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Risk limits for boron, silver, titanium, tellurium, uranium and organosilicon compounds in the framework of EU Directive 76/464/EEC

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This investigation has been performed by order and for the account of the Directorate-General for Environmental Protection, Directorate for Chemicals, External Safety and Radiation, within the framework of project "Setting Integrated Environmental Quality Standards", project no. 601501.



Preface

This report contains results obtained in the framework of the project "Setting Integrated Environmental Quality Standards". The results have been discussed in the "Setting Integrated Environmental Quality Standards Advisory Group". The members are M. Beek and J. Hendriks (Institute for Inland Water Management and Waste Water Treatment), M. v.d. Weiden, D. Jonkers and S. Boekhold (Minstry of Housing, Spatial Planning and the Environment), J. Lourens (National Institute for Coastal and Marine Management), P. v. Beelen, T. Crommentuijn, M. Janssen, D. Sijm, J. Struijs (National Institute of Public Health and the Environment), W. van Tilborg (BMRO), J. van Wensem (Technical Soil Protection Committee), T. Brock and J. Deneer (DLO Staring Centre), S. Dogger (Health Council of the Netherlands), K. den Haan (BMRO), J. Faber (DLO Institute for Forestry and Nature Research), M. Koene (Stichting Natuur en Milieu), W. Tas (CTB), D. v. Wijk (BMRO) and W.F. ten Berge (BMRO).

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Samenvatting

In het kader van EU richtlijn 76/464 dienen de lidstaten van de Europese Unie milieukwaliteitsnormen af te leiden voor de stoffen die in deze richtlijn genoemd worden. Voor een aantal van deze stoffen waren tot nu toe geen Nederlandse milieukwaliteitsnormen beschikbaar. Daarom heeft het ministerie van VROM het RIVM verzocht om voor deze stoffen risicogrenzen (het Maximaal Toelaatbaar Risiconiveau en het Verwaarloosbaar Risiconiveau, afgekort MTR en VR) af te leiden, die vervolgens door het ministerie gebruikt kunnen worden om te voldoen aan haar verplichtingen zoals in de EU richtlijn gesteld. Het gaat hierbij om de volgende stoffen: boor, zilver, titanium, tellurium, uranium en organische siliciumverbindingen.

De organische siliciumverbindingen betreft een diverse groep verbindingen. Uit deze groep werd de - gezien het marktaandeel - meest relevante gekozen, namelijk de polydimethylsiloxanen. Van deze groep bleek alleen voor octamethyltetrasiloxaan (OCMTS) voldoende informatie beschikbaar te zijn om risicogrenzen te kunnen afleiden.

Het MTR voor metalen is de som van de Maximaal Toelaatbare Toevoeging (MTT) en het achtergrondgehalte in water, sediment of bodem (het VR is dan de Verwaarloosbare Toevoeging - afgekort VT - opgeteld bij het achtergrondgehalte; VT = MTT/100). Voor de meeste metalen kon wel een MTT afgeleid worden, maar waren onvoldoende gegevens beschikbaar om een achtergrondconcentratie vast te stellen voor Nederland. Voor geen enkel metaal kon een achtergrondgehalte in zoetwater, zoutwater, grondwater of sediment afgeleid worden, terwijl alleen voor titanium en uranium een achtergrondgehalte in bodem afgeleid kon worden. Voor titanium kon echter geen MTT in bodem bepaald worden omdat onvoldoende ecotoxicologische gegevens beschikbaar waren. Zodoende kon alleen voor uranium een MTR afgeleid worden, en dan nog alleen voor het compartiment bodem.

In Duitsland zijn achtergrondgehaltes voor boor in zoetwater van 0,01 tot 0,2 mg/l gemeten. Of deze niveaus ook voor Nederland gebruikt kunnen worden is onduidelijk. In de onderstaande tabellen zijn de resultaten weergegeven.

	MTT (μg/	MTT (µg/l) zoetwater zoutwater grondwate			achtergrondgehalte (µg/l)			MTR (µg/l)		
	zoetwater	zoutwater	grondwater	zoetwater	zoutwater	grondwater	zoetwater	zoutwater	grondwater	
boor	650 ^a	650 ^a	650 ^a	-	-	-	-	-	-	
tellurium	-	-	-	-	-	-	-	-	-	
titanium	-	-	-	-	-	-	-	-	-	
uranium	1.0^{b}	1.0^{b}	1.0^{b}	-	-	-	-	-	-	
zilver	0.082^{a}	1.2 ^a	0.082^{a}	-	-	-	-	-	-	
OMCTS	nvt	nvt	nvt	nvt	nvt	nvt	0.44 ^b	0.44 ^b	0.44 ^b	
а •		1. A111.	0 Clab -	a a da a da						

gebaseerd op de Aldenberg & Slob methode,

nvt niet van toepassing,

MTT, achtergrondgehalte en MTT zijn uitgedrukt als opgeloste concentratie.

b gebaseerd op de EPA methode,

	VT (µg/l)			achtergrondgehalte (µg/l)			VR (µg/l)		
	zoetwater	zoutwater	grondwater	zoetwater	zoutwater	grondwater	zoetwater	zoutwater	grondwater
boor	6.5	6.5	6.5	_	_	-	_	_	grond water
tellurium	•	-	-	-	_	_	_	_	_
titanium	-	-	_	-	_	_	_	-	-
uranium	0.010	0.01	0.01	_	_	_	-	•	-
zilver	0.00082		0.00082	_	_	-	-	-	-
OMCTS	nvt			nvt		-	0.0044		-
nvt niet van toepassing,									0.0044

MTT, achtergrondgehalte en MTT zijn uitgedrukt als opgeloste concentratie.

	MTT (mg	MTT (mg/kg)		ondgehalte (mg/kg)	MTR (mg/kg)	
	bodem	sediment	bodem			sediment
boor	0.1ª	-	-	_	bodem	-
tellurium	-	-	-	_	_	
titanium	-	-	3465	_	_	-
uranium	25.4 ^a	-	2.915	_	28.3	-
zilver	0.010^{b}	5.5 ^b	-			-
OMCTS	nvt	nvt	nvt	nvt	1.3 ^b	- 2.0 ^a

gebaseerd op de EPA methode,

nvt niet van toepassing.

	VT (mg/kg) bodem	sediment	achtergro bodem	ndgehalte (mg/kg) sediment	VR (mg/kg) bodem	sediment
boor	0.001	-	_	-	-	seament
tellurium	-	_	_	_		-
titanium	-	_	3465	_	-	-
uranium	0.254	_	2.915	<u>-</u>	2.160	-
zilver	0.00010	0.055	2.713		3.169	-
OMCTS	nvt	nvt	nut		-	-
-	an toepassing.	· -	nvt	nvt	0.013	0.020

gebaseerd op de evenwichtspartitiemethode,

Summary

In the framework of EU directive 76/464/EEC member states of the European Union have to derive environmental quality standards for the substances mentioned in this directive. For some of these substances no environmental quality standards were available up to now in the Netherlands. The National Institute of Public Health and the Environment was asked by the Ministry of Housing, Spatial Planning and the Environment to derive risk limits (Maximum Permissible Concentrations or MPCs and Negligible Concentrations or NCs) for these substances. These risk limits can be used by the ministry to meet its obligations with respect to directive 76/464. The following substances were dealt with: boron, silver, titanium, tellurium, uranium and organosilicon compounds.

The organosilicon compounds consists of various groups. From these groups the most elevant one with respect to market share was chosen: polydimethylsiloxanes. Only for octamethyltetrasiloxane (OCMTS) sufficient information was available to derive risk limits.

The MPC for metals is the sum of the Maximum Permissible Addition (MPA) and the background concentration in water, sediment or soil (the Negligible Concentration is the Negligible Addition - NA - and the background concentration; VA = MPA/100). For the majority of the metals considered a MPA could be derived but insufficient data were available to derive a background concentration in the Netherlands. For all metals no background concentration could be derived in freshwater, saltwater, groundwater or sediment, while only for titanium and uranium a background concentration in soil could be derived. For titanium no MPA in soil could be derived, as insufficient ecotoxicological data were available. Subsequently, only for uranium a MPC could be derived in soil.

In Germany background concentration for boron in freshwater of 0.01 to 0.2 mg/l have been reported. Whether these levels can be extrapolated to the Dutch situation is unclear.

In the following table the results are presented.

	MPA (μg/l)			backgroun	d concentr	ation (µg/l)	MPC (μg/l)		
	freshwater	saltwater	groundwater	freshwater	saltwater	groundwater	freshwater	saltwater	groundwater
boron	650 ^a	650 ^a	650 ^a	-	-	-	-	-	-
tellurium	-	-	-	-	-	-	-	-	-
titanium	-	-	-	-	-	-	-	-	-
uranium	1.0 ^b	1.0 ^b	1.0^{b}	-	-	-	-	-	-
silver	0.082^{a}	1.2 ^a	0.082^{a}	-	•	-	-	-	-
OMCTS	na	na	na	na	na	na	0.44 ^b	0.44 ^b	0.44 ^b

based on the Aldenberg & Slob method;

MPA, background concentration and MPC are expressed as dissolved concentration.

based on the EPA method;

na not applicable;

	VA (µg/l)			background concentration (μg/l) VA (μg/l)					
•	freshwater	saltwater	groundwater	freshwater	saltwater	groundwater	freshwater	saltwa er	groundwater
boron	6.5	6.5	6.5	_	-	_	_	_	Broana water
tellurium	-	-	-	_	-	_	_	_	-
titanium	-	-	-	_	_	_	_	-	-
uranium	0.010	0.01	0.01	-	-	_		-	=
silver	0.00082	0.012	0.00082	_	_	_		-	-
OMCTS	na	na	na	na	na			-	-
na not	applicable	; ;		114	na	na	0.0044	0.0044	0.0044

MPA, background concentration and MPC are expressed as dissolved concentration.

	MPA (mg/k	g)	backgroun	nd concentration (mg/kg)	MPC (mg/kg)	
	soil	sediment	soil	sediment	soil	sediment
boron	0.1 ^a	-	-	-	_	-
tellurium	-	-	-	-	_	_
titanium	-	-	3465	-	_	_
uranium	25.4ª	-	2.915	-	28.3	_
silver	0.010^{b}	5.5 ^b	-	-	20.5	-
OMCTS	na	na	na	na	1.3 ^b	2.0ª
a 1					1.5	2.0

based on the EPA method,

na not applicable.

	VA (mg/kg) soil	sediment	00:1		=	VA (mg/kg)	
boron	0.001	_	3011	sediment	soil	sediment	
tellurium		-	-	-	-	=	
	-	-	-	~	-	-	
titanium	-	-	3465	•	_	_	
uranium	0.254	-	2.915	-	3.169	_	
silver	0.00010	0.055	_		3.103	-	
OMCTS	na			<u>-</u>	-	-	
-	pplicable.	na	na	na	0.013	0.020	

based on the equilibrium partitioning method;

1. Introduction

The present report is produced in the context of the RIVM project "Setting Integrated Environmental Quality Standards" (Crommentuijn et al., 1997). In this project risk limits expressed as concentrations in the compartments air, water, sediment and soil are derived based on the risk philosophy of the Ministry of Housing, Spatial Planning and the Environment (VROM, 1989).

Environmental Quality Standards (Maximum Permissible Concentrations and target values) are set by the Ministry of Housing, Spatial Planning and the Environment. These standards are based on two risk limits: the Maximum Permissible Concentration (MPC) and the Negligible Concentration (NC). The NC is obtained by dividing the MPC by 100. The MPC and NC are derived by the National Institute of Public Health and the Environment.

In the framework of EU Dangerous Substances Directive 76/464/EEC member states of the European Union have to derive environmental quality standards for selected List II substances. For some of these substances no environmental quality standards were available up to now in the Netherlands. The National Institute of Public Health and the Environment was asked by the Ministry of Housing, Spatial Planning and Environment to derive risk limits for these substances in the framework of the project "Setting Integrated Environmental Quality Standards". These risk limits can be used by the ministry to meet its obligations with respect to directive 76/464/EEC. The following substances had to be dealt with: boron, silver, titanium, tellurium, uranium and organosilicon compounds.

2. Methods

2.1 Literature search and evaluation

Sources used for the collection of single-species toxicity data and data on soil/water and sediment/water partition coefficients are both in-house and external documentation centers and libraries, and bibliographic databases. A detailed description of the parameters searched for and criteria applied when performing the literature search and evaluation is presented in CSR (1996).

Toxicological criteria, which may affect the species at the population level are taken into account. In general these are survival, growth and reproduction and are commonly expressed as an L(E)C50 (short-term tests, duration four days or less) or NOEC (long-term tests, duration more than four days, with the exception of micro-organisms and algae for which a NOEC may be derived from experiments during less than four days). For the terrestrial environment also effect data on microbiological processes and enzymatic activity are searched for, commonly expressed as a NOEC or ECx value.

Not all the tests described in the literature are performed under the same conditions. Therefore ecotoxicological test results for soil organisms are normalised as proposed by Denneman and Van Gestel (1990). All L(E)C50 and NOEC data are normalised to a standard soil containing 10% organic matter and 25 % of clay.

For metals the following equation is used:

$$ECx_{(ssoil)} = ECx_{(exp)} \frac{R_{(ssoil)}}{R_{(exp)}}$$
 (1)

in which: EC

 $ECx_{(ssoil)}$ = normalised Effect Concentration (NOEC or LC50) in

standard soil;

 $ECx_{(exp)}$ = Effect Concentration (NOEC or LC50) in soil used in the

experiment;

R_(ssoil) = reference value for standard soil;

 $R_{(exp)}$ = reference value for soil used in experiment.

The reference values for soil are based on the so-called reference lines. For metals these reference lines were derived by correlating measured ambient background concentrations (total concentrations in the soil-matrix) at a series of remote rural sites in the Netherlands to the percentage clay and the organic matter content of these soils (Edelman, 1984; De Bruijn and Denneman, 1992). In the present report reference lines have been derived for titanium and uranium.

For organic substances the following equation is used:

$$ECx_{(ssoil)} = ECx_{(exp)} \frac{H_{(ssoil)}}{H_{(exp)}}$$
 (2)

in which:

 $ECx_{(ssoil)}$ = normalised Effect Concentration (NOEC or LC50) in

standard soil;

 $ECx_{(exp)}$ = Effect Concentration (NOEC or LC50) in soil used in the

experiment;

 $H_{(ssoil)}$ = organic matter content of standard soil (10%); $H_{(exp)}$ = organic matter content of soil used in experiment.

If H< 2% the percentage is set to 2%, if H>30 % the percentage is set to 30%.

In case no data on terrestrial/sediment species are available the Equilibrium Partitioning method or EP-method is applied to derive risk limits for soil and sediment. To be able to apply the EP-method data on partition coefficients are required. Sorption coefficients (Kp) are derived by evaluating batch experiment studies. When no or only few experimental data are available, the Koc for organic substances can be estimated using the regression equations derived by Sabljic et al. (1995) and DiToro et al. (1991). Both give empirical formulas from which a log Koc can be derived using a log Kow. The log Kow is derived from the MEDCHEM (1992) data base.

2.2 Data selection

The aim of selecting toxicity data is firstly to derive one single toxicity data for each compound and species, and secondly, to select reliable toxicity data. One parameter per species is necessary as input in the extrapolation methods. Therefore chronic as well as acute toxicity data are weighed over the species as follows (Slooff, 1992):

- If for one species several toxicity data based on the same toxicological endpoint are available, these values are averaged by calculating the geometric mean;
- If for one species several toxicity data based on different toxicological endpoints are available, the lowest value is selected. The lowest value is determined on the basis of the geometric mean, if more than one value for the same parameter is available;
- In some cases data for effects of different life-stages are available. If from these data it becomes evident that a distinct life-stage is more sensitive, this result may be used in the extrapolation.

