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Environmental risk limits for antifouling substances

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Abstract

In 1989, the EU restricted the use of tributyl-tin (TBT) and the International Maritime Organisation (IMO) decided for a world-wide ban on TBT in 2003. As a replacement for TBT, new antifouling agents are entering the market. Environmental risk limits (ERLs) are derived for substances that are used as TBT-substitutes, i.e. the compounds Irgarol 1051, dichlofluanid, ziram, chlorothalonil and TCMTB. ERLs represent the potential risk of the substances to the ecosystem and are derived using data on (eco)toxicology and environmental chemistry. Only toxicity studies with endpoints related to population dynamics are taken into account.

For Irgarol 1051 especially plants appear to be sensitive; the mode of action is inhibition of photosynthetic electron transport. Despite the higher sensitivity of the plants, the calculated ERL for water based on plants only is higher than the ERL based on all data due to the lower variability in the plant only dataset. Because there is a mechanistic basis to state that plants are the most sensitive species, we propose to base the ERL for water on the plants only dataset. As dichlofluanid is highly unstable in the water phase, it is recommended to base the ERL on the metabolites formed and not on the parent compound.

No toxicity data of the studied compounds for organisms living in sediments were found, the ERLs for sediment are derived with help of the equilibrium partitioning method. For dichlofluanid and chlorothalonil the ERL for soil is directly based on terrestrial data, for Irgarol 1051 and ziram the ERL for soil is derived using equilibrium partitioning.

Except for Irgarol 1051, no information was encountered in the open literature on the environmental occurrence in The Netherlands of the chemicals studied. The measured concentrations for Irgarol 1051 are close to the derived ERL. For this compound it is concluded that the species composition and thereby ecosystem functioning cannot be considered as protected.
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Keywords: Irgarol 1051; Dichlofluanid; Ziram; Chlorothalonil; TCMTB

1. Introduction

Environmental quality standards in Dutch environmental policy are based on environmental risk limits (ERLs) for the compartments air, water, sediment and soil. ERLs are derived using data on (eco)toxicology and environmental chemistry, and represent the potential risk of the substances to the ecosystem. ERLs that are derived in The Netherlands until 1997 are summarised by De Bruijn et al. (1999). Reuther et al. (1998) derived ERLs for aniline derivatives. Risk limits for boron, silver, titanium, tellurium, uranium and

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an organosilicon compound are derived in Van de Plassche et al. (1999), and ERLs were derived for PCBs and phthalates (Van Wezel et al., 2000a,b), and for rare earth elements (Sneller et al., 2000). Here, ERLs for the compartments water, sediment and soil are presented for five compounds that are used as antifouling substances.

Biofouling, the settlement and growth of micro- and macro-organisms on surfaces, can be prevented by the use of antifouling substances, by cleaning or by nutrient limitation (Flemming et al., 1996). On ships tributyl-tin (TBT) has been used as major antifouling substance in the past. Many adverse ecotoxicological effects caused by TBT are reported in laboratory and field studies in marina's and the open sea (Crommentuijn et al., 2000a; Ten Hallers-Tjabbes et al., 1994) and butyltin contamination is widespread (Tanabe et al., 1998). The ecotoxicological problems associated with the use of TBT have been recognised. In 1989, the European Community introduced a directive to restrict the use of TBT-based antifouling paints on boats under 25 m. The International Maritime Organisation (IMO) has decided for a complete world-wide ban on TBT for all boats in 2003. As a replacement for TBT, new antifouling agents are coming up the market (e.g. Voulvoulis et al., 1999a,b). Examples of these substances can be found in Table 1. The substances are partly well known chemicals for which ERLs were derived earlier. However, also relatively unknown chemicals that have not been the subject of many ecotoxicological studies are used to replace TBT.

In the present work, ERLs are derived for Irgarol 1051, dichlofluanid, ziram, chlorothalonil and TCMTB. For SeaNine 211 and TCMS pyridine, information appeared to be insufficient to derive an ERL. The selected compounds are authorised in The Netherlands by the Board for the Authorization of Pesticides as an antifouling substance (Irgarol 1051, dichlofluanid, and ziram), or often mentioned in the literature as an alternative to TBT (chlorothalonil, SeaNine). General information on the evaluated antifouling substances can be found in Table 2 .

2. Methods

2.1. General scheme

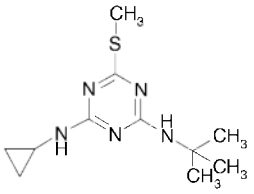
The ERLs are derived as described in Traas (2001). In short, data on chronic and acute toxicity for aquatic and terrestrial species and terrestrial processes are searched for the compound of interest. The data are evaluated, and selected or rejected. For compounds with a log K_{ow} (*n*-octanol/water partition coefficient) higher than 5.0, or for compounds for which there is an expectation for secondary poisoning, in addition toxicity data for mammals and birds are searched for. The ERL is derived using either the refined assessment method as described by Aldenberg and Jaworska (2000), or using assessment factors as laid down in the Technical Guidance Document (ECB, 1996, developed for EU council regulation 793/93). The ERLs are harmonised according to the equilibrium partition

Table 1
Substances used to replace TBT in antifouling paints

Chemical name	ERL derived	Chemical name	ERL derived
2,3,5,6-Tetrachloro-4-(methyl sulphonyl) pyridine	N	Zineb	Y
2-Methylthio-4-tertiary-butylamino-6-cyclopropylamino-*s*-triazine	N	*cis*-1-(3-Chloroallyl)-3,5,7-triaza-1-azonia adamantane chloride	N
Cuprous thiocyanate	Y (Cu)	Dichlofluanid	N
2,4,5,6-Tetrachloro-*iso*-phthalo-nitrile	N	2-(Thiocyanomethyl thio)benzthiazole	N
4,5-Dichloro-2-*n*-octyl-4-isothiazolin-3-one	N	Deltamethrin	Y
Dichlorophenyl dimethylurea	Y	Farnesol	N
Folpet	N	Thiram	Y
Zinc pyrithione	N	Oxy-tetracycline-hydrochloride	N
4-Chloro-meta-cresol	N	Ziram	N
Arsenic trioxide	N	Bitumen	N
Maneb	Y		

Table 2
General information and physical–chemical properties of the studied compounds

