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INTEGRATED CRITERIA DOCUMENT ZINC

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CONTENTS

Title	Integrated Criteria Document Zinc
Key words	Criteria document, zinc, soil quality, water quality, air quality, standards, measurement techniques, measuring strategies, sources, emissions, production, distribution, conversion, concentrations in the environment, human toxicity, ecotoxicity, emission-control techniques, cost of emission control, financial consequences, risk analysis
Summary	This report contains a systematic review and a critical evaluation of the most relevant data on the priority substance zinc for the purpose of effect-oriented environmental policy
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SUMMARY

This document on the subject of zinc contains data concerning sources and distribution, the risks based on a comparison of exposure levels and toxic concentrations, and technical possibilities of reducing these risks.

In the Netherlands, 210,000 tonnes of zinc are produced annually, 80,000 tonnes of zinc are processed, and approximately 50,000 tonnes of zinc are consumed (1989 data). The production of zinc generates annually a waste stream containing about 3500 tonnes of zinc, and releases about 25 tonnes of zinc per year to the atmosphere. At present, the solid waste is stored, but will be processed in the future. There is an emission to water of 22 tonnes of zinc per year from waste stored in the past. In the Netherlands, zinc metal and zinc alloys constitute over 90 % of the Dutch consumption, and zinc compounds, primarily zinc oxide and products obtained from it, almost 10 %.

The principal emissions of zinc to the Dutch environment and the quantity of dumped/stored zinc-bearing waste, in rounded tonnes, is categorized in Table 1. Because of the extensive use of zinc, this metal is present in practically all waste streams. The zinc emissions from the industrial processing of zinc are relatively small, and therefore possible reductions in these emissions have only a limited effect.

Table 1. Categorization of the principal emissions of zinc to the Dutch environment, in tonnes per year (1989 data)

category	*soil*	*water*	*air*	*dumped/stored (in the Netherlands)*
industry	-	*130*	*170*	*ca 6000*
agriculture	*1740*	-	-	-
corrosion	*2000*	*1650*	-	-
waste (various)	-	-	*70*	*ca 7000*
traffic	*130*	*75*	-	-
net imports	-	*600*	*300*	-

Corrosion is the principal term in the emission to soil and to water. This term represents the zinc contamination in rainwater which runs off corroded material. A characteristic feature of the emission to soil from corrosion is that it is highly localized: in the vicinity of zinc or

galvanized structures (such as crash barriers, electricity pylons, etc.), with a total surface area exposed to the atmosphere of about 125 million square metres. There is a lack of information on soil zinc concentrations in localized areas due to corrosion. The zinc released to the environment through corrosion could be reduced by coating galvanized structures, using zinc alloys, and employing alternative construction materials.

The zinc input to the soil from agriculture (primarily from animal manure) is almost as great as that from corrosion, which affects mainly non-agricultural land. The emission into and deposition of zinc on agricultural soils result in an accumulation of about 1400 tonnes of zinc per year, which corresponds to an annual increase in the zinc concentration in the topsoil of approximately 0.2 $mg.kg^{-1}$. In terms of accumulation, this increase is no cause for concern, considering the soil zinc levels of 6-150 $mg.kg^{-1}$ in the Netherlands.

The zinc imported annually into the Netherlands via the large rivers has fallen dramatically in the past decade, from over 7000 tonnes in the early 1980s to 2000 tonnes by 1990. The airborne zinc concentrations have also fallen in this period, from about 0.6 $\mu g.m^{-3}$ to about 0.2 $\mu g.m^{-3}$. Foreign sources contribute almost 70 % to the atmospheric zinc deposition and about 45 % to the zinc input to surface water.

Zinc contamination of soil and water occurs in two regions, South Limburg and de Kempen, which is primarily attributable to a centuries-old input from the zinc mines in the neighbouring region of Belgium and from the production methods previously used at the smelters in de Kempen. Partly because of this historical input, the reference value for soil (140 mg $Zn.kg^{-1}$ dry weight for the standard soil) is often exceeded in these regions. Elevated zinc concentrations also occur locally in surface water (Geul/Meuse rivers) and groundwater (de Peel, a region in the province of North Brabant).

The average adult human intake of zinc, primarily via food, in the Netherlands ranges from 8 to 14 mg per day, and is approximately the same as the daily requirement for zinc. Harmful effects of environmental zinc on human health are nil. It should be noted that the possibility of too low a zinc intake seems to be greater than that of excessive intake, especially for risk groups such as lactating women.

With regard to the aquatic environment, a maximum tolerable concentration (MTC; 95 % protection level) of 25 $\mu g.l^{-1}$ total zinc has been derived in this document, for both fresh and salt water. The present-day average concentrations in the Dutch rivers are higher than this MTC. The protection levels for aquatic organisms are, at the current zinc concentrations in surface waters, generally greater than 82 %. A MTC for soil cannot be derived in a straightforward manner. If the present soil zinc concentrations are increased by 30-70 $mg.kg^{-1}$ dry weight by a single application of zinc in a bioavailable form, adverse effects on microbe-mediated processes can be expected. Sandy soils with a low humus content and (silty) clay loam soils are the most vulnerable.

Desirable levels and limit values for zinc, among other substances, in soil and water have recently been proposed by the Ministry of VROM (memorandum "Environmental Quality Objectives for Soil and Water" - 1991). Since zinc is a naturally occurring element and, moreover, an essential nutrient, it is obvious that the desirable level should be based on its "natural occurrence". When choosing a level as measured in relatively unpolluted areas as a starting point, the formulation of one desirable level for soil and groundwater should be called into question, considering the natural variations in zinc concentrations. Possibly, a more appropriate framework for the elaboration of the desirable level is the special environmental quality, so that different areas are distinguished. The current proposal for zinc in soil, 140 $mg.kg^{-1}$ dry weight, is too high for one area and too low for another.

INTRODUCTION

In the Netherlands, environmental policy at government level is first of all aimed at attaining and maintaining an environmental quality which ensures the general health and wellbeing of man and the preservation of animals, plants and goods, as well as specific uses of the substance in question (Indicative Multi-year Programme-Environmental Management, 1986-1990). However, with insufficient knowledge it is impossible for the time being to describe fully the general environmental quality desired. Attention is therefore being concentrated on factors which are believed to entail considerable risks, such as environmentally harmful substances. A selection has been made of the many substances of relevance, because of emission or use, and a priority list compiled. So-called integrated criteria documents are drawn up for most of these priority substances.

Integrated criteria documents contain, per substance or substance group, data on the sources and the distribution pattern (soil, water, air, biota), the risks of actual exposure concentrations for man, (parts of) ecosystems and materials, and the technical possibilities and financial consequences for the industries concerned of reducing these risks. This information serves as the scientific basis for formulating the effect-oriented environmental policy. This policy is aimed at attaining as large a risk reduction as possible, the desirable level being the ultimate goal. This level is the concentration in the environment at which no adverse effects (i.e. effects the risks of which are considered to be negligible) occur for man, plants, animals and materials. If the desirable level cannot be reached within a reasonable period of time, a limit value is established for a limited period, with the risks lying between the maximum tolerable and the desirable levels. In addition to the possible risk reduction, economic and social factors are also determinants in setting this limit value. This document is confined to the provision of information necessary for the establishment of the above-mentioned environmental quality criteria in terms of policy; the information supplied may also result in a general task-setting for the emission reductions per source type. The sections of this document do not, therefore, contain a policy statement.

The National Institute of Public Health and Environmental Protection (RIVM) is responsible for drawing up integrated criteria documents. The Institute for Environmental Issues (IvM) and the engineering firm Haskoning participated in the realization of this document. The section on the human toxicity of zinc was supplied by the U.S. Environmental Protection Agency (EPA) as part of the international cooperation agreement. Government, business and industry, and representatives from scientific institutes were involved in the preparation of this document. For example, the document has been checked in its entirety by a Review Committee of the RIVM, while an Advisory Board comprised of staff from the Ministry of Housing, Physical Planning and the Environment (VROM), the National Institute for Inland Water Management and Waste Water Treatment (RIZA), and the Ministry of Agriculture, Nature Management and Fisheries (LNV) gave guidance in its compilation. Business and industry supplied important, partly confidential, information through the ad hoc Working Group on Integrated Criteria Documents of the Office of Environment and Physical Planning of the Council of Dutch Employers' Unions, VNO and NCW. In case of differences of opinion, an addendum drawn up by the ad hoc Working Group may be added to the document. This possibility also exists for environmental groups through the Nature and Environment Foundation (Stichting Natuur en Milieu). At a later stage, the Health Council will publish a brief report on the document, including any addenda.

This document deals with the heavy metal zinc. Zinc is an essential element and so occurs naturally in the environment. In accordance with the commission given to the RIVM, which is also based on the Exploratory Report Zinc published previously (Slooff et al., 1989), special emphasis has been laid in the section on sources on the most relevant point sources and diffuse sources in the Netherlands, and the foreign sources insofar as they contribute substantially to the zinc input to the environment in the Netherlands. Attention is also paid to the effects on the zinc concentrations in the environment of measures already taken or being prepared, which are not specifically aimed at zinc.

1. PROPERTIES AND EXISTING STANDARDS

1.1. PROPERTIES

1.1.1. Forms of occurrence

Zinc (symbol Zn, atomic number 30, relative atomic mass 65.38) is found in nature only in combined form, chiefly with sulphur (sphalerite and wurtzite), carbon (smithsonite) and silicon (hemimorphite). Naturally occurring zinc comprises the isotopes 64/30Zn (48.6%), 66/30Zn 27.9%), 67/30Zn (4.1%) and 68/30Zn (18.8%). Sphalerite (zinc blende) is the principal source of zinc for the zinc industry (Holleman and Wiberg, 1985). Zinc ore usually contains 4-8% zinc and is concentrated at the mine to 50-60% zinc. These concentrates are the raw material for zinc production. The main impurities in zinc ore are Fe (1-14%), Cd (0.1-0.6%) and Pb (0.1-2%), depending on the location of the deposit (Rocher, 1990). Zinc metallurgy rests on two basic processes: extraction from its ores by a dry (thermal) process and by a wet (electrolytic) process. Zinc oxide, usually obtained by roasting zinc blende, is used as the raw material in both the dry and the wet process. Zinc is the most widely used metal in the world after iron, aluminium and copper. Zinc and zinc compounds are used chiefly in galvanizing, alloys, paints, cathodic protection, the construction industry, reagents, batteries, as a protective coating for metals, in white pigment, as solubilizing agents in medicine, and in the carpet industry. Zinc is an essential trace element. It is, among other things, a component of many enzymes.

1.1.2. CAS registration numbers

zinc	7440-66-6	zinc permanganate	23414-72-4
zinc chloride	7646-85-7	zinc hydroxide carbonate	5970-47-8
zinc cyanide	557-21-1	zinc nitrate tetrahydrate	19154-63-6
zinc acetate	557-34-6	zinc acetate dihydrate	5970-45-6
zinc iodide	101339-47-6	zinc sulfate heptahydrate	7446-20-0
zinc selenate	13597-46-1	zinc sulfate monohydrate	7446-19-7
zinc oxide	1314-13-2	zinc trifluoromethane sulfate	54010-75-2

zinc sulfide	1314-98-3	zinc nitrate hexahydrate	10196-18-6
zinc iodate	7790-37-6	zinc chromate(VI) hydroxide	13530-65-9
zinc nitrate	7779-88-6	zinc carbonate	3486-35-9
zinc sulfate	7733-02-0	zinc silicate	13597-65-4
zinc nitrite	10102-02-0	zinc perchlorate	13637-61-1
ziram	137-30-4	zineb	12122-67-7

1.1.3. Physical properties

Zinc is a lustrous, bluish-white metal with a density of 7.14 g cm-3 (25 °C) which crystallizes in the hexagonal system and exhibits a slaty crystalline fracture. It melts at 419.4 °C and boils at 908.5 °C under atmospheric pressure (Holleman and Wiberg, 1985). Zinc is malleable and can be rolled at temperatures between 100 and 150 °C. It becomes brittle at higher temperatures (> 200 °C). Its vapour pressure reaches 1 mm Hg at 487 °C. It has low ductility, but can be drawn out into wire. The mechanical resistance depends on the purity of the metal: the purer the metal, the less tensile it is. The purest grade of zinc is used for chemical and electrochemical applications. Table 1.1 contains physical properties of a number of zinc compounds.