For soil, toxicity data on terrestrial species as well as for microbial and enzymatic processes may be available. The latter are in principle summed parameters expressing the performance of a process. The process in question may be performed by more than one species. Under toxic stress the functioning of the process may be taken over by less sensitive species. According to Van Beelen and Doelman (1996) the results of ecotoxicological tests with microbial processes can not be used together with single species tests in a single extrapolation. Therefore, data for species and processes are selected separately.

For selection of toxicity data to be used in extrapolation for terrestrial species the selection criteria as described above are used. For the data on microbial processes and enzymatic activity more than one value per process is included in the extrapolation method. As mentioned above NOECs for the same process but using a different soil as substrate are regarded as NOECs based on different populations of bacteria and/or microbes. Therefore these NOECs are treated separately.

2.3 Calculating the Maximum Permissible Concentration and Negligible Concentration

In the Netherlands the extrapolation methods used for effect assessment are the refined effect assessment and the preliminary effect assessment. The first one is applied if chronic data for more than 4 different taxonomic groups are available. The second one if chronic data for less than 4 species of different taxonomic groups, or less than 4 different processes, or only acute data are available. For metals, having a natural background concentration, the Added Risk Approach is applied. In case, for the terrestrial/sediment environment no toxicity data are available, risk limits are derived on the basis of aquatic toxicity data applying the Equilibrium Partitioning Method or EP-method.

2.3.1 Refined Effect Assessment

The refined effect assessment or statistical extrapolation method is based on the assumption that the sensitivities of species in an ecosystem can be described by a statistical frequency distribution. This statistical frequency distribution describes the relationship between the concentration of the substance in a compartment and a certain percentage of species unprotected, the Potentially Affected Fraction of species or PAF. For a detailed overview of the theory and the statistical adjustments since its introduction, it is referred to the original literature (Kooijman, 1987; Van Straalen and Denneman, 1989; Wagner and Løkke, 1991, Aldenberg and Slob, 1993).

The method of Aldenberg and Slob (1993) assumes that the NOECs used for estimating the distribution fit the log-logistic distribution. The advantage of the log-logistic distribution is that it allows the analytical evaluation of the cumulative distribution of PAF by integration:

$$PAF(x) = 1/(1 + \exp((\alpha - x)/\beta))$$
(3)

in which:

PAF(x) = potentially affected fraction of all possible species at concentration x;

 α = mean value of the log-logistic distribution;

β = scale parameter of the log-logistic distribution;

x = log(c): logarithm of the concentration.

The log-logistic distribution can be characterised by α and β . The α indicates the mean value of the distribution which determines the location of the distribution on the concentration axis (log(NOEC) or log(c)) and β is the scale parameter of the distribution which determines the width or shape of the distribution and is equal to approximately half times σ ($\beta = \sigma \sqrt{3/\pi}$).

PAF(x) has a value between 0 and 1 and is the fraction of species that have log(NOEC) values smaller than x. The aim of the MPC is protection of all species in an ecosystem. However, in order to be able to use extrapolation methods like the one of Aldenberg and Slob (1993), a 95% protection level is chosen as a sort of cut-off value (VROM, 1989). The concentration corresponding with a 95% protection level - equal to a Potentially Affected Fraction of 5% (PAF = 0.05) - is called the Maximum Permissible Concentration (MPC). The Negligible Concentration (NC) is derived by dividing the MPC by a factor 100. This factor is applied to take combination toxicity into account (VROM, 1989).

The MPC can be derived by rewriting equation 4 into:

$$x = \alpha - \beta \ln ((1-PAF)/PAF)$$

(4)

in which:

x = MPC (PAF = 0.05)

2.3.2 Preliminary Effect Assessment

The preliminary effect assessment method is a method in which assessment factors are applied to toxicity data. The size of this factor depends on the number and kind of these toxicity data. The factors and conditions used for deriving MPCs are shown in Table 1 and 2 for aquatic MPCs, terrestrial MPCs, respectively. For deriving MPCs the method is often referred to as the modified EPA-method (van de Meent et al., 1990).

Table 1. Modified EPA-method for aquatic ecosystems to derive the MPC.



Available information	Assessment factor
lowest acute L(E)C50 or QSAR estimate for acute toxicity lowest acute L(E)C50 or QSAR estimate for acute toxicity	1000
for minimal algae/crustacean/fish	100
lowest NOEC or QSAR estimate for chronic toxicity [†]	10
lowest NOEC or QSAR estimate for chronic toxicity for minimal algae/crustacean/fisl this value is compared to the extrapolated value based on cause I/(E) QSO and it is a second or cau	h 10

this value is compared to the extrapolated value based on acute L(E)C50 toxicity values. The lowest one is selected.

Table 2. Modified EPA-method for terrestrial ecosystems to derive the MPC.

Available information	Assessment factor
lowest acute L(E)C50 or QSAR estimate for acute toxicity	1000
lowest acute L(E)C50 or QSAR estimate for acute toxicity	1000
of microbe-mediated processes, earthworms or arthropods and plants	100
lowest NOEC or QSAR estimate for chronic toxicity [†]	100
lowest NOEC or QSAR estimate for chronic toxicity for three representatives	10
of microbe-mediated processes or of earthworms, arthropods and plants	10
this value is compared to the extrapolated value based on acute L(E)C50 toxicity one is selected.	values. The lowest

2.3.3 The Added Risk Approach

The added risk approach is used to calculate risk limits for the different environmental compartments. The approach starts with calculating a maximum permissible addition (MPA) on the basis of available data from laboratory toxicity tests. This MPA, which may be related to anthropogenic activities, is considered to be the maximum concentration to be added to the background concentration (Cb). The MPC is then the sum of the Cb and the MPA:

$$MPC = Cb + MPA$$

The MPA is calculated using a similar approach as the MPC for substances having no natural background concentration. The NC is defined as the background concentration (Cb) plus the Negligible Addition (NA): NC = Cb + NA, where NA = MPA/100.

The theoretical description of the added risk approach as described by Struijs et al. (1997) includes the bioavailable fraction of the background concentration that can vary between 0% and 100%. Crommentuijn et al. (1997) derived MPCs for metals assuming a bioavailability of 0%, because from a policy point of view the effects of the natural background concentration may be neglected or even be considered desirable due to its contribution to the biodiversity. Also, not enough information was available to determine the bioavailable fraction of the background concentrations for metals.

2.3.4 Equilibrium Partitioning Method

The equilibrium partition method (EP method) was originally proposed by Pavlou and Veston (1984) to develop sediment quality criteria. The concept has been described in detail by Shea (1988) and DiToro et al. (1991). Three assumptions are made when applying this method: i) bioavailability, bioaccumulation and toxicity are closely related to the pore water concentration; ii) the sensitivity of aquatic organisms is comparable with the sensitivity of sediment dwelling organisms; iii) an equilibrium exists between the chemical sorbed to the particulate sediment organic carbon and the pore water and these concentrations are related by a partition coefficient (Koc).

The MPC for soil and sediment organisms using equilibrium partitioning is calculated applying the following equation:

$$MPC(sed \mid soil_{EP}) = MPC(water) * Kp_{(ssoil/ssed)}$$
 (6)

in which: MPC(sed/soilEP)= MPC for soil organisms species using the equilibrium

partition method;

MPC(water) = MPC for aquatic organisms;

Kp_(ssoil/ssed) = partition coefficient for standard soil or standard sediment in

l/kg

2.4 Harmonisation

When independently derived MPCs for water and sediment or soil are available, MPCs for water, sediment and soil have to be harmonised. This is done by calculating the MPC for sediment or soil from the MPC for water applying the equilibrium partition method and comparing this value with the MPC based on ecotoxicological data for soil or sediment organisms. In principle the lowest value of both MPC is selected as the harmonised MPC. However, the uncertainties in both MPCs and the partition coefficient have to be taken into account.

3. Maximum Permissible Concentrations (MPCs)

3.1 Boron (B)

3.1.1 Introduction

Boron is rarely found in the elemental form in nature but occurs primarily as borates of Ca and Na. The most common compound is borax: Na₂B₄O₇.10H₂O. An important source of boron is the mineral kernite: Na₂B₄O₇.4H₂O. From borax, sodium perborates are produced. These are used as bleaching agent in detergent powders and bleaching powders (ECETOC, 1995). The two main forms of commercial importance are sodium perborate tetrahydrate (NaBO₃.4H₂O) and sodium perborate monohydrate (NaBO₃.H₂O). According to the EU echnical Guidance Document boric acid is used in the leather industry.

The following reviews were available - and have been used as data source - on the effects of boron in the environment:

- US Fish and Wildlife Service published a review on boron (Eisler, 1990);
- Raymond and Butterwick (1992) and Butterwick et al. (1989) focus on the environmental aspects with respect to the use of sodium perborates as a bleach;
- Guhl (1992) reviewed the effects of boron in the aquatic environment;
- Environmental Health Criteria 204: Boron (IPCS, 1998);
- Crommentuijn et al. (1995) derived an Ecotoxicological Serious Soil Contamination Concentration upon which the Dutch intervention values for soil clean-up are based;
- report of the UK Technical Committee on Detergents and the Environment from 1994;
- an interim report of ECETOC entitled "Ecotoxicology of some Inorganic Borates" dated March 1997.

Perborate is on the third priority list of the EU Existing Chemicals Program with Austria being lead-country. No risk assessment report has been published yet.

The MPC is derived from the MPA based on ecotoxicological data, and the natural background concentration (C_b). In the following paragraphs only an MPA could be derived for boron in surface water, sediment and soil due to the absence of a natural background concentration for all compartments. Subsequently, no MPCs are derived.

3.1.2 Background concentrations

Ambient concentrations of boron in <u>freshwater</u> are readily available. An extensive survey is given by ECETOC (1997). Boron is often used as a tracer to study the hydrodynamic behaviour of sewage treatment plants and for verifying the accuracy of model predictions (Matthijs et al., sub.). ECETOC (1997) report influent and effluent concentrations from a monitoring study in the Netherlands on surfactants of 0.27-0.78 and 0.39-0.75 mg B/l, respectively. ECETOC (1997) also report measurements at unspecified sites in the Netherlands in 1992: ranges of medians were 0.090 to 0.145 mg B/l. In a recent study concerning the quality of drinking water boron was determined in 232 surface water and groundwater samples from drinking water pump stations (Jonker et al., 1998). The corresponding median concentration was 27.5 μ g/l. This value appears to be higher than the

'average' value found for freshwater systems according to Buffle (1988) of 10 μ g/l. Also a value of 10 μ g/l for stream water is reported by Winter (1998). ECETOC (1997) reports results of a monitoring study in Germany. More than 100 samples taken from areas in Baden-Württemberg - not influenced by anthropogenic activities - resulted in a 90th percentile of <0.05 mg B/l with a maximum of 0.2 mg B/l. Other German studies resulted in concentrations of 0.01-0.05 mg B/l in surface waters not influenced by anthropogenic activities (Metzner and Nitschke, 1998). If more information on these studies becomes available, they can probably be used to derive a natural background in fresh surface water for the Netherlands.

For <u>seawater</u>, boron concentrations are certainly higher compared to freshwater, which is also stated by ECETOC (1997). Typically concentrations are 5 mg B/l and the inorganic borate concentration varies in almost direct ratio to salinity: 0.24 mg boron per chloride expressed as Cl. Also, 'average' concentrations of 4.4 mg/l (Winter) and 5 mg/l (Buffle, 1988) are reported. However, no information for the Netherlands is available.

For commercially available mineral waters in Germany (n=31), which is a 'form' of groundwater, boron concentrations ranged from 0.3 up to 2.1 mg/l with an average of 0.36 mg/l (Abke et al. 1997). Concentrations in groundwater have been measured by in the Netherlands in 1996 at a depth of 10 and 25 m (Bronswijk and Absil, 1998). Concentrations beneath forests on a sandy soil were all less than the detection limit of 0.1 mg/l. In agricultural soil - arable land and grassland on clay and peat - higher concentration were measured up to 1.4 mg/l. From these data no natural background concentration can be derived as all measurements were < 0.1 mg/l.

No measured data are available for boron in Dutch <u>soils</u>. Lindsay (1979) reported that the boron content usually varies from 2 up to 100 mg/kg with an avergae of 10 mg/kg. For crustal rock material 8.7 mg/kg is reported (Winter, 1998). Tikaku (1998) summarized literature data of boron found in various igneous rocks and the earth crust. These data are comparable with the data of Lindsay (1979) and Winter (1998). They reported concentration of 3 up to 12 mg/kg. ECETOC (1997) reports that in most soils the boron content is < 10 mg B/kg.

Concluding: the existing information is too scarce for boron to derive a background concentration in Dutch soils, sediment, surface water and groundwater.

3.1.3 Water

The predominant species of boron in most natural freshwaters with a pH of 6-9 is undissociated boric acid H_3BO_3 (pKa₁ of 9.15 (ECEOC, 1997)). Boric acid can form complexes with carbohydrates and proteins (ECETOC, 1997). Other species like boric oxide B_2O_3 and the sodium borates will rapidly be converted to H_3BO_3 . In salt waters weakly dissociated boric acid is the predominant species, accounting for circa 75% of the total boron. The remaining 25% consists of the borate ion and borate complexes of sodium, magnesium and calcium (IPCS, 1998).

Boron is an essential element for cyanobacteria and diatoms (Loomis and Durst, 1992). The former require boron for the formation of nitrogen-fixing heterocysts and specifically for protection of the nitrogenase enzyme from oxygen. In the latter boron probably has a role in cross-linking polymeric carbohydrates of the cell wall matrix.

Toxicity data for aquatic organisms - expressed in mg B/l - are presented in Table 1.1 and 2.1 of Appendix 3. The data-base on aquatic toxicity tests with boron is large, especially for freshwater organisms: chronic test results are available for bacteria, protozoa, algae,

crustaceans, insects, fish and amphibians. Subsequently, no attempt has been made to collect all acute toxicity data.

Almost all chronic tests have been carried out with boric acid or borax under various conditions. In his review on boron toxicity Guhl (1992) compared the toxicity of borax and perborate and concluded that perborate is a factor 20 to 436 more toxic due to the formation of hydrogen peroxide, which gives off oxygen readily. As boric acid will be the species to which aquatic organisms will be exposed to due to the use of perborates in bleaches and detergents, the ecotoxicological results for perborate are not used for the calculation of the MPA.

In Table 3 results for borax ($Na_2B_4O_7$) and boric acid tested at 50 and 200 mg $CaCO_3/I$ are presented (Raymond and Butterwick, 1992).

Table 3. NOECs (mg B/l) from embryo-larval tests with borax and boric acid tested at 50 and 200 mg CaCO₃/l are presented (Raymond and Butterwick, 1992).

	O. mykiss		C. auratus		I. punctatus		B. fowleri	R. pipiens	
- 2"	-	$Na_2B_4O_7$	H ₃ BO ₃	$Na_2B_4O_7$	H_3BO_3	$Na_2B_4O_7$	H_3BO_3	H_3BO_3	$Na_2B_4O_7$
50	0.11	0.96	9.2	26.5	1.01	9	48.7	32.5	7.04
200	0.001	9.6	6.8	8.5	0.75	0.49	22.3	45.7	7.04

For *C. auratus*, *I. punctatus* and *O. mykiss* boric acid was more toxic than borax, while for *R. pipiens* the opposite result was found. Raymond and Butterwick (1992) report results of a study in which no differences were found between boric acid and borax regardless of water hardness when LC50 data for aquatic organisms were compared. The same conclusions are drawn in the ECETOC report (1997). Therefore, toxicity data for all boron species are combined for deriving the MPA.