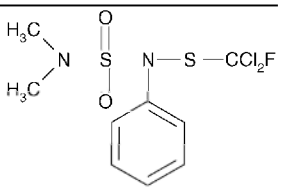
Irgarol 1051



2-Methylthio-4-tertiary-butylamino-6-cyclopropylamino-*s*-triazine
CAS no. 28159-98-0

Property	Value	Reference
Water solubility (mg/l)	6	Jongbloed and Luttik, 1996
	7	Jongbloed and Luttik, 1996
log K_{ow}	4.1	SRC, 1997
log K_{oc} (l/kg)	2.38	Rogers et al., 1996
	3.0	Tolosa et al., 1996
Henry's constant (Pa m^3 mol^{-1})	2×10^{-6}	Jongbloed and Luttik, 1996
	5.4×10^{-4}	Rogers et al., 1996
Vapour pressure (Pa)	8.8×10^{-5}	Jongbloed and Luttik, 1996
	1.5×10^{-5}	Rogers et al., 1996

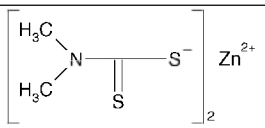
Dichlofluanid



N′-Dimethyl-*N*-phenylsulfamide
CAS no. 1085-98-9

Property	Value	Reference
Water solubility (mg/l)	1.3	Tomlin, 1997
log K_{ow}	3.7	Tomlin, 1997
log K_{oc}		Tomlin, 1997
Henry's constant (Pa m^3 mol^{-1})	<1.9	Tomlin, 1997
Vapour pressure (Pa)	$<15 \times 10^{-6}$	Tomlin, 1997

Ziram

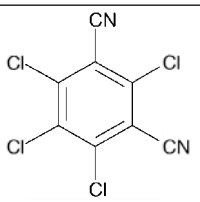


Zinc dimethyldithiocarbamate
CAS no. 137-30-4

Property	Value	Reference
Water solubility (mg/l)	1.58–18.3	Tomlin, 1997
log K_{ow}	1.23	Tomlin, 1997
log K_{oc}	0.8–1.3	Ordelman et al., 1993
Henry's constant (Pa m^3 mol^{-1})	<1.9	Tomlin, 1997
Vapour pressure (Pa)	$<1 \times 10^{-6}$	Tomlin, 1997

Table 2 (*Continued*)

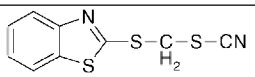
Chlorothalonil



2,4,5,6-Tetrachloro-isophtalonitrile
CAS no. 1897-45-6

Property	Value	Reference
Water solubility (mg/l)	0.9	Caux et al., 1996
log K_{ow}	2.6–4.4	Caux et al., 1996
log K_{oc} (l/kg)	2.9–3.8	Caux et al., 1996
Henry's constant (Pa m^3 mol^{-1})	1.7×10^{-2}	Caux et al., 1996
Vapour pressure (Pa, 25 °C)	4.3×10^{-12}	Caux et al., 1996

TCMTB



(2-Thiocyanomethylthio)benzothiazole
CAS no. 21564-17-0

Property	Value	Reference
Water solubility (mg/l)	20	Van der Pol and Van der Linde, 1999
	45	Van der Pol and Van der Linde, 1999
	40	Brownlee et al., 1992
log K_{ow}	3.1	Brownlee et al., 1992
log K_{oc} (l/kg)	2.74	Predicted acc. to Karickhoff (1981); in an experimental set-up TCMTB was hydrolysed and methylated so an K_{oc} could not be measured (Brownlee et al., 1992)
Henry's constant (Pa m^3 mol^{-1})	1.2	Van der Pol and Van der Linde, 1999
Vapour pressure (Pa)	607	Van der Pol and Van der Linde, 1999
	193	Van der Pol and Van der Linde, 1999

method. For further discussions on the methods and the implications of ERLs we refer to Sijm et al. (2001) and Posthuma et al. (2002).

2.2. Data collection

An on-line literature search was performed for the period 1983–summer 1999. The TOXLINE and BIOSYS databases were used. In addition to the open literature advisory reports were used as source of information. These reports are prepared at RIVM for the authorisation of pesticides, under account of the Dutch Board for the Authorisation of Pesticides.

2.3. Data selection

A toxicity study is considered reliable if the design of the experiment is in agreement with international accepted guidelines, e.g. OECD guidelines. To judge studies that have not been performed according to these guidelines, criteria have been developed at our institute. Only effects on growth, reproduction or survival are used in the derivation of ERLs, as they can directly be related to population dynamics. So toxicity studies with endpoints related to, e.g. biochemistry or animal behaviour are not taken into account. The NOEC/EC10, LC50 or EC50 was

recalculated when the method of derivation was not clearly stated in the original work. A logistic equation was fitted through effect data versus the logarithms of concentrations (using Graphpad Prism, 1996). Toxicity data from sediment or soil studies are normalised to 10% organic matter. A conversion factor from organic carbon to organic matter was assumed of 1.724.

Per compound, the most sensitive toxicity test is selected for each species. If for a single species several toxicity values are found for the same effect parameter, the geometric mean of these data is used.

2.4. Extrapolation to environmental risk limits

For the derivation of ERLs salt and freshwater data are combined if a two-tailed *t*-test with Welch correction (GraphPad Prism) shows there are no statistical reasons to keep the data separated.

2.4.1. Preliminary effect assessment

If chronic or acute toxicity data are available for less than four taxonomic groups, assessment factors are used. The assessment factors used are laid down in the Technical Guidance Document (ECB, 1996), which is developed within the framework of EU council regulation 793/93. In case there is no complete base-set (acute toxicity to algae, daphnia and fish), the modified EPA method is used (Kalf et al., 1999).

2.4.2. Refined effect assessment

The aim of ERLs is to protect all species in the ecosystem. For statistical considerations the ERL is set equal to the concentration at which 95% of the species is protected, the HC5, assuming thereby to protect the whole ecosystem (VROM, 1989; Van Leeuwen et al., 1992). A detailed description of the statistical background of the refined effect assessment method is given in the literature (Aldenberg and Jaworska, 2000). It is assumed that sensitivities of species in an ecosystem can be described by a log-normal frequency distribution. Using the Kolgomorov–Smirnov $D^*\mathrm{sqrt}(n)$ test this assumption is tested. The mean, standard deviation, and the number of underlying data define the frequency distribution. Extrapolation factors as derived by Aldenberg and Jaworska (2000) are used to estimate the HC5, and its 5–95% confidence interval.