1.1.4. Chemical properties

Zinc belongs to the group of IIB elements in the periodic table. The configuration of the outermost electrons is 4s(2)3d(10). Zinc is a reactive, amphoteric metal. It has reducing and also several transition-metal properties. In aqueous environments it is always in the divalent state (Williams, 1971). It remains lustrous and does not oxidize in dry air. In moist air, it becomes covered with an adherent film of zinc oxide or basic zinc carbonate, so isolating the underlying metal and retarding further corrosion (Holleman and Wiberg, 1985). This characteristic accounts for the use of zinc for construction purposes. However, if the atmosphere contains much SO2, zinc roofings can be corroded owing to the formation of insoluble zinc sulphate. A protective film of Zn(OH2) builds up when exposed to water. Because zinc is amphoteric, it dissolves in mineral acids and strong alkalies. It is insensitive to most organic substances if these are not acidic or moist. Zinc is capable of reducing most metals, with the exception of aluminium and magnesium. The standard electrode potential of zinc is 0.32 V less than that of iron, hence its use for protection of ferrous metals against corrosion. The chemical and electrochemical properties of zinc account for the importance of this metal as an electrode in dry cells (Leclanché cell). They also underlie the use of zinc dust in hydrometallurgy, where the zinc reduces the ions of heavy and noble metals to their metallic state. Zinc burns upon heating in air with a green-blue light. In solution, 4 to 6 ligands are coordinated to the zinc ion. Zinc salts are generally white or colourless.

Tabel 1.1 Meltingpoint, boilingpoint (by 1 bar) and dissolvebility in water (15 - 30 °C) of a few zinccompounds (Weast, 1975; Merck, 1989).

Compounds	*Formula*	*Melting point (°C)*	*Boil. point (°C)*	*Solvabil. (g/100 ml)*
zinc bromide	$ZnBr^2$	394	650	447
zinc acetate	$Zn(C^2H^3O^2)^2$	200,d*)	-	30
zinc carbonate	$ZnCO^3$	300,d	-	0,001
zinc chloride	$ZnC1^2$	283	732	432
zinc nitratehexahydrate	$Zn(NO^3)^2.6H^2o$	36,4	d	184
zinc oxide	ZnO	1975	-	0,0002
zinc orthofosfate	$Zn^3(PO^4)^2$	900	-	unsolv.
zinc sulfate	$ZnSO^4$	600,d	-	unsolv.
zinc sulfateheptahydrate	$ZnSO^4.7H^2O$	100	280,d	97
zinc sulfidemonohydrate	$ZnS.H^2O$	1049	-	unsolv.
zinc sulfidedihydrate	$ZnSO^3.2H^2O$	100,d	200,d	0,16
zineb	$C^4H^6N^2S^4Zn$	-	-	unsolv.
ziram	$C^6H^{12}N^2S^4Zn$	250	-	unsolv.

**)d = decomposition*

1.2. EXISTING STANDARDS AND GUIDELINES

1.2.1. Development in standards and guidelines

Standards and guidelines for zinc in soil, water, groundwater and sediment have been in a state of flux in the past few years, coinciding with the preparation and realization of this integrated criteria document. This is illustrated in Table 1.2. A system of limit values and desirable levels has been given by the Ministry of VROM in the memorandum "Quality Objectives for Soil and Water (VROM, 1991). This system has been revised with respect to zinc on the basis of the draft Integrated Criteria Document Zinc. With the discussion of the policy document on this memorandum by the Lower House (VROM, 1992), these standards have been put into effect. There is no national standard for zinc in ambient air.

1.2.2. Soil and groundwater

The reference values for zinc in soil and groundwater (dissolved) given in the Environmental Programme 1988-1991 (MPV-88, 1987) are 50 + 1.5(2C + H) $mg.kg^{-1}$ dry weight and 150 $\mu g.l^{-1}$ respectively, where C is percent clay (diameter < 2 um) by weight and H is percent organic matter by weight of the soil. For a standard soil with a clay content of 25 % and an organic matter content of 10 %, the reference value is thus 140 $mg.kg^{-1}$ dry weight. The above reference values for soil have been retained as desirable levels in the memorandum "Environmental Quality Objectives for Soil and Water" (VROM, 1991). According to the current insights, at this or lower zinc concentrations the soil can in general be considered to be multifunctional, that is, zinc is not expected to cause detrimental effects. When assessing the soil quality, the technical manual must be used. The desirable level for zinc in groundwater has been adjusted in the policy document to a value of 65 $\mu g.l^{-1}$, on the advice of the Technical Committee on Soil Protection (TCB, 1991).

A testing framework for the assessment of the concentration levels in soil has been given in the Soil Cleanup Guide (VROM, 1990) (Table 1.3).

Table 1.2. *Sketch of the development in various standards and guidelines for zinc in water, sediment, soil and groundwater*

	water (µg/l)		*sediment (mg/kg dry wt)*	*soil (mg/kg dry wt)*	*ground-water (ug/l)*	*Source:*
	dissolved	*total*				
lowest NOEC)*	*0.75*			*7.3*		*SNW**)*
MTR	*1.6*	*(6.9)***)*	*120*	*0.73*		*SNW*
NR	*0.016*	*(0.069)*	*1.2*	*0.0073*		*SNW*
background conc. (unpolluted areas)	*1*	*2.6*	*68*			*SNW*
reference value for soil quality	*(1.9)*		*140****)*	*150*		*MPV88*
general environmental quality of sediment			*140*			*MPV89*
ecotoxicological value	*6.5*	*28*	*477*			*KVW*
K2000	*(7.0)*	*30*	*480*			*DNW*
limit value	*7*	*30*	*480°)*			*VROM'92*
desirable level	*2*	*9*	*140*	*140*	*65*	*VROM'92*

**) Abbreviations: NOEC = no-observed-effect concentration; MTR = maximum tolerable risk level; NR = negligible risk level; K2000 = Quality Objectives 2000*

***) References:*
SNW: van de Meent et al. (1990)
MPV88: MPV-88 (1987)
MPV89: MPV-89 (1988)
KVW: RIZA (1989)
DNW: V&W/VROM/L&V (1989)
VROM'92: VROM (1992)

****) In parentheses: calculated consequences of the value(s) formulated elsewhere in the row*

*****) For standard soil*

o) For newly formed sediment

Table 1.3. *Testing framework for the assessment of the concentration levels of zinc in soil (VROM, 1990)*

Compartment	*A*	*B*	*C*
Soil (mg per kg dry weight)	*50 + 1.5(2C + H)*	*500*	*3000*
Groundwater (ug per litre)	*150*	*200*	*800*

C = percent clay (diameter < 2 µm) by weight
H = percent organic matter by weight
A = reference value, 140 mg.kg^{-1} dry weight for a standard soil, equal to MPV-88 value
B = testing value for the purpose of further research
C = testing value for the purpose of clean up research

The indicative guidelines reported in Table 1.3 should not be regarded as standards but as an assessment framework.

For the use of cleaned soil, without restrictions, the draft working paper "Standards for Use of Cleaned Soil" (DGM, 1988) has adopted the same A value (DGM,1988).

The EEC (1986) limit for zinc in soil is 150 to 300 mg.kg^{-1} dry weight. This value may be exceeded by 50 % at most at pH > 7, thereby posing no risk to man, environment or groundwater. The EEC limit for zinc in sewage sludge intended for use on agricultural land is 2.5 to 4 g kg^{-1} dry weight, and the maximum amount of zinc which may be applied annually is 30 kg per ha, based on a 10-year average. This corresponds to about 10 mg.kg^{-1} of topsoil (the upper 20 cm).

The LAC (Agricultural Advisory Committee) "signal" value, which indicates the lowest concentration in the soil above which problems in agriculture may be expected, is 200 mg.kg^{-1} for sandy soils, and 350 mg.kg^{-1} for clay and peat soils (LAC, 1991).

The EEC (1980a) has issued a directive for the protection of groundwater, making it obligatory for the member states to restrict the introduction of list II substances (including zinc) into groundwater.

1.2.3. Sewage sludge and compost

The "Draft Decree on Quality and Use of other Organic Fertilizers", January 1990 (Meeuwissen, 1989), gives the maximum permissible zinc concentrations in sewage sludge, compost and organic soil, when used as a fertilizer (see Table 1.4), as well as the maximum amounts which may be applied onto the land.

The use of very clean compost, that is, compost containing less than 75 mg Zn.kg^{-1}, is not subject to restrictions, nor is that of organic soil, which is permitted to have a zinc content of 50 + 1.5(2C + H), where C is percent clay and H is percent organic matter (maximum, 15 %).

<u>Table 1.4.</u> *Maximum permissible concentrations of zinc in sewage sludge and compost, and the maximum amounts which may be applied to the land; all zinc levels are given in mg.kg^{-1}, and the maximum permissible amounts in tonnes of dry matter per hectare*

	Sewage sludge (up to 1995)		Clean sludge (up to 1995)		Sewage sludge (after 1995)	
Zn concentration:	1400		560		300	
	Liquid	Firm	Liquid	Firm	Liquid	Firm
Use on:						
grassland	1 t/y	2 t/y	2.5 t/y	5 t/2 y	Same amounts as up to 1995	
arable land	2 t/y	4 t/2 y	5 t/y	10 t/2 y		

	Compost (up to 1995)			Clean compost (up to 1995)			Compost (after 1995)
Zn concentration:	900			280			200
prepared from:	s.sl.	cl.sl.	waste	s.sl.	cl.sl.	waste	s.sl. or waste
Use on:							
grassland	2 t/ 2 y	5t/ 2 y	1.5 t/ y or 3 t/ 2 y or 6 t/4 y	2 t/ 2 y	5 t/ 2 y	3 t/ y or 6 t/ 2 y	Same amounts as up to
arable land	4 t/ 2 y	10 t/ 2 y	3 t/ y or 6 t/ 2 y or 12 t/4 y	4 t/ 2 y	10 t/ 2 y	6 t/ y or 12 t/ 4 y	
other soil	irr.	irr.	6 t/y	irr.	irr.	12 t/y	

* s.sl. = sewage sludge cl.sl.= clean sludge

** irr. = irrelevant

1.2.4. Water and sediments

As indicated in Table 1.2, the previous standard, as reported in the Third Water Management Memorandum (V&W/VROM/L&V, 1989), has been adopted in the policy document as the limit value for zinc in surface water: 30 $\mu g.l^{-1}$, related to 30 mg of suspended solids per litre. The desirable levels for total zinc and dissolved zinc in surface water are 9 and 2 $\mu g.l^{-1}$, respectively. The Quality Objectives and Surface Water Measurements Decree stipulates that the zinc concentration in surface water intended for the production of drinking water should not exceed 200 $\mu g.l^{-1}$. The EEC and Dutch standards, which surface water intended for the production of drinking water must meet, are summarized in Table 1.5. The international association of water companies along the Rhine (IAWR, 1986) prescribes that the zinc concentration in the River Rhine should not exceed 1 $mg.l^{-1}$ when drinking water is produced by a physicochemical process, and 0.5 $mg.l^{-1}$ when only natural purification techniques are used.

To protect salmon and carp, the zinc concentration in fishing waters should not exceed 200 $\mu g.l^{-1}$ (Staatsblad [Gazette], 1983).

CUWVO guidelines have been drawn up for discharges by industries.

Table 1.5. Standards for the zinc concentration in surface water intended for the production of drinking water ($mg.l^{-1}$) (Waterleidingbesluit [Water Board Decree], 1984)

Reference	*Waterleidingbesluit (1984)*			
Quality class)*	*I*	*II*		*III*
Guideline/Limit	*L*	*G*	*L*	*L*
Zinc concentration	*0.2*	*0.2*	*1*	*3*

**) The quality classes relate to the treatment methods used in the production of drinking water:*
I: simple treatment and disinfection
II: standard physical and chemical treatment, and disinfection
III: thorough treatment, removal of impurities, and disinfection

The establishment of standards for sediments is still in a state of flux. In 1988, the initial impetus was given to establish recommended standards

(MPV-89, 1988), with the assumption that the general environmental quality of sediments and the reference value for soil quality (Table 1.3) would indicate in principle an identical protection level. Subsequently, in advance of the Third Water Management Memorandum, the National Water Authority (RIZA, 1988) developed an interim system for the assessment of the quality of bottom sediments and dredged sediments. New proposals for standards, more effect-oriented, were presented in the Third Water Management Memorandum (V&W/VROM/L&V, 1989), and adjusted in conformity with the policy document (VROM, 1992). The various standards are summarized in Table 1.6.