Several abiotic factors may influence the toxicity of boron. Most important factors studied are water hardness and type of test water. Only for fish hardness seems to exert an effect on the toxicity of boron (see Table 1). However, the effect is not consistent, although for most fish species boron is more toxic in soft water. This can be explained by the formation of ion pairs with cations like Mg²⁺ and Ca²⁺ in water with a higher hardness (Raymond and Butterwick, 1992). Maier and Knight (1991) studied the effect of water hardness and sulfate on boron acute toxicity to *Daphnia magna*. No influence was observed for the ranges 10-170 mg/l CaCO₃ and 10.2-325.4 mg/l SO₄²⁻.

Sensitivity of fresh versus saltwater organisms can only be compared based on acute toxicity data. Raymond and Butterwick (1992) conclude that the toxicity of boron is similar in seawater and freshwater. IPCS (1998) report results of two studies with fish in which saltwater species are more sensitive than freshwater species. Although there are some indications that saltwater organisms are more sensitive, it is decided to combine both datasets and derive one single MPA for surface water.

It should be noted that probably all test waters also contain a certain amount of boron. For most tests this was not reported, although e.g. for seawater this will be in the order of mg B/l. Birge and Black (1993) did measure boron in their tests: for 1 and 10 mg/l measured concentrations are 140% and 122% of nominal, while at the other - lower as well as higher - test concentrations no differences between measured and nominal concentrations are observed. As information is lacking it is decided to regard the results of these as well as the other test results presented in Appendix 2, as 'added concentrations'.

Enough chronic toxicity data are available to apply statistical extrapolation. The interspecies variation in NOECs is very high: from 0.001 mg/l for *Oncorhynchus mykiss* to 109 mg/l for *Uronema pardaczi*. Fish are clearly the most sensitive taxonomic group. No information was found on the toxicological working mechanism for boron in fish. Fish do not accumulate boron: ECETOC (1997) report BCFs <2 l/kg for four fish species.

For fish also a high intra-species variation is found, especially for *Ictalurus punctatus* and *Oncorhynchus mykiss*. For the latter species this has been investigated by Black et al. (1993) in detail (several other tests are reported by Raymond and Butterwick (1992); the original reference could not be retrieved). They performed the following experiments:

- 8-days post-hatch embryo-larval tests in reconstituted water with O. mykiss (Soap Lake strain) using test concentrations varying from 0.001 to 10.0 mg/l;
- same test with O. mykiss (Wytheville strain) in reconstituted and three natural waters with ambient concentrations of 0.023, 0.091 and 0.75 mg/l using test concentrations of 1.0 and 10.0 mg/l. In the tests in natural water, dissolved versus total boron was measured by filtration through an acid-washed 0.45 μ m \varnothing membrane filter;
- 60-days post-hatch early life-stage test in well water with O. mykiss (Hildebrand strain) using test concentrations varying from 0.0017 to 1.7 mg/l.

Results can be summarized as follows:

- O. mykiss appeared to be most sensitive in reconstituted water with NOECs as low as 0.009 mg/l (measured concentration). However, the concentration-response curve was very flat¹: an extreme example is a test response of 13.8% at 10.0 mg/l and 3.4% at 0.01 mg/l for teratogenesis at hatching. It should be noted that observed statistically significant effects in the controls were relatively low ranging from 6.4 to as low as 0.7%. Therefore, the original data were used to calculate an EC10 applying a concentration-response model.
- O. mykiss appeared to be less sensitive in natural waters. Effect percentages were consistently approximately 10% lower in all three natural waters compared to reconstituted water. In all test waters significant effects were observed at 1.0 mg/l. Results in the controls of tests in reconstituted water were similar to the natural waters. In the natural waters all boron was present predominantly in the dissolved phase, irrespective of ambient or added concentrations. In well water no effects were observed up to the highest concentration tested of 1.7 mg/l.
- in reconstituted water results differed by one order of magnitude for different strains. This might implicate a difference in sensitivity between these strains, although it may also be a result of intra-laboratory variation.

No unequivocal conclusion can be drawn with respect to the NOEC for O. mykiss - and also other fish species. Experimental design - test concentrations and type of test water - do influence the outcome of the test. According to Black et al. (1993) added boron seems to behave differently from ambient boron due to the formation of stable complexes of boric acid with organic chemicals like α -hydroxy carboxylic acids. After assessing all fish tests ECETOC (1997) concludes the following:

- the type of dilution waters and the different trout strains used in the tests cannot explain the wide range of test results;
- as serial dilutions of a factor ten were used and control responses were very low, the NOEC overestimates the chronic toxicity;
- the difference between effects observed in natural waters versus reconstituted water is caused by the better health experienced by organisms exposed to boron in natural water. This may be due to nutrient deficiencies.

¹ This was also found by Black et al (1993) in a test with Micropterus salmoides.

The latter is rather unlikely as fish in the laboratory are reared under optimal conditions. Test design and determination of a NOEC by comparing control and test concentration response, seem the most likely explanation for some of the extreme low results found by Black et al. (1993). Repeating the early life-stage test with an improved test design is recommended.

Using expert judgement the NOEC seems to lie between 0.1 and 1.0 mg/l. Applying the standard procedure for deriving MPCs - taking the geometric mean of all values - the NOEC is 0.23 mg/l. Although this might be an overestimation of the sensitivity of *O. mykiss* it is decided to use this procedure - unless new information will become available - for this fish species as well as all other test results for aquatic species. The resulting sensitivity distribution is presented in Figure 1.

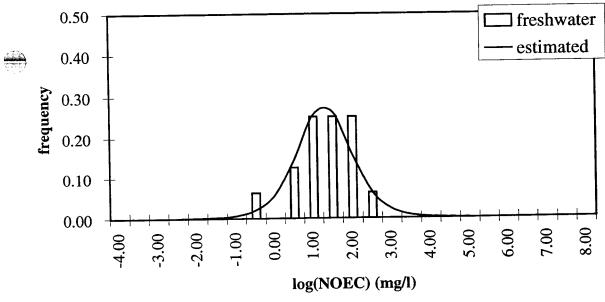


Figure 1. Estimated species sensitivity distribution of ecotoxicological data available for boron ($\alpha = 1.0$ and $\beta = 0.44$) and frequency of experimental NOECs (frequency of experimental data within a category is obtained by dividing the number of data in a category by the total number of data).

Using the input data given in Appendix 2 an MPA of 0.65 mg/l (50/95% ratio of 5.0) is calculated applying the method of Aldenberg and Slob (1993).

Black et al. (1993) collected data from field-surveys on surface water boron concentrations and the distribution of wild trout as well as data on boron concentrations in trout hatcheries; both in California, USA. Boron concentrations in surface waters (14 rivers and one lake) with viable trout populations varied from 0.01 to 13.1 mg/l, while boron concentrations in ten trout hatcheries varied from 0.02 to 0.10 mg/l. ECETOC (1997) report results from several recent studies: e.g. boron concentrations in trout hatcheries in the UK and Germany with healthy populations were up to 0.107 mg B/l. They conclude that "rainbow trout populations do not become limited at boron levels below 1 mg B/l".

Several authors and authorities have recommended "safe values" for boron:

• in Canada a Water Quality Guideline has been set for irrigation water of 0.5-6.0 mg total B/l (Health Canada and Environment Canada, 1995);

- UK Governement has recommended an Environmental Quality Standard for the protection of freshwater and saltwater life of 2 and 7 mg/l, respectively (Technical Committee on Detergents and the Environment, 1994). No information is presented on how these values have been derived;
- US Fish and Wildlife Service recommended a concentration of <1.0 mg B/l for the protection of sensitive aquatic species (Black et al., 1993);
- Black et al. (1993) recommended a concentration between 0.75 and 1.0 mg B/l as an environmentally acceptable limit;
- IPCS (1998) concludes: "Comparison of the environmental no-effect concentration (1 mg/litre) with the general ambient environmental levels of boron indicates that the risk of adverse effects of boron on the aquatic ecosystem is low. In a few boron-rich environments, natural levels will be higher. It is reasonable to assume that aquatic organisms in such habitats may be adapted to the local conditions."
- Maier and Knight (1992) state that systems with concentrations of 1-2 mg B/l will probably not experience direct effects on aquatic animals.

The MPA of 0.65 mg B/l is lower than these values. However, the natural background concentration still has to be included. The "safe values" given above do probably include the natural background concentration.



Concluding: since no natural background concentration in surface water is available for the Netherlands no MPC can be derived for boron. The MPA is 0.65 mg B/l. In freshwater the natural background concentration may be <0.05 mg B/l, while in seawater the natural background concentration will be much higher, approximately two orders of magnitude.

The MPA derived for surface water can be used for groundwater also. As also for groundwater no natural background concentration is available for the Netherlands no MPC can be derived for boron.

3.1.4 Sediment

No toxicity data are available for sediment dwelling organisms. The equilibrium partitioning method can be used to derive an MPA for sediment, using the equation:

$$MPA_{sediment} = Kp * MPA_{water}$$
(7)

However, no data are available on sorption of boron in sediment. Therefore no MPA for sediment can be derived.

3.1.5 Soil

Boron is an essential element for plants (Mortvedt et al., 1991). As boron deficiency produces a wide variety of symptoms, many hypotheses have been postulated on the function of boron related to for example cell wall formation and stabilization, lignification, xylem differentation and at the cellwall plasma membrane interface (Loomis and Durst, 1992; Mortvedt et al., 1991).

Most studies have focussed on the relationship between deficiency-toxicity of various crops for boron expressed as concentrations of boron in nutrient or soil solutions or boron levels in plant tissue. The majority of the data are available for agricultural crops. Raymond and Butterwick (1992) present an overview of threshold concentration ranges defined as the maximum concentration that a given plant species tolerates without manifesting visual injury symptoms and/or a decrease in yield. For 51 plant species the treshold concentration - given as mg B/l in soil water, field capacity basis - varied from 0.30-0.50 mg/l for sensitive crops to 10.05-15.03 mg/l for tolerant crops. Adriano (1986) presents an overview of deficient, sufficient and toxic levels in plants expressed as mg B/kg dry matter plant tissue. For 24 plant species the deficient and toxic levels varied from <0.3-40 and 43->800 mg/kg dw. From these studies it is clear that there is a wide range in deficiency levels for plants. Unfortunately, no concentrations in soil expressed as mg/kg dw - preferably measured as total and extracted with the hot water solubility method (ECETOC, 1997) - are reported.

Toxicity data, expressed as a concentration in the solid phase, for boron are presented in Table 3.1 and 4.1 of Appendix 3. Data are available for plants, nitrification and the activities of the following enzymes: urease, arylsulfatase and dehydrogenase. The lowest value is a NOEC of 1.0 mg/kg for barley (*Hordeum vulgare*). The test was carried out in a sand with a boron content of <0.5 mg/kg dw extracted with 0.05 M mannitol/0.01 M CaCl₂, to which 0.5-8 mg/kg B was added as B(OH)₃ (Riley, 1987). Applying an assessment factor of 10 leads to an MPA of 0.1 mg/kg. This is not a concentration in standard soil as no soil type correction factor is available for boron.

Mortvedt et al. (1992) give rates of boron application for correction of boron deficiency of various crops: alfalfa, cole crops, grape, pine trees, rapeseed, soybean, strawberry, sugarbeet and table beet. Optimum rates vary from 0.45 to 5.7 kg/ha. Assuming that this amount is homogeneously mixed in a soil layer with a depth of 0.20 m and a density of 1400 kg/m³ this results in 0.16-2.0 mg B/kg. This agrees with boron contents of soils for optimum growth given by Butterwick et al. (1989) for 31 crops, which vary from 0.1 to 0.5 mg/kg. The MPA of 0.1 mg/kg dw is at the lower end of this range, so it could be argued that toxic effects do not occur at this concentration.

The equilibrium partitioning method is used to harmonize the MPA for soil and the one for surface water, using the equation:

$$MPA_{soil} = Kp * MPA_{water}$$
 (8)

Van den Berg et al. (1994) report a Kp for boron of 10 l/kg. Using the MPA for water of 0.55 mg/l this leads to a MPA for soil of 5.5 mg/kg. Considering the uncertainties in the Kp value - in most soils no sorption was detected - the MPA based on ecotoxicological data is preferred. Since no natural background concentration for boron is available, no MPC can be derived.

3.2 Silver (Ag)

3.2.1 Introduction

Silver is a metal that is extensively utilized in the photographic industry as well as in electronics and electrical applications. The data base on environmental fate and effects of silver is growing rapidly the last decade due to research funded by the Silver Coalition and the Silver Council. Immediate cause for this research were discussions between industry and the US-EPA on the acute water quality criteria for freshwater and saltwater. Results of the research program have been published in Environmental Toxicology and Chemistry (Gorsuch and Klaine, 1998). In January 1999 a review issue of silver was published in the same journal (Gorsuch and Klaine, 1999). New data are presented on the environmental chemistry of silver and the toxicity of silver focussing on sediment dwelling organisms and fresh- and saltwater fish. The results published in this special issue could not be incorporated anymore. However, it can be stated that the conclusions drawn in the next paragraphs are in line with the conclusions in this review issue. As Andren and Armstrong state in the editorial: "Recent research has resolved several important questions, but additional challenges remain before we can reach a full understanding of the environmental chemistry and toxicology of silver. Environmental risk assessment for aquatic silver should be based on exposure of aquatic organisms to Ag+ ion. Thus, we need to be able to measure of model the speciation of silver, including association with all important ligands."

The behaviour of silver is different in freshwater and saltwater (Hogstrand and Wood, 1998): in seawater the concentration of ionic Ag⁺ - the most toxic form of silver - is extremely low due to the higher chloride concentrations compared to freshwater. These types of water are therefore discussed separately. Speciation of silver is an essential factor with respect to the toxicity of silver to aquatic and sediment dwelling organisms and will be dealt with in these paragraphs.

Almost no measured concentrations are available for the Netherlands for any of the compartments water, sediment and soil. Subsequently, no natural background concentrations (C_b) are available for silver. Therefore, in the following paragraphs only MPAs and no MPCs are derived.

3.2.2 Background concentrations

Average background concentrations of Ag in <u>freshwater</u> systems appear to decrease over the years, which is explained by the increasing use of 'clean technology' techniques (Mukherjee, 1995). Hence, the reported data vary considerably, from less than 2 ng/l up to 2 μ g/l (Mukherjee, 1995). Lytle (1984) summarized results of a survey in the USA from the sixties. In 130 natural waters analyzed in the USA silver was detected in 6.6% of the samples with total concentrations ranging from <0.1 to 38 μ g/l with a mean of 2.6 μ g/l. Dissolved Ag concentrations in the North East Pacific Ocean were found to be depending on the depth of sampling and varied between 0.3 to 5.8 ng/l (Mukherjee, 1995). Winter (1998) reported average Ag concentrations of 0.1 and 0.3 μ g/l for <u>seawater</u> and streamwater, respectively. For the Colorado River, upstream unfiltered concentrations of Ag were found to be in the fairly narrow range of 3.1 to 21 ng/l (Gill et al., 1997). Pavlostathis and Maeng (1998) summarize results of a recent study on the fate of silver in sewage treatment plants of photoprocessing

facilities. Total silver influent concentrations ranged from 0.004 to 0.10 mg/l with removal efficiencies of >98%.

For groundwater in forest areas in the Netherlands, indicative silver concentrations were found to range from less than 20 ng/l (detection limit of analytical technique) to about 90 ng/l (Bronswijk, pers. com.).

Silver content of the earth crust varies from circa 0.01 up to approximately 0.1 mg/kg (Winter, 1998; Tikaku, 1998). For Finnish stream sediments (n=1164) average Ag contents were found to be 0.11 mg/kg with the maximum of 0.65 mg/kg (Mukherjee, 1995). For not contaminated sediments in the USA, silver concentration is about 0.1 mg kg⁻¹ (Mukherjee, 1995). For the Netherlands, Ag values in soil from Nieuwlanden in the provence Zeeland were found to range from 0.05 to 0.13 mg/kg and 0.03 to 0.11 mg/kg for the upper (5-25 cm) and lower (35-65 cm) soil layers, respectively (De Jong, pers. com). This is in line with the common range of Ag found in soil, i.e 0.03 to 0.09 mg/kg (Kabata-Pendias and Pendias, 1984). Increased values are reported for mineralized soils and soils rich in organic matter, 0.7 and 2-5 mg/kg, respectively (Mukherjee, 1995).

