dw	–
Secondary poisoning	2.78	–

5.3 Analysis

The data quality requirements are that, at a third of the EQS, the total error of measurement should not exceed 50 per cent. Using this criterion, it is evident that current analytical methodologies (non-standard) employing GC-MS, which are capable of achieving detection limits as low as 15 pg l⁻¹, should offer adequate performance for analysis for cypermethrin.

5.4 Implementation issues

Before PNECs for cypermethrin can be adopted as EQSs, it will be necessary to address the following issues:

1. The relevance of standards for cypermethrin in the water column should be considered because the high lipophilicity of cypermethrin means it is more likely to occur in sediment and biota.
2. Further data from manufacturers may be forthcoming once these standards are released for consultation. These are unlikely to affect the freshwater long-term PNEC, but could influence other PNECs.
3. Given the short persistence of cypermethrin in the water column, consideration needs to be given to the usefulness of the long-term and short-term PNECs.

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List of abbreviations

AA	annual average
AF	assessment factor
a.i.	active ingredient
ATSDR	Agency on Toxic Substances and Disease Registry
BCF	bioconcentration factor
bw	body weight
CAS	Chemical Abstracts Service
DMSO	dimethyl sulfoxide
dw	dry weight
EC50	concentration effective against 50% of the organisms tested
ECD	electron capture detection
EHC	Environmental Health Criteria
EQS	Environmental Quality Standard
GC	gas chromatography
GC-MS	gas chromatography/mass spectrometry
GLP	Good Laboratory Practice (OECD)
HSDB	Hazardous Substances Data Bank
IRIS	Integrated Risk Information System
IUPAC	International Union of Pure and Applied Chemistry
LC50	concentration lethal to 50% of the organisms tested
LOAEL	lowest observed adverse effect level
LOAEC	lowest observed adverse effect concentration
LOD	limit of detection
LOEC	lowest observed effect concentration
lt	long term
MAC	maximum allowable concentration
NOAEL	no observed adverse effect level
NOEC	no observed effect concentration
OECD	Organisation for Economic Co-operation and Development
PNEC	predicted no-effect concentration
PPP	plant protection product
secpois	secondary poisoning
SEPA	Scottish Environment Protection Agency
SNIFFER	Scotland & Northern Ireland Forum for Environmental Research

SPE	solid-phase extraction
SSD	species sensitivity distribution
st	short term
TGD	Technical Guidance Document
UKTAG	UK Technical Advisory Group
US EPA	US Environmental Protection Agency
WFD	Water Framework Directive
WHO	World Health Organization

ANNEX 1 Data quality assessment sheets

Identified and ordered by reference number (see References & Bibliography).

Data relevant for PNEC derivation were quality assessed in accordance with the so-called Klimisch Criteria (Table A1).

Table A1 Klimisch Criteria*

Code	Category	Description
1	Reliable without restrictions	Refers to studies/data carried out or generated according to internationally accepted testing-guidelines (preferably GLP**) or in which the test parameters documented are based on a specific (national) testing guideline (preferably GLP), or in which all parameters described are closely related/comparable to a guideline method.
2	Reliable with restrictions	Studies or data (mostly not performed according to GLP) in which the test parameters documented do not comply totally with the specific testing guideline, but are sufficient to accept the data or in which investigations are described that cannot be subsumed under a testing guideline, but which are nevertheless well-documented and scientifically acceptable.
3	Not reliable	Studies/data in which there are interferences between the measuring system and the test substance, or in which organisms/test systems were used that are not relevant in relation to exposure, or which were carried out or generated according to a method which is not acceptable, the documentation of which is not sufficient for an assessment and which is not convincing for an expert assessment.
4	Not assignable	Studies or data which do not give sufficient experimental details and which are only listed in short abstracts or secondary literature.

* Klimisch H-J, Andreae M and Tillmann U, 1997 *A systematic approach for evaluating the quality of experimental toxicological and ecotoxicological data*. Regulatory Toxicology and Pharmacology, **25**, 1–5.

** OECD Principles of Good Laboratory Practice (GLP). See:

http://www.oecd.org/departement/0,2688,en_2649_34381_1_1_1_1_1,00.html

Reference	2
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Information on the test species	
Test species used	<i>Acartia tonsa</i>
Source of the test organisms	Continuous cultures maintained at the Institute of Aquaculture, Stirling, Scotland
Holding conditions prior to test	Tanks supplied with 0.2 µm filtered natural seawater maintained at 20°C under a photoperiod of 16 hours:8 hours light/dark cycle with the water changes every 2 days
Life stage of the test species used	Range of life stages (eggs, nauplii, copepodites and adults)

Information on the test design	
Methodology used	The test method is described
Form of the test substance	40% <i>cis</i> -, 58% <i>trans</i> -cypermethrin of 99.5% purity
Source of the test substance	Supelco, Bellefonte, PA, USA
Type and source of the exposure medium	Filtered natural seawater collected from St Andrews, Scotland
Test concentrations used	For the short-term and longer-term toxicity tests: 0 (control), 4.2, 7.4, 29, 89 and 259 µg l ⁻¹
Number of replicates per concentration	For the short-term nauplii survival test: 1 For the longer-term test: 1
Number of organisms per replicate	
Nature of test system (static, semi-static or flow-through, duration, feeding)	Semi-static with replacement of test solutions every 48 hours; no feeding
Measurement of exposure concentrations	No, but measurement of stock solutions at the beginning and end of the exposure period.
Measurement of water quality parameters	
Test validity criteria satisfied	Not stated
Water quality criteria satisfied	Not stated
Study conducted to GLP	Not stated
Overall comment on quality	Generally good study, but analysis only of stock solutions.