It should be noted that the "signal" value in Table 1.6 has a function similar to the C value in the Soil Cleanup Guide.

Table 1.6. *Standards for zinc in sediments*

Type of standard	*value (mg.kg^{-1} dry wt)*	*Reference*
Desirable level	*140*	*VROM (1992)*
Limit value (newly formed sediment)	*480*	*VROM (1992)*
Testing value	*1000*	*V&W/VROM/L&V (1989)*
"Signal" value	*2500*	*V&W/VROM/L&V (1989)*

1.2.5. Air

Table 1.7 lists the quality criteria in the workplace (MAC - maximum acceptable concentration) (IDC, 1985).

Table 1.7. *Air quality criteria in the workplace (MAC values, time-weighted average, TWA, for an 8-hour day, 40-hour workweek), in mg.m^{-3}*

Country	*MAC value*	*Comment*	*Reference*
The Netherlands	*1*	*zinc chloride (fume)*	*Nationale MAC lijst (1986)*
	0.05	*zinc chromate (as Cr)*	
	5	*zinc oxide (fume)*	
	10	*zinc stearate*	
US	*5*	*zinc oxide (fume)*	*SCMO/TNO (1977)*
Germany	*5*	"	"
Sweden	*5*	"	"
Former USSR	*6*	"	"

In Germany an ambient air quality criterion of < 0.05 mg.m^{-3} (annual mean) is in force (IDC, 1985).

1.2.6. Drinking water

The WHO guideline for zinc in drinking water is 5.0 mg.l^{-1} (WHO, 1984). Standards for drinking water are summarized in Table 1.8.

Table 1.8. Drinking-water standards (mg.l^{-1})

Country	*Standard*	*Comment*	*Reference*
The Netherlands	*0.1*	*on leaving pumping station*	*Waterleiding-besluit (1984)*
	5	*after standing for 16 h in a galvanized metal pipe*	
EEC	*0.1*	*on leaving pumping station*	*EEC (1980b)*
	5	*after standing for 12 h*	
Germany	*2*		*SCMO/TNO (1977)*
US	*5*		*ATSDR (1989)*

1.2.7. Other

The Designation of Chemical Waste Decree (BACA) (Staatsblad, 1991) specifies a number of processes which by definition generate chemical waste. Several processes resulting in zinc-bearing waste streams are also mentioned, for example, zinc production, zinc oxide production, metal-surface treatments, blasting operations, iron and steel production, and the production and formulation of pesticides. According to BACA, zinc-bearing waste streams originating from processes which are not included in the BACA list of processes can be regarded as chemical waste when the zinc concentration exceeds 20 g kg^{-1} (VROM, 1991a).
The total zinc in animal feed, for all animal species, added in the form of zinc lactate trihydrate, zinc acetate dihydrate, zinc carbonate, zinc chloride monohydrate, zinc oxide, zinc sulphate (hepta- and monohydrate) should be no more that 250 mg.kg^{-1} (containing 12 % liquid) (Diervoederverordening, 1986).

2. PRODUCTION AND APPLICATIONS, SOURCES AND EMISSIONS

This chapter outlines the production, applications, sources and emissions of metallic zinc and zinc compounds. Applications and consumption are discussed in Section 2.1, while national sources and emissions are considered in Sections 2.2 and 2.3. The representation of the emissions is derived for the most part from written and/or oral company information based on the year 1989. Older data were extrapolated to that year, if possible. The emissions have all been expressed in zinc.

2.1. PRODUCTION AND APPLICATIONS

World consumption of zinc is estimated at about 7 Mtonnes (Anonymus, 1990). The distribution of worldwide uses of zinc is given in Table 2.1, in percentages. It is seen that the major use of zinc is in (hot-dip) galvanizing. The total zinc consumption in the Netherlands is about 50,000 tonnes per year, while Dutch industry processes about 80,000 tonnes of zinc a year. In addition, the Netherlands produces 210,000 tonnes of zinc annually. The quantities of zinc consumed and processed in the Netherlands per area of applications are given in Table 2.2. The major use of zinc in the Netherlands is for hot-dip galvanizing, brass, and rolled zinc (gutters).

Table 2.1. Applications of zinc on a global scale (WBMS, 1990)

Application	*Consumption*
Galvanizing (chiefly hot-dip)	*49 %*
Rolling	*8 %*
Zinc compounds	*11 %*
Die-casting	*17 %*
Alloys	*15 %*

Zinc oxide is used in a wide variety of industries. An estimate of the zinc oxide processed by each industry is given in Table 2.3. A summary of the applications of the other zinc compounds (from Table 2.3) is given in Table 2.4.

Table 2.2. *Consumption and processing of zinc in the Netherlands, in tonnes per year (company inf.)*

Area	*Consumption*	*Industrial processing*
Galvanizing		
hot dip	*14,000*	*22,000*
electrolytic	*600*	*600*
zinc spraying	*170*	*170*
Rolling	*15,000*	*14,000*
Zinc compounds		
zinc oxide production		*16,000*
zinc oxide use	*3,500*	*4,800*
Die-casting	*5,000*	*1,000*
Alloys		
brass	*10,000*	*25,000*
Other	*300*	*300*
Total	*ca 50,000*	*ca 80,000*

Table 2.3. *Summary of zinc oxide processing in various Dutch industries (company inf.)*

Industry	*Consumption (tonnes of zinc)*
Ceramics	*200*
Production of frits	*1,500*
Production of magnetic tapes	*100*
Rayon manufacture	*275*
Rubber	*1,100*
Animal feeds	*500*
Textile finishing (carpet backings)	*100*
Paint production (estimate)	*180*
Production of other zinc compounds	*800*
Total	*4,800*

Table 2.4. Summary of the applications of zinc compounds manufactured in the Netherlands (company inf.)

Zinc compound	*Uses*
Zinc acetate	*raw material in pharmaceutical industry*
Zinc bromides	*sealant in oil and gas drilling (not used in the Netherlands)*
Zinc chromates	*paint pigment, primer*
Zinc thiocarbamates	*pesticides zineb, mancozeb and ziram*
Zinc gluconate	*cough syrup, adjustment of mineral balance of man and animals*
Zinc naphthenate	*paint drier, (wood) preservative*
Zinc octoate	*paint drier, catalyst in pharmaceutical industry*
Zinc stearate	*PVC stabilizer, additive in ointments, animal feed supplement*

2.2. INDUSTRIAL SOURCES AND EMISSIONS

2.2.1. Zinc production

Major deposits of zinc ores are found in Canada, Peru and Australia. In the Netherlands, zinc is produced hydrometallurgically from zinc sulphide ore concentrates by the jarosite process (since 1973). In this process, the iron present in the zinc ore concentrate is precipitated out of the liquid as ferrous ammonium sulphate. Without the removal of iron in the form of jarosite, 12-14 % of the zinc would be lost due to the formation of zinc ferrite. The hydrometallurgical zinc winning process involves four stages: roasting, leaching, purification, and electrolysis. In roasting, the zinc sulphide is burned in the presence of air to convert it to zinc oxide. This operation generates thermal energy, a waste gas containing sulphur dioxide from which sulphuric acid is made, and zinc ferrite. In leaching, the zinc oxide and zinc ferrite are dissolved in dilute sulphuric acid. The dissolved iron resulting from the dissolution of zinc ferrite is precipitated as ammoniojarosite by the addition of ammonia. In the purification step, the resulting zinc sulphate solution is cleansed of other elements present in the ore which have entered it, and which may interfere with the electrolytic process. The purified zinc sulphate solution is then transferred to electrolytic cells in which zinc metal of a purity greater than 99.9 % is deposited on aluminium cathodes. In this way, 210,000 tonnes of zinc, and jarosite waste with a zinc content of about 3000 tonnes are produced annually in the Netherlands.

In addition, gypsum generated by the wastewater neutralization plant, filter material and rubble contain a total of about 500 tonnes of zinc. For the time being, these waste streams are stored on the factory site (Meijer, 1990).

The zinc emission into air arises from the transshipment of ore (as dust) and production (as zinc chloride-, zinc sulphate- or zinc oxide - aerosols), and totals about 25 tonnes per year.

The zinc emission into surface water from the current zinc manufacturing process is about 1 tonne per year. The emission into water originating from the factory site is about 16 tonnes per year, and is due mainly to zinc that has been leached out of stored "cellar ashes" (zinc-containing aluminium oxide silicates) by rainwater and seepage water (company inf.). The figure of 16 tonnes mentioned varies, depending on whether it is a wet or dry year.

2.2.2. Production of zinc alloys

Brass (ca 25 % zinc and 75 % copper) is produced in the Netherlands, partly by reprocessing scrap brass. The brass industry processes about 25,000 tonnes of zinc annually. In addition, relatively small quantities of zinc (< 500 tonnes) are utilized in the Netherlands for the production of other alloys.

The zinc input to surface water from brass manufacturing is about 0.8 tonne and arises from the effluents from the detoxification/neutralization/ dewatering systems which treat contaminated cooling and rinse water (company inf.).

The sources of the releases to air are the melting of zinc and transfer of the melt to the casting ladle and/or casting machines. The zinc emissions from the melting furnace itself are exhausted and treated in a filter system, yielding a residual emission of about 2 tonnes of zinc. The largest emission sources, however, are situations in which the zinc fumes evolving from the melt are not, or are insufficiently, exhausted. This occurs, for example, during the filling of the furnaces, pouring of the melt, and transportation of the ladle. The total zinc input to the atmosphere resulting from these operations has been calculated to be about 25 tonnes (company inf.).

The brass production process generates waste in the form of filter dust, filter cake, slag and spent pickling baths, involving a total of about 1200 tonnes of zinc per year. At present, the filter dust and slag are reprocessed abroad to recover zinc. The pickling baths are also sent abroad. The filter cake is (partly) reprocessed in the Netherlands (company inf.).

2.2.3. Production of zinc oxide

Zinc oxide is produced in the Netherlands by the direct and the indirect processes. In the direct process, zinc clinker (waste material from hot-dip galvanizing operations which has been reprocessed abroad, with a zinc content of about 70 %) is used as a starting material. The starting material for the indirect process is zinc metal (so-called "hard zinc" with a zinc content of 93-95 %, derived from the bottom of the zinc baths of hot-dip galvanizing plants) or electrolytic zinc (99.9 % purity). Approximately 20,000 tonnes of zinc oxide are produced annually in the Netherlands by these two processes. Cinders, a by-product of zinc oxide production, are partly reused and partly stored on the factory site (about 300 tonnes of zinc) (company inf.).

The zinc input to the atmosphere from zinc oxide production is about 9 tonnes per year. The largest emission source is the breakthrough of the cloth filter system (about 10 mg ZnO m^{-3}) (company inf.).

Process water is not utilized in the manufacture of zinc oxide. Zinc releases into water are due mainly to runoff of contaminated water from the factory site, and are estimated to be about 1 tonne a year (company inf.; ER, 1990).

2.2.4. Production of other zinc compounds

Ten zinc compounds are produced in the Netherlands, using zinc oxide and zinc chloride or zinc sulphate as starting materials. The total amount of zinc used for this purpose is about 800 tonnes per year. The production of the zinc compounds generates filter cake (about 50 tonnes of zinc) and filter dust (about 10 tonnes of zinc). These waste streams are disposed of as chemical waste. In addition, the production operations discharge about 12.5 tonnes of zinc per year into water. The manufacture of zinc-based pesticides accounts for 85 % of the water emission (company inf.). This source is also responsible for 75 % of the total atmospheric emission of about 0.7 tonne per year (company inf.).

2.2.5. Zinc-consuming industries

Zinc and zinc compounds are used in the Netherlands in the following industries:

Manufacture of Batteries

Batteries are produced in the Netherlands on a limited scale. Zinc consumption for this purpose is estimated to be < 50 tonnes per year. Zinc emissions into air and water are negligible (Meijer and Lohuizen, 1991). The total battery consumption in the Netherlands involves about 600 tonnes of zinc per year. About 40 % of this is collected separately and stored at AVR (a waste incineration facility), while 360 tonnes of zinc end up in household waste.

Pharmaceutical industry

The annual discharge of zinc into surface water by the pharmaceutical industry, from the production of zinc ointments and other preparations, is estimated to be about 2-3 tonnes per year. The waste contains about 25-40 tonnes of zinc, and the sludge from the in-house wastewater treatment facility about 5-8 tonnes (Ros and van der Poel, 1989).