Concluding: the existing information is too scarce for silver to derive a background concentration in Dutch soils, sediment, surface water and groundwater.

3.2.3 Freshwater

The ecotoxicological database for silver is large. In Table 1.2.1 of Appendix 3 the chronic data for $AgNO_3$ are presented, and in Table 1.2.2 acute as well as chronic data are presented for the other silver species. Most ecotoxicological information on silver is available for $AgNO_3$. In freshwater $AgNO_3$ will almost dissociate completely to free ionic Ag^+ in solution (accompanying dissociation constant log K = -0.3) (Hogstrand and Wood, 1998). The environmental relevance of the $AgNO_3$ data is debated due to the following:

- in the environment Ag⁺ will bind to a variety of anionic ligands, organic as well as inorganic. These complexes are far less toxic than ionic Ag⁺. Important ligands are DOC, sulfide, chloride and thiosulfate.
- almost all silver will enter the environment in forms other than ionic silver or $AgNO_3$. Ag_2S is the major silver species or silver form after reduction in sewage treatment plants, while the majority of silver discharged to sewage treatment plants by the photographic industries is $Ag(S_2O_3)_n^2$.

The following procedure will be used for deriving an MPA for silver. First an MPA will be derived based on the ecotoxicological data for AgNO₃. This value is regarded as the MPA expressed as the dissolved silver concentration. Subsequently, a relationship is derived to obtain an estimate of the MPA expressed as the total concentration of silver, as will be monitored in surface waters.

MPA for silver based on ecotoxicological data for AgNO₃

Acute data are not presented in this report. An overview of acute data for fish is given by Hogstrand and Wood (1998). They conclude that the 96 hr LC50 lies in the range of 5 to

² Silver is found in the environment in four oxidation states: 0, 1+, 2+ and 3+. Two species of silverthiosulfate - $Ag(S_2O_3)_n^{n-}$ can be formed: $AgS_2O_3^{-}$ and $Ag(S_2O_3)_2^{2-}$ (Hogstrand et al., 1996), with dissociation constants of 10^{-9} and $5*10^{-14}$, respectively (Pavlostathis and Maeng, 1998).

70 µg total Ag/l, which makes AgNO₃ one of the most toxic metal salts in laboratory tests. Silver appears to be a surface-active toxicant, exerting damage on or in the gills starting with branchial Na⁺ and Cl⁻ loss.

Enough chronic data are available in order to apply statistical extrapolation. Studies have been carried out with bacteria, algae, protozoa, crustaceans, insects, molluscs and fish. A distribution of the resulting NOECs is presented in Figure 2. NOECs range from $580 \,\mu\text{g/l}$ for *Entosiphon sulcatum* (Bringmann and Kühn, 1978) to $0.23 \,\mu\text{g/l}$ for *Oncorhynchus mykiss* (Davies et al., 1978). Fish are the most sensitive taxonomic group after chronic exposure³. It appears that the toxic mechanism for fish does not change compared to acute exposure, although there are indications of interference with zinc metabolism (Hogstrand and Wood, 1998).

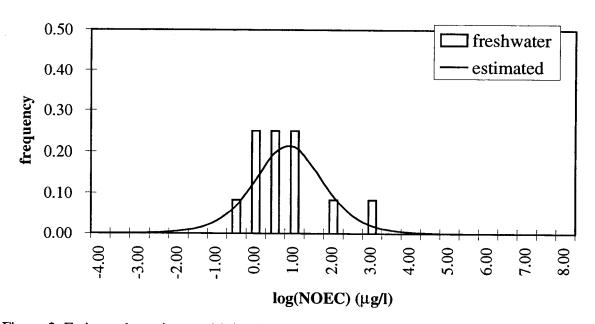


Figure 2. Estimated species sensitivity distribution of ecotoxicological data available for $AgNO_3$ ($\alpha = 0.59$ and $\beta = 0.57$) and frequency of experimental NOECs (frequency of experimental data within a category is obtained by dividing the number of data in a category by the total number of data).

Using the method of Aldenberg and Slob an MPA of $0.082 \,\mu g$ Ag/l is derived with a 50/95 confidence ratio of 13. Comparing this value to MPAs for other metals derived by Crommentuijn et al. (1997) shows that AgNO₃ is also one of the most toxic metals after chronic exposure. The MPA for cadmium e.g. is $0.34 \,\mu g$ Cd/l for freshwater.

³ After acute exposure daphnids and mayflies are more sensitive (pers. com. J.W. Gorsuch, Eastman Kodak Company).

MPA for silver expressed as total silver

Other species than AgNO₃ are clearly less toxic. This was already shown by LeBlanc et al. in 1984. They determined 96 hr LC50 values for *Pimephales promelas* of >280, >13->240 and >4.6 mg Ag/l for Ag(S_2O3)_n, Ag₂S and AgCl_n⁴, respectively. Embryo-larval tests with the same species resulted in NOEC values of 16 mg Ag/l for Ag(S_2O3)_n, and >11 mg Ag/l for AgS. The acute results have been confirmed by Hogstrand et al. (1996).

Hardness does not seem to influence toxicity of silver as greatly as chloride, as several studies cited by Hogstrand and Wood (1998) have shown. However, Cl ameliorates silver toxicity due to the formation of AgCl_n complexes. This has been shown by Galvez and Wood (1997) who determined LT50 and 7 day LC50 values for Oncorhynchus mykiss in test water with different water Cl concentrations, over widely different ranges of water hardness and AgNO₃ concentrations. A 168 hr LC50 of 3.2 µg Ag/I was found in test water with 1.77 mg Cl/l while 40% mortality occurred at the highest concentration of 4.5 µg Ag/l for test water with 7.98 mg Cl'/l. Hogstrand and Wood (1998) elaborated these data and showed that at 88.6 mg Cl⁻/l the LC50 is 97 µg Ag/l. Speciation calculations showed that the ionic Ag⁺ ncentration is equal for all LC50 values, being 3.2 µg Ag/l. Some mean chloride concentrations for 1997 in Dutch surface waters are: Meuse: 39 mg/l, Rhine: 147 mg/l, Haringvliet: 83 mg/l and IJsselmeer: 89 mg/l (per. com. G. Rijs, RIZA). Chloride concentrations in ecotoxicological studies with AgNO₃ performed more than 5-10 years ago have not been reported. It can be concluded that chloride can have a substantial influence on the toxicity of silver, but that this cannot be quantified at the moment. More information on this aspect is needed.

Hogstrand and Wood (1998) report some results of unpublished studies on the toxicity of Ag-DOC complexes. The 96 hr LC50 values of AgNO₃ to *Pimephales promelas* increased by a factor of two and four by raising DOC (reagent-grade humic acid) from 0 to 1 to 10 to 12 mg/l, respectively. In natural river water the LC50 values for the same species and *Daphnia magna* increased 10- to 60-fold.

Summarizing, the toxicity of silver is modified by complexation with chloride, DOC and sulfide, while hardness has a minor influence. Therefore, a relationship should be established between dissolved or even Ag⁺ and total silver including these complexing agents. At the moment such a relationship cannot be established, although Hogstrand and Wood (1998) state that "research currently in progress may help meet this goal". Clearly, the MPA expressed as total silver will be higher. Janes and Playle (1995) estimated a log K of approximately 9.0 for natural DOC collected from a marsh⁵, while log K values for AgCl_n complexes are 3.3-5.5 (Hogstrand and Wood, 1998). For the time being the MPA of 0.082 $\mu g/l^6$ - equal to the dissolved silver concentration - can be converted to a total silver concentration with the log K_p for suspended matter - water. Wen et al. (1997) determined a log K_p of 5.0 \pm 0.6 l/kg (based on filtration through a 0.45 μm filter) from measurements in several rivers in Texas. This leads to a total silver concentration of 0.35 $\mu g/l$ assuming a suspended matter concentration of 30 mg/l.

⁴ Several silver chloride complexes - AgCl_n¹⁻ⁿ - can be formed: in oxygenated freshwater the uncharged AgCl_(aq) dominates; in brackish and seawater the species AgCl₂², AgCl₃² and AgCl₄³ are formed. The insoluble AgCl_(s) complex cerargyrite - often found in laboratory testing - is unlikely to form in natural waters as high silver concentrations are needed for its formation (Hogstrand and Wood, 1998). Depending on salinity, precipitation occurs at silver concentrations of approximately 1 mg/l (Ferguson and Hogstrand, 1998).

⁵ The unit of the log K was not given by Janes and Playle (1995). Therefore, this log K value cannot be directly compared with the log K value for AgCl_n as the unit can be for example g/l, g C/l or mol C/l which has consequences for the absolute value of K.

 $^{^6}$ Canada and Switserland have set water quality criteria for water of 0.1 µg/l (total concentration) and 0.1 µg/l (dissolved concentration), respectively (Behra et al., 1994).

As free ionic Ag+ is probably the main source of toxicity in freshwater system insight into the relationship between total, dissolved and Ag+ in solution is crucial and will underpin the assumption that the MPA based on ecotoxicological data for AgNO₃ can be regarded as the dissolved silver concentration. Speciation calculations by Ferguson and Hogstrand (1998) show that in freshwater (chloride: 28 mg/l) approximately 40% of total silver will be present as Ag⁺. Concentrations of Ag⁺ - as the activity of Ag⁺ - have been measured by a potentiometric technique by Chudd (1983) and Lytle (1984). The first author reports Ag+ activities ranging from 0.0001 to 0.2 µg/l in 8 selected natural waters. Unfortunately, dissolved and total concentrations are not reported. The second author reports Ag+ activities downstream and upstream of sewage treatment plants and in influent and effluent. Based on only two samples, Ag+ activities downstream and upstream were 0.01-7% of total silver concentrations. Unfortunately, no dissolved concentrations are reported. If it is assumed that 25% of silver is present in the dissolved form - using the Kp and suspended matter concentration given above - it can be concluded that the speciation calculations lead to an overestimation of the Ag+ concentration. This can be explained by the fact that these calculations do not include all potential ligands, which reduce the free silver concentration in combination with dissolved organics and suspended matter.

Summarizing, an MPA of $0.082~\mu g$ Ag/l is derived. Since no background concentration is available for Dutch freshwater no MPC can be derived.

3.2.4 Saltwater

As already stated in paragraph 3.2.1 in seawater the concentration of ionic Ag^+ is extremely low due to the higher chloride concentrations compared to freshwater. Ferguson and Hogstrand (1998) performed speciation calculations with salinity ranging from freshwater (0.051 ‰) to seawater (35 ‰) and total silver concentrations from 21.5 μ g Ag/l to 1.0 mg Ag/l. Ag⁺ was present only at salinities of less than 3 ‰. In seawater silver will be present as $AgCl_n^{1-n}$: the dissolved neutral $AgCl_{(aq)}$ is reduced and the species $AgCl_2^{-1}$, $AgCl_3^{-1}$ and $AgCl_4^{-1}$ dominate. Subsequently, the toxicity of silver to marine organisms is lower compared to freshwater organisms.

Acute toxicity studies are summarized by Crommentuijn et al. (1995). LC50 values for molluscs and fish were 0.10-1.0 and 5.8 mg Ag/l, respectively. Shaw et al. (1998) present several other acute results for fish, ranging from 8-140 µg Ag/l for embryonic stages of *Paralichthys dentatus* to 2.7 mg/l for *Fundulus heteroclitus*. Hogstrand and Wood (1998) present LC50 values for 7 fish species, with a lowest value of 330 µg Ag/l for juvenile *Oligocottus masculosus*. Shaw et al. (1998) determined LC50 values for *Oligocottus maculosus*, resulting in 119-664 µg Ag/l for various salinities. Excluding the values with embryos and larvae presented by Shaw et al. (1998) this is the lowest acute LC50 value. Chronic data are available for fish and molluscs with a lowest NOEC of 20 µg/l for *Crassostrea gigas* and *Mytilus galloprovincialis* (Metayer et al., 1995). Thomulka et al. (1993) tested two bacteria species leading to 1-5 hr EC50 values of 38-83 µg/l.

The modified EPA method has to be used to derive an MPA, as insufficient data are available to apply statistical extrapolation. Applying a factor 100 on the lowest LC50 value for Oligocottus maculosus of 119 µg Ag/l and comparing this to a factor of 10 on the lowest NOEC of 20 µg Ag/l, leads to an MPA of 1.2 µg Ag/l.

This concentration is expressed as dissolved silver. As no Kp value is available, no total concentration can be calculated. Only measurements of Wen et al. (1997) in Galveston

Bay in Texas are available, one of the largest estuaries on the USA coastline. They determined a log Kp value of 5.0 ± 0.3 l/kg, but consider their measurements as "preliminary data".

Summarizing, an MPA of $1.2 \,\mu g$ Ag/l is derived. Since no background concentration is available for Dutch saltwater no MPC can be derived.

3.2.5 Sediment

Toxicity data for sediment dwelling organisms are presented in Table 5.1 of Appendix 2. Data are available for one species: *Hyalella azteca*. 10 Day LC50 values have been derived by Rodgers et al. (1997) and Hirsch (1998a) for several Ag species. Only when AgNO₃ was used was toxicity observed, resulting in LC50 values ranging from 1.6 to 380 mg Ag/kg dw depending on sediment characteristics like redox, CEC, pH, % om, % clay and Acid Volatile Sulfide (AVS). No relationship could be established between the bioavailability of silver added as AgNO₃ and these characteristics. The LC50 of 1.6 mg Ag/kg dw was determined in an extremely sandy sediment. Concentrations of the other Ag species were >500 mg Ag/kg. No conversion to standard sediment was possible as no correction factor for silver is available.

In the sediment Ag will most likely be present as silver sulfide Ag_2S . This complex is chemically inert with an estimated solubility product of 10^{-29} (Hirsch, 1998b). A low accumulation factor of 0.18 was determined for *Lumbriculus variegatus* in sediment spiked with Ag_2S at a concentration of 444 mg Ag/kg dw after 28 days exposure (Hirsch, 1998b).

Due to the variability of the data for $AgNO_3$ and the absence of a reference line to recalculate concentrations to standard sediment, the derivation of an MPA from these toxicological data is problematic. An MPA can also be determined using the equilibrium partitioning method applying equation (7). From the K_p for suspended matter of 10^5 l/kg (Wen et al., 1997) a K_p for sediment can be derived by dividing this value by a factor 1.5 (Van de Meent et al., 1990). Applying this K_p value and the MPA for silver an MPA for freshwater sediments can be derived of 5.5 mg Ag/kg dw. Since no background concentration is available for Dutch sediments no MPC can be derived.

3.2.6 Soil

Almost no ecotoxicological data are available. Crommentuijn et al. (1995) presents some studies on effects of silver on microbial processes but these data were too scarce in order to derive a Ecotoxicological Serious Soil Contamination Concentration. No new data could be located. According to Gorsuch (pers. com.) Eastman Kodak Company studied the effects of silver sulfide on the earthworm *Lumbricus terrestris*. In a limit test no effects were observed on survival, burrowing time and growth after 14 days exposure at a measured concentration of 1595 mg Ag/kg dw.

Using equation (8) and the MPA for silver for freshwater and a K_p of 128 l/kg as given by Kreule et al. (1995) an MPA for soil of 10 μ g/kg dw is calculated based on equilibrium partitioning. Considering the earthworm test described above the MPA based on toxicity data for soil organisms may be much higher. Since no background concentration is available for Dutch soils no MPC can be derived.