2.4.3. Biomagnification

For compounds that accumulated in the food chain, ERLs are derived that take into account this extra risk (Van de Plassche, 1994; Van Wezel et al., 2000a). The compounds studied in the present work do not appear to be very hydrophobic (see K_{ow} or K_{oc} (organic carbon/water partititon coefficient), Table 2) and are therefore not expected to biomagnify in the food chain.

2.5. Equilibrium partitioning and harmonisation between the compartments

According to (DiToro et al., 1991) the partition coefficient between organic carbon in soil/sediment and water (K_{oc}) is used to derive an ERL for soil/sediment when no data on terrestrial or sediment-dwelling organisms are available. In addition, the K_{oc} is used to harmonise the ERLs between the different compartments.

3. Results

3.1. Toxicity data and derivation of ERLs for water

Aquatic toxicity data for Irgarol 1051, dichlofluanid, ziram, chlorothalonil and TCMTB are presented in Table 3a–e . Rejected tests are not listed. For more detailed information on the toxicity data it is referred to the underlying report (Van Wezel and Van Vlaardingen, 2001). For an overview of the derived ERLs for water (ERL_{water}) see Table 4.

3.1.1. Irgarol 1051

Acute toxicity data are found for algae, macrophytes, crustaceans, and fish (Table 3a). Especially algae and macrophytes appear to be sensitive taxonomic groups. The sensitivity of freshwater and marine organisms to acute exposure can be compared for the crustaceans and fish. The marine crustacean is 100 times more sensitive than the freshwater crustacean. The sensitivity of the two marine fish falls well within the range of sensitivities encountered for the freshwater species. Chronic toxicity was tested for algae, macrophytes, crustaceans, and fish (Table 3a). Again, algae and macrophytes are more sensitive than crustaceans and fish. For algae both saltwater species ($n = 2$) and freshwater species ($n = 4$) are tested; the

Table 3
Aquatic toxicity data

Organism	Experimental time[a]	Criterion	End-point[b]	Result (μg/l)	Reference
(a) **Irgarol 1051**					
Acute toxicity to freshwater organisms					
Algae					
Selenastrum capricornutum	72 h	EC50	g	4.2[c]	Jongbloed and Luttik, 1996
Crustacea					
Daphnia magna	24 h	EC50	i	49000	Jongbloed and Luttik, 1996
Pisces					
Brachydanio rerio	96 h	LC50	s	4000	Jongbloed and Luttik, 1996
Lepomis macrochirus	96 h	LC50	s	2900	Jongbloed and Luttik, 1996
Leuciscus idus	48 h	LC50	s	6200	Jongbloed and Luttik, 1996
Oncorhynchus mykiss	96 h	LC50	s	940	Jongbloed and Luttik, 1996
Oncorhynchus mykiss	96 h	LC50	s	860	Jongbloed and Luttik, 1996
Acute toxicity to saltwater organisms					
Macrophyta					
Enteromorpha intestinalis	144 h	NOEC	g	0.022[c]	Scarlett et al., 1997
Enteromorpha intestinalis	72 h	EC50	f	2.5	Scarlett et al., 1997
Zostera marina	10 d	LOEC	g	10	Scarlett et al., 1997
Crustacea					
Mysidopsis bahia	96 h	LC50	s	430	Jongbloed and Luttik, 1996
Pisces					
Cyprinodon variegatus	96 h	LC50	s	3400	Jongbloed and Luttik, 1996
Menidia beryllina	96 h	LC50	s	1770	Jongbloed and Luttik, 1996
Chronic toxicity to freshwater organisms					
Algae					
Anabaena flos-aquae	120 h	NOEC	g	0.54	Jongbloed and Luttik, 1996
Navicula pelliculosa	120 h	EC10	g	0.017[c]	Jongbloed and Luttik, 1996
Scenedesmus subspicatus	72 h	NOEC	g	0.23	Jongbloed and Luttik, 1996
Selenastrum capricornutum	120 h	NOEC	g	0.65	Jongbloed and Luttik, 1996
Macrophyta					
Lemna gibba	14 d	NOEC	g	0.4	Jongbloed and Luttik, 1996
Pisces					
Oncorhynchus mykiss	98 d	LOEC	g	<29	Jongbloed and Luttik, 1996
Chronic toxicity to saltwater organisms					
Algae					
Skeletonema costatum	120 h	NOEC	g	0.14	Jongbloed and Luttik, 1996
Periphiton community	21 d	LOEC	g	1	Dahl and Blanck, 1996
Crustacea					
Mysidopsis bahia	28 d	NOEC	g	110	Jongbloed and Luttik, 1996
Organism	Experimental time[a]	Criterion	End-point[b]	Result (mg/l)	Reference
(b) **Dichlofluanid**					
Acute toxicity to freshwater organisms					
Crustacea					
Daphnia magna	48 h	LC50	s	>1.8	Heimbach, 1983
Daphnia magna	48 h	LC50	s	0.37	Frazier et al., 1986

Table 3 (*Continued*)

