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RIVM report 601501 008

Maximum permissible concentrations and negligible concentrations for antifouling substances

Irgarol 1051, dichlofluanid, ziram, chlorothalonil and TCMTB

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Abstract

In this report maximum permissible concentrations and negligible concentrations are derived for various antifouling substances, which are used as substitute for TBT such as Irgarol 1051, dichlofluanid, ziram, chlorothalonil and TCMTB.

Preface

Thanks are due to dr. M. van der Weiden, who was contact person at the ministry of housing, spatial planning and the environment (VROM-DGM/SAS). We want to acknowledge dr. D. Sijm, and drs. T. Traas who are involved in the RIVM-project 601501 in which the work was performed.

The results as presented in this report are discussed by the members of the ‘Setting Integrated Environmental Quality Standards Advisory Group’, who are acknowledged for their contribution. The members are: dr. T. Brock (Alterra), drs. S. Dogger (Health Council of the Netherlands), dr. J. Faber (Alterra), dr. K. den Haan (Shell International Chemical BV), drs. J. Peijnenburg (National Institute for Coastal and Marine Management), drs. M. Koene (Foundation for Nature and Environment), dr. D. Sijm (National Institute of Public Health and the Environment), dr. E. Sneller (National Institute of Inland Water Management), dr. J. Appelman (Board for the Authorisation of Pesticides), dr. W. van Tilborg (VTBC), dr. J. van Wensem (Technical Soil Protection Committee), dr. T. Traas (National Institute of Public Health and the Environment).

The work described in this report relies partly upon recently published CSR-advisory reports: nr. 06456a00 on TCMTB, nr. 06105a00 on chlorothalonil and nr. 8241a01 on chlorothalonil. Therefore we want to acknowledge J. van der Pol, A. van der Linde, M.H.M.M. Montforts, R. Posthumus and C.E. Smit (all RIVM-CSR) who contributed to these reports.

Contents

Samenvatting

In dit rapport zijn maximaal toelaatbare risiconiveaus (MTRs) en verwaarloosbare risiconiveaus (VRs) afgeleid voor vijf verbindingen die gebruikt worden als aangroeiwerend middel op onder andere schepen. MTRs worden afgeleid met gebruik van ecotoxicologische en milieuchemische data, en representeren het potentiële risico van stoffen voor een ecosysteem. MTRs vormen de wetenschappelijke basis voor milieukwaliteitsnormen die worden vastgesteld door het ministerie van VROM.

In het verleden werd tributyltin (TBT) als belangrijk aangroeiwerend middel toegepast. Echter vanwege de aantoonbare ecotoxicologische effecten, en de wijdverbreide verspreiding die samenhangen met het gebruik van TBT, zijn politieke maatregelen genomen welke leiden tot een wereldwijd verbod op TBT in 2003. Als vervanger voor TBT komen nieuwe aangroeiwerende middelen op de verfmarkt. In dit rapport worden MTRs afgeleid voor deze TBT-vervangers.

Voor de stoffen Irgarol 1051, dichlofluanid, ziram, chlorothalonil en TCMTB is een MTR afgeleid, voor de verbindingen SeaNine 211 en TCMS pyridine was te weinig informatie voorhanden om een MTR af te leiden. Naast de openbare literatuur is gebruik gemaakt van zogenaamde adviesrapporten om de toelating van bestrijdingsmiddelen te beoordelen. Deze adviesrapporten zijn opgesteld door het RIVM, Centrum voor Stoffen en Risico's, in opdracht van het College Toelating Bestrijdingsmiddelen (CTB). Alleen toxiciteitstudies met eindpunten die gerelateerd zijn aan overleving, groei of reproductie zijn in beschouwing genomen.

Ten opzichte van de tot nog toe gebruikte methodieken in het project 'Integrale normstelling stoffen' is een verandering aangebracht overeenkomstig Aldenberg and Jaworska (2000).

Voor Irgarol 1051 blijken vooral de planten gevoelig te zijn; het mechanisme van toxiciteit is inhibitie van het fotosynthetisch elektronen transport. Een log-normale fit aan de toxiciteitgegevens van alle soorten, maar ook aan alleen de plantgegevens was statistisch acceptabel. Ondanks de hogere gevoeligheid van de planten is het berekende MTR_{water} die gebaseerd werd op alleen de plant gegevens hoger dan het MTR_{water} die is berekend over alle gegevens, dit is te verklaren uit de lagere spreiding in de plantendataset. Er wordt voorgesteld het MTR_{water} te baseren op de plantgegevens.

Dichlofluanide is erg instabiel in water, de stof is niet meer te detecteren aan het eind van toxiciteittesten. Er wordt aanbevolen om het MTR_{water} te baseren op de gevormde metabolieten in plaats van op de moederverbinding.

Voor de toxiciteit in sediment van de onderzochte verbindingen zijn geen specifieke gegevens gevonden, de $MTR_{sediment}$ is voor alle stoffen afgeleid met behulp van de evenwichts-partitie theorie. Voor TCMTB kan geen K_{oc} gemeten worden, en dus ook geen evenwichts-partitie toegepast worden, vanwege de hydrolyse en methylatie van TCMTB in 2-(methylthio)benzothiazol.

Voor bodem waren voor dichlofluanide, ziram en chlorothalonil bruikbare gegevens voorhanden over de toxiciteit naar terrestrische organismen of processen. Voor dichlofluanid en chlorothalonil is de MTR_{bodem} afgeleid op basis van deze terrestrische gegevens, en voor

Irgarol 1051 en ziram is de MTR$_{bodem}$ afgeleid met gebruik van de evenwichts-partitie theorie. Voor een overzicht van de afgeleide MTRs zie tabel I.

Tabel I. MTRs en VRs voor aangroeiwerende middelen, respectievelijk voor water (opgelost), standaard sediment en standaard bodem

Stof	**Methode**	**MTR$_{water}$ (ng/l)**	**VR$_{water}$ (ng/l)**	**Methode**	**MTR$_{sediment}$ (µg/kg)**	**VR$_{sediment}$ (ng/kg)**	**Methode**	**MTR$_{bodem}$ (µg/kg)**	**VR$_{bodem}$ (ng/kg)**	**K$_p$[b] (l/kg)**
Irgarol 1051	A&J[c]	24 (2.7-73)	0.24	EP	1.4	14	EP	1.4	14	58
Dichlofluanide[a]	-	-	-	-	-	-	NOEC/50	190	1900	-
Ziram	LC50/1000	9.7	0.097	EP	0.011	0.11	EP	0.011	0.11	1.16
Chlorothalonil	A&J	530 (38-2300)	5.3	EP	50.6	506	NOEC/50	10	100	92
TCMTB	NOEC/10	380	3.8	-	-	-	-	-	-	-

[a] Onstabiele verbinding
[b] Berekend uit K$_{oc}$
[c] Volgens Aldenberg and Jaworska, 2000

Behalve voor Irgarol 1051, is geen informatie aangetroffen in de open literatuur over het voorkomen in het milieu in Nederland van de hier behandelde verbindingen. Irgarol 1051 komt wijdverbreid voor in Europese estuariene en kust- wateren en sedimenten. Concentraties zijn gevonden tot 0,19 µg/l in water en tot 1,7 µg/l in havens. Er is een seizoensgebonden patroon in de concentraties, welke pieken in de vroege zomer. Langs een saliniteitsgradiënt in de Westerschelde werden concentraties gevonden tussen de 1 en 10 ng/l. Concentraties in havens zullen vermoedelijk hierboven liggen. De gemeten concentraties liggen dicht bij het MTR.

Milieuconcentraties van TBT-vervangers anders dan Irgarol kunnen geschat worden met behulp van modellen. Het 'MAM-PEC' model (Van Hattum et al., 1999) is speciaal voor dit doeleinde ontwikkeld. Wanneer de geschatte concentraties gecombineerd worden met de informatie uit het huidige rapport, kunnen de milieurisico's van de diverse TBT-vervangers met elkaar vergeleken worden.

Summary

In this report maximum permissible concentrations (MPCs) and negligible concentrations (NCs) are derived for five compounds used as antifouling substances on e.g. ships. MPCs are derived using data on (eco)toxicology and environmental chemistry, and represent the potential risk of the substances to the ecosystem. They are the scientific basis for Environmental Quality Standards (EQSs) set by the Ministry of VROM.

Tributyl-tin (TBT) was used as major antifouling substance on ships in the past. Many adverse ecotoxicological effects caused by TBT are reported, and butyltin contamination is widespread. In 1989 the EU restricted the use of TBT on boats under 25 m and the International Maritime Organisation decided for a world-wide ban on TBT in 2003. As a replacement for TBT, new antifouling agents are coming up to the paint market. In this report MPCs are derived for substances that are used as TBT-substitutes.

MPCs are derived for the compounds Irgarol 1051, dichlofluanid, ziram, chlorothalonil and TCMTB. For SeaNine 211 and TCMS pyridine, there appeared to be insufficient information to derive an MPC. In addition to the open literature, advisory reports that are prepared for the authorisation of pesticides were a source of information. These advisory reports are prepared by RIVM, for the account of the Dutch Board for the Authorisation of Pesticides (CTB). Only toxicity studies with endpoints related to survival, growth or reproduction are taken into account. A modification to the generally used procedures in the project ‘Setting Integrated Environmental Quality Standards’ is made according to Aldenberg and Jaworska (2000).

For Irgarol 1051 especially plants appear to be sensitive; the mode of action is inhibition of photosynthetic electron transport. The log-normal fit to toxicity data of all species as well as to only the plant data was statistically acceptable. In spite of the higher sensitivity of the plants, the calculated MPC_{water} based on the ‘plants only’ dataset is higher than the MPC_{water} calculated over all data, due to the lower variability in the plant only dataset. It is proposed to base the MPC_{water} on the plants only dataset.

Dichlofluanid is highly unstable in the water phase, the parent compound was below detection limit at the end of the toxicity tests. Therefore, it is recommended to base the MPC on the metabolites formed and not on the parent compound.

No data for toxicity of the studied compounds to organisms living in sediments were found. For all compounds the $MPC_{sediment}$ is derived with help of the equilibrium partitioning theory. For TCMTB 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.

Data on the toxicity to soil organisms or soil processes are available for dichlofluanid, ziram and chlorothalonil. For dichlofluanid and chlorothalonil MPC_{soil} is directly based on these terrestrial data, for Irgarol 1051 and ziram the MPC_{soil} is derived using equilibrium partitioning. For an overview of the MPCs derived in this report see Table I.