3.3 Tellurium (Te)

Almost no ecotoxicological data are available for tellurium. Posthumus et al. (1998) report one aquatic toxicity study with *Tubifex tubifex* resulting in an EC50 of 126 mg/l (see Table 1.2 of Appendix 3) and a log Kp of 2.48 l/kg. They did not derive an Ecotoxicological Serious Soil Contamination Concentration due to this scarcity of data. For the same reason also here no MPA is derived.

Also data on tellurium concentrations in the natural environment are very scarce. For the earth crust, Te contents are found to be in the order of 1 μ g/kg (Winter, 1998; Tikaku, 1998).



3.4 Titanium (Ti)

For titanium almost no data are available, although titanium dioxide TiO₂ is used as a white pigment in many applications, e.g. surface coatings, paper and textile industries.

For sea water, large variations in concentrations are reported, 1 μ g/l 'on average' by Winters (1998) and 0.013 μ g/l for Atlantic Sea water by Laane (1992). Titanium contents in soils from Nieuwlanden in The Netherlands, were found to range from 0.6 up to 1.0 g/kg for the upper soil layer of 5 to 25 cm (De Jong, pers. com.). Comparable concentrations were found for the lower soil layer (35-65 cm). Tikaku (1998) summarized a number of data with respect to igenous rocks and the earth crust, which were found to vary from 0.44 to 0.63 g/kg.

A background concentration in <u>soil</u> in the Netherlands can be derived:
Starting point is the data set of Edelman, who sampled approximately 40 Dutch soils regions which are assumed to be less influenced by human activities (Edelman, 1984). In most cases, these areas are (protected) natural systems, including a large variety of Dutch ecosystems like forests, dunes, outer marches etc. The samples have been analysed for titanium by neutron activation analysis. In addition, these soils are characterised with respect to content of clay, organic matter, carbonates, pH etc. Data are related to the upper 10 cm of the soil layer.

A reference line is derived. First, using multiple linear regression analysis, a correlation analysis is performed for the concentration of the element in the soil sample and the soil characteristics clay and organic matter content. From the most reliable line, the slope of the final reference line is obtained. Then, the line is shifted in such a direction that approximately 90% of the original samples lie below the line. In Figure 3 such an analysis is carried out for titanium. The best correlation is obtained by the clay content of the soil only (the dotted line). The slope of this line is 46.6 ± 8.3 with an r^2 of 0.504 (n = 33). Shifting the line results in a reference line with the equation:

$$[Ti] = 2300 + 46.6 * L$$
 (9)

where:

L: clay content.

Subsequently, the background concentration for titanium in standard soil is 3465 mg/kg.

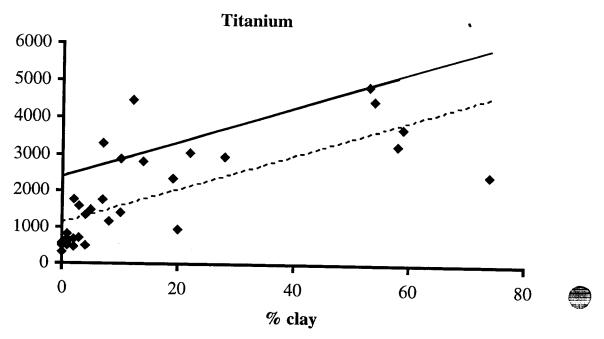


Figure 3: Measured background concentrations of Titanium in Dutch soils as a function of the clay content. Dotted line represents best fit and the solid line represents the reference line. Data adapted from Edelman (1984).

Only two ecotoxicological studies are available (see Table 1.3 and 4.2 of Appendix 3): one in freshwater with *Tetrahymena pyriformis* and one in which the effects on the activity of arylsulphatase in soil is studied. This information is considered insufficient to derive MPAs for soil or surface water.

3.5 Uranium (U)

3.5.1 Introduction

Uranium is a naturally occurring radioactive element. The natural element consists of $99.28\%^{238}$ U (half-life $4.5*10^9$ years), $0.71\%^{235}$ U (half-life $7.1*10^8$ years) and $0.006\%^{234}$ U (half-life $2.5*10^5$ years) (Uvarov and Isaacs, 1986). 235 U is capable of sustaining a nuclear chain reaction and is used in nuclear reactors and nuclear weapons.

Uranium can induce radiation stress as well as chemical toxicity. Although information is scarce, the latter seems to occur at lower concentrations than the former. Sheppard et al. (1992) concluded from germination tests with *Pinus banksiana* Lamb., that ²³⁸U concentrations that would be chemically toxic to plants were 720 times lower than those that would cause radiation stress.



3.5.2 Background concentrations

Concentrations of uranium are expressed in two ways, as usual in chemistry by concentration per volume of mass unit or in radiation unit (Bq) as done for radionuclides.

Winters (1998) reports uranium concentrations of 3.3 μ g/l and 0.04 μ g/l for seawater and stream water, respectively. Du Preez (1980) reports uranium concentrations in sea water of 2-3 μ g/l. For river waters in Japan, mean uranium concentrations of 0.57 μ g/l are reported (Miyake et al.,). In river waters, background activity concentrations of 0.185 to 62.9 Bq/kg are reported for ²³⁸U (Laane, 1992). For groundwater in forest areas in the Netherlands, indicative uranium concentrations were found to range from less than <0.01 μ g/l (detection limit of analytical technique) to about 1.3 μ g/l (Bronswijk, pers. com.). These values agree well with data (0.04 - 5 μ g/l) obtained for a number of groundwater samples (depth 15-25 m) as carried out by Van Dongen et al. (1983). In this research, it was concluded that the sampled groundwaters were not contaminated through radioactive waste present at the particular spot.

For the earth crust, uranium contents vary from circa 2 up to 80 mg/kg (Winters, 1998; Tikaku, 1998). A background concentration in <u>soil</u> in the Netherlands can be derived (see paragraph 3.3 on titanium for the data source and methodology). It is found that the soil concentration depends on both the clay content and the organic matter content. Hence, the slope of the reference line becomes a function of both parameters (r² of 0.776 and n=37):

$$[U] = 0.073 (\pm 0.008) * L + 0.009 (\pm 0.010) * OM$$
 (10)

where:

L: clay content;

OM: organic matter content.

In Figure 4 the calculated uranium concentration is plotted versus the measured concentration. The dotted line represents the 1:1 line, which is shifted up with one unit to fulfill the requirement that 90% of the samples will have an uranium concentration which is below the reference line. The reference line becomes then:

$$[U] = 1 + (0.073 * L) + (0.009 * OM)$$
(11)

Subsequently, the background concentration for uranium in standard soil is 2.915 mg/kg. Adding the MPA of 25.4 mg/kg leads to an MPC of 28.3 mg/kg.

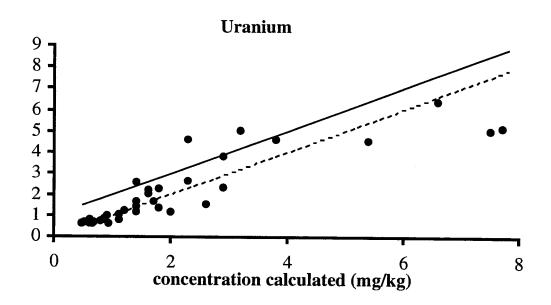


Figure 4: Measured versus calculated background concentrations of uranium in Dutch soils: [U] = 0.58 + (0.073*L) + (0.009*OM) with r^2 of 0.776 (n=37). Data adapted from Edelman (1984).

Concluding: the existing information is too scarce for uranium to derive a background concentrations in Dutch sediment, surface water and groundwater. A background concentration for Dutch soils can be derived.

3.5.3 Surface water

Release of uranium to the aquatic environment mainly occurs due to mining activities. Uranium does occur as the uranyl ion: UO_2^{2+} . In fresh surface water with a pH of more than 6 the uranyl ion forms complexes with carbonate ions (Poston et al., 1984).

The available ecotoxicological information is presented in Table 1.4 and 2.2 for freshwater and saltwater organisms, respectively. Only a few studies are available; most being acute. According to Poston (1984) the toxicity of uranium is influenced by the water hardness: 48 h LC50 values for *D. magna* decreased from 29.6-74.3 mg/l in water with a hardness of 188-205 mg CaCO₃/l to 5.3-7.6 mg/l in water with a hardness of 66-73 mg CaCO₃/l. This is confirmed by results of Bywater et al. (1991) who tested serveral typical Australian fish and crustacean species in extremely soft natural water (hardness: 4.35 mg CaCO₃/l). They reported LC50 values ranging from 0.41 to 3.46 mg/l. Hamilton (1995) tested 3 fish species in water with a hardness of 196 mg CaCO₃/l leading to a 96 LC50 value of 46 mg/l for all fish species.

In the Figure 5 the relationship between water hardness and acute toxicity for 15 fish species is depicted. Not enough data-points are available to determine a quantitative relationship. Especially in the - for the Netherlands relevant - range of $50-200 \text{ mg CaCO}_3/1 \text{ data}$ are lacking.

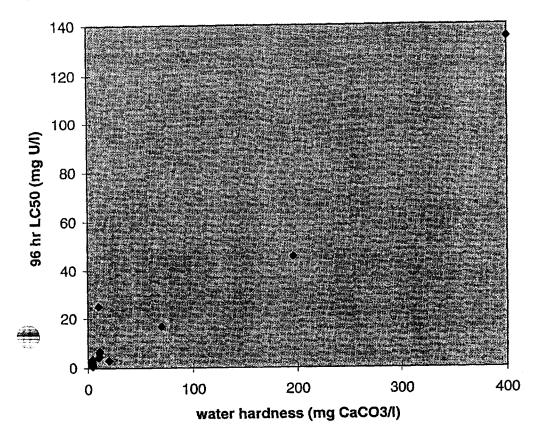


Figure 5: Relationship between water hardness and acute fish toxicity for uranium ($\dot{n} = 15$).

For deriving an MPA for uranium the following selection procedure is followed:

- the test results with typical Australian species in extreme soft water of 4.35 CaCO₃/l of Bywater et al. (1991) are excluded;
- test results for freshwater and saltwater species are combined.

The lowest acute LC50 value is 2.8-3.1 mg/l for *Pimephales promelas*. The lowest chronic NOEC is 10 μ g/l for *Moinodaphnia macleayi*. Hyne et al. (1993) investigated the effects of several diets on survival and fecundicity of this cladoceran species in a life-cycle toxicity test. Survival appeared to be the most sensitive parameter.

The modified EPA method has to be used to derive an MPA, as not enough data are available to apply statistical extrapolation. Subsequently, the lowest value is selected after applying a factor 1000 on the LC50 and 10 on the NOEC, leading to an MPA of 1.0 μ g/l.

No Dutch background concentration for uranium is available in freshwater, saltwater or groundwater. Therefore, no MPC can be derived.

3.5.4 Sediment

No toxicity data are available for sediment dwelling organisms. The equilibrium partitioning method can be used to derive an MPA for sediment, using the equation (7). However, no data are available on sorption of uranium in sediment. Therefore no MPA for sediment can be derived.

3.5.5 Soil

Only one ecotoxicological study is available: Sheppard et al. (1992) studied the effects of uranium on plants, earthworms and phosphatase activity. Unfortunately, only the results for the concentrations in which effects occurred are presented. Therefore, only for green beans (*Phaseolus vulgaris*) an NOEC of 254 mg/kg in standard soil can be derived for effects on germination. It is clear however, that no or only minor effects occurred at higher concentrations up to 1523 mg/kg in standard soil for several other plants, the earthworm *Lumbricus terrestris* and phosphatase activity. Applying a factor 10 on the NOEC of 254 mg/kg leads to an MPA(species) in standard soil of 25.4 mg/kg. No MPA(processes) is derived.

The equilibrium partitioning method can be used to harmonize the MPA for soil and the one for surface water, using the equation (8). Only one study is available on sorption of uranium: Willett and Bond (1995) determined sorption properties of three highly weathered soils in batch experiments. From these experiments an average log Kp of 2.23 ± 2.3 l/kg can be derived. Using the MPA for water of $2.8 \,\mu$ g/l an MPA for soil of $0.47 \, \text{mg/kg}$ is derived. This value is much lower than the MPA for soil based on ecotoxicological data derived above. Considering the uncertainties in the Kp value (sorption of uranium is highly pH dependent) the latter value is preferred.

3.6 Organosilicon compounds

3.6.1 Introduction

Of the organosilicon compounds the methylsiloxanes are the most important group (Frye, 1988). Siloxanes - characterized by the Si-O-Si linkage - are a group of compounds with the general formula $R_n SiO_{(4-n)/2}$, where R stands for an organic group or hydrogen. Siloxanes are produced as fluids, elastomers and resins. Since the elastomers and resins are high-molecular polymers they will probably be immobile in the environment and will therefore not be considered here. Two types of fluids can be distinguished (Hamelink, 1992):

1. non-volatile linear and volatile cyclic polydimethylsiloxanes (PDMS)

2. polyethermethylsiloxanes (PEMS).

PEMS comprise only a few percent of the total market (Hamelink, 1992). They will not be considered further here. For PDMS information was collected on ecotoxicology and invironmental fate parameters. The high molecular weight PDMS will probably not be taken up⁷. Subsequently, the search for information was focussed on the following substances based on a study by Montforts and Van de Plassche (1996):

- linear PDMS: hexamethyltrisiloxane, octamethyltrisiloxane, decamethyltetrasiloxane, dodecamethylpentasiloxane and tetradecamethylsiloxane;
- branched PDMS: 1,1,1,3,5,5,5-heptamethyl-3-[(trimethylsilyl)oxy]-trisiloxane, 1,1,1,5,5,5-hexamethyl-3,3bis[(trimethylsilyl)oxy]-trisiloxane and pentamethyl[(trimethylsilyl)oxyl]-cyclotrisiloxane;
- cyclic PDMS: hexamethylcyclotrisiloxane, octamethylcyclotetrasiloxane, decamethylcyclopentasiloxane and dodecamethylcyclohexasiloxane;
- the breakdown product of PDMS: dimethylsilanediol.

Data appeared to be very scarce for PDMS: almost no ecotoxicological information was retrieved. Hobbs et al. (1975) tested some commercial formulations to several freshwater and marine species. Since exposure times were only 48-96 hr and test concentrations far above the water solubility, these tests are not suitable to derive MPCs. The only compound for which sufficient information was available is octamethyltetrasiloxane (OMCTS). An extensive testing programme for OMCTS has been carried out as part of a Toxic Substances Control Act (TSCA) Section 4 Consent Order (C) agreed on between the U.S. Environmental Protection Agency (US-EPA) and the Silicones Environmental Health and Safety Council, an industrial organization (Hobson, 1995). Resuls of this program were published in Environmental Toxicology and Chemistry in 1995. Based on the results of the program the US-EPA concluded in 1994 that OMCTS would present low risk to aquatic species (Walker and Smock, 1995).

More than 90% of OMCTS is used as an on-site intermediate in the synthesis of PDMS and other high molecular weight silicones (Hobson, 1995). The remainder is used in personal care and consumer products: anti-perspirants, skin and hair care products, automobile polishes etc. The structure of OMCTS is given in Figure 4.

⁷ The EU Technical Guidance Document gives a molecular weight of 700 as a cut-off value.

Figure 4. Structure of octamethylcyclotetrasiloxane (OMCTS) (Hobson, 1995).

OMCTS is a highly volatile substance with the following physico-chemical properties (Hobson, 1995):

- vapour pressure: 133 Pa;
- log Kow: 5.1;
- water solubility: in freshwater 74 μg/l and in saltwater 33 μg/l;
- dimensionless Henry's law constant: > 17.

Due to these properties "totally enclosed exposure systems", i.e. flow-through systems with no headspace, were used to maintain stable exposure concentrations (Hobson and Silberhorn, 1995). Also, a method was developed to prepare OMCTS-saturated stock solutions. In the following paragraph MPCs will be derived based on the ecotoxicological data presented in Table 1.5, 2.3 and 5.1 in Appendix 3.