Organism	Experimental time[a]	Criterion	End-point[b]	Result (mg/l)	Reference
Pisces					
Lepomis macrochirus	96 h	LC50	s	0.025	Swigert et al., 1986a
Leuciscus idus melanotus	96 h	LC50	s	0.12[d]	Anonymus, 1980
Leuciscus idus melanotus	96 h	LC50	s	0.12[d]	Jansma and Linders, 1992
Oncorhynchus mykiss	96 h	LC50	s	0.05[d]	Anonymus, 1979
Oncorhynchus mykiss	96 h	LC50	s	0.011	Swigert et al., 1986b
Chronic toxicity to freshwater organisms					
Crustacea					
Daphnia magna	24 d	NOEC	r	0.04[d]	Jansma and Linders, 1992
Pisces					
Oncorhynchus mykiss	21 d	LC50	s	0.016	Grau, 1989
(c) **Ziram**					
Acute toxicity of ziram to freshwater organisms					
Algae					
Chlorella pyrenoidosa	96 h	EC50	g	1.2	Van Leeuwen et al., 1985a
Selenastrum capricornutum	96 h	EC50	g	0.066	European Commision, concept
Crustacea					
Daphnia magna	48 h	EC50		0.048	Van Leeuwen et al., 1985b
Insecta					
Culex fatigans	24 h	LC50	s	0.18	Strufe, 1968
Culex fatigans	24 h	LC50	s	0.55	Strufe, 1968
Culex fatigans	24 h	LC50	s	1.31	Strufe, 1968
Culex fatigans	24 h	LC50	s	8.1	Strufe, 1968
Mollusca					
Dreissena polymorpha	5 d	LC50	s	1.8	Hoestlandt, 1972
Pisces					
Carassius auratus	96 h	LC50	s	2.3	Tibosch et al., 1993
Carassius auratus	48 h	LC50	s	0.095	Nischiuchi, 1974
Cyprinus carpio	48 h	LC50	s	0.075	Nischiuchi, 1974
Lepomis macrochirus	96 h	LC50	s	0.0097	European Commision, concept
Misgurnus anguillacaudatus	48 h	LC50	s	0.15	Nischiuchi, 1974
Oryzias latipes	48 h	LC50	s	0.056	Nischiuchi, 1974
Poecilia reticulata	96 h	LC50	s	0.75	Van Leeuwen et al., 1985a
Oncorhynchus mykiss	96 h	LC50	s	0.3	Tibosch et al., 1993
Oncorhynchus mykiss	96 h	LC50	s	1.78	European Commision, concept
Acute toxicity to saltwater organisms					
Bacteria					
Vibrio fisheri	15 min	EC50		0.15	Van Leeuwen et al., 1985a
Chronic to freshwater organisms					
Crustacea					
Daphnia magna	21 d	LC50	s	0.011	Van Leeuwen et al., 1985b
Daphnia magna	21 d	NOEC	s	0.0033[e]	Van Leeuwen et al., 1985b
Pisces					
Oncorhynchus mykiss	60 d	LC50	s	0.002	Van Leeuwen et al., 1985c
Oncorhynchus mykiss	60 d	NOEC	s	0.0006[e]	Van Leeuwen et al., 1985c
(d) **Chlorothalonil**					
Acute toxicity to freshwater organisms					
Crustacea					
Astacopsis gouldi	96 h	LC50	s	0.012	Davies et al., 1994
Daphnia magna	48 h	EC50	i	0.054	Montforts, 1999

Table 3 (*Continued*)

Organism	Experimental time[a]	Criterion	End-point[b]	Result (mg/l)	Reference
Daphnia magna	48 h	EC50	i	0.117	Montforts, 1999
Daphnia magna	48 h	EC50	i	0.115	Montforts, 1999
Daphnia magna	24 h	LC50	s	0.195	Montforts, 1999
Parataya australiensis	96 h	LC50	s	0.016	Davies et al., 1994
Pisces					
Cyprinus carpio	96 h	LC50	s	0.06	Montforts, 1999
Galaxias auratus	96 h	LC50	s	0.029	Davies and White, 1985
Galaxias maculatus	96 h	LC50	s	0.016	Davies and White, 1985
Galaxias truttaceus	96 h	LC50	s	0.019	Davies and White, 1985
Ictalurus punctatus	96 h	LC50	s	0.047	Montforts, 1999
Ictalurus punctatus	96 h	LC50	s	0.052	Gallagher et al., 1992
Lepomis macrochirus	96 h	LC50	s	0.059	Montforts, 1999
Oncorhynchus mykiss	96 h	LC50	s	0.017	Montforts, 1999
Oncorhynchus mykiss	96 h	LC50	s	0.076	Ernst et al., 1991
Oncorhynchus mykiss	96 h	LC50	s	0.043	Montforts, 1999
Acute toxicity to saltwater organisms					
Crustacea					
Penaeus duorarum	96 h	LC50	s	0.162	Montforts, 1999
Penaeus duorarum	48 h	EC50		0.320	Mayer, 1987
Mollusca					
Crassostrea virginica	96 h	EC50	g	0.005	Montforts, 1999
Crassostrea virginica	96 h	EC50		0.026	Mayer, 1987
Pisces					
Cyprinodon variegatus	96 h	LC50	s	0.033	Montforts, 1999
Leiostomus xanthurus	48 h	LC50	s	0.032	Mayer, 1987
Chronic toxicity to freshwater organisms					
Algae/Chlorophyta					
Pseudokirchneriella subsp.	96 h	NOEC	g	0.05	Montforts, 1999
Scenedesmus subspicatus	96 h	NOEC	g	0.06	Montforts, 1999
Anabaena flos-aquae	120 h	NOEC	g	0.02	Montforts, 2001
Navicula pelliculosa	120 h	NOEC	g	0.0035	Montforts, 2001
Plants					
Lemna gibba	72 d	NOEC	g	0.29	Montforts, 2001
Crustacea					
Daphnia magna	21 d	NOEC	r	0.035	Montforts, 1999
Daphnia magna	21 d	NOEC	s	0.0006	Montforts, 1999
Daphnia magna	21 d	NOEC	r	0.019	Montforts, 1999
Daphnia magna	21 + 21 d	NOEC	r	0.035	Montforts, 1999
Insecta					
Chironomus riparius	28 d	NOEC	r	0.125	Montforts, 1999
Pisces					
Pimephales promelas	45 w	NOEC	r	0.003	Montforts, 1999
Oncorhynchus mykiss	21 d	NOEC	g	0.0069	Montforts, 1999

Organism	Experimental time[a]	Criterion	End-point[b]	Result (μg/l)	Reference
(e) **TCMTB**					
Chronic toxicity to freshwater organisms					
Crustacea					
Daphnia magna	21 d	NOEC	s	3.8	Van der Pol and Van der Linde, 1999

Table 3 (*Continued*)

Organism	Experimental time[a]	Criterion	End-point[b]	Result (μg/l)	Reference
Acute toxicity to freshwater organisms					
Crustacea					
Daphnia magna	48 h	EC50	s	24	Van der Pol and Van der Linde, 1999
Pisces					
Oncorhynchus mykiss	96 h	LC50	s	21	Van der Pol and Van der Linde, 1999

[a] min: minute, h: hour, d: day, w: week.
[b] g: growth, s: survival, r: reproduction, i: inhibition, f: fotosynthesis.
[c] Effect concentration recalculated.
[d] Result based on nominal values: the parent compound was below detection limit after 48 h.
[e] The NOEC is calculated by LOEC/3.

sensitivities of saltwater and freshwater species are not statistically different.