Reliability of study	Reliable
Relevance of study	Relevant
Klimisch Code	2

Reference	12
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Information on the test species	
Test species used	<i>Cyprinus carpio</i>
Source of the test organisms	Not stated
Holding conditions prior to test	Not stated
Life stage of the test species used	Eggs at early cleavage stage

Information on the test design	
Methodology used	Eggs examined every 12 hours until 2 days after hatching
Form of the test substance	Cypermethrin 25 emulsifiable concentrate
Source of the test substance	Not stated
Type and source of the exposure medium	Tap water
Test concentrations used	0.00001–40 mg l ⁻¹
Number of replicates per concentration	3
Number of organisms per replicate	100
Nature of test system (static, semi-static or flow-through, duration, feeding)	Static
Measurement of exposure concentrations	No
Measurement of water quality parameters	Yes
Test validity criteria satisfied	Not stated
Water quality criteria satisfied	Not stated
Study conducted to GLP	No
Comments	This study exposed eggs for several days but only one dose of cypermethrin was applied at the start of the experiment and there was no chemical analysis.

Reliability of study	Not reliable
Relevance of study	Relevant
Klimisch Code	3

Reference	13
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Information on the test species	
Test species used	<i>Palaemonetes africanus</i>
Source of the test organisms	Obtained from Lagos lagoon
Holding conditions prior to test	According to FAO Fisheries Technical Paper
Life stage of the test species used	Juveniles

Information on the test design	
Methodology used	The test procedure is described, but not in detail
Form of the test substance	Research grade cypermethrin
Source of the test substance	Allied Products Limited, Apapa, Lagos
Type and source of the exposure medium	Brackish water, source not stated
Test concentrations used	Not stated
Number of replicates per concentration	Not stated
Number of organisms per replicate	10 per test vessels
Nature of test system (static, semi-static or flow-through, duration, feeding)	Semi-static with replacement of test solutions daily; no feeding
Measurement of exposure concentrations	No
Measurement of water quality parameters	pH, dissolved oxygen and salinity at start of the test
Test validity criteria satisfied	Not stated
Water quality criteria satisfied	Not stated
Study conducted to GLP	Not stated
Overall comment on quality	Lack of analysis makes this study unreliable.

Reliability of study	Not reliable
Relevance of study	Relevant
Klimisch Code	3

Reference	17
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Information on the test species	
Test species used	<i>Gambusia affinis</i>
Source of the test organisms	Laboratory culture
Holding conditions prior to test	Laboratory
Life stage of the test species used	Four weeks old

Information on the test design	
Methodology used	96-hour LC50 tests under either 12-hours light: 12-hours dark or 24-hours light: 24-hours dark photoperiod
Form of the test substance	Ripcord 30% emulsifiable concentrate
Source of the test substance	Not stated
Type and source of the exposure medium	Dechlorinated water
Test concentrations used	Not stated
Number of replicates per concentration	3
Number of organisms per replicate	20
Nature of test system (static, semi-static or flow-through, duration, feeding)	Static
Measurement of exposure concentrations	No
Measurement of water quality parameters	No
Test validity criteria satisfied	Not stated
Water quality criteria satisfied	Not stated
Study conducted to GLP	Not stated
Comments	The lack of exposure measurement means that this study cannot be considered reliable.

Reliability of study	Not reliable
Relevance of study	Relevant
Klimisch Code	3

Reference	19
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Information on the test species	
Test species used	<i>Polydora cornuta</i> <i>Strongylocentrotus droebachiensis</i>
Source of the test organisms	Not stated
Holding conditions prior to test	Not stated
Life stage of the test species used	Not stated

Information on the test design	
Methodology used	The test procedure is not described in detail
Form of the test substance	Cypermethrin formulation (Excis)
Source of the test substance	Not stated
Type and source of the exposure medium	Seawater
Test concentrations used	Not stated, paper hints that it could only be one concentration, i.e. the recommended treatment dose of the formulation
Number of replicates per concentration	Not stated
Number of organisms per replicate	Not stated
Nature of test system (static, semi-static or flow-through, duration, feeding)	Not stated
Measurement of exposure concentrations	Not stated
Measurement of water quality parameters	Not stated
Test validity criteria satisfied	Not stated
Water quality criteria satisfied	Not stated
Study conducted to GLP	Not stated
Overall comment on quality	Lack of information on analysis and test conditions means this study cannot be considered reliable.