3.6.2 MPCs for surface water, sediment and soil for OMCTS

Water

Acute or prolonged toxicity studies were carried out with the freshwater species Daphnia magna, Chironomus tentans and Oncorhynchus mykiss and the saltwater species Mysidopsis bahia and Cyprinodon variegatus (Kent et al., 1994; Sousa et al., 1995). Mean measured exposure concentrations varied from 0.49 to 22 μ g/l. Only in the test with Oncorhynchus mykiss effects were observed, leading to an LC50 of 10 μ g/l. Results of several other studies are reported also by Sousa et al. (1995): studies with larger fish showed no effects at the same concentrations after 14 days exposure.

A 21 day life-cycle study and an early life-stage study were carried out with *Daphnia magna* and *Oncorhynchus mykiss*, respectively. Mean measured exposure concentrations were 1.7-15 µg/l for *Daphnia magna* and 0.25-4.4 µg/l for *Oncorhynchus mykiss*. In the daphnid study 77% survival was measured at the highest concentration compared to 93% in the control. At the other concentrations no effects were observed, giving a NOEC of 7.9 µg/l. No effects were detected on reproduction, measured as mean cumulative offspring per female daphnid. In the study with *Oncorhynchus mykiss* no effects were observed on reproduction measured as % viability of embryos, % survival at hatch and larval survival post-hatch, leading to a NOEC of >4.4 µg/l.

OMCTS appears to act by a non-specific narcosis mechanism of toxicity: mortality occured after 7-14 days exposure and was the only endpoint affected. Therefore a factor 10 on the lowest NOEC seems justified - combining the data-sets for freshwater and saltwater species - to derive an MPC for surface water, although no studies with algae are available. QSAR estimations, using the QSARs for substances which act by non-polar narcosis derived

 μ g/l for fish, *Daphnia magna* and *Selenastrum capricornutum*, respectively. Although the validity of the log Kow could not be checked as the original study could not be retrieved⁸, these calculations substantiate the application of an assessment factor of 10. This leads to an MPC of 0.44 μ g/l.

Bioconcentration has been determined with *Pimephales promelas* using radiolabeled OMCTS leading to a BCF of 12,400 l/kg after 28 days exposure (Fackler et al., 1995). HPLC analysis showed that OMCTS was not metabolized. With the LC50 for *Oncorhynchus mykiss* a LBB of 0.4 mmol/kg can be calculated, which is another indication - although different fish species are used - that OMCTS is acting by non-polar narcosis.

The potential effects on organisms higher in the food-chain could not be studied as no toxicological information is available. Walker and Smock (1995) report that OMCTS has been recommended for health effects testing in 1992. From these tests a No Effect Concentration for predators can be derived using toxicity studies with mammals. Whether tests have been carried out is unknown, however.

Sediment

One spiked sediment test was carried out with *Chironomus tentans* using exposure concentrations of 2.6 to 250 mg/kg dw (Kent et al., 1994). Three sediment types were used varying in organic matter content, prepared from one pond sediment. Effects on survival and growth were observed at the highest exposure concentrations only, leading to NOECs of 54-120 mg/kg dw. Taking the geometric mean of these values leads to an NOEC of 198 mg/kg dw for standard sediment. Since results for only one species are available, an MPC for sediment is derived applying a factor 100 on the NOEC of 198 mg/kg dw. This leads to an MPC of 2.0 mg/kg dw.

From the MPC for water a MPC for sediment can be calculated using equation (7). Using the log Kow of 5.1 a log Koc is derived of 4.7 l/kg. Subsequently, a log Kp of 3.5 l/kg for standard sediment is derived. Applying equation (7) gives an MPC for sediment of 1.3 mg/kg dw. This value is in agreement with the MPC for sediment based on ecotoxicological data. Therefore, the MPC of 2.0 mg/kg dw is preferred.

Soil

No ecotoxicological data are available for soil organisms. Using equilibrium partitioning an MPC for soil can be derived applying equation (8). With the log Kp of 3.47 l/kg and the MPC for water of 0.44 μ g/l a MPC for standard soil of 1.3 mg/kg dw can be derived.

⁸ The log Kow was referred to as Manufacturer submissions (4, 8d, 8e, FYI) to the US-EPA of the TSCA Test Submissions Database. The Syracuse Research Corporation calculated value for the log Kow is 5.09.

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Appendix 1 Mailing list

- 1-10 Directoraat Generaal Milieubeheer, Directie Stoffen, Veiligheid en Straling, afdeling Normstelling, d.t.v. M. v.d. Weiden
- 11 plv. DG Milieubeheer
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- 13 Directoraat Generaal Milieubeheer, Directie Bodem
- 14 Directoraat Generaal Milieubeheer, Directie Lucht en Energie, hoofd afdeling Luchtkwaliteit en Verzuring
- 15 Directoraat Generaal Milieubeheer, Directie Drinkwater, Water en Landbouw
- 16-36 Onderzoeksbegeleidingsgroep INS d.t.v. D. Sijm
- 37-47 Stuurgroep INS d.t.v. M. v.d. Weiden
- 48 A. Berends, Solvay, Brussel, België
- 49 F. Balk, Haskoning, Nijmegen
- 50 J.H. Burema, Nederlandse Vereniging van Zeepfabrikanten, Zeist
- 51 H. Davies, NSW EPA, Sydney, Australië
- 52 T. Feijtel, Procter & Gamble, Brussel, België
- 53 J.W. Gorsuch, Eastman Kodak Company, New York, USA
- 54 C. Hogstrand, University of Kentucky, Lexington, USA
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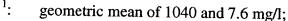
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Appendix 2: Toxicity data used for extrapolation

Boron (expressed	as	mg	B/1)	
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species	NOEC	species	NOEC
	mg/l		mg/l
Pseudomonas putida	89 ¹	Chironomus decorus	10
Chilomonas paramaecium	38	Carassius aurata	11 ⁵
Entosiphon sulcatum	3.2^{2}	Ictalurus punctatus	1.4^{6}
Uronema pardaczi	109	Micropterus salmoides	1.4
Microcystus aeruginosa	73	Oncorhynchus mykiss	0.23^{7}
Scenedesmus quadricauda	6.9^{3}	Pimephales promelas	18 ⁸
Ceriodaphnia dubia	10	Bufo fowleri	33 ⁹
Daphnia magna	13 ⁴	Rana pipiens	17 ¹⁰



geometric mean of 1.0 and 10 mg/l;

Silvernitrate (expressed as µg Ag/l)

NOEC	species	NOEC
μg/l		μg/l
6	Daphnia magna	3.6^{1}
0.7	Hyalella azteca	0.9
9.5	Isonychia bicolor	3.1
2.6	Corbicula fluminea	2.6
580	•	0.23^{2}
100	Pimephales promelas	0.37
	μg/l 6 0.7 9.5 2.6 580	μg/l 6 Daphnia magna 0.7 Hyalella azteca 9.5 Isonychia bicolor 2.6 Corbicula fluminea 580 Oncorhynchus mykiss

geometric mean of 1.6, 8.8 and 3.4 μ g/l;

geometric mean of 0.58, 24 and 24 mg/l;

^{2:} 3: 4: 5: geometric mean of 27, 6, 29, 6.4, 10 and 18 mg/l;

geometric mean of 26.5, 8.5, 9.2 and 6.8 mg/l;

geometric mean of 1.01, 0.75, 9.0 and 0.49 mg/l;

geometric mean of 0.19, 0.57, 2.1, 0.11, 0.001, 0.96, 9.6, 0.01 and 0.75 mg/l (EC10 values calculated from tests by Black et al. (1993) are included)

geometric mean of 14 and 24 mg/l;

geometric mean of 48.7 and 22.3 mg/l;

geometric mean of 32.5, 45.7, 7.04 and 7.04 mg/l.

geometric mean of 0.09, 0.17, 0.34, 0.36 and 0.1 μ g/l.

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Appendix 3 Toxicity data

TABLE 1.1: TOXICITY OF BORON TO FRESHWATER SPECIES

species	anal.	test type	species	Hq	hardness mg CaCO ₃ /I	test water	exp. time	criterion	value (mg B/l)	reference
CHRONIC TOXICITY							:			
bacteriophyta Peudomonas putida Peudomonas putida	Z,	ω,	Na ₂ B ₄ O ₇	7.0	42.5	am -	16 h 16 h	NOEC EC10	1040 ^{1.6} 7.6	Bringmann and K hn, 1977a Schr berl and Huber, 1989 in ECETOC, 1997
protozoa Chilomonas paramaecium Entosiphon sulcatum Entosiphon sulcatum Uronema pardaczi	ZZıZ	ωω _ι ω	Na ₂ B ₄ O ₇ Na ₂ B ₄ O ₇ - Na ₂ B ₄ O ₇	6.9 6.9 - 6.9	42.3 35.3 - 35.3	am am am	48 h 72 h 72 h 20 h	NOEC NOEC NOEC NOEC	38¹ 1.0¹ ≥10 109¹	Bringmann and K hn, 1980a Bringmann, 1978a Guhl, 1996 in ECETOC, 1997 Bringmann and K hn, 1980b
cyanophyta Microcystis aeruginosa	z	S	Na ₂ B ₄ O ₇	7.0	28.7	am	p 8	NOEC	731.7	Bringmann and K hn, 1978b
chlorophyta Scenedesmus quadricauda Scenedesmus subspicatus Scenedesmus subspicatus	Z , ,	ω , ,	Na ₂ B ₄ O ₇ NaBO ₃ H ₃ BO ₃	7.0	28.7	am - -	7 d -	NOEC EC10 EC10	0.58¹ 24 24	Bringmann and K hn, 1977a Guhl, 1992 in ECETOC, 1997 Kopf and Wilk, 1995 in ECETOC, 1997
crustacea Ceriodaphnia dubia Daphnia magna Daphnia magna Daphnia magna Daphnia magna	z >> >> .	S R R R R .	H,BO; H,BO; H,BO; H,BO; H,BO;	7.9 7.1-8.7 7.1-8.7 8.1 7.3-8.0	250 166 166 148 148	am nw nw nw nw	14 d 21 d 21 d 21 d 21 d 21 d	NOEC NOEC NOEC NOEC NOEC NOEC	10 ² 27 ¹ 6 ² 29 ³ 6.4 ⁴	Hickey, 1989 Lewis and Valentine., 1981 Lewis and Valentine., 1981 Gersich, 1984 Gersich, 1984 Guhl, 1992 in ECETOC, 1997



	anal.	test type R	species H ₃ BO ₃	PHd 7.9	hardness mg CaCO ₃ /I 250	test water am	exp. time 14 d	criterion	value (mg B/l)	reference Hickey, 1989
Z	—— <u>—</u>	84	Na ₂ B ₄ O ₇	8.2	06	rw	96 h	NOEC	101	Maier and Knight, 1991
		Щ	Na ₂ B ₄ O ₇	1	50	M.I	7 d	NOEC	26.5	Ravmond and Butterwick 1992
			$Na_2B_4O_7$,	200	ΓW	7 d	NOEC	8.5	Raymond and Butterwick, 1992
		Щ 1	H ₃ BO ₃	,	50	ΙW	7 d	NOEC	9.2	
			H ₃ BO ₃		200	rw	7 d	NOEC	8.9	
4			H ₃ BO ₃		50	2	p 6	NOEC	1.01	
			H ₃ BO ₃		200	ΓW	p 6	NOEC	0.75	
			Na ₂ B ₄ O ₇	,	50	ΙW	p 6	NOEC	0.6	
			Na ₂ B ₄ O ₇	1	200	rw	p 6	NOEC	0.49	
×		ı,		7.5	204	rw	11 d	NOEC	$1.39^3\alpha$	Black et al., 1993
≻		<u> </u>	ı	7.4	197	rw	32 d	EC10	$0.19^8\alpha$	Black et al., 1993
X		Щ	•	7.4	197	IW	32 d	EC10	$0.57^9 \alpha$	Black et al., 1993
\succ		Щ	H ₃ BO ₃	6.8-7.1	24-39	mu		NOFC	>> 13 0	Black et al 1002
			1			 -			3	בומנה כן מוו, 1773
	_	щ	H ₃ BO ₃	,	50	2	28 d	NOEC	0.11	Raymond and Butterwick, 1992
1	-	<u> </u>	H ₃ BO ₃		200	rw	28 d	NOEC	0.001	Raymond and Butterwick, 1992
		<u> </u>	Na ₂ B ₄ O ₇		50	ľW	28 d	NOEC	96:0	Raymond and Butterwick, 1992
		L.	Na ₂ B ₄ O ₇	1	200	ľW	28 d	NOEC	9.6	Raymond and Butterwick, 1992
,		<u></u>	H ₃ BO ₃		200	M.	32 d	NOEC	0.01	Raymond and Butterwick, 1992
	-	<u>-</u>	H ₃ BO ₃	1	1	wu	36 d	NOEC	0.75	Raymond and Butterwick, 1992
	_	<u>н</u>	H ₃ BO ₃	7.1-7.9	38-46	wu	30 d	NOEC	141	Raymond and Butterwick, 1992



species	anal.	test type	species	Hd		test e	exp. time	critellon	value (mg B/l)	reference
		:			CaCO,/I					000111
Pimephales promelas, egg and fry		ഥ	H ₃ BO ₃	7.1-7.9	38-46	wa	p 09	NOEC	243	Raymond and Butterwick, 1992
amphibia		ħ	H,BO,	ı	50	M		NOEC	48.7	Raymond and Butterwick, 1992
Bifo fowleri, embryo-iarvai Rufo fowleri, embryo-larvai	1 1	, IL	H ₃ BO ₃		200			NOEC	22.3	Raymond and Butterwick, 1992
Rana pipiens, embryo-larval	,	ഥ	H ₃ BO ₃	•	50		_	NOEC	32.5	Raymond and Butterwick, 1992 Desired and Butterwick, 1902
Rana pipiens, embryo-larval	1	ᄄ	H ₃ BO ₃		200	A A	7 d	NOEC	7.04	Raymond and Butterwick, 1992 Raymond and Butterwick, 1992
Rana pipiens, embryo-larval Rana pipiens, embryo-larval	<u> </u>	L	Na ₂ B ₄ O ₇		200			NOEC	7.04	Raymond and Butterwick, 1992
ACUTE TOXICITY										
crustacea Simocephalus vetulus	Z	S	H ₃ BO ₃	7.9	250	am	24 h	EC50	123	Hickey, 1989 Hickey, 1989
Ceriodaphnia dubia Ceriodaphnia cf. pulcella	zz	nω	H ₃ BO ₃	7.9	250		24 h	EC50	101	Hickey, 1989
Daphnia carinata	ΖZ	so so	H ₃ BO ₃ H ₃ BO ₃	7.9	250 250	am am	24 h 24 h	EC50	320	Hickey, 1909 Hickey, 1980
Daphnia magna Daphnia magna	ZZ	s os c	Na ₂ B ₄ O ₇	9.7	272	am	24 h	LC50	73	Bringmann and Kühn, 1977b Maier and Knight. 1991
Daphnia magna Daphnia magna	Z ,	n n	Na ₂ B ₄ O ₇ H ₃ BO ₃	6.7-8.1	150	. wu	48 h	PCS0	133	Raymond and Butterwick, 1992
insecta Chironomus decorus (4 th instar)	Z	S	Na ₂ B ₄ O ₇	8.2	06	Ν	48 h	rcs0	1376	Maier and Knight, 1991
pisces Gambusia affinis, female, adult		S	Na ₂ B ₄ O ₇	8.6-9.1		ı	96 h	LC50	408	Raymond and Butterwick, 1992
Gambusia affinis, female, adult		so so	H ₃ BO ₃ Na ₂ B ₄ O ₇	5.4-7.3	- 84-163	- ¥	24 h	rcso rcso	9/0 4.6	Raymond and Butterwick, 1992
Lepomis macrochirus, 7 cm, 5 g	1	S	BF ₃	1	- 77	¥ i	24 h 283 h	LC50	2389	Raymond and Butterwick, 1992 Raymond and Butterwick, 1992
Oncorhynchus kisutch, alevins Oncorhynchus kisutch, < 1 year		o o	Na ₂ B ₂ O ₄ H ₃ BO ₃	7.1-8.7	4, 166	nw h	48 h	LC50	226	Raymond and Butterwick, 1992

The section of the se

reference	Raymond and Butterwick, 1992
value (mg B/l)	40.35
спієпоп	EC50
exp. time	32 d
test water	wu
hardness mg CaCO3/I	ı
рН	ı
species	B ₄ O ₇ -
test	1
anal. test type	
species	macrophyta Myriophyllum spicatum

reproduction

mortality

growth and reproduction

reduction of root weight

Bringmann and Kühn (1976) report a NOEC of 73 mg/l. However, in another publication by Bringmann and Kühn (1980b) again 1040 mg/l is reported. All test

results from Bringmann and Kühn are expressed as the "effective ion" which is considered here as mg B/I.