Chronic toxicity tests are available for species of four different taxonomic groups, so the refined assessment (Aldenberg and Jaworska, 2000) can be applied. The log-normal fit to the most sensitive chronic data per species was statistically accepted according to the Kolgomorov–Smirnov test. The ERL_{water} is 9.0 ng/l (0.26–61 ng/l), which is a factor of two below the lowest chronic toxicity value of 17 ng/l for the algae *Navicula pelliculosa*.

According to the mechanism of action of Irgarol 1051, i.e. inhibition of photosynthetic electron transport (Holt, 1993), plants can be considered the most sensitive species. This is confirmed by the available data. A one-tailed *t*-test (with GraphPad Prism) shows that the data for plants differ significantly ($P = 0.0007$) from the remaining toxicity data. A log-normal fit to only the plant data (algae and macrophytes) is statistically accepted. The variability in the plants-only dataset is smaller than in the dataset for all species. Despite the higher sensitivity of the plants, the calculated ERL_{water} based on the plants only dataset is higher than the ERL_{water} calculated over all data: 24 ng/l (2.5–73 ng/l). This is due to the lower variability and lower resulting standard deviation in the plants-only dataset (Fig. 1). As there is a mechanistic basis to state that plants are the most sensitive species, it is proposed to base the ERL_{water} on the plants only dataset.

Hall et al. (1999) also fitted species sensitivity distributions to—mainly unpublished—data. They used the statistical methods as described by Solomon et al. (1996). The data used were slightly different from the ones used in the current study. The 5th percentile of the most sensitive group, i.e. aquatic plants, was 80 ng/l, which is a factor 3–4 above the ERL derived in the current study.

3.1.2. Dichlofluanid

Aquatic toxicity tests with dichlofluanid can be found in Table 3b. Only freshwater species

Table 4
ERL_{water} (dissolved), $ERL_{sediment}$ and ERL_{soil}

Compound	Method used	ERL_{water} (ng/l)	Method used	$ERL_{sediment}$ (μg/kg)	Method used	ERL_{soil} (μg/kg)	K_p[a] (l/kg)
Irgarol 1051	A&J[b]	24 (2.7–73)	EP	1.4	EP	1.4	58
Dichlofluanid[c]	–	–	–	–	NOEC/50	190	–
Ziram	LC50/1000	9.7	EP	0.011	EP	0.011	1.16
Chlorothalonil	A&J	530 (38–2300)	EP	50.6	NOEC/50	10	92
TCMTB	NOEC/10	380	–	–	–	–	–

[a] Calculated from K_{oc}, assuming standard sediment with 10% organic matter.
[b] According to Aldenberg and Jaworska (2000).
[c] Highly unstable compound, no ERL derived.

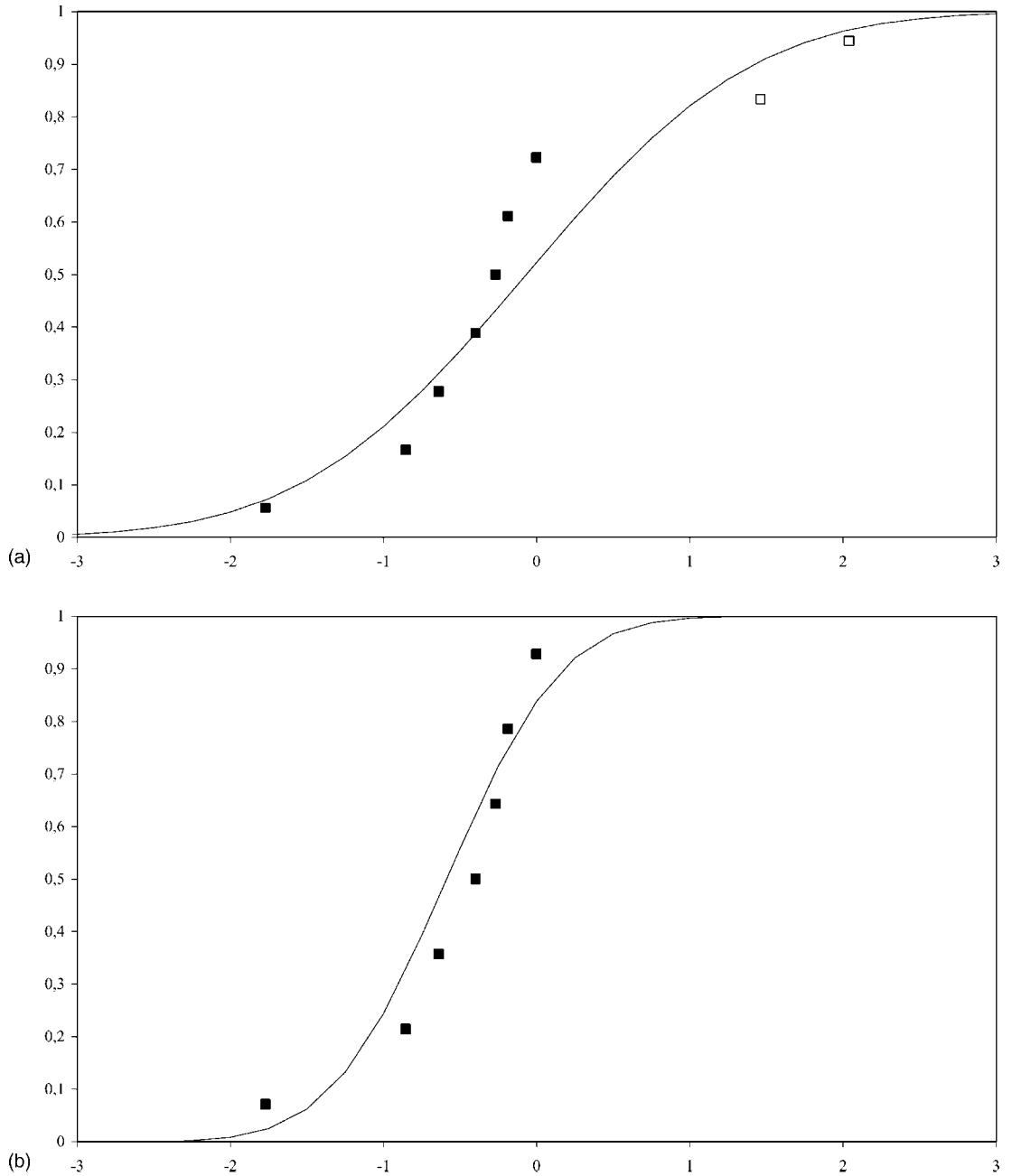


Fig. 1. Frequency distributions of the toxicity data for Irgarol 1051 for all species (a) or for plants only (b). Filled symbols are plant data.

are tested, acute and chronic data are available for two taxonomic groups: crustaceans and fish. However, the substance is highly unstable in the water phase. The parent compound is below detection limit at the end of all toxicity tests. Therefore, it is recommended to base the ERL on the metabolites formed and not on the parent compound.