Table I. MPCs and NCs for antifouling substances, respectively for water (dissolved), standard sediment and standard soil

Compound	**Method used**	**MPC$_{water}$ (ng/l)**	**NC$_{water}$ (ng/l)**	**Method used**	**MPC$_{sediment}$ (µg/kg)**	**NC$_{sediment}$ (ng/kg)**	**Method used**	**MPC$_{soil}$ (µg/kg)**	**NC$_{soil}$ (ng/kg)**	**K_p[b] (l/kg)**
Irgarol 1051	A&J[c]	24 (2.7-73)	0.24	EP	1.4	14	EP	1.4	14	58
Dichlofluanid[a]	-	-	-	-	-	-	NOEC/50	190	1900	-
Ziram	LC50/1000	9.7	0.097	EP	0.011	0.11	EP	0.011	0.11	1.16
Chlorothalonil	A&J	530 (38-2300)	5.3	EP	50.6	506	NOEC/50	10	100	92
TCMTB	NOEC/10	380	3.8	-	-	-	-	-	-	-

[a] Highly unstable compound
[b] Calculated from K_{oc}
[c] According to Aldenberg and Jaworska, 2000

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. A clear seasonally bound pattern is observed, with a maximal concentration in early summer. Along a salinity gradient in the Scheldt, the Netherlands, concentrations between 1 and 10 ng/l are found. Concentrations encountered in harbours are expected to exceed these values. The measured concentrations are close to the derived MPC. It is concluded that the species composition and thereby ecosystem functioning cannot be considered as protected.

To estimate the environmental concentration 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 report should be combined with information on predicted concentrations. For this purpose the ‘MAM-PEC model’ (Van Hattum et al. 1999) could be used.

1 Introduction

1.1 The project 'Setting Integrated Environmental Quality Standards'

This report is produced in the framework of the project 'Setting Integrated Environmental Quality Standards'. The aim of the project is to derive environmental risk limits for substances in the environment for the compartments air, water, sediment and soil. The environmental risk limits are referred to as Environmental Quality Standards (EQSs) in Dutch Environmental Policy and are set by the Ministry of VROM. The EQSs are based on maximum permissible concentrations (MPCs) and negligible concentrations (NCs). MPCs are derived using data on (eco)toxicology and environmental chemistry, and represent the potential risk of the substances to the ecosystem. Applying a factor of 100 towards the MPC yields the NCs. The process of deriving integrated EQSs is shown schematically in Figure 1.1.

In this report MPCs are derived for five compounds that are used as antifouling substances. The results obtained until now in the project 'Setting Integrated Environmental Quality Standards' are laid down in several reports. The MPCs and NCs derived until 1997 are summarised by De Bruijn et al. (1999). Reuther et al. (1998) derived MPCs and NCs for aniline derivatives. Risk limits for boron, silver, titanium, tellurium, uranium and an organosilicon compound are derived in Van de Plassche et al. (1999), and MPCs have been proposed for PCBs and phthalates (Van Wezel et al., 1999ab).

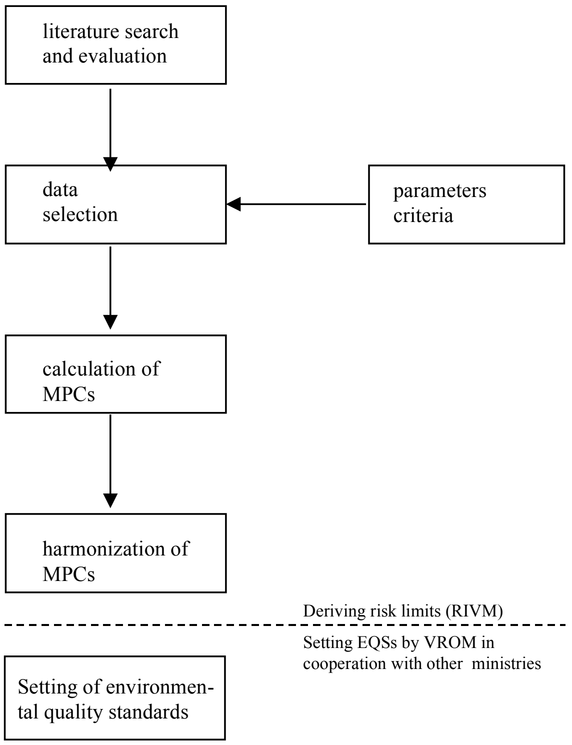


Figure 1.1. The process of deriving Integrated Environmental Quality Standards

1.2 Antifouling substances

1.2.1 Background

Biofouling is the settlement and growth of micro- and macro-organisms on surfaces. Biofouling on ships increases the fuel consumption (by 6% for every 100 μm increase in hull roughness, cited in Voulvoulis et al., 1999a). Biofouling can be prevented by the use of antifouling substances. Other ways of preventing biofouling is by cleaning or nutrient limitation (Flemming et al., 1996).

On ships tributyl-tin (TBT) was used as major antifouling substance in the past. Many adverse ecotoxicological effects caused by TBT are reported in laboratory studies (see for example Crommentuijn et al. 1997a for an overview) and field studies in marina's and the open sea (Ten Hallers-Tjabbes et al., 1994). Butyltin contamination is not only found in harbours, but is more widespread (Tanabe et al., 1998). The ecotoxicological problems associated with the use of TBT have been recognised, and have led to policy action. 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 to the paint market (e.g. Voulvoulis et al., 1999ab). Examples of these substances can be found in Table 1. These substances are partly well known chemicals for which environmental risk limits have been derived. However, also relatively unknown chemicals that have not been the subject of many ecotoxicological studies are used to replace TBT. The different TBT-substitutes are commonly used in combination with copper or zinc compounds. Additional to copper and zinc, organic biocides are needed, because of the relative tolerance of (micro-) algae species to these metals (Voulvoulis et al., 1999a). Several of the TBT-substitutes have in addition to application as an antifouling agent other agricultural uses (Voulvoulis et al., 1999a).

Table 1.1: Substances used to replace TBT in antifouling paints

Chemical name	MPCs derived	Common name	Chemical name	MPCs derived	Common name
2,3,5,6-tetrachloro-4-(methyl sulphonyl) pyridine	N	TCMS Pyridine	zineb	Y	
2-methylthio-4-tertiary-butylamino-6-cyclopropylamino-s-triazine	N	Irgarol 1051	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	Chlorothalonil	2-(thiocyanomethyl thio)benzthiazole	N	TCMTB
4,5-dichloro-2-n-octyl-4-isothiazolin-3-one	N	SeaNine 211 Kathon 5287	deltamethrin	Y	
Dichlorophenyl dimethylurea	Y	Diuron	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				

Research on natural product antifouling is still in its infancy. Clare (1996) reviewed natural products against biofouling produced by cnidaria, porifera (sponges), chordata, thallophyta, angiospermae and micro-organisms. However, very few of these products have really been tested for their antifouling action when applied on boats, and on their toxicity.

1.2.2 Authorisation in the Netherlands

Antifouling substances that are presently authorised in the Netherlands are (information from the Board for the Authorisation of Pesticides, CTB):

- Irgarol 1051 (0.6-5%) in combination with
  - Copper (I) oxide (28-43%)
  - or Copperthiocyanate (14-17%)
  - or copperthiocyanate (5-6.6%) and zinc oxide (3.2-4.3%)
  - or copper (I) oxide (40%) and zinc oxide (9%)
- bitumen (5.9%) in combination with copper (I) oxide (21%)
- dichlofluanid (9%)
- diuron (3.5-4.3%) in combination with
  - copper (I) oxide (40-43%)
  - or copper thiocyanate (24%)
  - or copper thiocyanate (20%) and zinc oxide (13%)
  - or copper (I) oxide (29-46%) and zinc oxide (9.5-12%)
- copper (17-25%)
- copper (I) oxide (10-50%)
- a combination of zineb (4.4%) and copper oxide (40%)
- a combination of zinc oxide (11-18%) and copper (I) oxide (41-45%)
- a combination of ziram (4.6%) and copper (I) oxide (39.3%)
- antifouling substances with tributyltinoxides and tributyltinmethacrylates (also in combination with copper (I) oxides(5-40%)

1.2.3 Antifouling substances evaluated in the present report

The purpose of the present report is to derive MPCs for water, sediment and soil for substances that are used as TBT-substitutes.

MPCs are derived for Irgarol 1051, dichlofluanid, ziram, chlorothalonil and TCMTB. For SeaNine 211 and TCMS pyridine, there appeared to be insufficient information to derive an MPC. The compounds are selected as they are authorised in the Netherlands (Irgarol 1051, dichlofluanid, and ziram) as an antifouling substance, or often mentioned in the literature as an alternative to TBT (chlorothalonil, SeaNine). Mixture toxicity of the different TBT-substitutes with among themselves or with copper or zinc, was not taken into account in the MPC-derivation. If compounds are accumulated in the food chain, this poses an extra risk for species at the top of the food chain and MPCs are derived that take into account this extra risk (Van de Plassche, 1994; Van Wezel et al., 1999a). The compounds studied in the present report do not appear to be very hydrophobic (see K_{ow} or K_{oc} in Table 1.2.). Therefore they are

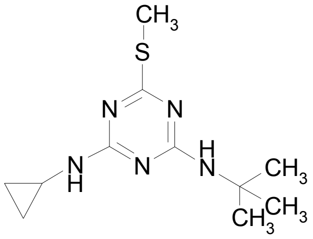
not expected to biomagnify in the food chain, and it is considered not necessary to derive MPCs that take into account biomagnification.
General information on the evaluated antifouling substances can be found in Table 1.2.