Bringmann and Kühn (1976) report a NOEC of 5 mg/I. However, in two other publications by Bringmann and Kühn (1978c; 1980b) 73 mg/l is reported. % %

Soap strain of rainbow trout. EC10 calculated using a concentration-response model applying Graphpad for results "mortality and teratogenesis at 8 days posthatching" (control: 6.4%; 0.001 mg/l: 7.0%; 0.009 mg/l: 8.9%; 0.10: 12.5%; 1.26: 22.1%; and 10.20 mg/l: 33.5% effect).

Whyteville strain of rainbow trout. EC10 calculated using a concentration-response model applying Graphpad for results "mortality and teratogenesis at 8 days oosthatching" (control: 7.0%; 0.001 mg/l: 13.8%; 0.016 mg/l: 6.6%; 0.103: 12.6%; 1.34: 24.4%; and 11.46 mg/l: 34.3% effect). 9

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TABLE 1.2.1: TOXICITY OF SILVER TO FRESHWATER SPECIES: CHRONIC DATA FOR AGNO3

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secies	anal.	test type	species	Hd	hardness mg CaCOyll	test water	exp. time	criterion	value (µg Ag/l)	reference
bacteriophyta Pseudomonas putida	Z	S	AgNO ₃	7.0	42.5	am	16 h	NOEC	61	Bringmann and Kühn, 1977
cyanophyta Microcystis aeruginosa	z	S	$AgNO_3$	7.0	28.7	am	p 8	NOEC	0.71	Bringmann and Kühn, 1978
chlorophyta Scenedesmus quadricauda	Z	S	$AgNO_3$	7.0	28.7	am	p &	NOEC	9.5²	Bringmann and Kühn, 1978
protozoa Chilomonas paramaecium Entosiphon sulcatum Uronema parduczi	ZZZ	S S S	AgNO3 AgNO3 AgNO3	6.9 5.9 6.9	42.3 35.3 35.3	am am	48 h 72 h 20 h	NOEC NOEC NOEC	2.6^{1} 580^{1} 100^{1}	Bringmann and Kühn, 1980a Bringmann, 1978 Bringmann and Kühn, 1980b
crustacea Daphnia magna, , 24 h Daphnia magna, , 24 h Daphnia magna, , 24 h Hyalella azteca	****	8888	AgNO3 AgNO3 AgNO3 AgNO3	7.2 7.2 7.2 7.8	60 75 180 34.8	nw nw nw	21 d 21 d 21 d 21 d	NOEC NOEC NOEC NOEC	1.6 ³ 8.8 ³ 3.4 ³	Nebeker et al., 1983 Nebeker et al., 1983 Nebeker et al., 1983 Diamond et al., 1990
insecta Isonychia bicolor	>	æ	AgNO ₃	7.8	34.8	wu	14 d	NOEC	3.14	Diamond et al., 1990
mollusca Corbicula fluminea Corbicula fluminea	7 7	8 8	AgNO ₃ AgNO ₃	7.8	43.8 43.8	wu wu	21 d 21 d	NOEC	7.8 ⁴ 2.6 ¹	Diamond et al., 1990 Diamond et al., 1990
pisces Oncorhynchus mykiss, eyed eggs Oncorhynchus mykiss, eyed eggs Oncorhynchus mykiss, eyed eggs Oncorhynchus mykiss, eyed eggs	* * * *	5555	AgNO3 AgNO3 AgNO3 AgNO3	6.8-7.3 6.6-7.4 6.6-7.7 6.6-7.4	30.4 27.5 27.5 27.5	nw nw nw	10 w 18 m 2 m 3 m	NOEC NOEC NOEC NOEC	< 0.6 ⁴ 0.09 ⁴ 0.09 ¹ 0.17 ¹	Davies et al, 1978 Davies et al, 1978 Davies et al., 1978 Davies et al., 1978

reference	Davies et al., 1978 Nebeker et al., 1983 Nebeker et al., 1983 Holcombe et al., 1983 Holcombe et al., 1983
([/8/	0.34 ¹ D. 0.36 ¹ N. 0.1 ¹ N. 1.07 ² H. 0.65 ¹ H.
4	NOEC NOEC NOEC NOEC NOEC
exp. time	3.5 m 60 d 60 d 28 d 28 d 28 d
test water	0 m m m m m m m m m m m m m m m m m m m
hardness mg CaCO ₂ /I	27.5 36 36 45.1 45.1
Hd	6.6-7.4 7.0 7.0 7.2-7.7 7.2-7.7
species	AgNO3 AgNO3 AgNO3 AgNO3 AgNO3 AgNO3
test type	~ ~ ~ CF CF
anal.	*************************************
Species	Oncorhynchus mykiss, eyed eggs Oncorhynchus mykiss, eggs Pimephales promelas, < 24 h Pimephales promelas, < 24 h Pimephales promelas, < 24 h

- 4 % 4

growth abnormality of larvae alive adults, total young and mean number of young per adult per day mortality

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TABLE 1.2.2: TOXICITY OF SILVER TO FRESHWATER SPECIES: DATA FOR OTHER AG SPECIES THAN AGNO,

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reference	Hogstrand et al., 1996 Hogstrand et al., 1996 LeBlanc et al., 1984 LeBlanc et al., 1984 LeBlanc et al., 1984 LeBlanc et al., 1984	LeBlanc et al., 1984 LeBlanc et al., 1984
value (mg Ag/l)	161 α >100° α >280¹ α >240³ α >13³ α >4.6⁵ α	16 α >11 α
criterion	LC50 LC50 LC50 LC50 LC50 LC50 LC50	NOEC
exp. time	96 hr 96 hr 96 hr 96 hr 96 hr	emlar. ⁶ emlar. ⁶
test water	N N N N	rw rw
hardness mg CaCO ₂ /I		38 38
Hd	7.9-8.2 7.9-8.2 7.2-8.4 7.2-8.4 7.2-8.4 7.2-8.4	7.2-8.4 38
species	Ag(S ₂ O ₃) _n AgCl _n Ag(S ₂ O ₃) _n AgS ⁴ AgCl _n	Ag(S ₂ O _{3)n} AgS ⁴
test type	SS SS CG	CF CF
anal.	******	* *
sbecies	ACUTE TOXICITY Oncorhynchus mykiss Oncorhynchus mykiss Pimpehales promelas Pimpehales promelas Pimpehales promelas	CHRONIC TOXICITY Pimpehales promelas Pimpehales promelas

calculated ionic Ag⁺ concentration: 0.12 ng/l

tested as dispersion

calculated ionic Ag⁺ concentration: <10⁻⁵ ng/l

tested as slurry

tested in the presence of 2,000 mg/l CI-; calculated ionic Ag⁺ concentration: 0.103 µg/l; percent mortality was 40 at 4.6 mg/l

embryo-larval test with exposure until 30 days post-hatch [Na⁺] = 0.6 mM; [C1] = 0.7 mM; [Ca²†] = 1.0 mM and [HCO₃] = 1.9 mM

water supplemented with 50 mM NaCl; fish acclimated to test water for 2 weeks prior to testing and then exposed to AgNO3; speciation calculations showed that almost all Ag was present as AgCl_n

dissolved AgCl, was 120 µg Ag/l using speciation calculations; no effects were observed when AgCl, was directly added to test water up to 1 mg/Ag l

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TABLE 1.3: TOXICITY OF TELLURIUM TO FRESHWATER SPECIES

reference	Khangarot, 1991
value (mg Te/l)	126
criterion	EC50
exp. time	ч 96
test water	am
hardness test mg water CaCO ₃ A	245
Hq	7.6
sbecies pH	K ₂ TeO ₃ 7.6
type	R
anal.	Z
species annilida	Tubifex tubifex

TABLE 1.4: TOXICITY OF TITANIUM TO FRESHWATER SPECIES

	**	-
reference	Sauvant et al., 1997	
value (mg Ti/l)	20	
criterion	IC50	
exp. time	ı	_
hardness test mg water CaCO ₃ /I	1	
hardness mg CaCO ₃ /I	•	
cies pH	ı	
species	TiCl4	
test type	1	
anal.		
species	protozoa Tetrahymena pyriformis	

TABLE 1.5: TOXICITY OF URANIUM TO FRESHWATER SPECIES

secies	anal	test type	species.	Hd	nardness mg CaCO ₃ /1	test water	exp. time	criterion	value (mg U/I)	reference
CHRONIC TOXICITY										
crustacea Daphnia magna Moinodaphnia macleayi	X	~ ~	UO ₂ (NO ₃₎₂ UO ₂ SO ₄	7.9-8.0 5.9-6.3	66-73	nw nw	21 d 5 d	NOEC	1.29¹ 0.010³	Poston et al., 1984 Hyne et al., 1993
ACUTE TOXICITY						100				
hydrozoa Hydra viridissima Hydra vulgaris	7 7	S S	UO ₂ SO ₄ UO ₂ SO ₄	6.1-6.7		wu nw	96 h 96 h	NOEC	0.15 0.40	Hyne et al., 1992 Hyne et al., 1992
crustacea Dadaya macrops, < 6 h Daphnia magna	> Z Z Z	SSS	UO ₂ SO ₄ UO ₂ (NO ₃) ₂ UO ₂ (NO ₃) ₂	6.57 7.9-8.0 7.9-8.0	4.35 66-73 126-140	nw nw nw	24 h 48 h 48 h 48 h	LC50 LC50 LC50	1.10 ² 5.3-7.6 30.4-44.6 29 6-74 3	Bywater et al., 1991 Poston et al., 1984 Poston et al., 1984 Poston et al., 1984
Diaphanosoma excisum, < 6 h Latonopsis fusciculata, < 6 h Moinodaphnia mecleayi, < 6 h	Z >> >>	n n n n	UO ₂ (NO ₃₎₂ UO ₂ SO ₄ UO ₂ SO ₄ UO ₂ SO ₄	6.57 6.57 6.57 6.57	4.35 4.35 4.35	nu nw nw	24 h 24 h 24 h	1CS0 1CS0 1CS0	$\frac{1.0^2}{0.41^2}$	Bywater et al., 1991 Bywater et al., 1991 Bywater et al., 1991
pisces Ambassis macleayi, juv.	7 .	<u>~</u> ,	UO ₂ SO ₄	6.57	4.35	wu -	96 h 96 h	LC50 LC50	0.80 ² 25	Bywater et al., 1991 Bywater et al., 1991
Craterocephalus marianae, juv	> .	~ .	UO ₂ SO ₄	6.57 6.9-7.1	4.35	wu -	96 h 96 h	LC50 LC50	1.22²	Bywater et al., 1991 Bywater et al., 1991
Gila elegans Hypseleotris compresssa I eignotheranon unicolor	Z , ,	s	1 1 1	7.8 - 6.9-7.1	196 2-20 10	rw -	96 h 96 h 96 h	LC50 LC50 LC50	46 6.6 4.1	Hamilton, 1995 Bywater et al., 1991 Bywater et al., 1991
Leadpoint up on mission.										

species	anal	anal test	species.	Hu	hardness	fact	ava	To the state of		
		type			mg	water	time	211511011	value (mg U/l)	reference
					CaCO ₃ /I					
Melanotaenia nigrans, 7 days	<u>>-</u>	2	100204	6.57	4.35	иw	96 h	1.050	1 702	Branctor of ol 1001
90 days	×	2	10,50,	6 57	4 35	210	1 70	1 050	1.70	Dywalci ci al., 1991
Molanotaenia niarans	1	i	*00700		6.6	MII W	11 02		1.90	Bywater et al., 1991
inclumenta nigrans		,		,	2-20		l 96 h	LC50	4.5	Bywater et al 1991
Melanotaenia splendida inornata	<u>_</u>	<u>ح</u>	$ \text{UO}_2 \text{SO}_4$	6.57	4.35	wu	96 h	1,050	2 662	Dynamic of al., 1771
7 days						:	:	2	00.3	Dywatel et al., 1991
90 days	X	8	UO,SO	6.57	4.35	M.	1 96 h	1 050	3 162	D
Melanotaenis splendida inornata					200	:	7	000	2.	Dywater et al., 1991
Molanotoponic contondida inconto			1	, \	07-7		96 h	LCS0	9	Bywater et al., 1991
menunoidenis spiendida mornaid	,			6.3	,	ı	96 h	LC50	1.39	Bywater et al 1991
Mogurnda mogurnda, 7 days	>	2	100_2SO_4	6.57	4.35	nw	96 h	1,050	1 112	Burnoter of al 1001
90 days	>-	2	NO,SO	6.57	4.35	wn	06 h	1 050	1.11	Dywatci et al., 1991
Mogurnda mogurnda 6 days	-	1	•)	: :	#	רכיי	1.40	Bywater et al., 1991
10 day		_	<u>. </u>	0.0		_	96 h	LC50	1.57	Bywater et al., 1991
40 days			•	6.3	,		96 h	LC50	3.29	Bywater et al 1901
/0 days	,			6.3		_	4 96 h	1,050	3 20	Burneter et al 1001
Oncorhynchus mykiss	1	,	_	,		-	1 yo	0507	7:50	Dywater et al., 1991
Pimephales promelas	,			1	20		100	1000	7.0	bywater et al., 1991
Pimenhales prometas				ı	07		90 n	LCSO	2.8-3.1	Bywater et al., 1991
Dimonhalos promodas im.			<u> </u>	, , ,	909		96 h	LC50	135	Bywater et al., 1991
I imephates prometas, juv		,	•	7.9-8.0	66-73		96 h	LC50	16.7	Rywater et al 1001
Pseudomugil tenellus, juv	Y	~	UO ₂ SO ₄	6.57	4.35	wu	96 h	1 0.50	0.732	D
Ptychochelius lucius	z	v.	· •	7.8	104		100		67.0	bywater et al., 1991
Salvelinus fontinalis)	_	 	130	<u> </u>	70 n		46	Hamilton, 1995
Vincental Johnson	. ;	. (_	ı		96 h	LC50	∞	Bywater et al., 1991
Ayraucnen texanus	z	S)		7.8	196	ΙW	96 h	LC50	46	Hamilton, 1995
						-				

test was carried out in duplo; only result of test 2 is used due to high mortality in test 1; concentration of U in test medium was 0.56 µg/l; reproduction measured as mean young per female; concentration of U in test medium was $0.2\pm0.1~\mu g/l$ parental survival

3; 5;

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TABLE 1.6: TOXICITY OF OCTAMETHYLCYCLOTETRASILOXANE TO FRESHWATER SPECIES