Reliability of study	Not reliable
Relevance of study	Relevant
Klimisch Code	3

Reference	23
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Information on the test species	
Test species used	1. <i>Pseudomonas putida</i> 2. <i>Vibrio fischeri</i>
Source of the test organisms	1. Biosensors and freeze-dried substrate obtained from Terra Nova Systems (Cambridge, UK) 2. Liquid-dried photo-bacteria reagent <i>V. fischeri</i> (NRRL B-111 77) Merck KgaA, Darmstadt, Germany
Holding conditions prior to test	Not applicable
Life stage of the test species used	Not applicable

Information on the test design	
Methodology used	1. Referred to other references 2. ToxAlert 100 system (Merck)
Form of the test substance	Pure pesticide
Source of the test substance	Riedel-de-Haën (Seelze, Germany)
Type and source of the exposure medium	1. Ultrapure Milli Q water used to prepare a 0.85% saline solution 2. High performance liquid chromatography (HPLC) water
Test concentrations used	Not stated (range 0.3–14 mg l ⁻¹)
Number of replicates per concentration	Not stated
Number of organisms per replicate	Not stated
Nature of test system (static, semi-static or flow-through, duration, feeding)	Static
Measurement of exposure concentrations	Yes
Measurement of water quality parameters	Not applicable
Test validity criteria satisfied	Yes
Water quality criteria satisfied	Not applicable
Study conducted to GLP	Not stated
Comments	This study was well performed using a standard test system.

Reliability of study	Reliable
Relevance of study	Relevant
Klimisch Code	2

Reference	29
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Information on the test species	
Test species used	<i>Rana arvalis</i>
Source of the test organisms	Egg clutches collected from wetland pond in north-east Germany in April 2002.
Holding conditions prior to test	Eggs and tadpoles kept in tanks with artificially salted (100 mg l ⁻¹ sodium chloride, 200 mg l ⁻¹ calcium chloride dihydrate, 103 mg l ⁻¹ sodium hydrogen carbonate) demineralised water. Temperature 20°C
Life stage of the test species used	Eggs, embryos (stage 10–12), tadpoles (stage 20)

Information on the test design	
Methodology used	Non-standard but well described
Form of the test substance	alpha-cypermethrin (purity >99%)
Source of the test substance	Fluka, Seelze, Germany
Type and source of the exposure medium	Well water
Test concentrations used	0.1, 1 and 10 µg l ⁻¹ plus solvent and water only controls
Number of replicates per concentration	Three, and experiments repeated three times
Number of organisms per replicate	10
Nature of test system (static, semi-static or flow-through, duration, feeding)	Static
Measurement of exposure concentrations	No
Measurement of water quality parameters	Not stated
Test validity criteria satisfied	Not stated
Water quality criteria satisfied	Not stated
Study conducted to GLP	Not stated
Comment	The lack of exposure measurement means that this study cannot be considered reliable.

Reliability of study	Not reliable
Relevance of study	Relevant
Klimisch Code	3

Reference	37
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Information on the test species	
Test species used	<i>Chironomus riparius</i>
Source of the test organisms	Laboratory culture maintained at Jealott's Hill International Research Centre, UK
Holding conditions prior to test	Larvae reared at low density, unlimited food ration, 20 ± 1°C, life-cycle completed in 3–4 weeks
Life stage of the test species used	Newly hatched larvae <24 hours old

Information on the test design	
Methodology used	Non-standard but well described
Form of the test substance	¹⁴ C-phenoxy-labelled cypermethrin in acetone with a specific activity of 2.1 GBq mmol l ⁻¹ ; purity >95%
Source of the test substance	Syngenta, Jealott's Hill International Research Centre
Type and source of the exposure medium	Reconstituted water: deionised water + 122.5 mg MgSO ₄ •7H ₂ O, 96 mg NaHCO ₃ , 60 mg CaSO ₄ •2H ₂ O and 4 mg KCl per litre
Test concentrations used	Three with solvent control (0, 0.015, 0.0225 and 0.03 µg l ⁻¹ nominal)
Number of replicates per concentration	4 (different organism densities, see below)
Number of organisms per replicate	64, 128, 256 and 512 larvae/vessel
Nature of test system (static, semi-static or flow-through, duration, feeding)	Flow-through – each population fed 25 mg Tetramin® fish flakes daily
Measurement of exposure concentrations	Yes
Substrate composition	Formulated sediment: 70% sand, 20% kaolin clay and 10% peat (OECD 1984*)
Measurement of water quality parameters	Yes
Test validity criteria satisfied	Yes
Water quality criteria satisfied	Yes
Study conducted to GLP	Not stated
Comment	This is a well-performed study with chemical analysis of exposure concentrations.

Reliability of study	Reliable
Relevance of study	Relevant
Klimisch Code	1

* Organisation for Economic Co-operation and Development (OECD), 1984 *OECD guideline for testing chemicals 207: earthworm acute toxicity test*. Adopted: 4 April 1984. Paris: OECD.