Formulation of pesticides

A number of zinc-containing pesticides (metiram, ziram, zinc phosphide, mancozeb and zinab) are formulated in the Netherlands by five companies. The total zinc consumption for this purpose is estimated at 125 tonnes per year. In the Netherlands, zinc-containing pesticide formulations are produced mainly by dry processes. Approximately 1 tonne of zinc ends up in the industrial waste. The zinc input to water is estimated to be < 1 kilogram. Less than 0.1 tonne of zinc (dust) is released into the atmosphere (CUWVO, 1989; Haskoning, 1989b).

Frit production

Approximately 1500 tonnes of zinc (as zinc oxide) are used annually in the Netherlands for the production of frits, which are used in the ceramics industry. The associated zinc emission into water is about 0.2 tonne. Zinc emissions into air are negligible (company inf.).

Printing industry

The printing industry uses relatively little zinc oxide. The wastes generated are spent etching fluid and spent plates, with a total zinc content of 0.7 tonne per year. The zinc input to water, due to wastewater discharge, is about 0.06 tonne per year (VROM, 1990; Klingenberg, 1986). Atmospheric emissions are negligible.

Ceramics industry

In the ceramics industry zinc compounds are used in glazes. It is estimated that the industry utilizes annually about 200 tonnes of zinc in the form of zinc oxide (in glazes) and frits. The waste (chiefly filter cake) contains about 60 tonnes of zinc, and is reused in the coarse ceramics industry. The amount of zinc discharged into water is about 0.5 tonne. The zinc emission into air, resulting from exhaustion of the spray booths and discharge from the furnaces, is estimated at about 1 tonne a year (company inf.; Berkens, 1990; ER, 1990).

Magnetic tape production

Approximately 100 tonnes of zinc are used annually in the production of magnetic tapes. The "rejects" contain about 10 tonnes of zinc, which are disposed of as chemical waste. Zinc emissions into air and water are negligible (company inf.).

Metal surface treatments

In the Netherlands, zinc coatings are applied to metal surfaces by zinc spraying, electrogalvanizing, and hot-dip galvanizing.

Approximately 100 mostly small establishments use 170 tonnes of zinc per year for zinc spraying (metallization). This coating technique is employed chiefly for steel constructions, truck bodies, appliances and machines (Roovers, 1989; Anonymus, 1977). Much of the zinc emitted during zinc spraying ends up on the ground and is removed together with the blasting grit and the waste. It is estimated that about 17 tonnes of zinc are involved. The sources of atmospheric emissions are spray material missing the object (deposition efficiency, ca 90 %), spraying in the open air without protection (2 %), spraying in booths without a filter system (about 1/3) and spraying in booths equipped with a filter system (2/3). A total of 6 tonnes of zinc is estimated to be released into the atmosphere. A small discharge into water can occur when spraying in the open air (company inf.).

In electrogalvanizing, objects are immersed in a solution containing various zinc salts, after which a continuous, even layer of zinc is deposited on the metal base by electrolysis. Electrogalvanizing is employed for a wide variety of articles. However, it can be stated that these objects are usually used indoors. The zinc layer is then 5 to 10 um thick. Electrogalvanizing consumes about 600 tonnes of zinc per year (company inf.). The waste generated is a mixed sludge, usually derived from detoxification/neutralization/dewatering systems. This sludge contains about 30 tonnes of zinc and is mainly tipped on the C2 dump in the Maasvlakte. The zinc input to water resulting from electrogalvanizing is estimated at about 7.5 tonnes (ER, 1990; CUWVO, 1987).

In the Netherlands, hot-dip galvanizing is performed at about 25 establishments. In hot-dip galvanizing, objects, after degreasing and pickling, are activated in a bath containing so-called "prefluxes" (an aqueous solution of $ZnCl_2$ and NH_4Cl), after which they are immersed in a tank of molten zinc (450 °C). The flux melts and the article becomes coated with a zinc film of about 50-100 um. Hot-dip galvanized articles are used mostly outdoors. Hot-dip galvanizing consumes about 22,000 tonnes of zinc per year (CBS, 1991). The zinc emissions into water are due to rinsing and scrubbing activities and drainage of rainwater, and are estimated to be about 2.5 tonnes a year. The atmospheric emission arises from the reaction of molten zinc with relatively cold steel, and is estimated at < 1 tonne.

The wastes generated during hot-dip galvanizing are hard zinc, zinc ashes, ammonium chloride slags, and spent pickling baths. Hard zinc contains about 2900 tonnes of zinc, and zinc ashes contain about 3200 tonnes. Both waste streams are reused abroad. Pickling baths which contain too much iron or zinc are for the most part sent abroad for further processing. The remaining part is dumped after immobilization, and has a zinc content of about 700 tonnes.

Rayon manufacture

The rayon industry uses annually about 275 tonnes of zinc as coagulation retardants in spinning. The spinning bath contains zinc sulphate, so is also the principal emission source. The manufacture of rayon generates wastewater sludge with a zinc load of 243 tonnes. The sludge is stored on site (215 tonnes of zinc) or incinerated (28 tonnes of zinc). In view of the temperature during the manufacturing process, among other things, zinc is not released into air. About 18 tonnes of zinc are discharged into water by the wastewater treatment plants. In addition, 7 tonnes of zinc are retained in a sodium sulphate residue and 13 tonnes are incorporated in the yarns (company inf.; Walpot, 1985).

Rubber industry

The rubber industry uses zinc oxide as a vulcanization activator. The Dutch rubber industry consumes annually about 1600 tonnes of zinc in the form of zinc oxide and/or ready-made masterbatches. About 1000 tonnes of zinc are utilized for the manufacture of car tyres, 100 tonnes for bicycle tyres and 500 tonnes for other rubber products. The production waste contains about 20 tonnes of zinc. Releases of zinc to the atmosphere during rubber manufacturing are negligible (ER, 1990; Haskoning, 1989a). The zinc input to water is about 1 tonne and is due chiefly to rinsing activities (company inf.).

Textile finishing

A smooth rubberlike backing is often applied to carpets. Zinc oxide or zinc latex are used in the vulcanization of foam backings. It is estimated that 100 tonnes of zinc are required annually for this purpose. The discharge into water is only about 0.2 tonne of zinc. About 15 tonnes of zinc are estimated to end up in the waste (company inf.; CUWVO, 1989b; Tebodin, 1987).

Processing of plastics

Zinc-containing stabilizers are used in the processing of chlorine-containing polymers such as polyvinyl chloride (PVC). A number of stabilizers are used in the Netherlands; for example, 400 tonnes of Ba/Zn stabilizer per year for various types of foil, and about 320 tonnes of Ba/Zn and Ca/Zn stabilizers for floor coverings and other coatings. A total of 860 tonnes of zinc-containing stabilizers is consumed annually for plasticized PVC articles. Assuming a zinc (stearate) content of 10-20 % would imply a zinc load of about 25-30 tonnes (company inf.). Although a large proportion of the production waste is reused directly, the processing of plasticized PVC generates a waste stream representing about 0.25 % of the total production, which is dumped. The processing of plastics does not give rise to significant zinc emissions into air. The zinc input to water is about 0.1 tonne (company inf.).

Petrochemical industry

In the petrochemical industry, small quantities of zinc are utilized in catalysts. Oil refineries discharge annually about 1 tonne of zinc to surface water. After use, the catalysts are exported, regenerated in Germany or Belgium, or dumped. Small amounts of zinc alkyl dithiophosphates are added to lubricating oils as an anti-wear agent. About 175 tonnes of zinc are used annually for this purpose. The zinc compounds mentioned are not produced in the Netherlands; however, the additives mixture is prepared. Emissions during mixing are negligible.

Others

In addition to the zinc-consuming industries mentioned above, there are also a number of industries which do not utilize zinc directly but do discharge it, because it is present in the products, equipment, raw materials, or cooling and tap water. Table 2.5 summarizes the zinc emissions to water from these industries. Approximately 50 % of this stream is discharged directly to surface water (for example, paint industry, wood cleaning, and a quarter of the discharge from the food and allied products industry). Indirect discharges make up the remaining 50 %. Using the Emissions Registration, a large number of industrial sources have been identified, each emitting little to very little zinc to the atmosphere (less than one tonne a year). The total air emission from these small sources is about 40 tonnes per year.

2.2.6. Zinc-bearing primary and secondary raw materials

This subsection deals with the industries which process the zinc-bearing primary raw materials titanium dioxide ore, phosphate ore, iron ore and coal, and the zinc-bearing secondary raw material steel scrap.

Titanium dioxide ore

In 1989 the white pigment titanium dioxide was obtained from titanium dioxide ore by the so-called sulphate process. About 10 tonnes of zinc were discharged into water. The so-called "chlorine process" has been employed since early 1990 (see 6.1.6).

Phosphate ore

Phosphate ore is the starting material for the manufacture of phosphoric acid. One of the impurities in the ore is zinc. Phosphoric acid is used in the manufacture of phosphate fertilizers (see 2.3.2. Agriculture) and animal feedstuffs, and contained in 1990 about 180 tonnes of zinc. The water emission from the discharging of phosphoric acid gypsum totalled about 12 tonnes of zinc. Zinc emissions into air were negligible (Hoogenkamp, 1990).

Primary iron and steel production

In the Netherlands, the production of primary iron and steel is accomplished by the oxygen steelmaking process. In this process the iron-bearing agglomerates are reduced to molten pig iron in blast furnaces using coke as a reducing agent, followed by refining of the product to steel. Scrap (200 to 300 kg of scrap per tonne of crude steel) is used as a cooling agent in the refining process. The atmospheric discharge from the production process is about 26 tonnes of zinc per year (company inf.), the major emission sources being the oxygen steelmaking converters.

About 4 tonnes of zinc are discharged annually to water via the outfall of the wastewater treatment plant for the wash water used in the cleaning of the blast furnace gas and the primary and secondary dust from the oxygen steelmaking converters (ER, 1990; Anonymus, 1985; Welvaadt, 1983; company inf.). In 1990, a nonstructural zinc emission to water of about 15 tonnes per year which had occurred during the preceding years, owing to a leak, became known. The principal waste streams from primary iron and steel production are blast furnace sludge (920 tonnes of zinc) and oxylime sludge (110 tonnes of zinc). Other waste streams are steel slag (10 tonnes of zinc) and oxygen steelmaking dust (23 tonnes of zinc), which are used in road construction and the cement industry, and dry blast furnace bag filter dust (80 tonnes of zinc), which is reused in the blast furnaces (Van Deelen et al., 1989; VROM, 1989; Welvaadt, 1983; company inf.). The blast furnace sludge originates from the scrubbing of the blast furnace gas which is released during the manufacture of pig iron. The blast furnace gas is cleaned in a wet scrubber. The wash water is cleaned physicochemically, whereby the blast furnace sludge precipitates out. The blast furnace sludge is separated in a hydrocyclone into a high-zinc fraction (850 tonnes of zinc) which is stored, and a low-zinc fraction which is reused in the process (60 tonnes of zinc). At present, the oxylime sludge (110 tonnes of zinc) is reused in the process (Van Deelen et al., 1989; Heywegen and Kat, 1985).

Secondary steel production

In the Netherlands, secondary steel production is by the electrosteelmaking process. In this process, scrap (including galvanized steel), after selection and preconditioning, is remelted in electric furnaces to a new product. The zinc emission to the atmosphere is about 32 tonnes per year, while less than one tonne of zinc is discharged to water (ER, 1990). When the cold scrap is added to the electric furnace bath, a considerable amount of dust is produced which escapes past the electrode openings. Most of the dust is captured by an exhaust hood. The filter dust contains about 375 tonnes of zinc and is disposed of as chemical waste. In addition, lime slag is produced, which is sold as road metal.