Table 1.2: General information and physical-chemical properties of the studied compounds

Irgarol 1051

2-methylthio-4-tertiary-butylamino-6-cyclopropylamino-s-triazine

CASnr. 28159-98-0

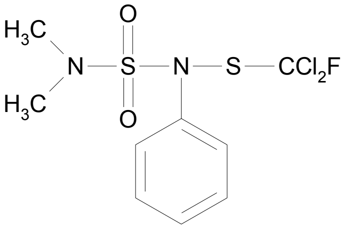


Property	**Value**	**Reference**
Water solubility (mg/l)	6	Jongbloed & Luttik, 1996
	7	Jongbloed & Luttik, 1996
log K_{ow}	4.1	SRC, 1997
log K_{oc} (l/kg)	2.38	Rogers et al., 1996
	3.0	Tolosa et al., 1996
Henry's constant ($Pa.m^3.mol^{-1}$)	2.10^{-6}	Jongbloed & Luttik, 1996
	$5.4.10^{-4}$	Rogers et al., 1996
Vapour pressure (Pa)	$8.8.10^{-5}$	Jongbloed & Luttik, 1996
	$1.5.10^{-5}$	Rogers et al., 1996

Dichlofluanid

N'-dimethyl-*N*-phenylsulfamide

CASnr. 1085-98-9

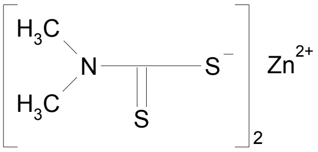


Property	**Value**	**Reference**
Water solubility (mg/l)	1.3	Tomlin, 1997
log K_{ow}	3.7	Tomlin, 1997
log K_{oc}		Tomlin, 1997
Henry's constant ($Pa.m^3.mol^{-1}$)	<1.9	Tomlin, 1997
Vapour pressure (Pa)	$<15.10^{-6}$	Tomlin, 1997

Ziram

Zinc dimethyldithiocarbamate

CASnr. 137-30-4



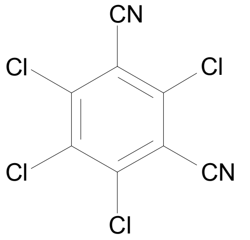
Property	**Value**	**Reference**
Water solubility (mg/l)	1.58-18.3	Tomlin, 1997
log K_{ow}	1.23	Tomlin, 1997
log K_{oc}	0.8-1.3	Ordelman et al., 1993
Henry's constant ($Pa.m^3.mol^{-1}$)	<1.9	Tomlin, 1997
Vapour pressure (Pa)	$<1.10^{-6}$	Tomlin, 1997

Table 1.2., continued

Chlorothalonil

2,4,5,6-tetrachloro-isophtalonitrile

CASnr. 1897-45-6

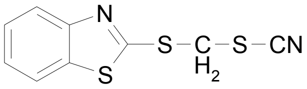


Property	Value	Reference
Water solubility (mg/l)	0.9	Caux et al., 1996
log K_{ow}	2.6-4.4	Caux et al., 1996
log K_{oc} (l/kg)	2.9-3.8	Caux et al., 1996
Henry's constant ($Pa.m^3.mol^{-1}$)	$1.7 \cdot 10^{-2}$	Caux et al., 1996
Vapour pressure (Pa, 25ºC)	$4.3 \cdot 10^{-12}$	Caux et al., 1996

TCMTB

(2-thiocyanomethylthio)benzothiazole

CASnr. 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 Karickhof, 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

2 Methods

2.1 General scheme

The maximum permissible concentrations and negligible concentrations are derived as described in Kalf et al. (1999), and according to the methods generally applied within the project ‘Setting Integrated Environmental Quality Standards’. A modification to the generally used procedures is made according to Aldenberg and Jaworska (2000).

In short, data on chronic and acute toxicity for aquatic and terrestrial species and terrestrial processes of a compound are searched for. They are evaluated, and selected or rejected. For compounds with a log K_{ow} higher than 5.0, or for compounds for which there is an expectation for secondary poisoning, also toxicity data for mammals and birds are searched for. The maximum permissible concentration (MPC) is derived using either the refined assessment method as described by Aldenberg and Jaworska (2000), or assessment factors as laid down in the Technical Guidance Document (ECB, 1996, developed for EU council regulation 793/93). The MPCs are harmonised according to the equilibrium partition theory. In this way it is prevented that a concentration on an MPC-level in one compartment leads to an exceeding of the MPC in another compartment.

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 that are prepared for the authorisation of pesticides were a source of information. The National Institute of Public Health and the Environment (RIVM) prepares the advisory reports, for the account of the Dutch Board for the Authorisation of Pesticides (CTB). Relevant references are Jongbloed and Luttik (1996) which reviewed data for Irgarol 1051, Jansma and Linders (1992) which served as a basis for the information on dichlofluanid. Tibosch et al. (1993) summarised data on ziram. Van der Pol and Van der Linde (1999) served as a basis for information on TCMTB, and Montforts (1999) and Posthumus (1999) summarised data for chlorothalonil.

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 are developed within the framework of the project ‘Setting Integrated Environmental Quality Standards’.

Effects on growth, reproduction or survival are used in the derivation of MPCs, as they are directly related to population dynamics. Toxicity data from sediment studies are normalised to 10% organic matter.

When the method of derivation of a NOEC, LC50 or EC50 was not clearly stated in the original work, a recalculation was performed. A logistic equation was fitted through effect data versus the logarithms of concentrations (preferably measured values) using nonlinear regression (Graphpad Prism, 1996). Either the EC50 (LC50) or the EC10 was calculated. When data of a chronic experiment were fitted, an EC10 was calculated, which was interpreted as NOEC. Recalculation of data is mentioned in the footnotes of the tables in Appendix 2 and 3 by 'Effect concentration recalculated'.

For each species and each compound, the most sensitive toxicity test is selected. If for a single species several toxicity values are found for the same effect parameter, the geometric mean is calculated.

2.4 Extrapolation towards MPCs and NCs

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; Kalf et al., 1999), which is developed in the framework of EU council regulation 793/93.

In the case that there is no complete base-set (acute toxicity to algae, daphnia and fish), the modified EPA method is used.

2.4.2 Refined effect assessment

The aim of environmental quality standards as derived in the project 'Setting Integrated Environmental Quality Standards' is to protect all species in the ecosystem. For statistical considerations the MPC is set equal to the concentration at which 95% of the species is protected, i.e. 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 (Kooijman, 1987; Van Straalen and Denneman, 1989; Aldenberg and Slob, 1993; 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 computer package GraphPad Prism it is tested, with the Kolmogorov-Smirnov D*sqrt(n) test, if a normal distribution to the log-transformed data adequately describes the underlying data. The average, the standard deviation, and the number of the underlying data define this distribution. Extrapolation factors as derived by Aldenberg and Jaworska (2000) are used to estimate the HC5, and its upper (95%) and lower (5%) estimate, constituting a 90% two-sided confidence interval.

2.4.3 Derivation of negligible concentrations (NCs)

Multiplying the MPCs with a factor 0.01 derives NCs. This factor is supposed to be needed as protection against mixture toxicity, since species are always exposed in the environment to mixtures of chemicals and chemicals act often as concentration-additive (Van Leeuwen et al., 1996; Deneer, 1988).

2.5 Equilibrium partitioning and harmonisation between the compartments

The partition coefficient between organic carbon in the soil/sediment and water (K_{oc}) is used to derive an MPC for soil/sediment when no data on terrestrial or sediment-dwelling organisms are available. In addition, it is used to harmonise the MPCs between the different compartments.

By applying this equilibrium-partitioning concept (DiToro et al., 1991), it is assumed that there is equilibrium between the concentration in organic carbon and (pore) water. The K_{oc} describes this equilibrium. It is furthermore assumed that toxicity is related to the pore water concentrations, and that aquatic organisms are comparable in their sensitivity to the compound to the organisms living in soil or sediment.

3 Toxicity data and derivation of MPCs and NCs for water

The aquatic toxicity data that are found for Irgarol 1051, dichlofluanid, ziram, chlorothalonil and TCMTB are presented in Appendix 2. The toxicity data that are found for terrestrial or benthic organisms are presented in Appendix 3 for the same compounds.
Only toxicity studies with endpoints related to survival, growth or reproduction are taken into account. Several toxicity studies are found with endpoints related to biochemistry or animal behaviour (MacKinnon and Farrell, 1992; Kruzynski et al., 1994ab; Davies et al., 1994). These endpoints are not taken into account for the derivation of MPCs, as they do not have a clear relationship with population dynamics.
For the derivation of MPCs salt and freshwater data are combined if there are no (statistical) reasons to keep the data separated. This means that the MPC is derived using the combined dataset. For an overview of the derived MPCs see Table 3.1.

3.1 Irgarol 1051

Aquatic toxicity data on Irgarol 1051 can be found in Tables 1.1. to 1.4. in Appendix 2. Acute and chronic toxicity data are given for freshwater and saltwater organisms.
Acute toxicity was tested for algae, macrophytes, crustaceans, and fish (Tables 1.1. and 1.2.). Especially algae and macrophytes appear to be sensitive taxonomic groups. This is explained as the mode of action of Irgarol 1051 is inhibition of photosynthetic electron transport (Holt, 1993). 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 (Tables 1.3. and 1.4.). 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 sensitivities of saltwater and freshwater species are not statistically different (Two-tailed T-test with Welch correction, GraphPad Prism).

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 data per species from Tables 1.3. and 1.4. was statistically accepted according to the Kolgomorov-Smirnov test. The MPC_{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, i.e. inhibition of photosynthetic electron transport, plants can be considered the most sensitive species. This is confirmed by the available data (Figure 3.1.). A one-tailed T-test (with GraphPad Prism) shows that the data for plants differed significantly (P=0.0007) from the remaining toxicity data. A log-normal fit to only the plant data (algae and macrophytes) was also statistically accepted. The variability in

the plant only dataset is smaller than in the dataset for all species. In spite of the higher sensitivity of the plants, the calculated MPC_{water} based on the plants only dataset is higher than the MPC_{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 (Figure 3.1.).
As there is a basis to state that plants are the most sensitive species, it is proposed to base the MPC_{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 as 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 MPC derived in the current study.

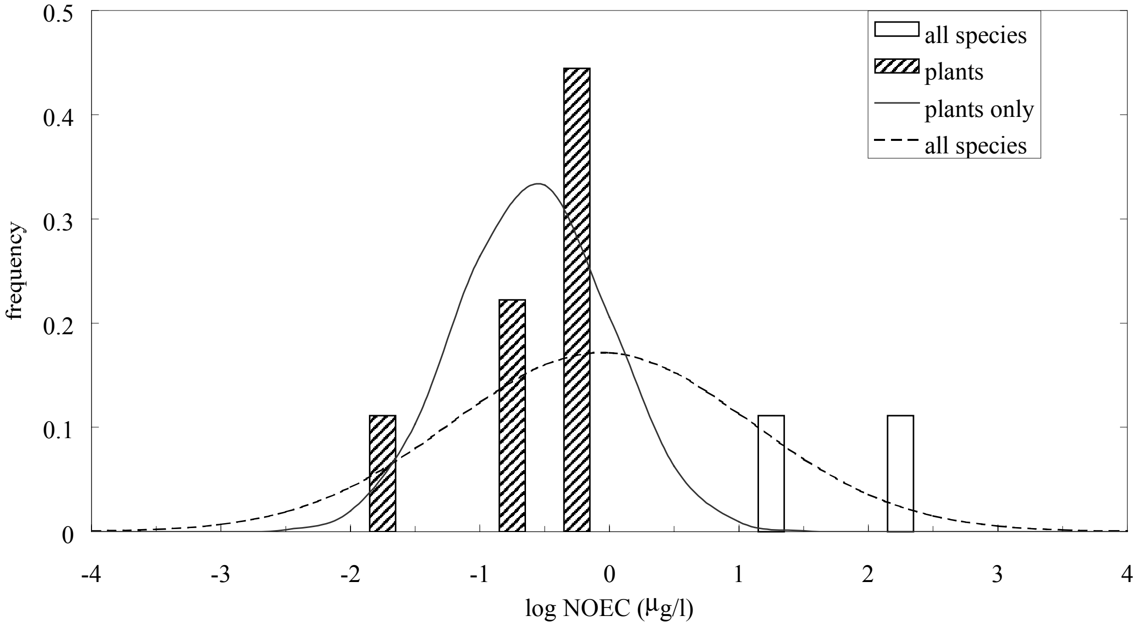


Figure 3.1. Frequency distributions of the toxicity data for Irgarol 1051 for all species or for plants only