Reference	42
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Information on the test species	
Test species used	<i>Lepidocephalichthys thermalis</i>
Source of the test organisms	Ponds near Madurai Kamaraj University, Tamil Nadu, India
Holding conditions prior to test	Acclimated in tap water for 15 days and fed on boiled egg white
Life stage of the test species used	0.4–0.5 g wet weight

Information on the test design	
Methodology used	96-hour survival tests (APHA 1985*)
Form of the test substance	Not stated
Source of the test substance	Not stated
Type and source of the exposure medium	Not stated
Test concentrations used	Not stated
Number of replicates per concentration	2
Number of organisms per replicate	10
Nature of test system (static, semi-static or flow-through, duration, feeding)	Static
Measurement of exposure concentrations	No
Measurement of water quality parameters	No
Test validity criteria satisfied	Not stated
Water quality criteria satisfied	Not stated
Study conducted to GLP	Not stated
Comments	The lack of exposure measurement means that this study cannot be considered reliable.

Reliability of study	Not reliable
Relevance of study	Relevant
Klimisch Code	3

* American Public Health Association (APHA), 1985 *Standard methods for the examination of water and waste water*. Washington, DC: APHA.

Reference	50
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Information on the test species	
Test species used	<i>Salmo salar</i>
Source of the test organisms	Not stated
Holding conditions prior to test	Not stated
Life stage of the test species used	Unfertilised eggs and milt

Information on the test design	
Methodology used	Non-standard
Form of the test substance	Not stated
Source of the test substance	Not stated
Type and source of the exposure medium	Not stated
Test concentrations used	2 + control (0.05 and 0.10 µg l ⁻¹)
Number of replicates per concentration	2
Number of organisms per replicate	600
Nature of test system (static, semi-static or flow-through, duration, feeding)	Static
Measurement of exposure concentrations	No
Measurement of water quality parameters	Temperature; others not stated
Test validity criteria satisfied	Not stated
Water quality criteria satisfied	Not stated
Study conducted to GLP	Not stated
Comment	No measurement of exposure concentrations and the lack of a number of other details in this brief communication mean that it cannot be regarded as a reliable.

Reliability of study	Not reliable
Relevance of study	Relevant
Klimisch Code	3

Reference	53
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Information on the test species	
Test species used	1. <i>Daphnia magna</i> 2. <i>Hyalella azteca</i> 3. <i>Chironomus tentans</i>
Source of the test organisms	Laboratory cultures
Holding conditions prior to test	Not stated
Life stage of the test species used	1. Adult female 2. 7–14 days old 3. 3rd–4th instar

Information on the test design																	
Methodology used	Non-standard but well documented																
Form of the test substance	¹⁴ C-phenoxy-labelled cypermethrin with a specific activity of 2.1 GBq mmol I ⁻¹ ; purity >99%																
Source of the test substance	Not stated																
Type and source of the exposure medium	Not stated																
Test concentrations used	Three bioavailability (40, 100 and 150 µg/kg – <i>C. tentans</i> ; 423, 1,260 and 5,320 µg/kg – <i>D. magna</i>) Not stated for toxicity studies (ranged from 2.2–450 µg/kg for <i>C. tentans</i> dependent on sediment type; and 0.74–150 µg/kg for <i>H. azteca</i> dependent on sediment type)																
Number of replicates per concentration	6 (toxicity studies) 2 (bioavailability studies)																
Number of organisms per replicate	10																
Nature of test system (static, semi-static or flow-through, duration, feeding)	Static																
Measurement of exposure concentrations	Yes																
Substrate composition	<table border="0"> <thead> <tr> <th>Parameter</th> <th>Range of values in substrates</th> </tr> </thead> <tbody> <tr> <td>% organic carbon</td> <td>1–13</td> </tr> <tr> <td colspan="2">Textural properties</td> </tr> <tr> <td>% clay</td> <td>10–25</td> </tr> <tr> <td>% sand</td> <td>6–61</td> </tr> <tr> <td>% silt</td> <td>29–70</td> </tr> <tr> <td>Cation exchange capacity (mEq/100 g)</td> <td>4.0–43.6</td> </tr> <tr> <td>pH</td> <td>4.9–7.2</td> </tr> </tbody> </table>	Parameter	Range of values in substrates	% organic carbon	1–13	Textural properties		% clay	10–25	% sand	6–61	% silt	29–70	Cation exchange capacity (mEq/100 g)	4.0–43.6	pH	4.9–7.2
Parameter	Range of values in substrates																
% organic carbon	1–13																
Textural properties																	
% clay	10–25																
% sand	6–61																
% silt	29–70																
Cation exchange capacity (mEq/100 g)	4.0–43.6																
pH	4.9–7.2																
Measurement of water quality parameters	Not stated																
Test validity criteria satisfied	Not stated																

Water quality criteria satisfied	Not stated
Study conducted to GLP	Not stated
Comments	This is a well-performed study with chemical confirmation of test concentrations, but a few methodological details are missing.