Coal (electricity generating stations)

The Dutch electricity generating stations burned 7.8 Mtonnes of pulverized coal in 1989. The solid wastes produced by burning pulverized coal are bottom ash (6 tonnes of zinc), pulverized-coal fly ash (153 tonnes of zinc), and flue-gas desulphurization gypsum (< 3 tonnes of zinc) (Meij and Koops, 1992). The source of the atmospheric zinc emissions, a total of about 20 tonnes, is escaping fly ash (Meij and Koops, 1992). Almost all the pulverized-coal fly ash is reused as a filler, mixing element or lightweight aggregate in the asphalt, concrete or cement industry. The flue-gas desulphurization gypsum is processed by the gypsum industry. Leaching of zinc from cement, concrete or asphalt is not to be expected because the pulverized-coal fly ash is used in bound form on the one hand, and in strongly diluted form on the other (Bolt, 1983, 1985; Bolt and Snel, 1985). A large part of the collected bottom ash is reused, for example, in road construction. The leaching of zinc from (temporary) bottom ash and pulverized-coal fly ash dumps is much less than 1 %.

<u>*Table 2.5.*</u> *Summary of zinc emissions to water from industries which do not utilize zinc directly (ER, 1990; TNO, 1989)*

industrial sector	*zinc emission (tonnes per year)*	*source*
automobile industry	*1.0*	*galvanized metal products*
electrotechnical industry	*4.1*	*galvanized metal products*
glass industry	*0.05*	*leaching*
wood cleaning	*8.0*	*paint*
paper and paper products	*1.0*	*old photocopying paper*
paint industry	*10.0*	*paint*
other chemical industry	*2.2*	*diffuse*
other chemical raw materials	*5.0*	*diffuse*
food and allied products	*8.0*	*diffuse*
other industries	*2.4*	*diffuse*
Total	*ca 42*	

2.3. NON-INDUSTRIAL SOURCES

Table 2.6 summarizes the non-industrial, diffuse zinc emissions. The most relevant flows - traffic, agriculture, and corrosion - are considered in the following subsections.

2.3.1. Traffic

The wear of zinc-containing car tyres is the largest source of zinc emissions from traffic. Based on a CBS report, which gives the number of car tyres in use every year, the average wear upon replacement, and a tyre zinc content of 1.6 %, it is estimated that the zinc emission from passenger cars is 100 tonnes. Using analogous calculation methods, the diffuse zinc emission from trucks, delivery vans, agricultural machinery, bicycles and motorbikes was found to be about 100 tonnes per year (Meijer and van Lohuizen, 1991; CUWVO, 1986; company inf.). In addition, about 2 tonnes of zinc are released by the wearing away of road surfaces under traffic. Of the circa 200 tonnes of zinc emitted, about 50 tonnes end up in surface water (of which ca 16 tonnes via the sewage system), 112 tonnes on the soil, and 38 tonnes in the sewage treatment plant (STP) sludge (from CUWVO, 1986). Another source of diffuse zinc emissions from traffic is the use of zinc-containing motor oils and lubricating grease: ca 40 tonnes, of which about 25 tonnes to surface water and 15 tonnes to the soil. Zinc dialkyl dithiophosphates are much-used anti-wear additives in mineral oils (0.1 % on a zinc basis). Transport vehicles use 100,000 tonnes of oils and greases annually.

2.3.2. Agriculture

A considerable input of zinc to the soil comes from the agricultural sector (van Driel and Smilde, 1990). Agriculture itself is responsible for a number of direct sources of zinc to agricultural soil: production and use of animal manure, and the use of chemical fertilizers, pesticides and sewage sludge (see Table 2.7). In addition, atmospheric deposition, corrosion of galvanized structures, and settling of suspended sediments following the overflowing of a river also cause zinc contamination of agricultural soil.

Table 2.6. Summary of the zinc emissions from non-industrial sources (partly based on: RIZA, 1990; TNO, 1989)

source	emission (tonnes of zinc per year)					
	surface water	*of which via sewage system*	*STP sludge*	*soil*	*air*	*total*
households	45	29	67	5	-	117
corrosion	1,650	190	450	2,025	-	4,125
traffic	75	16	38	127	-	240
agriculture 1)	80	-	-	1,660	-	1,740
non-industrial lubricating oil usage	10	4	10	10	-	30

1) only: production and use of animal manure, and use of chemical fertilizers, pesticides and sewage sludge

The zinc input to agricultural soils is at least about 1990 tonnes per year. The zinc carried to surface water in runoff from the land is estimated to be about 80 tonnes per year [based on about 1 % of the total amount of zinc in animal manure on grassland (Jansen, 1988) and 88 g ha^{-1} on arable land], while removal by crops (mainly grass and grass products) is estimated at 550 tonnes a year. The minimum net input to agricultural soils is then about 1360 tonnes of zinc per year. The principle source of zinc to agricultural soils is animal manure. Animal manure has a relatively high zinc content because, in addition to the zinc concentration in feed of about 40 $mg.kg^{-1}$, another 40 $mg.kg^{-1}$ may have been added to concentrates, depending on the animal species.

Table 2.7. The annual zinc input to agricultural soil (based on Gorter, 1991, among others)

Source	*Amount (tonnes)*	*Comment*
Animal manure	*1,450*	*Minimum estimate: based on Zn content of animal feed*
Chemical fertilizers	*135*	
Pesticides	*60*	
Sewage sludge	*93*	*Zn content: ca 1300 mg kg dry weight*
Deposition	*250*	*Based on this document*
Corrosion	*p.m.*	*Probably a few hundred tonnes per year*
Other	*p.m.*	*e.g., settling of suspended sediment after overflowing of a river*
Total	*> 1,988*	

In estimating the minimum accumulation, the contribution from corrosion of zinc to the total soil burden was not taken into account.

2.3.3. Corrosion

The corrosion of galvanized structures, such as balustrades, electricity pylons, crash barriers, lampposts, gutters and pipes, makes a substantial contribution to the zinc pollution of the environment.

The amount of zinc lost to the environment through corrosion is difficult to estimate and therefore uncertain. For a description of the methodology followed, the reader is referred to Annema et al. (1991).

The rate of corrosion of zinc from galvanized steel depends upon many factors, important among which are the amount of salt and pollutants (particularly SO^2) in the atmosphere, the rate and amount of rainfall, the relative humidity, and the acidity of precipitation. Consequently, the corrosion rate of zinc varies with the location of the zinc structure: it has been assumed that zinc structures located in rural areas have the lowest corrosion rate (14 g per m^{-2} per year) and those erected around highways have the highest rate (50 g per m^{-2} per year). By dividing the total zinc surface area which was exposed to the atmosphere in 1989 (about 125 million m^{-2}) among the various locations, the total amount of zinc lost by corrosion was calculated to be 4000 ± 1000 tonnes. A flow model

(STRAVERA) was used to determine where in the environment the corroded zinc ends up (Table 2.8). According to this calculation, a total zinc load of 450 tonnes due to corrosion would end up in sewage sludge and drain-hole sludge. This stream contains an estimated total of 430 tonnes of zinc (Table 2.9). Since in addition to corrosion, there are a number of other (small) sources which determine the concentration of zinc in sludge, it can be concluded that the calculated and estimated figures do not entirely agree. This reflects the fact that for the calculation of the zinc concentration and of the zinc removal situation, many assumptions had to be made. Nevertheless, it is clear that the corrosion term has been estimated reasonably well.

Table 2.8. Calculated amounts of zinc entering surface water, sludge and soil due to corrosion of zinc structures

Fresh surface water	*1,650*
Sludge	*450*
Soil	*2,025*

2.4. ZINC-BEARING WASTE

Practically every waste stream contains zinc. Table 2.9 summarizes the principal waste streams and a rough estimate of their destinations. The processing of zinc-bearing waste streams releases annually about 70 tonnes of zinc into the atmosphere, mainly through the incineration of household waste (about 30 tonnes) and of spent oil (40 tonnes). Important sources of zinc in household waste are nonferrous components (12 g kg^{-1} dry weight), ceramics (0.4 g kg^{-1} dry weight), carpets (0.8 g kg^{-1} dry weight), and batteries (106 g kg^{-1} dry weight) (van de Beek et al., 1989). Figure 2.1 summarizes the zinc flow occurring in waste processing.

Export concerns primarily old sheet zinc (from buildings) and various industrial waste streams from, for example, the hot-dip galvanizing plants (see Section 2.5), which are reprocessed abroad to recover zinc. The fate of this waste stream is not exactly known, but it can be assumed that the greater part will be processed.

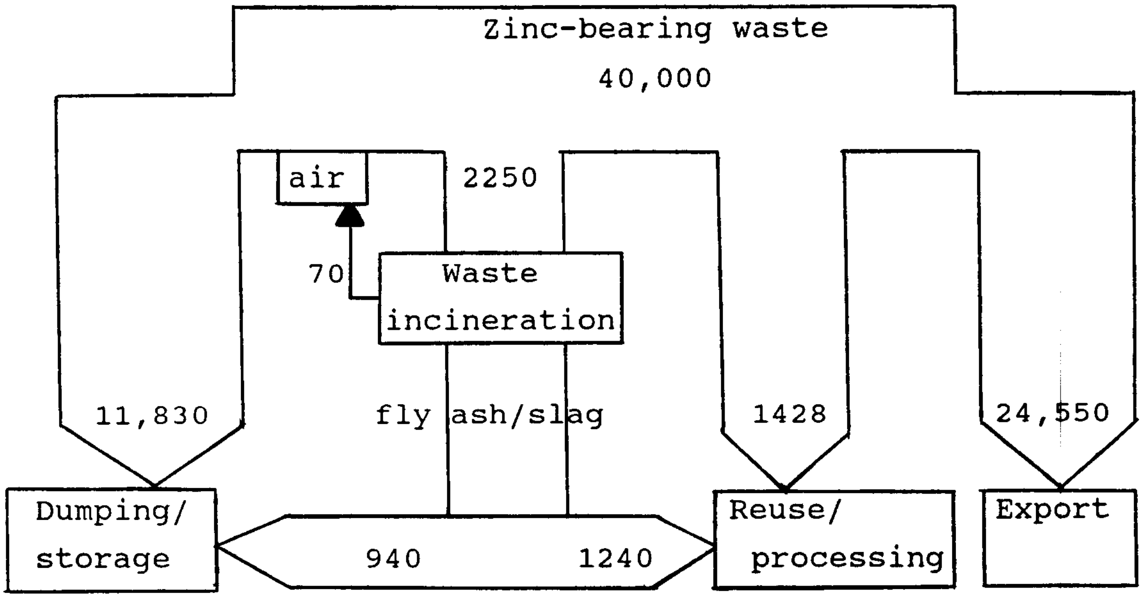

Figure 2.1. *Zinc flow (tonnes per year) resulting from the production and processing of zinc-bearing waste streams and residual streams*

2.5. SUMMARY AND CONCLUSIONS

Table 2.10 summarizes the zinc emissions in the Netherlands in 1989. The total zinc emission to soil, water and air was about 6,000 tonnes. The corrosion of galvanized steel (construction steel, crash barriers, electricity pylons and the like) and rolled zinc (gutters and roofing) is by far the most important source. More than 85 % of the zinc input to water and about 50 % of that to soil is attributable to this source. The production and use of animal manure, and the use of chemical fertilizers, pesticides and sewage sludge in agriculture also result in a significant zinc pollution to the soil: about 45 % of the total input to soil. Industrial sources account for only about 6 % of the total input to water. The incineration of zinc-bearing waste materials is the principal source of atmospheric zinc emissions. In addition, there are four important industrial point sources of zinc air emissions: secondary steel production, primary iron and steel production, primary zinc production, and production of zinc alloys.

Of the zinc load in zinc-bearing waste streams and residual streams, which was about 40,000 tonnes in 1989, about 60 % was shipped to other countries, where the greater part will be reprocessed. Zinc-bearing waste, with a zinc content of about 13,000 tonnes, is dumped or stored in the Netherlands.

Table 2.11 gives a summary of the zinc input (not only direct emissions but also transport pathways such as atmospheric deposition, import and runoff) to soil and water in 1989.

The total input to agricultural soil, corrected for removal by crops (app. 550 tonnes per year) and runoff (80 tonnes per year), amounts to a minimum annual zinc accumulation in agricultural soil of 1,360 tonnes.