3.2 Dichlofluanid

Aquatic toxicity tests with dichlofluanid can be found in Tables 2.1. to 2.2., and rejected tests in Table 2.3. and 2.4. in Appendix 2. Only freshwater species are tested, acute and chronic data are available for two taxonomic groups: crustaceans and fish. Since the base set is incomplete (there are no data for three taxonomic groups) and according to Kalf et al. (1999), the modified EPA method is used. The lowest chronic (21 d) test is an LC50 value of 0.016 mg/l for *Oncorhynchus mykiss*, an assessment factor of 10 is applied, which yields an MPC_{water} of 1.6 µg/l. As chronic data are only available for two taxonomic groups, this is compared with the extrapolated value based on acute toxicity values. The lowest acute toxicity value is 0.011 mg/l again for *Oncorhynchus mykiss*. An assessment factor of 1000 yields an MPC_{water} of 11 ng/l. The lowest of both extrapolation methods is chosen, yielding an MPC_{water} of 11 ng/l.
However, the substance is highly unstable in the water phase. The parent compound was below detection limit at the end of the toxicity test. Therefore, it is recommended to base the

MPC on the metabolites formed and not on the parent compound (see discussion for further details).

3.3 Ziram

Aquatic toxicity data on ziram can be found in Tables 3.1. to 3.3. in Appendix 2.
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. In this taxonomic group no freshwater species is tested. Acute aquatic toxicity data are available for six taxonomic groups (bacteria, algae, crustacea, insects, mollusca and pisces, Tables 3.1. and 3.2.). 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*. According to the EU/TGD (ECB, 1996) and Kalf (1999) an assessment factor of 1000 is applied which gives an MPC_{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 3.3.). Since the taxonomic group showing the lowest acute effect (i.c. 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 MPC_{water} of 0.6/50 = 0.012 µg/l or 12 ng/l. The MPC based on extrapolation of acute data is (only slightly) lower than the MPC based on extrapolation of chronic data, therefore the former is selected (Kalf, 1999; ECB, 1996). Hence, the MPC_{water} for ziram is **9.7 ng/l**.

3.4 Chlorothalonil

Chlorothalonil possesses multiple electrophilic centres, and is therefore reactive towards GSH and can be detoxified thereby (Gallagher and Di Giulio, 1992). If channel catfish were depleted in their GSH, the acute toxicity of chlorothalonil was elevated (Gallagher et al., 1992).
Acute aquatic toxicity data of chlorothalonil are presented in Tables 4.1. and 4.2. for freshwater species and marine species respectively. Acute toxicity tests are performed with crustaceans, molluscs and fish. For crustaceans and fish both freshwater and marine species are tested, for both species the data for fresh- and salt water do not differ statistically (unpaired T-test with Welch's correction, GraphPad Prism).
Chronic aquatic toxicity data are available for freshwater species only, and can be found in Table 4.3. Toxicity data are available for four different taxonomic groups (algae, plants, crustaceans, insects and fish), so a MPC_{water} can be derived with help of the refined assessment method. The data were found to be log-normal distributed (Kolgomorov-Smirnov test). The **MPC_{water}** which was derived is **0.53 µg/l** (0.038-2.3 µg/l).

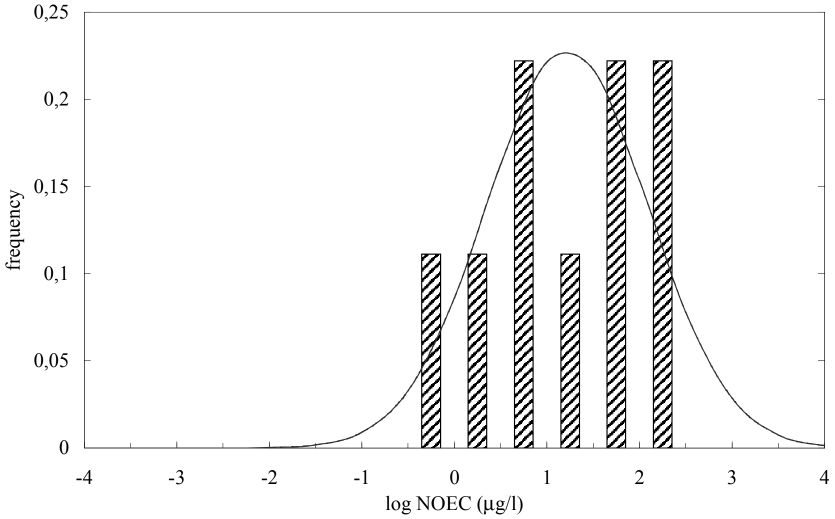


Figure 3.2. Frequency distributions of the toxicity data for chlorothalonil

3.5 TCMTB

Information on the aquatic toxicity of TCMTB can be found in Table 5.1. and 5.2. of Appendix 2. The amount of data is limited, and only data for freshwater organisms are available. Acute data are available for a crustacean and a fish, only for daphnia magna a chronic toxicity value is available. There is no complete base set, according to Kalf et al. (1999) an assessment factor of 10 is applied to the NOEC, this yields an **MPC_{water}** of **0.38 µg/l.**

Table 3.1. MPC_{water} (dissolved) for antifouling substances

Compound	**Method used**	**MPC_{water} (ng/l)**	**NC_{water} (ng/l)**
Irgarol 1051	A&J[c]	24 (2.7-73)	0.24
Dichlofluanid[a]	-	-	-
Ziram	LC50/1000	9.7	0.097
Chlorothalonil	A&J	530 (38-2300)	5.3
TCMTB	NOEC/10	380	3.8

[a] Highly unstable compound, no MPC derived

[b] Calculated from K_{oc}, assuming standard sediment with 10% organic matter

[c] According to Aldenberg and Jaworska, 2000

4 Toxicity data and derivation of MPCs and NCs for soil and sediment

4.1 MPCs for sediment

No specific data are found for sediment toxicity of the studied compounds, only for ziram a test was found that was rejected (Table 2.3.). As no sediment toxicity data are available, the MPCs are derived with help of the equilibrium partitioning theory as described earlier (2.5.). In conclusion, for Irgarol 1051, ziram and chlorothalonil K_p's are found, and using equilibrium partitioning an $MPC_{sediment}$ is derived of respectively 0.5, 0.011 and 27.6 μg/kg (Table 3.1.).

4.1.1 Partition coefficients used for the antifoulings

For Irgarol 1051 a log K_{oc} of 3.0 was used (Tolosa et al., 1996), so a K_p to standard sediment with 10% organic matter (conversion factor from organic carbon to organic matter is assumed 1.724) is 58.

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

For ziram a log K_{oc} was used of 1.3 was used, the higher in the range 0.8-1.3 reported by Ordelman et al. (1993), which corresponds with a K_p of 1.16 l/kg.

Experimental log K_{oc} values for chlorothalonil vary between 2.5 and 3.8, the mean of 11 experimental data is 3.2 (Posthumus, 1999). Normalised to standard sediment with 10% organic matter, the K_p is 92 l/kg.

For TCMTB no information in the industrial dossiers is available on sorption to organic carbon (Van der Pol and Van der Linde, 1999), and 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.

Table 4.1. MPC_{water} (dissolved) and $MPC_{sediment}$ for antifouling substances

Compound	**MPC_{water} (ng/l)**	**Method used**	**$MPC_{sediment}$ (μg/kg)**	**$NC_{sediment}$ (ng/kg)**	**K_p[b] (l/kg)**
Irgarol 1051	24 (2.7-73)	EP	1.4	14	58
Dichlofluanid[a]	-	-	-	-	-
Ziram	9.7	EP	0.011	0.11	1.16
Chlorothalonil	530 (38-2300)	EP	50.6	506	92
TCMTB	380	-	-	-	-

[a] Highly unstable compound, no MPC derived

[b] Calculated from K_{oc}, assuming standard sediment with 10% organic matter

4.2 MPCs for soil

4.2.1 Irgarol 1051

For Irgarol, no specific toxicity tests related to soil are available. As for sediment, equilibrium partitioning is used to derive an MPC_{soil} of 1.4 µg/kg standard soil with 10% organic matter.

4.2.2 Dichlofluanid

For dichlofluanid, Tables 1.1. and 1.2 from Appendix 3 show that the chronic data on microbial processes (only data on nitrification are available) are more critical than the chronic toxicity data on *Eisenia fetida*. Therefore these data are used to derive an MPC_{soil} for dichlofluanid. The lowest value of 9.3 mg/kg d.w. is used. This value is considered a NOEC (9% effect). Three NOECs are available, so normally the lowest will be divided by a factor 0f 10. However, according to Kalf et al. (1999) here the NOEC is divided by a factor of 50 as no acute data are available for the same parameter and process. This yields an MPC_{soil} of **0.19 mg/kg**. For comparison; a risk limit based on the earthworm data would yield >0.913 mg/kg, this is based on the LC50/1000 which is more critical than the NOEC/100 (2.88 mg/kg).

4.2.3 Ziram

For ziram one use-full chronic test was found, a NOEC on the process sulfur oxidation of 292 mg/kg standard soil. This value is divided by 100 to yield an MPC_{soil} of 2.92 mg/kg. The MPC_{soil} based on equilibrium partitioning is 0.011 µg/kg (Table 4.1.) and therefore is more stringent than the MPC based on sulfur oxidation. Therefore, for ziram an MPC_{soil} is proposed of 0.011 µg/kg.

4.2.4 Chlorothalonil

For terrestrial processes 6 chronic data are available for three processes (nitrification, sulfur oxidation and respiration), and 14 acute data are available for processes. In addition, 5 data on enzyme activity are found (Tables 3.1. and 3.2.). No refined assessment was used for 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 is 0.3 mg/kg (NOEC/50) which is also protective for the acute effects on terrestrial processes and enzyme activity.

For terrestrial species, chronic data for three species (Table 3.3.), i.e. fungi, bacteriophyta and earthworm. The lowest observed toxicity 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 methods generally applied within the project 'Setting Integrated Environmental Quality Standards'. Using preliminary extrapolation, a risk limit is derived of 0.01 mg/kg standard soil. A factor of 50 is used as no acute data of the same species are available for comparison.