Reliability of study	Reliable with restriction
Relevance of study	Relevant
Klimisch Code	2

Reference	55
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Information on the test species	
Test species used	<i>Salmo salar</i> <i>Homarus americanus</i> <i>Crangon septemspinosa</i>
Source of the test organisms	Not stated
Holding conditions prior to test	Not stated
Life stage of the test species used	Not stated

Information on the test design	
Methodology used	Non-standard but described well
Form of the test substance	Cypermethrin technical grade (98.5% pure)
Source of the test substance	Shell Canada
Type and source of the exposure medium	Not stated
Test concentrations used	Six concentrations
Number of replicates per concentration	9
Number of organisms per replicate	3
Nature of test system (static, semi-static or flow-through, duration, feeding)	Semi-static
Measurement of exposure concentrations	Yes, five times during test (found to be 70–80% of nominal)
Measurement of water quality parameters	Not stated
Test validity criteria satisfied	Not stated
Water quality criteria satisfied	Not stated
Study conducted to GLP	Not stated
Comments	Well-documented study though there is limited information on replication and a non-standard method is used.

Reliability of study	Reliable
Relevance of study	Relevant
Klimisch Code	2

Reference	57
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Information on the test species	
Test species used	<i>Daphnia magna</i>
Source of the test organisms	Laboratory culture
Holding conditions prior to test	Reared at 20°C; 14 hours:10 hours light/dark regime in artificial tank water (reverse osmosis water containing 100 mg l ⁻¹ sea salt, 200 mg l ⁻¹ CaCl ₂ ·2H ₂ O and 103 mg l ⁻¹ NaHCO ₃)
Life stage of the test species used	Adult females without eggs

Information on the test design	
Methodology used	Non-standard but well described
Form of the test substance	Cypermethrin
Source of the test substance	Not stated
Type and source of the exposure medium	<ol style="list-style-type: none"> 1. Artificial tank water (control) 2. Stream water from Svartberget coniferan forest, Norway 3. Suwannee River in Okefenokee Swamp, South Georgia, USA 4. HS1500, Sopar Pharma GmbH, Mannheim, Germany
Test concentrations used	0.001, 0.01, 0.1, 1 µg l ⁻¹ + solvent control
Number of replicates per concentration	3
Number of organisms per replicate	100
Nature of test system (static, semi-static or flow-through, duration, feeding)	Static
Measurement of exposure concentrations	No
Measurement of water quality parameters	Yes
Test validity criteria satisfied	Not stated
Water quality criteria satisfied	Not stated
Study conducted to GLP	Not stated
Comment	<p>Different concentrations of natural organic matter (humic substances – NOMs) from the sources described above were added in the following amounts: 0.5, 1, 5, 10, 50 mg l⁻¹ (+ 100 mg l⁻¹ Suwannee River). For combined exposures with NOMs, 0.1 µg l⁻¹ cypermethrin was used with either 5 or 50 mg l⁻¹ NOM.</p> <p>The lack of exposure measurement means that this study cannot be considered reliable.</p>

Reliability of study	Not reliable
Relevance of study	Relevant
Klimisch Code	3

Reference	58
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Information on the test species	
Test species used	<i>Ceratophyllum demersum</i>
Source of the test organisms	Wild population collected from the Möllensee near Berlin
Holding conditions prior to test	Cultivated axenically prior to experiments for some months in Provasoli's medium (ESI_{sp} 15 ml l ⁻¹) at 20–22°C.
Life stage of the test species used	Not stated

Information on the test design	
Methodology used	Non-standard but described well
Form of the test substance	(<i>S,R</i>)- α -cyano-3-phenoxybenzyl (1 <i>R</i> ,1 <i>S</i> , <i>cis,trans</i>)-3-(2,2-dichlorovinyl)-2,2-dimethylcyclopropanecarboxylate
Source of the test substance	Fluka, Germany
Type and source of the exposure medium	Assume same as culture medium.
Test concentrations used	0.5, 5, 50, 500 and 1,000 $\mu\text{g l}^{-1}$ + solvent control
Number of replicates per concentration	5
Number of organisms per replicate	10 g fresh weight
Nature of test system (static, semi-static or flow-through, duration, feeding)	Static
Measurement of exposure concentrations	Not stated
Measurement of water quality parameters	Not stated
Test validity criteria satisfied	Not stated
Water quality criteria satisfied	Not stated
Study conducted to GLP	Not stated
Comments	Although two of the parameters showed significant effects, mid-exposure levels returned to the same as controls by end of exposure, indicating a possible biotransformation response.
Comment	The lack of exposure measurement means that this study cannot be considered reliable.