Table 2.9. Significant zinc-bearing waste and residual streams (RIVM, 1991; Nagelhout et al., 1989; Bohman, 1989; Huiszoon, 1989; Jaartsveld Groen and Milieu BV, 1988; TAUW, 1988; Verhagen, 1989; van Weelden, 1989; Nieuwenhuis et al., 1990; de Weerd and Wieringa, 1990)

waste stream	*zinc content (mg.kg^{-1})*	*zinc load (tonnes)*	*disposal method*
old sheet zinc, brass scrap and Al-Cu-Zn alloy	*various*	*15,000*	*export*
household waste	*various*	*4,700*	*35% incineration* *60% dumping* *5% reuse*
bulky waste	*various*	*400*	*as above*
spent oil	*1,000*	*100*	*40% incineration* *55% reuse* *5% discharge*
batteries	*150,000*	*600*	*40% dumping* *40% storage* *20% incineration*
car tyres	*16,000*	*1,000*	*25% dumping* *50% export* *25% reuse*
scrap	*1,500*	*3,200*	*60% export* *40% dumping*
spraying/paint waste	*5,500/1,500*	*600*	*dumping/incineration*
blasting grit	*7,000*	*600*	*30% reuse* *70% dumping and loss to the environment*
industrial waste (see 2.2)	*various*	*13,200*	*54% export* *42% dumping/storage* *4% reuse/processing*
dredged sediments (class IV)	*500*	*300*	*dumping*
sewage sludge/drainhole sludge	*1,270/600*	*430*	*56% dumping/ incineration* *44% reuse/processing*
Total		*ca 40,000*	

Table 2.10. *Summary of zinc emissions in the Netherlands (tonnes of zinc per year)*

Source	emissions water	emissions air	emissions soil	Total
INDUSTRIAL SOURCES:				
zinc production	1*)	25	-	26
storage in the past	16	-	-	16
production of zinc alloys	0,8	25	-	25,8
zinc oxide production	1	9	-	10
production of zinc compounds	12,5	0,7	-	13,2
metal surface treatment				
zinc spraying	< 0,1	6	-	< 6,1
hot-dip galvanizing	2,5	< 1,0	-	< 3,5
electrogalvanizing	7,5	-	-	7,5
rayon production	18	-	-	18
primary iron/steel production	4	26	-	30
secondary steel production	< 1	32	-	< 33
phosphoric acid production	12	-	-	12
titanium dioxide production	10	-	-	10
other industries	45	42	-	87
ENERGY GENERATION				
coal	-	2	-	2
WASTE DISPOSAL				
incineration	-	70	-	70
AGRICULTURE	80	-	1,660	1,740
TRAFFIC	75	-	127	202
CORROSION (CONSTRUCTION)	1,650	-	2,025	3,675
HOUSEHOLDS	45	-	5	50
TOTAL	1,965	239	3,817	6,021

*) from current manufacturing process

Table 2.11. Summary of the zinc input to soil and surface water in the Netherlands in 1989

Pathway	*water*	*soil (total)*	*agricultural soil*
Corrosion	*1,650*	*2,025*	*p.m.*
Agriculture	*80*	*1,660*	*1,660*
Traffic	*75*	*127*	*p.m.*
Industry	*130*	-	-
Atm. deposition	*60*	*410*	*250*
Households	*45*	*5*	-
Other	*10*	*10*	*p.m.*
Import (rivers)	*2,000*	*p.m. 1)*	*p.m. 1)*
Total	*4,050*	*> 4,237*	*> 1,910*

1) Settling of suspended sediments following a flood

3. FORMS OF ZINC AND DISTRIBUTION

3.1. FORMS OF ZINC

Zinc is a common metal, ubiquitous in the human environment. It is the most abundant of all essential trace elements present in the environment, and its bioavailability almost certainly depends on its chemical form. Zinc is present in the environment only in the divalent state. Possible chemical forms of Zn(II) in fresh surface water and in seawater are presented in Tables 3.1 and 3.2., respectively. Zinc forms fairly stable complexes with chloride ions and cysteine, and can form stable complexes with humic and fulvic acids and sulphide ions. Although the speciation of zinc can be calculated in principle, the results of such model calculations indicate that they vary widely even for the simple inorganic complexes. Analytical-chemical methods remain indispensable for the determination of the distribution pattern of zinc species. There is controversy in the literature over the percentage of the total zinc in fresh surface water and seawater that is bound to organic matter (Florence, 1980). The dominant forms of a number of zinc compounds are presented graphically in Figure 3.1 as a function of pH, for the $Zn\text{-}CO^2\text{-}S\text{-}H^2O$ system (Hem, 1972). The concentrations of zinc in the soil solution are low at a pH between 7 and 8, but increase sharply at pH < 6 due to desorption and dissociation processes. The organically bound fraction decreases sharply at pH < 6 (Brummer, 1986). In sewage sludge over 50 % of the zinc was found to be organically bound, regardless of the amount of zinc present (Mehotra et al., 1989). The formation of $Zn(OH)^{-3}$ and $Zn(OH)^{2-4}$ ions is not to be expected in the environment. Under reducing conditions, precipitation of the sulphide (ZnS) may occur, and under pH-neutral conditions at higher concentrations, of the hydroxide and carbonate ($Zn(OH)^2$, $ZnCO^3$). In surface waters, these chemical reactions are of lesser importance for the speciation of zinc than the sorption of zinc onto oxides and oxyhydrates of iron and manganese, clay minerals and suspended organic matter (Malle, 1989). The bioavailable fraction of zinc from sediments is about 2 to 17 % (Prosi and Muller, 1987).

The distribution of zinc in soil is as follows: (1) dissolved in soil water, (2) exchangeably bound to soil particles, (3) bound to organic ligands, (4) occluded in secondary clay minerals and metal oxides and hydroxides, and (5) present in the primary minerals.

Table 3.1. *Possible chemical forms (speciation) of dissolved zinc in surface waters (Florence, 1980)*

Chemical form	*Examples*	*Approximate diameter (nm)*
particulate matter	*not retained by 0.45 um filter*	> 450
hydrated metal ion	$Zn(H_2O)_{2+6}$	0.8
labile inorg. complexes	$Zn(H_2O)_5Cl^+$, $Zn(H_2O)_5OH^+$	1
labile org. complexes	*Zn-citrate, Zn-glycinate*	1-2
stable inorg. complexes	ZnS, $ZnCO_3$, Zn_2SiO_4	1-2
stable org. complexes	*Zn-humate, Zn-cysteinate*	2-4
adsorbed on inorg. colloids	Zn^{2+}-Fe_2O_3, Zn^{2+}-SiO_2	10-500
adsorbed on org. colloids	Zn^{2+}-*humic acid* Zn^{2+}-*org. detritus*	10-500

Table 3.2. *Possible chemical forms (model calculations) of zinc species in seawater*

	percentage of total zinc			
Zn species	*Zirino and Yamamoto (1972)*	*Dyrssen and Wedborg (1974)*	*Morgan and Sibley (1975)*	*Florence and Batley 1977*
Zn^{2+}	17	16.1	12.5	5.7
$ZnCl^{n2-n}$ (n:1-4)	11.4	63.7	79	17.8
$ZnOH^+$, $Zn(OH)_2$	62.2	2.3	0.6	71.8
$ZnCO_3$	6	3.3	1.6	2.4
$ZnHCO_{+3}$	0.7	0.3	-	0.2
$ZnOHCl$	-	12.5	-	-
$ZnSO_4$	4	1.9	1.6	2.2

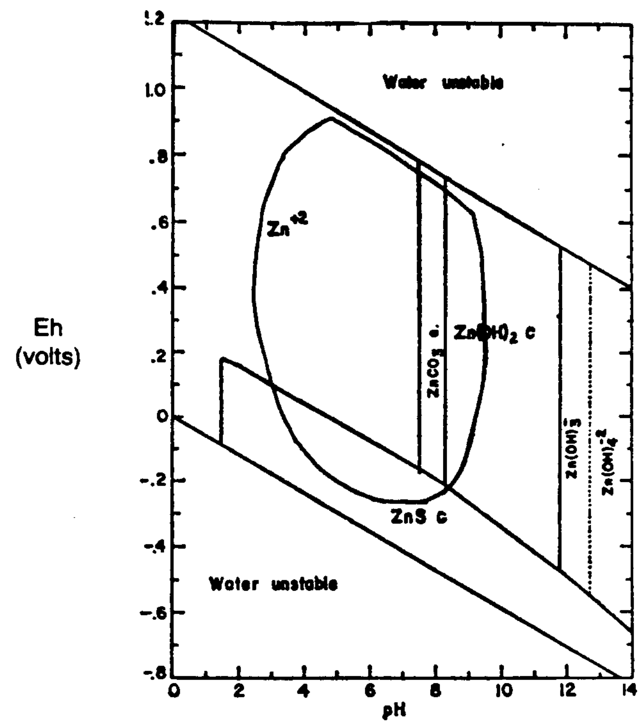

Figure 3.1. *Fields of stability of solid (c) and dissolved zinc species in the system $Zn+CO_2+S+H_2O$ at 25 °C and 1 atm pressure in relation to redox potential (Eh) and acidity (pH). Dissolved zinc activity, 10^{-5} moles.l^{-1}; dissolved carbon dioxide and sulphur species, 10^{-3} moles.l^{-1} (Hem, 1972). The area within the closed curve encompasses Eh-pH combinations most commonly found in the environment*

The relevant processes for the availability of zinc in soil are precipitation and dissolution, complexation, and adsorption and desorption. Inorganic and organic zinc species are present in the soil solution. The chemical speciation depends on the presence of organic matter in the soil, the soil pH, and the ionic strength and composition of the soil solution. The major inorganic species at $pH < 7.7$ is Zn^{2+}, while $ZnOH^+$ is more important at higher pH values. $Zn(OH)_2$ is the dominant species at $pH > 9.1$ (Figure 3.1). Zinc can form complexes with numerous anions. A number of equilibrium reactions with associated equilibrium constants are given in Table 3.3. Calculations indicate that under particular conditions, the $ZnSO_4$ and $ZnHPO_4$ complexes can increase the total amount of zinc in solution. At sulphate concentrations of 400-600 mg.l^{-1}, as measured in the Western Mining District (van Duijvenbooden, 1989), 40 to 50 % of the inorganic zinc can exist in the form of the $ZnSO_4$ complex.

Table 3.3. *Soluble zinc species in equilibrium with soil zinc and the log K values of the respective equilibrium reactions (Source: Kiekens (1990)*

Equilibrium reaction	*log K*
$Zn^{2+} + H_2O$ <-> $ZnOH^{+} + H^{+}$	-7.69
$Zn^{2+} + 2H_2O$ <-> $Zn(OH)_2 + 2H^{+}$	-16.80
$Zn^{2+} + 3H_2O$ <-> $Zn(OH)^{-}_3 + 3H^{+}$	-27.68
$Z^{n2}+ + 4H_2O$ <-> $Zn(OH)^{2-}_4 + 4H^{+}$	-38.29
$Zn^{2+} + Cl^{-}$ <-> $ZnCl^{+}$	0.43
$Zn^{2+} + 2Cl^{-}$ <-> $ZnCl_2$	0.00
$Zn^{2+} + 3Cl^{-}$ <-> $ZnCl^{-}_3$	0.50
$Zn^{2+} + 4Cl^{-}$ <-> $ZnCl^{2-}_4$	0.20
$Zn^{2+} + H_2PO^{-}_4$ <-> $ZnH_2PO^{+}_4$	1.60
$Zn^{2+} + H_2PO^{-}_4$ <-> $ZnHPO_4 + H^{+}$	-3.90
$Zn^{2+} + NO^{-}3$ <-> $ZnNO^{+}_3$	0.40
$Zn^{2+} + 2NO^{-}_3$ <-> $Zn(NO_3)_2$	-0.30
$Zn^{2+} + SO^{2-}_4$ <-> $ZnSO_4$	2.33

The two most stable forms of organic matter in the soil solution are humic and fulvic acids. Fulvic acids form complexes with zinc ions over a broad pH range, and so enhance the solubility and mobility of zinc. Verloo (1974) found in column experiments that 16 % of the zinc in the leachate existed as fulvates. In other studies, percentages as high as 60 to 75 % have been observed (Hodgson et al., 1966; Geering and Hodgson, 1969). The stability constants of these zinc complexes increase with increasing pH. The complexes exhibit almost no tendency to flocculate except at high ionic strength. The interactions between zinc and humic acids, too, are strongly affected by pH. Besides humic and fulvic acids, other simple organic compounds also play a role in complex formation.