So the lowest risk limit derived on direct terrestrial data is 0.01 mg/kg for species, and this value is also lower than the value derived using equilibrium partitioning (Table 4.1.). Therefore, and MPC_{soil} is proposed for chlorothalonil of 0.01 mg/kg standard soil, which is based on chronic toxicity data for terrestrial species.

4.2.5 TCMTB

For TCMTB no usable direct terrestrial data are found to base an MPC_{soil} upon (Table 4.1.). As no partition coefficient is available for TCMTB no MPC_{soil} can be derived.

Table 4.2. MPC_{soil} for antifouling substances

Compound	**Method used**	**MPC_{soil} (µg/kg)**	**NC_{soil} (ng/kg)**	**K_p[a] (l/kg)**
Irgarol 1051	EP	1.4	14	58
Dichlofluanid	NOEC/50	190	1900	-
Ziram	EP	0.011	0.11	1.16
Chlorothalonil	NOEC/50	10	100	-
TCMTB	-	-	-	-

[a] Calculated from K_{oc}, assuming standard soil

5 Discussion

5.1 Occurrence

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

Recent studies show that 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 ng/l, 41 ng/l 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 (R. Steen, VU, personal communication; Hall et al., 1999). In the Netherlands, along a salinity gradient in the Scheldt, concentrations between 1 and 10 ng/l were found (Steen et al., 1997). Although the Scheldt is a dense shipping lane, concentrations encountered in harbors are expected to exceed these values, in conformity with the aforementioned international studies. The measured concentrations are at a same level as the derived MPC. It is concluded that the species composition and thereby ecosystem functioning is not considered protected.

To estimate the environmental concentration 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 report should be combined with information on predicted concentrations.

Van Hattum et al. (1999) developed the ‘MAM-PEC model’, which can be used to predict environmental concentrations of antifouling substances in a number of ‘typical’ environments (harbour, estuary, marina, open sea, open sea, shipping lane). The model takes into account emission factors (e.g. leaching rates, shipping intensities), environmental parameters, and compound-related physico-chemical properties. A prediction of future environmental concentrations of the various antifouling chemicals is hampered by the lack of knowledge on their future market-share. Therefore an application factor was introduced, the percentage of ships within a length category to which a product is applied. The model was used to calculate expected concentrations for TBT, Irgarol and Cu. The predicted concentrations appeared to be comparable to concentrations measured in monitoring studies (Van Hattum et al., 1999).

5.2 Effects observed in the field

Field or mesocosm studies were searched for in the open literature for Irgarol 1051, dichlofluanid, ziram and TCMTB. The databases BIOSIS (1985-1996) and CCsearch (1996-2000) were used for literature search.

Ernst et al. (1991) published a field study on the use of chlorothalonil in a pond ecosystem. Effects as observed in the field study were lower than expected based upon laboratory data. Water samples were taken on the water surface for analysis directly after spray. Processes such as sorption to sediment, degradation, dilution, volatilisation and so forth diminished the exposure to chlorothalonil. The diminished exposure explains the differences observed in laboratory and field data.

5.3 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, which leads 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. Otherwise, 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 acute toxicity data as a basis to derive MPCs. The mostly used end-point in an acute test is lethality, while other endpoints such as growth and reproduction are used in chronic tests. Acute data can also be extrapolated with species sensitivity distributions. However the results should be extrapolated to other type of 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. These extrapolation factors are not generally available in the open literature. Therefore, we prefer to base the MPC on chronic data if available.

An extrapolation based on acute data can be used when compounds are instable. The compounds studied here, certainly if applied as antifouling agent, have a continuous input in the environment and thus can be monitored.

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

5.3.1 Irgarol 1051

Klisenko and Vekhstein (1971) found that Irgarol 1051 was hydrolysed relatively fast, especially at low pH (DT50=0.01 d at pH 3.8, DT50=0.38 d at pH 5.7, DT50=5 d at pH 7.0 and DT50=18 d at pH 8.0). More recent studies, however, 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 $ZnCl_2$ (Liu et al., 1999).
It is concluded that 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 and the compound is not readily biodegraded (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. The metabolite was stable under the test conditions (Liu et al., 1997). Ciba-Geigy (1995) reported a half-life of Irgarol 1051 in sediments of 100-200d.
Taken together, the interpretation of data on ecotoxicology and environmental fate of Irgarol 1051 used to derive an MPC is not hampered by a lack of stability.

5.3.2 Dichlofluanid

Dichlofluanid is unstable in an alkaline aqueous environment, it undergoes hydrolysis to the principal metabolite dimethylaminosulphanilide (DMSA, MW = 200.26 g/mol, Figure 4.1.) At pH 7.7 –7.9 and 21°C a DT50 was found of approximately 2 h (Jansma and Linders, 1992). A second hydrolysis study performed in buffered solutions, yielded DT50 values of 15.3 d at pH 4, 19 h at pH 7 and <10 minutes at pH 9 (Jansma and Linders, 1992). No parent compound could be detected at pH 9 even if analysis was performed immediately. The half-life of the parent compound is clearly depending on the pH.
As can be found in Table 2.1. of Appendix 2, in the static toxicity tests concentrations dropped fast from a nominal concentration 0.05 to 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. As the pH during the toxicity tests is between 7 and 8 (Table 2.1. in appendix 2), DT50 will in between 19 h and <10 minutes, according to the aforementioned information. Toxicity was observed however, and can presumably be attributed to the products formed (DMSA). The most critical toxicity study (based on nominal concentrations) to base an MPC upon, was a 96h acute toxicity test with fish performed at a pH 7.2-8.0. Although the toxicity was expressed as nominal concentration, also analyses were performed. DMSA was not analysed in the toxicity studies.
It is recommended to base an MPC for dichlofluanid on the important metabolites. Because of its instability no MPC is derived for the parent compound. Whenever dichlofluanid is measured in the field, this point to a severe situation that probably results in toxicity.

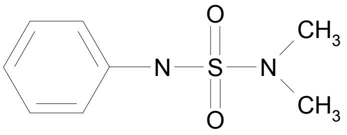


Figure 4.1. Structural formula of DMSA

5.3.3 Chlorothalonil

Laboratory investigations of the photodegradation by direct photolysis (lambda > 290 nm) show that the photolysis of chlorothalonil in water is low (Millet et al., 1998; Peñuela and Barceló, 1998). Extrapolating the laboratory data to half-lives in the environment yielded values of 30 to 200d (Millet et al., 1998).
In soil, chlorothalonil is degraded by microbial action. Motonaga et al. (1998) and others before them, showed that after first application the DT50 in soil is relatively short (approximately 2 weeks), but after repeated application the dissipation rate decreases which was explained by the toxicity of the metabolite 4-hydroxy-2,5,6-trichloroisophtalonitrile (TPN-OH) to the microbes. TPN-OH was proved to be stable in soil (Van der Pas et al., 1999). In situ (Dutch flower bulb plants) the amounts of TPN-OH found in soil correspond to up to 16% of the cumulative dose of chlorothalonil that was used (Van der Pas et al., 1999). As the MPC 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 MPCs.

5.3.4 Ziram

Ziram is not persistent. A study of Brisou and Denis (1969) reports hydrolysis DT50 values at 18-20 °C of 0.2 h (pH 3.8), 9.1 h (pH 5.7), 5 d (pH 7) and 18 d (pH 8). Again, hydrolysis is dependent on pH. A major product after hydrolysis 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.

5.3.5 TCMTB

TCMTB appears to be metabolised in soil under aerobic conditions (Fathulla, 1994). DT50 reported at 20°C is 3.4 d. 2-Mercaptobenzothiazole (MBT) appears the most important metabolite, the DT50 of the metabolite under the same circumstances is 1 d. In a water and sediment system, DT50 is 3 d. (Van der Pol and van der Linde, 1999).

Hydrolysis rates appear to depend on pH; at pH 5 and 7 DT50s are longer than 35 d, at pH 9 DT50 is 2-3 d (Van der Pol and van der Linde, 1999). TCMTB is rapidly photolysed in water, reported DT50s are 1.5 and 3.9 h, and main metabolite is again 2-mercaptobenzothiazole. 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 MPC derived is based on a study where the actual concentration is measured.

5.4 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. 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 MPC for the toxicity of copper and zinc was covered by Crommentuijn et al. (1997b). 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 MPC for ziram. As zinc is very commonly monitored, an exceeding of the MPC for zinc will be observed separately.

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47. prof. dr. N. van Straalen (VU)
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Appendix 2. Information on the aquatic toxicity of the antifoulings

Legend

L(E)C50$_{\text{aqua min}}$	lowest short term test result showing 50% effect or mortality
MPC	maximum permissible concentration
MPC$_{\text{chronic}}$	MPC derived using assessment factors, based solely on chronic test results
MPC$_{\text{short term}}$	MPC derived using assessment factors, based solely on short term test results
NOEC	no observed effect concentration
NOEC$_{\text{aqua min}}$	lowest no observed effect concentration
Organism	species used in the test, if available followed by age, size, weight or life stage
A	Y = test substance analyzed in test solution N = test substance not analyzed in test solution or no data
Test type	S = static, R = static with renewal, F = flow through
Test water	a.m. = artificial medium, a.s.w. = artificial seawater, n.f.s = natural filtered seawater, r.t.w. = reconsituted tap water (+additional salts)
Test substance purity	percentage active ingredient
Exposure time	h = hours, d = days, w = weeks, m = months, min. = minutes
Results	> and ≥ values = highest concentration used in the test

Table 1.1. Acute toxicity of Irgarol 1051 to freshwater organisms

Organism	Size (g)	A	Test-Type	Purity	Test-water	pH	Hardness	Exp. time	Criterion	End-point	Result µg/l	Notes	Reference
Algae													
Selenastrum capricornutum		N	S		a.m.	7.8-8.3		72 h	EC50	g	4.2	1	Jongbloed & Luttik, 1996
Crustacea													
Daphnia magna		Y	S	≥ 97%		7.7		24 h	EC50	i	49000		Jongbloed & Luttik, 1996
Pisces													
Brachydanio rerio	0.09-0.16	N		≥ 97%				96 h	LC50	s	4000		Jongbloed & Luttik, 1996
Lepomis macrochirus	0.18-0.40	N		≥ 97%				96 h	LC50	s	2900		Jongbloed & Luttik, 1996
Leuciscus idus		Y	S	≥ 97%		7.8		48 h	LC50	s	6200		Jongbloed & Luttik, 1996
Oncorhynchus mykiss	1.1-2.1	N		≥ 97%				96 h	LC50	s	940		Jongbloed & Luttik, 1996
Oncorhynchus mykiss	0.5-1.4	N		≥ 97%				96 h	LC50	s	860		Jongbloed & Luttik, 1996