3.1.3. Ziram

Aquatic toxicity data on ziram can be found in Table 3c. Acute data are found for freshwater and marine species. A comparison of sensitivities cannot be made, as for salt water the only species tested is a bacterium and no freshwater bacterium is tested. Acute aquatic toxicity data are available for six taxonomic groups (bacteria, algae, crustacea, insects, mollusca and pisces). No clear differences in sensitivity between the different taxonomic groups are observed. Chronic toxicity data are found for fresh water species of two taxonomic groups (crustacea and pisces). The lowest acute L(E)C50 is 9.7 μg/l for the fish *Lepomis macrochirus*. An assessment factor of 1000 is applied which gives an ERL_{water} of 9.7 ng/l. The lowest chronic toxicity value encountered is 0.6 μg/l for an early life stage test *Oncorhynchus mykiss* (Table 3c). Since the taxonomic group showing the lowest acute effect (i.e. pisces), is represented in the chronic toxicity data set by a NOEC value, an assessment factor of 50 is applied to the lowest NOEC value. This results in an ERL_{water} of $0.6/50 = 0.012$ μg/l or 12 ng/l. The ERL based on extrapolation of acute data is (only slightly) lower than the ERL based on extrapolation of chronic data, therefore the former is selected.

3.1.4. Chlorothalonil

Chlorothalonil is due to its multiple electrophilic centres reactive towards GSH, and can be detoxified thereby (Gallagher and Di Giulio, 1992; Gallagher et al., 1992). Aquatic toxicity data of chlorothalonil are listed in Table 3d. Acute toxicity tests are performed with crustaceans, molluscs and fish. Data for fresh and salt water do not differ statistically for crustaceans and fish. Chronic aquatic toxicity data are available for freshwater species only, for five different taxonomic groups (algae, plants, crustaceans, insects and fish). The data were found to be log-normal distributed (Kolgomorov–Smirnov test). Using the refined assessment method the ERL_{water} derived is 0.53 μg/l (0.038–2.3 μg/l).

3.1.5. TCMTB

Information on the aquatic toxicity of TCMTB can be found in Table 3e. The amount of data is limited, and restricted to freshwater organisms. Acute data are available for a crustacean and a fish, for *Daphnia magna* a chronic toxicity value is available. There is no complete base set, so an assessment factor of 10 is applied to the NOEC which yields an ERL_{water} of 0.38 μg/l.

3.2. Toxicity data, partition coefficients, and derivation of ERLs for sediment

No reliable sediment toxicity data are found for any of the studied compounds. Therefore, the ERLs for sediment are all derived with help of the equilibrium partitioning method. For an overview of the derived ERLs for sediment ($ERL_{sediment}$) see Table 4.

3.2.1. Partition coefficients used

For Irgarol 1051, a $\log K_{oc}$ of 3.0 (Tolosa et al., 1996) implies a K_p of 58 to 'standard sediment' with 10% organic matter.

Dichlofluanid is unstable in soil (Tomlin, 1997). It is first metabolised into dimethylsulfanilide and then further degraded. Therefore, the equilibrium partitioning theory cannot be applied to derive an $ERL_{sediment}$ for dichlofluanid.

For ziram a $\log K_{oc}$ of 1.3 was used, the higher value in the range 0.8–1.3 reported by Ordelman et al. (1993). This corresponds with a K_p of 1.16 l/kg for standard sediment.

Eleven experimental $\log K_{oc}$ values for chlorothalonil vary between 2.5 and 3.8, with a mean of 3.2 (Posthumus, 1999). Normalised to standard sediment with 10% organic matter, the K_p is 92 l/kg.

For TCMTB no information is available on sorption to organic carbon. A study of Brownlee et al. (1992) showed that in an experimental set-up the K_{oc} could not be measured due to hydrolysis and methylation of TCMTB into 2-(methylthio)benzothiazole (MTBT). Therefore, the equilibrium partitioning theory is not applicable for TCMTB.

3.3. Toxicity data and derivation of ERLs for soil

Terrestrial toxicity data for dichlofluanid, ziram, chlorothalonil and TCMTB are presented in Table 5a–c. Rejected tests are not listed. For more detailed information on the toxicity data it is referred to the underlying report (Van Wezel and Van Vlaardingen, 2001). For an overview of the derived ERLs for soil (ERL_{soil}) see Table 4.