3.2. BEHAVIOUR IN SOIL

3.2.1. Mobility

The mobility of zinc in soil depends on the degree of adsorption and the solubility of the species, which in turn depend on the composition of the soil solution and the properties of the soil material. In soils, zinc adsorbs strongly to oxides and hydroxides, silica, calcium carbonate, clay particles and organic matter. The active zinc species in adsorption is possibly $Zn(OH)^+$ (Sanders and El Kherbawy, 1987). Zinc tends to be more readily sorbed at higher pH (pH > 7) than lower pH (Callahan et al., 1979). Besides cation exchange (during the sorption of a zinc ion on the soil material, another - bivalent - cation is released from the soil complex to the soil solution), specific adsorption on soil constituents occurs, as shown in Table 3.4. It can be seen from this table that zinc occupies more adsorption sites on the metal oxides than would be present on the basis of the CEC determination with the barium ion as counterion. Kieken (1990) found that the adsorption-desorption curve of zinc, using calcium as the counterion, exhibited hysteresis whereby not all the zinc could be desorbed, which also points to specific sorption of zinc. Van Bladel et al. (1988) found that zinc can be readily displaced by calcium, which is commonly abundant in the soil solution. The chances for leaching will be greater in light (acid) soils than in soils high in organic matter and $CaCO_3$. Below pH 7, the amount of zinc in solution has been reported to be inversely related to soil pH (Saeed and Fox, 1977). Above pH 7, in the presence of sufficient organic matter, more zinc can actually be in solution than would be expected on the basis of the adsorption equilibrium, due to complexation (Sanders and El Kherbawy, 1987).

The pH of the soil determines not only the degree of complexation and adsorption of zinc but also the solubility of the various zinc minerals. The solubility of zinc in soil decreases with increasing pH (Lindsay, 1972). The strong sorption of zinc to soil particles makes the formation of, for example, smithsonite ($ZnCO_3$), zincite (ZnO) and willemite (Zn_2SiO_4) unlikely (Brummer, 1986; Kieken, 1990). Under anaerobic conditions, zinc sulphide is the controlling species (ATSDR, 1989). Zinc can become immobilized or less available in the course of time through slow diffusion into soil minerals.

Table 3.4. Cation exchange capacity (CEC) and adsorption maxima of zinc on a few materials in $CaCO_3$-buffered systems (Brummer, 1986)

Material	*CEC (pH 7.6) umoles g^{-1} (Ba^{2+}) (a)*	*Adsorption maximum *) µmoles g^{-1} (Zn^{2+}) (b)*	*b/a*
$CaCO_3$	-	0.44	-
Bentonite	450	44	0.10
Humic Acid	1,700	842	0.50
Amorphous Fe-oxide	160	1,190	7.4
Amorphous Al-oxide	50	1,310	26.2
d-MnO_2	230	1,540	6.7

**) Adsorption maximum calculated from the Langmuir isotherm for zinc concentrations in solution at the equilibrium concentration of zinc carbonate after a reaction time of seven days*

The distribution coefficient, Kd, is often used for quantifying the mobility of a substance. The Kd is the ratio between the concentration of a substance in the solid phase and its concentration in the liquid phase at equilibrium. The Kd values for zinc vary widely, from 0.1 to 8,000 $l.kg^{-1}$ (Baes and Sharp, 1983; Anderson and Christensen, 1989). Values of 0.2-4 $l.kg^{-1}$ have been reported for sandy soils and of 70-100 $l.kg^{-1}$ for sandy loam soils (Gerritse et al., 1982). Median values of 41 and 140 $l.kg^{-1}$ have been measured for the O-horizon (litter layer) and E-horizon (leached mineral layer), respectively, of a podzol forest soil (pH 3.7-4.6) (Bunzl and Schimmack, 1989). Anderson and Christensen (1989) found that the Kd value for zinc is strongly related to the pH. Furthermore, the presence of extractable manganese oxides and hydroxides and the magnitude of the cation exchange capacity are also important in this respect.

3.2.2. Availability in soil

The bioavailable fraction of zinc from soils to plants is assumed to be about 1-10 % (SDV, 1990). The plant takes up zinc primarily in the form of Zn^{2+}, but hydrated zinc and several other zinc complexes may also be absorbed. Factors influencing the availability of zinc to the plant are, in addition to total soil zinc, especially the pH, the concentration and type of organic matter, the number of adsorption sites, the microbial activity, and the soil moisture status. In addition, other factors such as interactions between zinc and other macro- and micronutrients also affect zinc availability (Kiekens, 1990).

Topical environmental issues such as "acid rain" and phosphate saturation of the soil are also related to the mobility of zinc in soil. The deposition of acidic substances leads not only to a decrease in the soil pH, which may or may not be temporary, but also to an increase in the sulphur loading of the soil, resulting in higher sulphate concentrations in the soil solution. The mean sulphur deposition rate in the Netherlands is 20 kg per ha per year, but varies from 15 kg per ha per year in the province of Friesland to 30 kg per ha per year in the province of Brabant (Erisman, 1991). This load is of the same order as the input from the use of animal manure, which, depending on manure type and land use, is 10-60 kg per ha per year (calculation based on van den Ham, 1988; van der Hoek, 1988). This yields a total sulphur input to agricultural soils of between 25 and 90 kg per ha per year. Using an evaporation factor of 3, the sulphate concentration in the soil solution can be calculated to be 33-120 $mg.l^{-1}$. Van Duijvenbooden (1989) reported values ranging from 70 to 110 $mg.l^{-1}$ for shallow groundwater, with peaks above 150 $mg.l^{-1}$. This implies that between 10 and 25 % of the zinc can exist as $ZnSO_4$ (calculated on the basis of the log K value in Table 3.3). The influence of phosphate in solution on zinc mobility is strongly pH dependent and will not play an important role under normal conditions. The concentration of orthophosphate in shallow groundwater usually remains below 0.4 $mg.l^{-1}$, due to fixation (van Duijvenbooden, 1989). This means that even at pH 7, at most 0.5 % of the zinc exists as $ZnHPO_4$. Van Riemsdijk (1990), however, calculated a phosphorus concentration of 91 $mg.l^{-1}$ for the soil solution of soils which have no binding capacity left for phosphate. In that case 25 % of the zinc could be in the form of $ZnHPO_4$ at pH 6.5. Note that a high soil phosphorus concentration will reduce zinc availability, due to chemical reactions in the rhizosphere. The Zn-P antagonism can be explained on a physiological basis (Kiekens, 1990).

3.3. BEHAVIOUR IN SURFACE WATER

3.3.1. General

In addition to chemical speciation, adsorption plays an important role in the behaviour of zinc in aquatic systems. Zinc can be bound in several ways in suspended and bottom sediments. The principal metal carriers in sediments are clay minerals, quartz, feldspars, calcium carbonate and organic matter. In particular, several hydroxides, clay minerals and organic matter are important in the adsorption of zinc (Salomons and Kerdijk, 1985). The various binding forms are subject to shifts when changes occur in the aquatic environment, for example, in the pH, the temperature, and at the transition from river water to freshwater basins and from fresh water to seawater. In natural aquatic systems, adsorption of zinc onto suspended solids is strongly pH dependent: as the pH increased from 6.5 to 9, the amount of metal adsorbed increased from 20 to 90 % (ZMAS, 1984a). Erosion of bottom sediments, which is important especially in the shallow Lake IJssel, has almost no influence on the concentration of dissolved zinc in the overlying water column (ZMAS, 1984b). The accumulation of zinc in the sediments from surface water increases with decreasing size of the sedimenting particles. Particles > 250 um show only very slightly increased zinc concentrations (Wachs, 1988). Diffusive transport of zinc to or from the pore water of the sediment is negligible compared with other physical processes.

3.3.2. River water: distribution and distribution coefficients

The water quality survey of State waters (RIZA, 1975-1988) indicates that the fraction of the total zinc load associated with the suspended sediment has increased with time. However, the amount of particulate-bound zinc has decreased. This is true for both the Rhine River at Lobith and the Meuse River at Eijsden (Figure 3.2). The quality survey of State waters also clearly shows another trend: the zinc load in both rivers has fallen by about a factor of 3 in the same period. It appears that the distribution coefficient increases with decreasing total zinc concentrations in the large rivers. Assuming that in this period the suspended solids concentration has remained constant at 37 $mg.l^{-1}$ (dry weight), the zinc concentration in suspended particulate matter (Cs in $mg.kg^{-1}$) and the distribution coefficient (Kd in $l.kg^{-1}$) can be estimated. The change in log Kd with time is given in Figure 3.3 and the Cs versus the concentration in the dissolved phase is plotted in Figure 3.4. A Langmuir isotherm has been drawn through the points in Figure 3.4. Golimowski et al. (1990) give ranges for the distribution coefficient of zinc in the Rhine, Waal and Meuse Rivers of 10,000 - 145,000, 10,000 - 190,000, and 75,000 - 230,000, respectively. The literature gives some indications that in rivers with a low pollution level, the proportion of zinc transported on suspended sediment is relatively high. Trefley and Presley (1971) found that in the uncontaminated stretch of the Missisippi River, 90 % of the zinc was carried in the particulate phase. In polluted rivers this was only 40 % (Kopp and Kroner, 1968).

3.3.3. Freshwater basins: retention

Before the closing off of the Zuider Sea and the Haringvliet from the sea, the zinc concentrations in the sediments were largely determined by mixing with marine sediment which had relatively low zinc levels. After the construction of the dams, the concentrations in precipitated bottom sediments, originating from the Rhine River, in the Lake Ketel/Lake IJssel and Hollands Diep/Haringvliet basins and in the Rotterdam harbour region rose considerably. The same is true for the sediments transported by the Meuse River which settle in the Amer/Hollands Diep. The concentrations are highest near river mouths: Hollands Diep/Haringvliet and Lake Ketel. In these basins the total zinc concentration (i.e., dissolved plus particulate) in the water column decreases due to sedimentation of suspended solids. Also, the concentrations of dissolved zinc decrease in the direction of the Haringvliet Sluices and the Lake IJssel Dam as a result of adsorption onto algae and coprecipitation with iron, manganese and calcium compounds (particularly in Lake IJssel). The sediments of Lake IJssel have a lower zinc concentration than those of Lake Ketel and the Haringvliet. These differences can be explained as follows (ZMAS, 1984a,b): in the relatively shallow Lake IJssel resuspension is extensive, resulting in mixing with uncontaminated older sediment. In addition, an important factor is the increase in pH caused by the algal bloom, so that a considerable amount of calcium carbonate precipitates. Through precipitation of locally-formed and thus relatively clean sediment (algae and calcium carbonate), there is a "dilution" of contaminated sediment supplied by the IJssel River, and of resuspended bottom sediments of Lake Ketel. The concentration of dissolved zinc falls due to adsorption onto the newly-formed sediment (Table 3.5). However, the magnitude of this process of "concentrating" in the sediment is smaller than that of the dilution process described above owing to lake bed erosion, whereby the amount of old sediment resuspended during a storm is many times greater than the annual sediment input to the lake. In the long run, a certain zinc level in the mixed sediment will have been reached and, therefore, with a constant loading, the zinc concentration in Lake IJssel sediments will increase further for some time. The sediments of the Haringvliet are by now fully "charged" with zinc because the sediment input is much greater, and deposition of this sediment dominates the retention of zinc. Moreover, because of a shorter residence time of the sediment input, there is less algal bloom and consequently less pH rise, and bed erosion in this basin with a greater depth and smaller surface area than Lake IJssel plays a less important role. Table 3.5 gives shows the total accumulation of zinc in the basins, from two studies made in 1977/1978 and 1985.