1 Effect concentration recalculated.

Table 1.2. Acute toxicity of Irgarol 1051 to saltwater organisms

Organism	Size	A	Test-type	Purity	Test-water	pH	Salinity o/oo	Exp. time	Criterion	End-point	Result µg/l	Notes	Reference
Macrophyta													
Enteromorpha intestinalis	Zoo-spores			>97%	a.m.			144 h	NOEC	g	0.022	1	Scarlett et al., 1997
Enteromorpha intestinalis	mature			>97%	a.m.			72 h	EC50	fotosyn-thesis	2.5		Scarlett et al., 1997
Zostera marina		N	R	>97%	seaw.		35‰	10 d	LOEC	g	10		Scarlett et al., 1997
Crustacea													
Mysidopsis bahia	2-4 d	N	S	98.6%		7.5-7.7	28-34‰	96 h	LC50	s	430		Jongbloed & Luttik, 1996
Pisces													
Cyprinodon variegatus	0.22 g	Y	F	98%		7.8		96 h	LC50	s	3400		Jongbloed & Luttik, 1996
Menidia beryllina		Y	S	98%	sea w.	8	2‰	96 h	LC50	s	1770		Jongbloed & Luttik, 1996

1 Effect concentration recalculated

Table 1.3. Chronic toxicity of Irgarol 1051 to freshwater organisms

Organism	Size	A	Test-Type	Purity	Test-water	pH	Hardness	Exp. Time	Criterion	End-point	Result µg/l	Notes	Reference
Algae													
Anabaena flos-aquae		Y	S	98.2%	a.m.	7.5		120 h	NOEC	G	0.54		Jongbloed & Luttik, 1996
Navicula pelliculosa		Y	S	98.2%	a.m.	7.6		120 h	EC10	G	0.017	1	Jongbloed & Luttik, 1996
Scenedesmus subspicatus		Y	S			7.7-9.6		72 h	NOEC	G	0.23		Jongbloed & Luttik, 1996
Selenastrum capricornutum		Y	S	98.2%	a.m.	7.5		120 h	NOEC	G	0.65		Jongbloed & Luttik, 1996
Macrophyta													
Lemna Gibba		Y	S	98.2%		7.9-9.4		14 d	NOEC	G	0.4		Jongbloed & Luttik, 1996
Pisces													
Oncorhynchus mykiss	e.l.s	Y		98%		7.8		98 d	LOEC	G	<29	2	Jongbloed & Luttik, 1996

1 Effect concentration recalculated.

2 No effects on hatch, fry survival or growth were observed in the study, yielding LOEC >37 µg/l. In a preliminary study all concentrations showed significant reduction and a LOEC <29 µg/l was determined. These results are combined.

Table 1.4. Chronic toxicity of Irgarol 1051 to saltwater organisms

Oganism	A	Test-Type	Purity	Test-Water	pH	Salinity o/oo	Exp. time	Criterion	End-Point	Result µg/l	Reference
Algae											
Skeletonema costatum	Y	S	98.2%	a.m.	8.3	30 ‰	120 h	NOEC	G	0.14	Jongbloed & Luttik, 1996
Crustacea											
Mysidopsis bahia	Y	F	≥ 97%		7.5-8.3	20 ‰	28 d	NOEC	G	110	Jongbloed & Luttik, 1996

Table 1.5. Acute toxicity of Irgarol 1051 to freshwater organisms: rejected tests

Organism	A	Test-type	Purity	Test-water	pH	Hardness	Exp. time	Criterion	End-point	Result µg/l	Reference
Crustacea											
Daphnia magna	Y	S	≥ 97%		7.8		48 h	EC50	I	8100	Jongbloed & Luttik, 1996

Rejected as test compound did not dissolve at t=0 in some test concentrations.

Table 2.1. Acute toxicity of dichlofluanid to freshwater organisms

Organism	Size (g)	A	Test-type	Purity	Test-water	pH	Hardness (mg $CaCO_3$/l)	Exp. Time	Crite-rion	End-point	Result mg/l	Notes	Reference
Crustacea													
Daphnia magna		N	S	94.1%	a.m.	~ 8		48 h	LC50	s	>1.8		Heimbach, 1983
Daphnia magna		Y	F	88.2	well water	8.2-8.3	225-275	48 h	LC50		0.37	3	Frazier et al., 1986
Pisces													
Lepomis macrochirus	1.5 ± 0.4	Y	F	88.5	well water	7.9-8.2	225-275	96 h	LC50		0.025	4	Swigert et al., 1986[a]
Leuciscus idus melanotus	1.5-1.8	A	S	90%	a.m.	7.2-8.0	255	96 h	LC50	s	0.12	1	Anonymus, 1980
Leuciscus idus melanotus	1.5	A	R	90%	a.m.	7.5-8.0	255	96 h	LC50	s	0.12	2	Jansma and Linders, 1992
Oncorhynchus mykiss	0.6-1.5	A	S	90%	a.m.	7.2-8.0	255	96 h	LC50	s	0.05	1	Anonymus, 1979
Oncorhynchus mykiss	0.35±0.071	Y	F	88.5	well water	8.0-8.2	225-275	96 h	LC50		0.011		Swigert et al., 1986[b]

1 Result based on nominal values: the parent compound was measured in test water without fish: a nominal concentration of 1 mg/l decreased to 0.34 mg/l after 2 h and to <0.02 (detection limit) after 48 h.

2 Result based on nominal values: the parent compound was measured in test water without fish: a nominal concentration of 1 mg/l decreased to 0.49 mg/l after 5 min, to 0.34 mg/l after 2 h, to 0.11 mg/l after 24 h and to <0.02 (detection limit) after 48 h.

3 Result based on actual concentrations:recovery is 50 ± 4% (average) of nominal at t=48 h, due to hydrolysis of analyte.

4 All test concentrations showed mortality throughout the test.

Table 2.2. Chronic toxicity of dichlofluanid to freshwater organisms

Organism	A	Test-type	Purity	Test-water	pH	Hardness	Exp. time	Crite-rion	End-point	Result mg/l	Notes	Reference
Crustacea												
Daphnia magna	Y	R	91.4%	a.m.	8.0-8.2		24 d	NOEC	r	0.04	1	Jansma and Linders, 1992
Pisces												
Oncorhynchus mykiss	Y	F	91.4	a.m.	6.6-7.6	40-60	21 d	LC50	m	0.016	2	Grau, 1989

1 parent compound could not be analyzed before renewal due to hydrolysis. 10 renewals were performed during the testperiod.

2 NOEC can not be determined from these data.

Table 2.3. Acute toxicity of dichlofluanid to freshwater organisms: rejected

Organism	Size (g)	A	Test-Type	Purity	Test-water	pH	Hardness mg $CaCO_3$/l	Exp. time	Crite-rion	End-point	Result mg/l	Notes	Reference
Pisces													
Oncorhynchus mykiss	0.84	A	R	90%	a.m.	7.5-8.0	255	96 h	LC50	s	0.02-	1	Jansma and Linders, 1992

0.05

1 no effect concentration established, 2 concentrations 0.02 and 0.05 mg/l.

Table 2.4. Chronic toxicity of dichlofluanid to freshwater organisms: rejected

Organism	A	Test-Type	Purity	Test-water	pH	Hardness	Exp. time	Crite-rion	End-point	Result mg/l	Notes	Reference
Algae												
Scenedesmus subspicatus	N	S	86.2%	a.m.	7.5-8.5		96 h	NOEC	g	≥1	1	Heimbach, 1985

1 only two concentrations tested: 0.1 and 1.0 mg/l, 23°C.

Table 2.5 Whole body bioconcentration factors of dichlofluanid for fish, based on wet weight

Organism	Test-type	Purity	Test-water	pH	Hardness mg $CaCO_3$/l	Exp. time	Conc. µg/l	equil. after	BCF	Notes	Reference
Lepomis macrochirus	F	99.0	a.m.	7.2 ± 0.2	48	28 d	4.4 ± 0.2		72 ± 14	1	Grau, 1991

1 concentration: all ^{14}C-radioactivity is assigned to dichlofluanid, temperature: 22°C

Table 2.6. Acute toxicity of DMSA to freshwater organisms

Organism	A	Test-type	Purity	Test-water	pH	Hardness (mg $CaCO_3$/l)	Exp. time	Crite-rion	End-point	Result mg/l	Notes	Reference
Crustacea												
Daphnia magna	Y	S	98.4%	a.m.	7.7-7.9	275	48 h	NOEC	imm	≥96	1	Caspers, 1997[b]

1 one concentration tested.

Table 2.7. Acute toxicity of DMSA to freshwater organisms

Organism	Size (g)	A	Test-Type	Purity	Test-water	pH	Hardness (mg $CaCO_3$/l)	Exp. time	Crite-rion	End-point	Result mg/l	Notes	Reference
Algae													
Scenedesmus subspicatus		Y	S	98.9%	a.m.	8.0-10.4		72 h	NOEC	inhib	≥98	1	Caspers, 1997[a]
Pisces													
Oncorhynchus myliss	1.26±0.28	Y	R	98%	a.m.	6.9-7.5	40-60	21 d	NOEC	g, m	≥10	2	Grau, 1990
									LOEC	g, m	≤100		

1 one concentration tested.
2 two concentrations tested, no effects at 10 mg/l, effect on growth and mortality significantly different from control at 100 mg/l.