Table 5
Terrestrial toxicity data

Organism/Process	Experimental time	Criterion	Result test soil (mg/kg d.w.)	Result standard soil (mg/kg d.w.)	Endpoint	Reference
(a) **Dichlofluanid**						
Chronic toxicity: microbial processes						
Nitrification	56 d	EC9	1.3	9.3	i	Jansma and Linders, 1992
Nitrification	56 d	EC21	13	92.9	i	Jansma and Linders, 1992
Nitrification	56 d	NOEC	≥1.3	≥3.0	i	Jansma and Linders, 1992
Nitrification	56 d	EC13	13	29.5	i	Jansma and Linders, 1992
Chronic toxicity: soil organisms						
Oligochaeta						
Eisenia fetida	28 d	LC50	>1000	–	s	Jansma and Linders, 1992
Eisenia fetida	14 d	LC50	>913	–	s	Jansma and Linders, 1992
Eisenia fetida	14 d	NOEC	288	–	s	Jansma and Linders, 1992
(b) **Ziram**						
Chronic toxicity: microbial processses						
sulfur oxidation	50 d	EC10	19	292	i	Ray, 1991
(c) **Chlorothalonil**						
Acute toxicity: microbial processes						
Nitrification	6 h	EC25	50	32	i	Hansson et al., 1991
	3 d	LOEC	1.8	1.7	i	Montforts, 1999
Respiration	18 h	EC47	100	165		Rashid and Mayaudon, 1974
Aerobic N-fixation	6 h	EC55	1.8	0.5	i	Montforts, 1999
Anaerobic N-fixation	6 h	NOEC	1.8	5	i	Montforts, 1999
Acute toxicity: enzyme activity						
Amylase	1 d	EC30	10	17		Tu, 1993
Dehydro-genase	4 d	NOEC	>10	> 50		Tu, 1993
Invertase	1 d	EC25	10	17		Tu, 1993
Phosphatase	2 h	NOEC	> 10	> 50		Tu, 1993
Urease	2 d	NOEC	> 10	> 50		Tu, 1993
Chronic toxicity: microbial processes						
Nitrification	2 w	EC44	10	17	i	Tu, 1993
	28 d	NOEC	4.4	15	i	Montforts, 1999
Sulfur oxidation	4 w	EC26	10	17	i	Tu, 1993
Respiration	28 d	NOEC	4.4	15	i	Montforts, 1999
Chronic toxicity to soil species						
Fungi						
Population growth	7 d	EC52	10	5	g	Tu, 1993
Bacteriophyta						
Population growth	7 d	EC29	10	17	g	Tu, 1993
Annelida						
Eisenia foetida	14 d	LC50	537	537	s	Montforts, 1999

3.3.1. Irgarol 1051

For Irgarol, no terrestrial toxicity tests are available. As for sediment, equilibrium partitioning is used to derive an ERL_{soil}.

3.3.2. Dichlofluanid

For dichlofluanid, Table 5a shows that the chronic data on nitrification are more critical than the chronic toxicity to *Eisenia fetida*. Therefore, these data are

used to derive an ERL_{soil} for dichlofluanid. The lowest value of 9.3 mg/kg d.w. is used. This value is considered a NOEC (9% effect), and is divided by a factor of 50 as no acute data are available for the same microbial process. This yields an ERL_{soil} of 0.19 mg/kg. For comparison; a risk limit based on the earthworm data would yield >0.913 mg/kg, which is based on applying an assessment factor of 1000 on the LC50, which is more critical than applying an assessment factor of 100 on the NOEC (2.88 mg/kg).

3.3.3. Ziram

For ziram one approved chronic test was found, a NOEC on the process sulfur oxidation of 292 mg/kg standard soil (Table 5b). By dividing this NOEC by an assessment factor of 100 the risk limit would be 2.92 mg/kg. However, the ERL_{soil} based on equilibrium partitioning is 0.011 μg/kg, and therefore more stringent.

3.3.4. Chlorothalonil

For terrestrial processes, six chronic data are available for nitrification, sulfur oxidation and respiration, and 14 acute data are available. In addition, five data on enzyme activity are found (Table 5c). No refined assessment was applied to the chronic data, as only three different processes are covered. The lowest chronic value is 15 mg/kg standard soil for nitrification, the lowest acute value is 0.5 mg/kg standard soil for aerobic nitrogen fixation. As three NOECs are available the risk limit becomes 0.3 mg/kg (NOEC/50), which is also protective for the acute effects on terrestrial processes and enzyme activity.

There are chronic data for three terrestrial species, i.e. fungi, bacteriophyta and earthworm. The lowest value is a LOEC (52% effect) of 5 mg/kg standard soil. This value is converted into a NOEC of 0.5 mg/kg, according to Kalf et al. (1999). Preliminary extrapolation with a factor of 50 is used, as no acute data of the same species are available for comparison. This yields a risk limit of 0.01 mg/kg standard soil. Thus, this value based upon species is lower than when based upon terrestrial processes, and also lower than the value derived using equilibrium partitioning.

3.3.5. TCMTB

For TCMTB no usable direct terrestrial data are found to base an ERL_{soil} upon. As no partition coefficient is available for TCMTB no ERL_{soil} can be derived.

4. Discussion

4.1. Concentrations in the environment

The concentrations of the studied substances as encountered in the environment cannot solely be attributed to their use as antifoulant, as many of the TBT-substitutes have other agricultural uses (see Voulvoulis et al., 1999a). Except for Irgarol 1051, no information was encountered in the open literature on the environmental occurrence in The Netherlands of the chemicals studied here.

Irgarol 1051 is widely distributed in European estuarine and coastal waters and sediments. Concentrations found are up to 0.19 μg/l in water and up to 1.7 μg/l in ports (Readman et al., 1993; Gough et al., 1994; Dahl and Blanck, 1996; Zhou et al., 1996; Tolosa et al., 1996; Scarlett et al., 1997, 1999; Peñalver et al., 1999). Hall et al. (1999) derived 90th percentiles of the concentrations as measured in several European monitoring studies and concluded that these were 316, 41 and 19 ng/l in marinas, estuaries and coastal waters, respectively. A clear seasonally bound pattern is observed, with a maximal concentration in early summer (Hall et al., 1999). In The Netherlands concentrations between 1 and 10 ng/l were found along a salinity gradient in the Scheldt (Steen et al., 1997). Although the Scheldt is a dense shipping lane, concentrations encountered in harbors are expected to exceed these values. The measured concentrations are at a same level as the derived ERL. It is concluded that the species composition and thereby ecosystem functioning is not considered protected.

To estimate environmental concentrations of the TBT-substitutes other than Irgarol and to compare the environmental risks between the various TBT-substitutes and TBT, the information from the present paper should be combined with information on predicted concentrations, e.g. according to Van Hattum et al. (1999).

4.2. Stability of the antifouling substances

Some of the antifouling substances seem to be relatively unstable. This can have consequences for the

fate of the substances during the toxicity tests. Nominal concentrations can differ substantially from actual concentrations, leading to an underestimation of the toxicity. However, if the test design is geared to the instability of the test compound (e.g. by using a flow through system) also chronic data can be considered as reliable. On the other hand, acute test results with a test design that is not designated to the instability of the test compound may not be reliable.