Reliability of study	Not reliable
Relevance of study	Relevant
Klimisch Code	3

Reference	61
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Information on the test species	
Test species used	<i>Salmo salar</i> L.
Source of the test organisms	Environment Agency, Cynrig Hatchery, Wales
Holding conditions prior to test	Kept in 1,000-litre tanks, under natural light conditions, with a constant flow of aerated dechlorinated water (flow rate of 85 litres per minute). Temperature 7.1–9.8°C. Other water properties reported in the journal article.
Life stage of the test species used	Spermiating male parr (length 126 ± 1.1 mm; weight 24.2 ± 0.7 g; gonadosomatic index (GSI) 7.1 ± 0.29%)

Information on the test design	
Methodology used	Non-standard – detection of priming pheromone PGF _{2α} by olfactory epithelium
Form of the test substance	Cypermethrin
Source of the test substance	Greyhound Chromatography and Allied Chemicals
Type and source of the exposure medium	Not stated
Test concentrations used	0.01 µg l ⁻¹ + control
Number of replicates per concentration	None
Number of organisms per replicate	10
Nature of test system (static, semi-static or flow-through, duration, feeding)	Semi-static renewal every 12 hours
Measurement of exposure concentrations	Yes
Measurement of water quality parameters	Not stated
Test validity criteria satisfied	Not stated
Water quality criteria satisfied	Not stated
Study conducted to GLP	Not stated
Comments	The measured cypermethrin concentration from the tank of parr used in the olfactory studies was <0.004 µg l ⁻¹ (the LOD).

Reliability of study	Reliable
Relevance of study	Relevant
Klimisch Code	2

Reference	61
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Information on the test species	
Test species used	<i>Salmo salar</i> L.
Source of the test organisms	Environment Agency, Cynrig Hatchery, Wales
Holding conditions prior to test	Kept in 1,000-litre tanks, under natural light conditions, with a constant flow of aerated dechlorinated water (flow rate of 85 litres per minute). Temperature 7.1–9.8°C. Other water properties reported in the journal article.
Life stage of the test species used	Spermiating male parr (length 130 ± 1.3 mm; weight 27.2 ± 0.8 g; gonadosomatic index (GSI) 7.9 ± 0.34%)

Information on the test design	
Methodology used	Non-standard – priming response of males to PGF _{2α}
Form of the test substance	Cypermethrin
Source of the test substance	Greyhound Chromatography and Allied Chemicals
Type and source of the exposure medium	Not stated
Test concentrations used	0.0001, 0.001, 0.01, 0.05, 0.1, 0.5 µg l ⁻¹ + control
Number of replicates per concentration	none
Number of organisms per replicate	7
Nature of test system (static, semi-static or flow-through, duration, feeding)	Semi-static renewal every 12 hours
Measurement of exposure concentrations	yes
Measurement of water quality parameters	Not stated
Test validity criteria satisfied	Not stated
Water quality criteria satisfied	Not stated
Study conducted to GLP	Not stated
Comments	The measured cypermethrin concentrations used in this study were between <0.004 and 0.33 µg l ⁻¹ . These are all measurements taken at the end of experimental exposure period.

Reliability of study	Reliable
Relevance of study	Relevant
Klimisch Code	2

Reference	61
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Information on the test species	
Test species used	<i>Salmo salar</i> L.
Source of the test organisms	Environment Agency, Kielder Hatchery
Holding conditions prior to test	Transported on ice to Lowestoft Laboratory
Life stage of the test species used	Unfertilised eggs and milt

Information on the test design	
Methodology used	Non-standard – effects on egg fertilisation
Form of the test substance	Cypermethrin
Source of the test substance	Greyhound Chromatography and Allied Chemicals
Type and source of the exposure medium	Not stated
Test concentrations used	0.001, 0.01, 0.05, 0.1, 0.5 µg l ⁻¹ + control
Number of replicates per concentration	none
Number of organisms per replicate	500
Nature of test system (static, semi-static or flow-through, duration, feeding)	Semi-static renewal every 12 hours
Measurement of exposure concentrations	Yes
Measurement of water quality parameters	Not stated
Test validity criteria satisfied	Not stated
Water quality criteria satisfied	Not stated
Study conducted to GLP	Not stated
Comments	The measured cypermethrin concentrations used in this study were between <0.004 and 0.33 µg l ⁻¹ . These are all measurements taken at the end of experimental exposure period.

Reliability of study	Reliable
Relevance of study	Relevant
Klimisch Code	2

Reference	64
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Information on the test species	
Test species used	<i>Cyprinus carpio communis</i>
Source of the test organisms	Local fish farms
Holding conditions prior to test	Acclimated for unspecified period and fed daily, with feed withdrawn one day before testing
Life stage of the test species used	3.23±0.84 g

Information on the test design	
Methodology used	96-hour survival test plus analysis of liver, gill and brain glycogen, lipid and protein content
Form of the test substance	Not stated
Source of the test substance	Not stated
Type and source of the exposure medium	Not stated
Test concentrations used	Not stated
Number of replicates per concentration	Not stated
Number of organisms per replicate	Not stated
Nature of test system (static, semi-static or flow-through, duration, feeding)	Static
Measurement of exposure concentrations	No
Measurement of water quality parameters	No
Test validity criteria satisfied	Not stated
Water quality criteria satisfied	Not stated
Study conducted to GLP	Not stated
Comments	The lack of exposure measurement means that this study cannot be considered reliable.