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species	anal	test type	subst. purity	Н	hardness mg CaCO ₃ /l	test	exp. time	criterion	value (mg/l)	reference
ACUTE/PROLONGED TOXICITY										
crustacea Daphnia magna, < 24 h	¥	Ľ	%66 <	6.8-7.2	28-36	wu	48 h	EC50	> 0.015¹ α	Sousa et al., 1995
insecta Chironomus tentans	Y	Щ	%66	6.9-7.5	20-40	wu	14 d	LC50	> 0.015 ¹ α	Kent et al., 1994
pisces Oncorhynchus mykiss, 0.42 g Oncorhynchus mykiss, 0.42 g	λ×	<u>г</u> т	%66 <	6.8-7.2	28-36 28-36	nw wu	14 d 14 d	LC50 NOEC	0.010 α 0.0044 α	Sousa et al., 1995 Sousa et al., 1995
CHRONIC TOXICITY										
crustacea Daphnia magna, < 24 h	Y	ц	%66 <	6.8-7.2	28-36	nw	21 d	NOEC	ο 6.0079 α	Sousa et al., 1995
pisces Oncorhynchus mykiss ELS-test	X	<u></u> [L	%66 <	6.8-7.2	28-36	wu	60 d post- hatch	NOEC	> 0.0044¹ α	Sousa et al., 1995

maximum achievable concentration

∷

TABLE 2.1: TOXICITY OF BORON TO MARINE ORGANISMS

species ACITE TOXICITY	anal.	test type	sbecies	ЬН	salinity (a/oo)	test water	exp. time	criterion	value (mg B/I)	reference
pisces Anouilla anouilla			0.00	,	ç		;	,		
11, 11, 11, 1	ı		1Nd2D4O7	7:7	71		74 h	rc100		IPCS, 1998
Anguilla anguilla			H ₃ BO ₃	7.2	12	,	24 h	LC100		IPCS, 1998
Anguilla anguilla			H ₃ BO ₃	9.9	25	1	24 h	LC100		IPCS, 1998
Anguilla anguilla	1	1	Na ₂ B ₄ O ₇	9.9	25	,	24 h	LC100		IPCS 1998
Anguila anguilla	,	1	NaBO ₃		12		24 h	LC100		IPCS 1998
Anguila anguilla	,		NaBO ₃		25	,	24 h	LC100		IPCS, 1998
Limanda limanda	1	ı	Na ₂ B ₄ O ₇	1	34.8	nw	96 h	LC50		Raymond and Butterwick 1002
Oncorhynchus kisutch, < 1 year	•	S	Na ₂ B ₄ O ₇		28	nw	283 h	1.050		Raymond and Butterwick 1000
Oncorhynchus kisutch, < 1 year		S	$Na_2B_4O_7$	ı	28	nw	ч 96	LC50	40	Raymond and Butterwick, 1992

TABLE 2.2: TOXICITY OF SILVER TO MARINE ORGANISMS

species	anal.	test type	species	Hd	salinity o/oo	test water	exp. time	спієпоп	value (μg Ag/l)	reference
CHRONICTOXICITY										
mollusca Crassostrea gigas, 10 month Mytilus edulis, juvenile Mytilus galloprovincialis, 3 year	z×z	& F &	AgNO ₃ AgNO ₃ AgNO ₃		35 25 35	nw nw nw	28 d 6 m 28 d	NOEC NOEC NOEC	20¹ 25² 20¹	Metayer et al., 1990 Calabrese et al., 1984 Metayer et al., 1990
fish Pseudopleuronectes americanus									54	Hostrand and Wood, 1998

mortality growth

TABLE 2.3: TOXICITY OF URANIUM TO MARINE ORGANISMS

20000000	×40
reference	Ahsanullah and Williams, 1986
value (mo 1/1)	11
criterion	NOEC
exp. time	4 w
test	nw
salinity o/oo	35
Hd	ı
species	UO ₂ (NO ₃) ₂
test type	S
anal.	X
species	crustacea Allorchestes compressa

: growth

TABLE 2.4: TOXICITY OF OCTAMETHYLCYCLOTETRASILOXANE TO MARINE ORGANISMS

species ACUTE/PROLONGED TOXICITY	anal.	test type	subst. pH purity	Hd	salinity 0/00	test	exp.	criterion	value (mg/l)	reference/remark
crustacea Mysidopsis bahia	¥	ᅜ	%66 <	7.9-8.1	20	wn	4 96	LC50	> 0.0091 ¹ α	$> 0.0091^{1} \alpha$ Sousa et al., 1995
pisces Cyprinodon variegatus	Y	Ħ	%66 <	7.9-8.1 20	20	wu	14 d	LC50	> 0.0063 ¹ α	$> 0.0063^{1} \alpha$ Sousa et al., 1995

maximum achievable concentration

∷



TABLE 3.1: TOXICITY OF BORON TO TERRESTRIAL SPECIES

species	soil type	Hd	шо %	% clay	temp.	exp. time	criterion	result test soil (mg B/kg dw)	reference
macrophyta Hordeum vulgare B(OH) ₃	sand	5.6	1.17	3.5	-	1	NOEC	1.01	Crommentuijn et al., 1995
Medicago sativa Na ₂ B ₄ O ₇	sandy clay loam sandy clay loam loamy sand loamy sand	7.3 7.3 7.4	4 7 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1	21 21 14 14	1 1 1	1 1 1 1	EC50 EC50 EC50 EC50	17.7-32.9 ¹ 16.1-30.9 ¹ 13.9-28.1 ¹ 17.2-21.5 ¹	Crommentuijn et al., 1995 Crommentuijn et al., 1995 Crommentuijn et al., 1995 Crommentuijn et al., 1995
Sorchum vulgare sudanense Na-tetraphenylboran Na-tetraphenylboran diphenyl boric acid	sand Ioamy sand sand	5.4 5.1 5.4	1.1	9 4 9	1 1 1	1 1 1	NOEC NOEC NOEC	14 t 1 8 1 8 1 8 1 8 1 8 1 8 1 8 1 8 1 8 1	Crommentuijn et al., 1995 Crommentuijn et al., 1995 Crommentuijn et al., 1995
Triticum durum	soil mix	8.1	0.45	-	5-30	1	NOEC	<25²	Yau and Saxena, 1997

^{1:} growth 2: several effects like shoot dry weight, grain yield and straw yield

TABLE 3.2: TOXICITY OF URANIUM TO TERRESTRIAL SPECIES

species	soil type	Hd	% ош	% clay	temp.	exp. time	спіепоп	result test soil (mgU/kg dw)	result stand, soil (mg U/kg dw)	reference
macrophyta Phaseolus vulgaris	fine sandy loam	7.5	18.4	18	ı	ı	EC50	>1000¹	>1176	Sheppard et al., 1992
Zea mais Lactuca sativa Brassica rapa Pine	loam clay loam fine sandy loam fine sandy loam fine sandy loam fine sandy loam	7.5 7.0 7.5 7.5 7.5 7.5	2.2 3.1 18.4 18.4 18.4 18.4	24 33 18 18 18		10 d	ECSO NOEC ECSO ECSO ECSO ECSO	>300° 300° 300° >1000° >1000° >1000°	>353 >1052 254 >1176 >1176 >1176	Sheppard et al., 1992 Sheppard et al, 1992 Sheppard et al, 1992 Sheppard et al., 1992 Sheppard et al., 1992 Sheppard et al., 1992 Sheppard et al., 1992
annelida Lumbricus terrestris	fine sandy loam	7.5	18.4	18	1	14 d	LC50	>1000	>1176	Sheppard et al., 1992

3 5 ::

seedling emergence seedling weight germination

all tests carried out with UO₂(NO₃)₂; background concentrations of uranium in soils varied from 0.6 to 4.9 mg U/kg



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TABLE 4.1: TOXICITY OF BORON TO MICROBIAL AND ENZYMATIC PROCESSES

1: soil enriched with 1% alfalfa

TABLE 4.2: TOXICITY OF SILVER TO MICROBIAL AND ENZYMATIC PROCESSES

		Crommentuijn et al., 1995	n et al., 1995	n et al., 1995	n et al., 1995	n et al., 1995	n et al., 1995	n et al., 1995	n et al., 1995	n et al., 1995	n et al., 1995	n et al., 1995		n et al., 1995	n et al., 1995 n et al. 1005	ı et al., 1993 ı et al 1995		1 et al., 1995	1 et al 1995	retal 1995	et al., 1995	ı et al., 1995	n et al., 1995	t et al., 1995	191 1905
	reference	Crommentuij	Crommentuijn et al., 1995	Crommentuijn et al., 1995	Crommentuijn et al., 1995	:	Crommentuijn et al., 1993	Crommentuijn et al., 1995	Crommentuijn et al.,	Crommentuijn et al.	Crommentuijn et al., 1995	Crommentivijn et al 1995	Crommentuin et al 1995	Crommentuijn et al., 1995	Crommentuijn et al., 1995	Crommentuijn et al.,	Crommentuijn et al., 1995	Crommentuijn et al. 1995							
	result test soil (ma Aolko dw)	50	400	50	400	539	539	539	539	539	539	539	2070	7607	7697	2697	269.7	2697	539	539	539	539	53.9	539	539
	criterion	EC15	EC27	EC65	EC97	EC96	EC73	EC85	EC59	EC98	EC54	EC41	EC07	100 H	ECS)	EC97	EC53	EC95	EC94						EC84
	exp. time	28 d	48 h	28 d	48 h	10 d	50 d	10 d	50 d	10 d	20 d	50 d	30 min	30 min		30 min		30 min	2 h	2 h	2 h	2 h		2 h	2 h
	temp.	-		•	1	30		30	ļ	30		30	···					ı	37	37	37	37		37	37
- 1	clay	0.21	0.21	0.21	0.21	23	1	30		34		45	20	3 6	<u> </u>	76		34	17	30	23	30		45	34
	шо %	7.14	7.14	7.14	7.14	4.39		6.36	(9.27		5.05	4 64	2.5	<u>:</u>	4.95		9.04	2.57	5.64	4.39	6.36		7.40	9.27
	rd.	8.4	8.4	8.4	8.4	5.8		7.8		4.		9.9	69	97	!	6.5		7.0	5.1	6.1	5.8	7.8	,	8.9	7.4
•	sou type	marl	marl	marl	marl	loam	•	clay loam		sifty clay loam	,	sifty clay	clav loam	clay loam		loam		clay loam	silt loam	silty clay loam	loam	silty clay loam		silty clay	silty clay loam
	hiocess	catalase	AgSO4	dehydrogenase	$AgSO_4$	nitrification							arylsulfatase						urease						



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TABLE 4.3: TOXICITY OF TITANIUM TO MICROBIAL AND ENZYMATIC PROCESSES

reference	Al-Khafaji and Tabatabai, 1979 Al-Khafaji and Tabatabai, 1979 Al-Khafaji and Tabatabai, 1979 Al-Khafaji and Tabatabai, 1979
stand soil (mg Tirkg dw)	1136 1121 1181 1068
result test soil (mg Ti/kg dw)	1197 1197 1197 1197
criterion	EC33 NOEC EC31 NOEC
exp. tíme	30 min 30 min 30 min 30 min
temp.	1 1 1 1
% clay	29 30 34 34
pH % om %	4.64 5.5 4.95 9.04
Hd	6.2 7.6 6.5 7.0
soil type	clay loam clay loam loam clay loam
species	arylsulphatase

TABLE 4.4: TOXICITY OF URANIUM TO MICROBIAL AND ENZYMATIC PROCESSES

	Sheppard et al., 1992
reference	Sheppard et al., Sheppard et al.,
result stand soil (mg U/kg dw)	>759 >673 >1052 >1176 >1984 >1376 >1457 >848
result test soil (mg U/kg dw)	>300 >300 >1000 >1000 >1000 >1000 >1000
criterion	EC50 EC50 EC50 EC50 EC50 EC50 EC50 EC50
exp. time	1 h 1 h 1 h 1 h 1 h 1 h 1 h 1 h 1 h 1 h
remp.	
% clay	2.0 4.0 24 18 6.0 15 13 33
% ош	0.7 0.8 2.2 18.4 3.5 2.6 5.7 3.1
Hd	4.9 7.5 7.5 7.5 7.0 7.0 7.8
soil type	fine sand fine sandy loam loam fine sandy loam sand fine sandy loam fine sandy loam clay loam fine sandy loam
species	phosphatase

all tests carried out with UO₂(NO₃)₂; background concentrations of uranium in soils varied from 0.6 to 4.9 mg U/kg

TABLE 5.1: TOXICITY OF SILVER TO SEDIMENT DWELLING ORGANISMS

sbecies	sbecies	шо %	% clay	Hd	CEC meg/	AVS µmol/g	exp. time	criterion	result test sediment (mg Ag/kg dw)	reterence
		,	ľ	(202	67.1	707	1 050	60.71	Rodoers et al 1997
Hvalella azteca	AgNO ₃	F 1.68	7.7	0.0	05.1	4.03	n 01	2	3	
Hvalella arteca	AgNO ₃	0.29	<0.01	08.9	0.11	0.36	10 d	LC50	1.62' α	
Hydrolla arteca	AgNO,	3.94	3.18	7.30	7.77	<0.01	10 d	LC50	$45.4^{1} \alpha$	Rodgers et al., 1997
Hydreita agreca	A GNO	231	95.0	7.48	2.40	70.8	10 d	LC50	379.7^{1} α	Rodgers et al., 1997
Hydrella azieca	Agrees	1 68	27.0	6.0	1.50	4.63	10 d	LC50	>2560 ¹ α	Rodgers et al., 1997
Hyalella azteca	AgCI _n	0.70	 	0.0	0.11	98.0	10.1	1,050	>25601 a	Rodgers et al., 1997
Hyalella azteca	AgCl _n	0.29	10.05	0.00	7.17	00)		5 0007	•
Hyalella azteca	AgC],	3.94	3.18	7.30	7.77	<0.01	10 d		>5200. α	Kodgers et al., 1997
Higher attood	AgCI	2.31	0.56	7.48	2.40	70.8	10 d	LC50	>2560¹ α	Rodgers et al., 1997
Hydreita deca	1.5C.n.	1 68	27	0.9	1.50	4.63	10 d	LC50	$ >1165^1 \alpha$	Rodgers et al., 1997
Hyalella azieca	Ag(32O3)n	00.1	; ;	00.7	0.11	980	10 d	1 050	>6481 a	Rodgers et al., 1997
Hyalella azteca	Ag(52U3)n	67.0	<0.02	0.00	0.11	00) ·		3 7 000	D. J. 2007
Hyalolla arteca	Ag(S,O ₃),	3.94	3.18	7.30	7.77	<0.01	10 d	0 2 1	>269. α	
II. alalla arteed	$\Delta \sigma(S_2 O_2)$	231	95.0	7.48	2.40	70.8	10 d	LC50	>682 ¹ α	Rodgers et al., 1997
nyaieiia azieca	0.50.20.3/n		2	· ·		202	10.4	1 050	-753 31.2 N	Hirsch 1998
Hyalella azteca	Ag ₂ S	CC.2	٥	,		5.55	7	25		

based on total acid-extractable Agbackground concentration 0.52 mg Ag/kg

TABLE 5.2: TOXICITY OF OCTAMETHYLCYCLOTETRASILOXANE TO SEDIMENT DWELLING ORGANISMS

species	hН	% ош	% clay	temp: ° C	exp. time	criterion result test sedir (mg/kg d	resu test (mg	nent w)	result stand, soil (mg/kg dw	result stand, soil mg/kg dw)	reference	
Chironomus tentans	,	0.46		_	14 d	NOEC	651	ಶ	325 α	ಶ	Kent et al., 1994	1
Chironomus tentans		3.9	,	1	14 d	NOEC	120	$120^2 \alpha$	308 α	ಶ	Kent et al., 1994	
Chironomus tentans	ı	7.0			14 d	NOEC	$54^2 \alpha$	ರ	77 a	.,	Kent et al., 1994	
											•	

growth measured as wet weight survival

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