It can be considered to use only acute toxicity data as a basis to derive ERLs. Lethality is often the end-point in an acute test, while endpoints such as growth and reproduction are used in chronic tests. In analogy to chronic data, acute data can be extrapolated with species sensitivity distributions. However, the results should be extrapolated both to other endpoints and to a chronic situation. For both types of extrapolation, information is needed on extrapolation factors related to the specific mode of action of the chemical considered. We prefer to base the ERL on chronic data if available, because of the lacking information for a correct extrapolation.

A literature inventory is made on the stability of the antifouling substances evaluated in this report.

4.2.1. Irgarol 1051

Klisenko and Vekhstein (1971) found that Irgarol 1051 was hydrolysed relatively fast, especially at low pH. More recent studies show Irgarol 1051 to be relatively stable. Liu et al. (1999) showed that Irgarol 1051 is stable in distilled water in the pH range 5.0–9.0. At low concentrations of $HgCl_2$ (20 mg/l), Irgarol 1051 concentrations quickly decreased, which points to catalysed chemical hydrolysis. Catalysed hydrolysis of Irgarol 1051 did not occur with other tested heavy metal salts, i.e. $AgNO_3$, $CdCl_2$, $CuSO_4$, $PbCl_2$ and $ZnCl_2$. Thus, in the pH range that is relevant for field circumstances and for toxicity tests hydrolysis does not hamper the interpretation of the literature data.

In sea and freshwater sediment, degradation of Irgarol 1051 is slow (cited in Scarlett et al., 1999 and Voulvoulis et al., 1999a). Irgarol 1051 was not transformed by a mixture of natural bacteria from Lake Ontario even after an incubation of 5 months (Liu et al., 1997). Irgarol is stable in the marine environment (Callow and Willingham, 1996; Readman, 1996). However, a fungus (*Phanerochaete chrysosporium*) was able to transform Irgarol 1051 by *n*-de-alkylation.

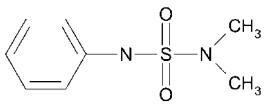


Fig. 2. Structural formula of DMSA.

The metabolite was stable under the test conditions (Liu et al., 1997). Taken together, we conclude that the interpretation of data on ecotoxicology and environmental fate of Irgarol 1051 used to derive an ERL is not hampered by a lack of stability.

4.2.2. Dichlofluanid

Dichlofluanid is unstable in an alkaline aqueous environment, as it undergoes hydrolysis to the principal metabolite dimethylaminosulphanilide (DMSA, Fig. 2). DT50 varies between 15.3 days and <10 min, depending on pH. No parent compound could be detected at pH 9 even if analysis was performed immediately.

In static toxicity tests concentrations dropped fast from a nominal concentration of 0.05–0.12 mg/l at the beginning of the exposure, to a concentration below the detection limit (0.02 mg/l) within a time frame of 48 h (Table 3b). Toxicity was observed however, and can presumably be attributed to the products formed (DMSA). DMSA was not analysed in the toxicity studies.

It is recommended to base an ERL for dichlofluanid on the important metabolites. Because of its instability no ERL is derived for the parent compound. Whenever dichlofluanid is measured in the field, this points to a severe situation that probably results in toxicity.

4.2.3. Chlorothalonil

Laboratory investigations show that the photolysis of chlorothalonil in water is low (Millet et al., 1998; Peñuela and Barceló, 1998). Extrapolating the laboratory data to the environment yielded half-lives of 30–200 days (Millet et al., 1998).

Chlorothalonil is degraded by microbial action in soil. Motonaga et al. (1998) and others showed that the DT50 in soil is relatively short after first application (approximately 2 weeks), but the dissipation rate decreases after repeated application. This is explained by the toxicity of the metabolite 4-hydroxy-2,5,6-trichloroisophtalonitrile (TPN-OH)

to the microbes. TPN-OH is stable in soil; in situ (Dutch flower bulb plants) the amounts of TPN-OH in soil correspond to up to 16% of the cumulative dose of chlorothalonil (Van der Pas et al., 1999).

As the ERL is derived based on aquatic toxicity studies, for sediment multiplied with a field-derived partition coefficient in which biodegradation is taken into account, it is not believed that instability of chlorothalonil troubles the interpretation of toxicity data nor the derivation of ERLs.

4.2.4. Ziram

Ziram is not persistent. A study of Brisou and Denis (1969) reports hydrolysis DT50 values ranging from 0.2 h (pH 3.8) to 18 days (pH 8). A major product is CS_2.

In the pH range in which the toxicity studies are performed (pH > 7.5), DT50 is higher than the test duration of at least acute toxicity tests, so the parent compound will mainly be responsible for the toxicity and the interpretation of the toxicity tests will not be hampered.

4.2.5. TCMTB

TCMTB is metabolised in soil under aerobic conditions (Fathulla, 1994). DT50 reported at 20 °C is 3.4 days. An important metabolite is 2-mercaptobenzothiazole (MBT), the DT50 of the metabolite is 1 day. In a water and sediment system, DT50 is 3 days (Van der Pol and Van der Linde, 1999). Hydrolysis rates depend on pH; at pH 5 and 7 DT50s are longer than 35 days, at pH 9 DT50 is 2–3 days (Van der Pol and Van der Linde, 1999). TCMTB is rapidly photolysed in water, reported DT50s are 1.5 and 3.9 h, and the main metabolite is again MBT. However, photolysis rate in a laboratory or a field situation may differ significantly. It is very plausible that especially photolysis plays an important role in the toxicity studies, and that 2-mercaptobenzothiazole is at least partly responsible for the observed toxic effects. The ERL derived is based on a study where the actual concentration is measured.

4.3. Mixture toxicity

As for antifouling various chemicals are used, and their main emittance will be in identical areas (i.e. shipping lanes, harbors, etc.), mixture toxicity will certainly play a role in the field situation. We did not consider mixture toxicity in this report, however a so-called 'toxic unit' approach can be used (Könemann, 1981) for assessing site-specific situations.

An ERL for the toxicity of copper and zinc was covered by Crommentuijn et al. (2000b,c). For ziram, zinc is used as a counterion, and the complex will partly dissociate in the water phase. The degree of dissociation will depend on environmental conditions such as pH and the presence of zinc ions and other counterions. For reason of the uncertainty in the speciation, we did not integrate the toxicity of zinc in the ERL for ziram. As zinc is very commonly monitored, an exceedance of the ERL for zinc will be observed separately.

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