Reliability of study	Not reliable
Relevance of study	Relevant
Klimisch Code	3

Reference	67
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Information on the test species	
Test species used	<i>Brachionus plicatilis</i> <i>Artemia franciscana</i>
Source of the test organisms	Cysts purchased
Holding conditions prior to test	Synthetic seawater 24 hours
Life stage of the test species used	Cysts and larvae

Information on the test design	
Methodology used	Followed standardised procedures for test species
Form of the test substance	Not stated. Cypermethrin
Source of the test substance	Supelco Inc. (USA)
Type and source of the exposure medium	Artificial seawater
Test concentrations used	6–8 concentrations plus controls
Number of replicates per concentration	Four
Number of organisms per replicate	10
Nature of test system (static, semi-static or flow-through, duration, feeding)	Static
Measurement of exposure concentrations	No
Measurement of water quality parameters	Yes
Test validity criteria satisfied	Yes
Water quality criteria satisfied	Yes
Study conducted to GLP	Not stated
Comments	Well-documented study, but no chemical analysis.

Reliability of study	Not reliable
Relevance of study	Relevant
Klimisch Code	3

Reference	68
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Information on the test species	
Test species used	<i>Gammarus pulex</i> <i>Cloeon dipterum</i>
Source of the test organisms	Field collected
Holding conditions prior to test	Held for 48 hours without food
Life stage of the test species used	<i>Gammarus pulex</i> : 3–8 mm long <i>Cloeon dipterum</i> : larvae

Information on the test design	
Methodology used	96-hour survival and motility tests
Form of the test substance	Technical cypermethrin (85%)
Source of the test substance	Not stated
Type and source of the exposure medium	Filtered and dechlorinated tap water
Test concentrations used	Not stated
Number of replicates per concentration	Not stated
Number of organisms per replicate	A total of 10 individuals per species were tested at each concentration
Nature of test system (static, semi-static or flow-through, duration, feeding)	Flow-through
Measurement of exposure concentrations	Yes
Measurement of water quality parameters	Yes
Test validity criteria satisfied	Not stated
Water quality criteria satisfied	Yes
Study conducted to GLP	Not stated
Comments	This was a well-performed study with chemical analysis.

Reliability of study	Reliable
Relevance of study	Relevant
Klimisch Code	1

Reference	70
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Information on the test species	
Test species used	<i>Scardinius erythrophthalmus</i> L.
Source of the test organisms	Commercial hatchery
Holding conditions prior to test	Held in laboratory for at least 10 days
Life stage of the test species used	Not stated

Information on the test design	
Methodology used	96-hour survival test
Form of the test substance	Technical cypermethrin (95%)
Source of the test substance	Not stated
Type and source of the exposure medium	Filtered, dechlorinated tap water
Test concentrations used	Five; 90.33–0.56 µg l ⁻¹
Number of replicates per concentration	1
Number of organisms per replicate	5
Nature of test system (static, semi-static or flow-through, duration, feeding)	Flow-through
Measurement of exposure concentrations	Yes
Measurement of water quality parameters	Yes
Test validity criteria satisfied	Not stated
Water quality criteria satisfied	Yes
Study conducted to GLP	Not stated
Comments	A well-performed study with chemical analysis.

Reliability of study	Reliable
Relevance of study	Relevant
Klimisch Code	1

Reference	80
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Information on the test species	
Test species used	<i>Acartia clausi</i> <i>Pseudocalanus elongatus</i> <i>Temora longicornis</i> <i>Oithona similis</i>
Source of the test organisms	Collected from sild
Holding conditions prior to test	Held in laboratory for a number of months in filtered seawater
Life stage of the test species used	Nauplii

Information on the test design	
Methodology used	48-hour survival test
Form of the test substance	Technical cypermethrin (95.8%)
Source of the test substance	Reidel-de Haen Germany
Type and source of the exposure medium	Filtered, seawater
Test concentrations used	0.15–5 µg l ⁻¹
Number of replicates per concentration	3
Number of organisms per replicate	10
Nature of test system (static, semi-static or flow-through, duration, feeding)	Semi-static
Measurement of exposure concentrations	Additional vessels were set up for chemical analysis, but the exposure water was not tested.
Measurement of water quality parameters	Yes
Test validity criteria satisfied	Not stated
Water quality criteria satisfied	Yes
Study conducted to GLP	Not stated
Comments	This was a well-performed study with chemical analysis, but of separate vessels and not the exposure water.

Reliability of study	Reliable
Relevance of study	Relevant
Klimisch Code	2

ANNEX 2 Cypermethrin analysis section of existing EQS report

This annex reproduces Section 3.2.1 and Table 3.1 of R&D Technical Report P2-115/TR prepared for the Environment Agency by WRC-NSF Ltd [9]. Readers should refer to this report for details of the references cited.