Table 3.1. Acute toxicity of ziram to freshwater organisms

Organism	Stage	A	Test-type	Purity	Test-water	pH	Hard-ness	Exp. time	Crite-rion	End-point	Result mg/l	Reference
Algae												
Chlorella pyrenoidosa			S	≥95%	a.m.			96 h	EC50	g	1.2	Van Leeuwen et al., 1985a
Selenastrum capricornutum		Y	S	98%	a.m.	7.5-8.8		96 h	EC50		0.066	European Commision, concept
Crustacea												
Daphnia magna		Y	S	98.9%	a.m.	8.0		48 h	EC50		0.048	Van Leeuwen et al., 1985b
Insecta												
Culex fatigans	2nd instar							24 h	LC50	s	0.18	Strufe, 1968
Culex fatigans	3rd instar							24 h	LC50	s	0.55	Strufe, 1968
Culex fatigans	4rd instar							24 h	LC50	s	1.31	Strufe, 1968
Culex fatigans	pupae							24 h	LC50	s	8.1	Strufe, 1968
Mollusca												
Dreissena polymorpha		N	S		a.m.	8.5		5 d	LC50	s	1.8	Hoestlandt, 1972
Pisces												
Carassius auratus		N	S					96 h	LC50	s	2.3	Tibosch et al., 1993
Carassius auratus				≥99%				48 h	LC50	s	0.095	Nischiuchi, 1974
Cyprinus carpio				≥99%				48 h	LC50	s	0.075	Nischiuchi, 1974
Lepomis macrochirus	1.01 ± 0.4 g	Y	F	98,9%	a.m.	7.5-7.7		96 h	LC50	s	0.0097	European Commision, concept
Misgurnus anguillacaudatus				≥99%				48 h	LC50	s	0.15	Nischiuchi, 1974
Oryzias latipes				≥99%				48 h	LC50	s	0.056	Nischiuchi, 1974
Poecilia reticulata			R	≥95%	a.m.			96 h	LC50	s	0.75	Van Leeuwen et al., 1985a
Oncorhynchus mykiss		N	S					96 h	LC50	s	0.3	Tibosch et al., 1993
Oncorhynchus mykiss	3.22 ± 1.2 g	Y	R	98.9%	a.m.	7.6-7.9		96 h	LC50	s	1.78	European Commision, concept

Table 3.2. *Acute toxicity of ziram to saltwater organisms*

Organism	A	Test-type	Purity	Test-water	pH	Salinity o/oo	Exp. time	Crite-rion	End-point	Result mg/l	Reference
Bacteria											
Vibrio fisheri	N	S	≥95%				15 min	EC50		0.15	Van Leeuwen et al., 1985a

Table 3.3. *Chronic toxicity of ziram to freshwater organisms*

Organism	Stage	A	Test-type	Purity	Test-water	pH	Hardness mg $CaCO_3$/l	Exp. time	Crite-rion	End-point	Result mg/l	Notes	Reference
Crustacea													
Daphnia magna	<24 h	N	R	≥95%	lake w.	8.1	225	21 d	LC50	s	0.011		Van Leeuwen et al., 1985b
Daphnia magna	<24 h	N	R	≥95%	lake w.	8.1	225	21 d	NOEC	s	0.0033	1	Van Leeuwen et al., 1985b
Pisces													
Oncorhynchus mykiss	e.l.s.		R	≥90%	a.m.	7.5-7.9	50	60 d	LC50	s	0.002		Van Leeuwen et al., 1985c
Oncorhynchus mykiss	e.l.s.		R	≥90%	a.m.	7.5-7.9	50	60 d	NOEC	s	0.0006	1	Van Leeuwen et al., 1985c

1 the NOEC is calculated by LOEC/3.

Table 4.1. Acute toxicity of chlorothalonil to freshwater organisms

Organism		A	Test type	Purity	Test water	pH	Hardness mg CaCO3/l	Exp. Time	Crite-rion	Type effect	Result mg/l	Reference
Crustacea												
Astacopsis gouldi	0.1 g	Y	S	>=98%	nw	6.5-7.0	-	96 h	LC50	s	0.012	Davies et al., 1994
Daphnia magna	< 24 h	Y	S	99.2%	-	7.1	150-200	48 h	EC50	i	0.054	Montforts, 1999
Daphnia magna	< 24 h	N	S	96%	-	7.2-7.4	60	48 h	EC50	i	0.117	Montforts, 1999
Daphnia magna	< 24 h	N	S	98.8%	-	7.8-8.2	172	48 h	EC50	i	0.115	Montforts, 1999
Daphnia magna	< 24 h	Y	S	98.1%	-	7.6-7.9	-	24 h	LC50	s	0.195	Montforts, 1999
Parataya australiensis	0.1 g	Y	S	>=98%	nw	6.5-7.0	-	96 h	LC50	s	0.016	Davies et al., 1994
Pisces												
Cyprinus carpio	1.7 g	Y	F	99.2%	-	7.4	150-200	96 h	LC50	s	0.06	Montforts, 1999
Galaxias auratus	7-11 g	Y	F	>=99%	-	-	-	96 h	LC50	s	0.029	Davies & White, 1985
Galaxias maculatus	7-10 g	Y	F	>=99%	-	-	-	96 h	LC50	s	0.016	Davies & White, 1985
Galaxias truttaceus	8-20 g	Y	F	>=99%	-	-	-	96 h	LC50	s	0.019	Davies & White, 1985
Ictalurus punctatus	1.77 g	N	S	96%	-	6.7-7.6	47	96 h	LC50	s	0.047	Montforts, 1999
Ictalurus punctatus	40-80 g	N	F	99%	tap	7.0-7.2	30	96 h	LC50	s	0.052	Gallagher et al., 1992
Lepomis macrochirus	1.0 g	N	S	96%	-	6.8-7.7	44	96 h	LC50	s	0.059	Montforts, 1999
Oncorhynchus mykiss	1.3 g	Y	F	99.2%	-	7.1	150-200	96 h	LC50	s	0.017	Montforts, 1999
Oncorhynchus mykiss	3.5-4g	N	S	97.8%	tap	7.8±0.2		96 h	LC50	s	0.076	Ernst et al., 1991
Oncorhynchus mykiss	1.0 g	N	S	96%	-	6.5-7.7	44	96 h	LC50	s	0.043	Montforts, 1999

Table 4.2. Acute toxicity of chlorothalonil to saltwater organisms

Organism		A	Test type	Purity	Test water	pH	salinity o/oo	Exp. time	Crite-rion	Type effect	Result mg/l	Reference
Crustacea												
Penaeus duorarum	1.1g	N	S	96%	-	7.4-7.7	22	96 h	LC50	s	0.162	Montforts, 1999
Penaeus duorarum		N	F	tech	-	-	27	48 h	EC50		0.320	Mayer, 1987
Mollusca												
Crassostrea virginica	2.6 g	Y	F	96%	-	8.0-8.2	22	96 h	EC50	g	0.005	Montforts, 1999
Crassostrea virginica		N	F	tech.	-	-	27	96 h	EC50		0.026	Mayer, 1987
Pisces												
Cyprinodon variegatus	0.5 g	N	S	96%	-	7.9-8.1	24	96 h	LC50	s	0.033	Montforts, 1999

Leiostomus xanthurus	N	F	tech.	-	-	22	48 h	LC50	s	0.032	Mayer, 1987

Tabel 4.3. Chronic toxicity of chlorothalonil to freshwater organisms

Organism	**Stage**	**A**	**Test type**	**Purity**	**Test water**	**pH**	**Hardness** mg CaCO3/l	**Exp. time**	**Crite-rion**	**End-point**	**Result mg/l**	**Reference**
Algae/Chlorophyta												
Pseudokirchneriella subsp.		N	S	97.9%	-	7.4-8.3	-	96 h	NOEC	g	0.05	Montforts, 1999
Scenedesmus subspicatus		Y	S	99.2%	-	7.2-7.7	-	96 h	NOEC	g	0.06	Montforts, 1999
Anabaena flos-aquae		N	S	98.1%	-	7.0-7.6	-	120 h	NOEC	g	0.02	Montforts, 2001
Navicula pelliculosa		N	S	98.1%	-	7.7-8.7	-	120 h	NOEC	g	0.0035	Montforts, 2001
Plants												
Lemna gibba		Y	SS	98.1%	-	4.6-5.8	-	72 d	NOEC	g	0.29	Montforts, 2001
Crustacea												
Daphnia magna	< 24 h	Y	F	98.8%	-	7.8-8.2	172	21 d	NOEC	r	0.035	Montforts, 1999
Daphnia magna		Y	SS	99.2%	-	7.0-7.4	150-200	21 d	NOEC	s	0.0006	Montforts, 1999
Daphnia magna		Y	SS	99.2%	-	7.0-7.4	150-200	21 d	NOEC	r	0.019	Montforts, 1999
Daphnia magna	F0 < 24 h	Y	F	98.8%	-	7.8-8.2	172	21+21 d	NOEC	r	0.035	Montforts, 1999
Insecta												
Chironomus riparius	1st instar	N	S	98.1%	-	6.2-8.4	-	28 d	NOEC	r	0.125	Montforts, 1999
Pisces												
Pimephales promelas	e.l.s.	Y	F	96%	-	6.5-7.3	-	45 w	NOEC	r	0.003	Montforts, 1999
Oncorhynchus mykiss	3.5 g	Y	F	99.2%	-	7.1	150-200	21 d	NOEC	g	0.0069	Montforts, 1999

Tabel 4.4. Chronic toxicity of chlorothalonil to freshwater organisms: rejected tests

Organism	**A**	**Test type**	**Purity**	**Test water**	**pH**	**Hardness** mg CaCO3/l	**Exp. time**	**Crite-rion**	**End-point**	**Result mg/l**	**Reference**
Chlorella pyrenoidosa	N	S	-	-	-	-	150 h	NOEC	g	0.0001	Montforts, 1999
Chlamydomonas dysos.	N	S	-	-	-	-	150 h	NOEC	g	0.0001	Montforts, 1999
Ulothrix dpp.	N	S	-	-	-	-	150 h	NOEC	g	0.0001	Montforts, 1999
Algae/Cyanophyta											
Anabaena variabilis	N	S	-	-	-	-	150 h	NOEC	g	< 0.0001	Montforts, 1999
Oscillatoria spp.	N	S	-	-	-	-	150 h	NOEC	g	0.00001	Montforts, 1999
Mycrocystis spp.	N	S	-	-	-	-	150 h	NOEC	g	<0.0001	Montforts, 1999

Table 4.5.Chronic toxicity of chlorothalonil to saltwater organisms: rejected tests

Organism	**Stage**	**A**	**Test type**	**Purity**	**Test water**	**pH**	**salinity o/oo**	**Exp. time**	**Crite-rion**	**End-point**	**Result mg/l**	**Reference**
Crustacea												
Mysidopsis bahia	< 24 h	Y	F	98%	-	7.7-8.0	31-33	28 d	NOEC	r	0.00083	Montforts, 1999

Table 5.1. Chronic toxicity of TCMTB to freshwater organisms

Organism	Stage	A	Test-type	Purity	Test-water	pH	Hardness mg $CaCO_3$/l	Exp. time	Crite-rion	End-point	Result µg/l	Notes	Reference
Crustacea													
Daphnia magna	<24 h	Y	F	84%		8.2		21 d	NOEC	s	3.8		Van der Pol & Van der Linde, 1999

Table 5.2. Acute toxicity of TCMTB to freshwater organisms

Organism	Stage	A	Test-Type	Purity	Test-water	pH	Hardness mg/l $CaCO_3$	Exp. time	Crite-rion	End-point	Result mg/l	Reference
Crustacea												
Daphnia magna	<24 h	Y	F	≥95%	a.m.	8.1-8.2	170-180	48 h	EC50	s	0.024	Van der Pol & Van der Linde, 1999
Pisces												
Oncorhynchus mykiss	0.76 g	Y	F	98.8%		6.8-7.1	42-44	96 h	LC50	s	0.021	Van der Pol & Van der Linde, 1999