A SCA "Blue Book" method for the analysis of cypermethrin and other synthetic pyrethroids exists [36] which utilizes solvent extraction, a clean up stage (3 alternatives are given) and GC-ECD for analysis with confirmation using negative ion chemical ionisation gas chromatography/mass spectrometry. The limit of detection is stated to be 10 ng l⁻¹.

The extraction method developed by Supelco (1996) can also be used for extraction of cypermethrin. Recoveries from a 0.5 ng l⁻¹ solution were found to be 100 +/- (5)% using ENVI-Carb cartridges and 83 +/- (7)% using charcoal/celite extraction cartridges.

Cypermethrin has also been determined by Legrand et al. (1991) using a multi-residue method. Samples of water (1 litre) were sequentially extracted by liquid-liquid extraction with dichloromethane. The resulting extracts were pooled and dried using sodium sulphate. The dried extracts were evaporated to 200 µl. Analysis of the extract was carried out using GCMS. The MS was operated in the electron impact mode at 70eV using selected ion monitoring. Using this approach, recoveries from samples spiked with cypermethrin at 50 ng l⁻¹ and 200 ng l⁻¹ were found to be 78 +/- (3)% and 80 +/- (7)%, respectively.

Hadfield et al. (1992) have described an analytical method for the pyrethroid insecticides cyhalothrin and cypermethrin in natural waters. The extraction technique involved solid phase extraction using columns containing a layer of Sepralyte bonded-phase strong anion exchange packing on a layer of Sepralyte bonded-phase octyl material. Prior to use the cartridges were conditioned with 25 ml methanol. Water samples were then passed through the cartridges at a rate of 50 ml/min. Cartridges were initially eluted with acetonitrile (3 x 5 ml), then treated with Clark and Lubs buffer followed by further elution using 5 ml diethyl ether/n-hexane (70:30) followed by acetonitrile. The resulting eluates were combined and cleaned up on a C8 column and a silica cartridge prior to analysis by GC-ECD. The mean recovery of cypermethrin from a samples spiked at 25 ng l⁻¹ was 90 +/- (7)% and analyse of pond water demonstrated the limit of detection for the technique to be 2 ng l⁻¹.

Other methods have been reported in the scientific literature, these are summarised in Table A2.

As part of an EA funded projects attempts were made by WRC-NSF to develop an analytical method for cypermethrin (in environmental waters) which had a limit of detection (LOD) below the minimum reporting value (MRV) (a concentration at which the confidence in the data is high – normally the limit of detection is lower than the MRV) of 0.01 ng l⁻¹.

However, cypermethrin was included in a group of seven pesticides for which a single method was developed, where the LOD achieved was just over 2 ng l⁻¹. Attempts to reduce the LOD possible for cypermethrin were not successful.

WRC-NSF is currently developing new methodology for the Environment Agency for cypermethrin and cyfluthrin. It is expected that a limit of detection of 0.1 ng l⁻¹ will be achieved for cypermethrin.

Table A2 Other Analytical Methods

Compounds Determined	Flumethrin, cypermethrin, deltamethrin, cyhalothrin	36 pesticides including cypermethrin	Cypermethrin and Lambda-cyhalothrin	Alpha-cypermethrin, chlorpropham, propham, atrazine, diflubenzuron and tetramethrin
Matrices	Milk and blood of lactating dairy cows	Groundwater	Pond water	Soils
Concentration Range		Low $\mu\text{g l}^{-1}$ levels	Up to at least $15 \mu\text{g l}^{-1}$	$1.2\text{--}30 \mu\text{g g}^{-1}$
Sample Size		500 ml	Up to 350 ml	10 g
Extraction	Acetonitrile, n-hexane partitioning	Liquid extraction using dichloromethane after addition of NaCl	Solid phase extraction using SAX/C8 cartridges	Sonicate twice with acetone, filter through a Whatman 40 filter and rotary evaporate to dryness, reconstitute in acetone
Clean-up	Silica gel column clean-up with n-hexane and diethyl ether			
Analysis	High performance liquid chromatography with ultra-violet detection (HPLC-UV)	GC-ECD	GC-ECD	Reverse phase thin layer chromatography
Limit of Detection	0.001 mg kg^{-1}	$0.5 \mu\text{g l}^{-1}$	2 ng l^{-1}	$0.5 \mu\text{g g}^{-1}$
Accuracy	Recovery averaged 78 to 91%	Mean recovery = 122% (n = 3)	Mean recovery at 10 ng l^{-1} = 100% (n = 47)	Mean recovery = 100.6% (n = 5) Conc. not stated
Precision		RSD = 6% (n=3)	RSD at 10 ng l^{-1} = 6% (n = 47)	RSD = 5.4%
Reference	Zuccari Bissacot and Vassilieff 1997	Hernandez <i>et al.</i> 1993	Hadfield <i>et al.</i> 1992	Babic <i>et al.</i> 1998

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