Appendix 3. Information on the soil or sediment toxicity of the antifoulings

Legend

L(E)C50$_{\text{aqua min}}$	lowest short term test result showing 50% effect or mortality
MPC	maximum permissible concentration
MPC$_{\text{chronic}}$	MPC derived using assessment factors, based solely on chronic test results
MPC$_{\text{short term}}$	MPC derived using assessment factors, based solely on short term test results
NOEC	no observed effect concentration
NOEC$_{\text{aqua min}}$	lowest no observed effect concentration
Organism	species used in the test, if available followed by age, size, weight or life stage
A	Y = test substance analyzed in test solution N = test substance not analyzed in test solution or no data
Test type	S = static, R = static with renewal, F = flow through
Test water	a.m. = artificial medium, a.s.w. = artificial seawater, n.f.s = natural filtered seawater, r.t.w. = reconsituted tap water (+additional salts)
Test substance purity	percentage active ingredient
Exposure time	h = hours, d = days, w = weeks, m = months, min. = minutes
Results	> and ≥ values = highest concentration used in the test

Table 1.1. Chronic toxicity of dichlofluanid to soil organisms: microbial processses

Organism	Soil type	pH	o.m. (%)	Clay (%)	Temp (°C)	Exp time	Crite-rion	Result test soil (mg/kg d.w)	Result stand. soil (mg/kg d.w)	Endpoint	Reference
Nitrification	sandy loam	5.3	1.4		20	56 d	EC9	1.3	9.3	inhib	Jansma & Linders, 1992
Nitrification	sandy loam	5.3	1.4		20	56 d	EC21	13	92.9	inhib	Jansma & Linders, 1992
Nitrification	silt loam	5.4	4.4		20	56 d	NOEC	≥1.3	≥3.0	inhib	Jansma & Linders, 1992
Nitrification	silt loam	5.4	4.4		20	56 d	EC13	13	29.5	inhib	Jansma & Linders, 1992

Table 1.2. Chronic toxicity of dichlofluanid to soil organisms

Organism	Stage	Soil type	pH	o.m. (%)	Clay (%)	Temp (°C)	Exp time	Crite-rion	Result test soil (mg/kg d.w)	Result stand. soil (mg/kg d.w)	End-point	Notes	Reference
Oligochaeta													
Eisenia fetida	adult	Art. soil	7			22±1	28 d	LC50	>1000	-	s	1	Jansma & Linders, 1992
Eisenia fetida	adult	Art. soil	5.8			20±1	14 d	LC50	>913	-	s	2	Jansma & Linders, 1992
Eisenia fetida	adult	Art. soil	5.8			20±1	14 d	NOEC	288	-	s	2	Jansma & Linders, 1992

Table 2.1. Chronic toxicity of ziram to soil organisms: microbial processses

Organism	Soil type	pH	o.m. (%)	Clay (%)	Temp (°C)	Exp time	Crite-rion	Result test soil (mg/kg d.w)	Result stand. soil (mg/kg d.w)	Endpoint	Notes	Reference
sulfur oxidation	Alluvial	6.3	0.65	-	28±2	50 d	EC10	19	292	inhib		Ray, 1991

Table 2.2. Chronic toxicity of ziram to soil organisms: microbial processes; rejected test

Process	Soil type	PH	o.m. (%)	Clay (%)	Temp (°C)	Exp time	Crite-rion	Result test soil (mg/kg d.w).	Result stand. soil (mg/kg d.w).	Type of effect	Note	Reference
Nitrification	sandy loam					150 d	EC50	<620		inhib	1	Jacques, 1959
Nitrification	sandy loam					150 d	NOEC	<62		inhib	1	Jacques, 1959

[1] two concentrations tested, at 62 mg/kg a slight lag in nitrification was observed, at 620 mg/kg NO_3-N was not detected until day 150. Test rejected as only two concentrations are tested.

Table 2.3. Acute toxicity of ziram to sediment organisms; rejected test

Organism	Age	A	Test-Type	Purity	Test-Water	pH	Hard-ness	Exp. time	Crite-rion	Result mg/l	Endpoint	Reference
Amphibia												
Bufo bufo	30 d							48 h	LC50	0.36	s	Nischiuchi, 1974

Too little information on type of test

Table 3.1. Acute toxicity of chlorothalonil to soil: microbial processes and enzyme activity

Process	Soil Type	pH	o.m. (%)	Clay (%)	T (°C)	Exp. time	Crite-rion	Result test soil (mg/kg dw)	NOEC standard soil (mg/kg dw)	Endpoint	Notes	Reference
Microbial processes												
Nitrification	--	6.4	5.3	39	24	6 h	EC25	50	32	Inhib	1	Hansson et al., 1991
	Loamy sand	7.0	1.3	-	22	3 d	EC22	1.6	2.7	Max. inhibition	2	Montforts, 1999
	Loamy sand	7.0	1.3	-	22	3 d	EC88	20		Max. inhibition	2	Montforts, 1999
	Silty loam	6.8	3.6	-	22	3 d	EC30	1.8	1.7	Max. inhibition	2	Montforts, 1999
	Silty loam	6.8	3.6	-	22	3 d	EC31	19	17.5	Max. inhibition	2	Montforts, 1999
Respiration	Sandy loam	7.6	1.5	10	5	18 h	EC47	100	165		2	Rashid & Mayaudon, 1974
aer. Nitrogen fixation	Loamy sand	7.0	1.3	-	22	6 h	EC43	1.6	2.7	Max. inhibition	2	Montforts, 1999
	Loamy sand	7.0	1.3	-	22	6 h	EC100	20		Max inhibition	2	Montforts, 1999
	Silty loam	6.8	3.6	-	22	6 h	EC55	1.8	0.5	Max. inhibition	2	Montforts, 1999
	Silty loam	6.8	3.6	-	22	6 h	EC200 +	19		Stimulation	2	Montforts, 1999
aner. Nitrogen fixation	Loamy sand	7.0	1.3	-	22	6 h	EC90 +	1.6		Stimulstion	2	Montforts, 1999
	Loamy sand	7.0	1.3	-	22	6 h	EC99	20		Max inhibition	2	Montforts, 1999
	Silty loam	6.8	3.6	-	22	6 h	NOEC	1.8	5		2	Montforts, 1999
	Silty loam	6.8	3.6	-	22	6 h	EC400 +	19		Stimulation	2	Montforts, 1999
Enzyme activity												
Amylase	Sandy loam	5.5	1.8	-	28	1 d	EC30	10	17		2	Tu, 1993
Dehydrogenase	Sandy loam	5.5	1.8	-	28	4 d	NOEC	>10	> 50		2	Tu, 1993
Invertase	Sandy loam	5.5	1.8	-	28	1 d	EC25	10	17		2	Tu, 1993
Phosphatase	Sandy loam	5.5	1.8	-	28	2 h	NOEC	> 10	> 50		2	Tu, 1993
Urease	Sandy loam	5.5	1.8	-	28	2 d	NOEC	> 10	> 50		2	Tu, 1993

1: added as a formulation, two concentrations tested (triplicate), 25 mg/kg was not significantly different from the control.

2: only one concentration is tested.

3: 9% stimulation was seen after 2 h (considered to be equal to the NOEC).

Table 3.2. Chronic toxicity of chlorothalonil to soil: microbial processes and enzyme activity

Process	Soil Type	pH	o.m. (%)	Clay (%)	T (°C)	Exp. time	Crite-rion	Result test soil (mg/kg dw)	NOEC Stand. soil (mg/kg dw)	Endpoint	Notes	Reference
Microbial processes												
Nitrification	Sandy loam	7.6	1.8	-	28	1 w	NOEC	> 10	> 50		1	Tu, 1993
	Sandy loam	7.6	1.8	-	28	2 w	EC44	10	17		1	Tu, 1993
	Sandy loam	6.6	2.9	-	20	28 d	NOEC	4.4	15	Max. inhibition	1	Montforts, 1999
sulfur oxidation	Sandy loam	7.6	1.8	-	28	4 w	EC26	10	17		1	Tu, 1993
	Sandy loam	7.6	1.8	-	28	8 w	NOEC	>10	> 50		1	Tu, 1993
Respiration	Sandy loam	6.6	2.9	-	20	28 d	NOEC	4.4	15	CO2 evolution	1, 2	Montforts, 1999

1: only one concentration is tested.
2: 9% stimulation was seen after 2 h (considered to be equal to the NOEC).

Table 3.3. Chronic toxicity of chlorothalonil to soil species

Process	Soil Type	pH	o.m. (%)	Clay (%)	T (°C)	Exp. time	Crite-rion	Result test soil (mg/kg dw)	Result stand. soil (mg/kg dw)	End-point	Reference
Fungi											
Population growth	sandy loam	7.6	1.8	-	28	7 d	EC52	10	5	g	Tu, 1993
Bacteriophyta											
Population growth	sandy loam	7.6	1.8	-	28	7 d	EC29	10	17	g	Tu, 1993
Annelida											
Eisenia foetida		5.9	10	-	25	14 d	LC50	537	537	s	Montforts, 1999

Table 3.4. Toxicity of chlorothalonil to soil: rejected tests

Process	Soil Type	pH	o.m. (%)	Clay (%)	T (°C)	Exp. Time	Crite-rion	Result test soil (mg/kg dw)	NOEC Stand. soil (mg/kg dw)	Endpoint	Notes	Reference
Fungi												
cellulose decompostion	clay loam	7.1	--	--	13/25	5 wk	--	--	--	inhib	1	Suyama et al., 1993
Sporidesmium sclerotivorum	Loamy sand	--	--	--	21-24	8 wk	EC100	10	--	inhib	2	Adams and Wong, 1991

1: fomulation tested, effects are not quantified.
2: complete inhibition at 10 mg/kg was named ‘toxicity’.

Table 4.1. Chronic toxicity of TCMTB to soil organisms: microbial processes; rejected tests

Process	Soil type	PH	o.m. (%)	Clay (%)	Temp (°C)	Exp time	Crite-rion	Result test soil (mg/kg d.w).	Result stand. soil (mg/kg d.w).	Type of effect	Note	Reference
Biomass		6.7	1.71	--	--	6 m		--	--	Composition	1	Van der Pol and Van der Linde, 1999
Ammonification		6.7	1.71	--	--	6 m		--	--	Inhib	1	Van der Pol and Van der Linde, 1999
Enzymes		6.7	1.71	--	--	6 m		--	--	Inhib	1	Van der Pol and Van der Linde, 1999

1: technical TCMTB (79% pure) shows effects on compostion, ammonification and enzyme activity at the lowest test concentration (50 mg/kg soil) but data are presented graphically. Quantitative results can not be be derived from these data.

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