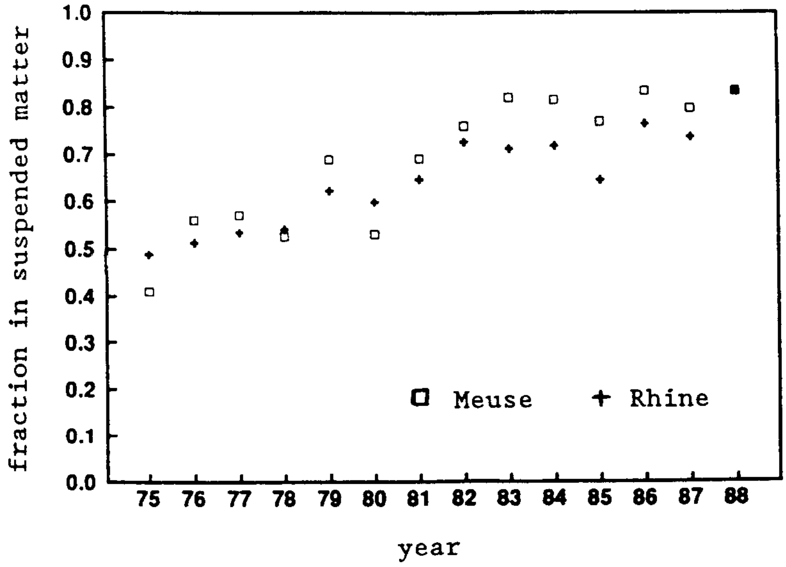

Figure 3.2. Fraction of zinc in suspended particulate matter in the Meuse and Rhine Rivers

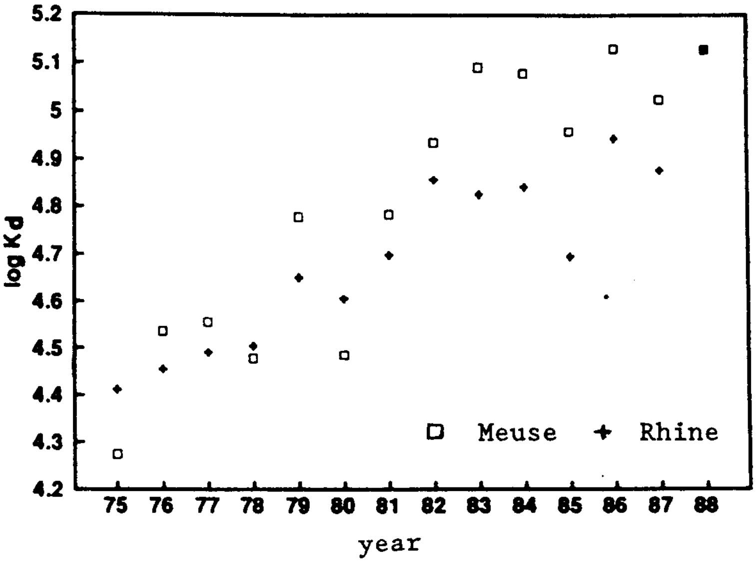

Figure 3.3. Log Kd (Kd in l.kg^{-1}) in the Meuse River (Eijsden) and Rhine River (Lobith), 1975-1988

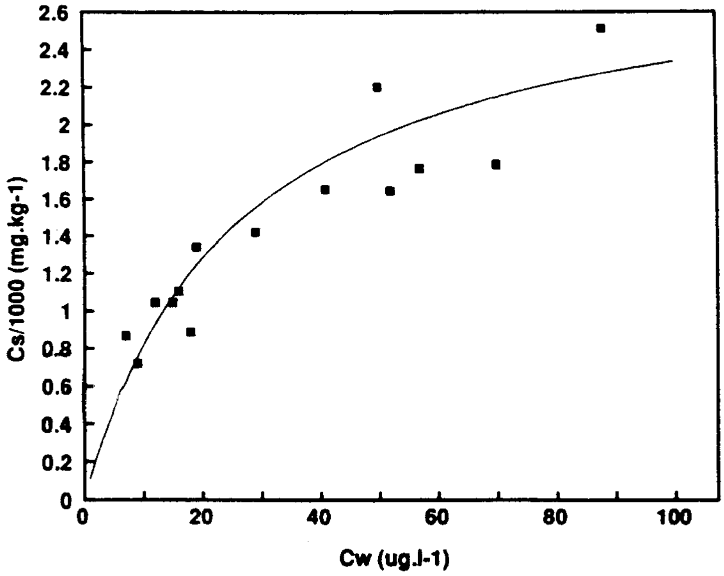

Figure 3.4. Partition of zinc in Rhine water; Langmuir isotherm

Table 3.5. Total accumulation of zinc in Hollands Diep/Haringvliet and Lake Ketel/Lake IJssel (ZMAS, 1984a,b 1991)

	Total accumulation of zinc (tonnes/year) *1977/1978 (ZMAS, 1984a,b)*	 *1985 (RIZA, 1991)*
Hollands Diep/ Haringvliet	*3,717*	*414*
Lake Ketel/ Lake IJssel	*1,003*	*305*

3.4. BEHAVIOUR IN AIR

In the atmosphere zinc occurs primarily bound to aerosols (Nriagu and Davidson, 1980; Thijsse and Huygen, 1985). Water-soluble forms of zinc account for about 25 % of the total particulate concentration (Lum et al., 1987). The proportion of zinc in the gaseous phase is reported to be no more than about one percent of the total atmospheric concentration. An important factor in determining the transport and deposition characteristics of zinc-containing aerosol particles is the particle-size distribution. The mass median diameter ranges from about 0.3 to 5 um (Milford and Davidson, 1985; Pacyna and Brynjulf, 1989). Because zinc in the atmosphere comes from a wide variety of sources, zinc-aerosol particles exhibit a rather flat size distribution. Waste incinerators release small zinc-containing particles to the atmosphere, while wear of automobile tyres produces larger particles (Sohn et al., 1989). Measurements of zinc in aerosols in the Netherlands (van Jaarsveld and Onderdelinden, 1986) indicate that in rural areas, zinc is present chiefly in the finest fraction (mass median diameter ca. 0.4 um, and 70 % of the total zinc mass below 1 μm). In urban and industrial areas (around metallurgical plants, and around brass and zinc production facilities), the median particle diameter can be as large as the afore-mentioned 5 um (Dorn et al., 1976; Nriagu and Davidson, 1980). In windblown soil and road dust, the particles are (super)coarse in size, with a diameter greater than a few tens of micrometres (van der Meulen, 1987). The effective dry deposition velocity of atmospheric aerosol-bound zinc ranges from 0.05 to 0.66 $cm.s^{-1}$ (Pacyna and Brynjulf, 1989). The dry deposition velocity for the Dutch situation was found to be 0.1-0.2 $cm.s^{-1}$ (van Jaarsveld and Onderdelinden, 1986). The initial value in the immediate vicinity of a source is 0.2 $cm.s^{-1}$. The deposition velocity decreases during transport of the atmospheric aerosol owing to preferential removal of the larger particles by dry and wet deposition. This leads to a representative value of about 0.1 $cm.s^{-1}$ for the dry deposition velocity of airborne zinc. The average rate of removal of zinc from the atmosphere by dry deposition is 0.5 % per hour. Under conditions pertaining in the Netherlands, the average rate of removal by wet deposition is ca 1.5 % per hour. From the above data it follows that the lifetime of atmospheric zinc aerosol is about 2 days. This residence time allows the zinc aerosols to be transported over a distance of about 800 km, quite independent of the source height. The deposition velocity of (super)coarse aerosol particles can be 10 times greater than the average value, so that the transport distance of the coarse fraction is 2 to 3 orders of magnitude smaller than the average value (Van der Meulen et al., 1984).

3.5. BEHAVIOUR IN BIOTA

The information in this section is partly based on data from Chapter 5. Most aquatic invertebrates and fish concentrate zinc only to a limited extent, from both fresh and salt water. The majority of the bioconcentration factors (BCFs) for invertebrates and fish lie between 100 and 1000, those for fish generally being lower than those for invertebrates. Certain benthic organisms such as crabs, oysters and insect larvae accumulate zinc to very high levels (BCFs in the range of 10,000 to 100,000). According to Hagel and Vos (1989), the zinc concentrations in fish are only weakly related to the degree of contamination of the water. In view of the decreasing BCF values with increasing trophic level in the food web ($BCF_{algae} > BCF_{invertebrates} > BCF_{fish}$), it is concluded that biomagnification (accumulation through food chains) is of little significance in the aquatic environment.

Zinc is concentrated by earthworms, an important group of soil invertebrates, even at relatively high soil zinc levels (concentration factor CF > 1). The CF value decreases with increasing soil zinc concentration, but only at extremely high soil zinc levels (> 1000 $mg.kg^{-1}$ dry weight) do earthworms not concentrate zinc. Other soil invertebrates such as wood lice, springtails, beetles and centipedes do not or scarcely concentrate zinc from the soil or the litter layer (CFs in the range of 0.03 to 3.0). The accumulation of zinc from soil by crops is strongly dependent on the chemical form of the metal. The bioavailability of zinc present in organic substrates such as compost is generally low, so that relatively high soil zinc concentrations lead only to a small increase in the concentrations in crop plants. Depending on the strength of the chemical bond between zinc and any ligands present, its bioavailability can be influenced both negatively and positively (Lee, 1972). The bioavailability of soluble inorganic zinc is (much) higher. The fraction of the total soil zinc which is available to plants is usually no more than 1 to 10 %. A deficiency of available zinc may occur in soils with high calcium carbonate and phosphorus contents. Zinc availability increases with decreasing soil pH. The presence of humic acids controls the availability of zinc. The zinc content of plants is usually (much) lower than that of the soil, even on a dry weight basis. The soil-crop relationships for zinc have not been clearly established. They are strongly dependent on soil pH, soil characteristics and degree of contamination.

Mammals have an effective control mechanism whereby the total body zinc is maintained within certain limits, both at low and high dietary zinc intakes (Chapter 5). In biota, zinc also plays an important, primarily antagonistic, role in the uptake of other elements, such as calcium, cadmium, lead, selenium and iron (Stoop and Rennen, 1990). At a soil zinc concentration of 200 $mg.kg^{-1}$, cadmium uptake can be reduced by 40 % (Sauerbeck, 1982) Excess zinc in the soil can lead to iron deficiency in plants (Kloke, 1974).

3.6. SUMMARY AND CONCLUSIONS

Zinc is the most abundant of all essential trace elements present in the environment. It can occur in various chemical forms: as free Zn^{2+} ion, particularly at $pH < 6$, bound to organic matter, and bound to inorganic ligands such as sulphide, hydroxide and carbonate ions and, in seawater, to chloride ions. In general, the speciation of zinc depends on the presence of organic matter, the pH, the ionic strength and the composition of the environmental matrix.

The mobility of zinc in soil depends on the degree of adsorption and the solubility of the species present. Zinc adsorption on hydroxides, clay particles and organic matter, among other materials, and precipitation (as, for example, $ZnCO_3$) is greater at higher pH than at lower pH. Values for the distribution coefficient (Kd) vary widely, from 0.1 to 8,000 $l.kg^{-1}$. The Kd value depends, among other factors, on the pH, the presence of manganese oxides and hydroxides, and the cation exchange capacity. The bioavailable fraction of zinc from soil is about 1 to 10 %.

In addition to chemical speciation, adsorption also plays an important role in the behaviour of zinc in surface waters. The adsorbents in sediments are chiefly clay minerals, quartz, feldspars, calcium carbonate and organic matter. The various binding forms are subject to shifts when changes occur in the aquatic environment, for example, at the transition from river water to freshwater basins and from fresh water to seawater. In aquatic systems, adsorption of zinc onto suspended particulate matter is strongly pH dependent. The Kd values for the partitioning of zinc between the solid and liquid phase in the large rivers range from 10,000 to 230,000 $l.kg^{-1}$. The total zinc concentration in the large freshwater basins decreases, due to the sedimentation of suspended solids. Also, the concentrations of dissolved zinc decrease in the direction of the Haringvliet Sluices and the Lake IJssel Dam as a result of adsorption and coprecipitation processes. The sediments of Lake IJssel have a lower zinc concentration than those of Lake Ketel and the Haringvliet, chiefly because of a greater effect of resuspension and because mixing with uncontaminated older sediment occurs in this lake.

In the atmosphere zinc occurs primarily bound to aerosols. The mass median diameter of zinc-containing aerosol particles ranges from 0.3 to 5 um. The dry deposition velocity for the Dutch situation is estimated to be 0.1-0.2 $cm.s^{-1}$. The average rate of removal of zinc from the atmosphere by dry deposition is 0.5 % per hour. Under conditions pertaining in the Netherlands, the average rate of removal by wet deposition is ca 1.5 % per hour.

With respect to biota, mammals have a mechanism for zinc homeostasis, whereby the levels of zinc in various organs are maintained within certain limits. In biota, zinc also plays an important role in the uptake of other heavy metals, such as cadmium, iron and copper. High zinc concentrations in soil and plants prevent the uptake of low doses of cadmium. The fraction of the total soil zinc which is available to plants is usually no more than 1 to 10 %. A deficiency of available zinc may occur in soils with high calcium carbonate and phosphorus contents.

4. CONCENTRATIONS, FLUXES AND EXPOSURE LEVELS

4.1. SAMPLING AND MEASUREMENT TECHNIQUES

During sampling, especially of unpolluted surface waters such as ocean water, the risk of contamination of the samples is great. Because zinc occurs wherever there is human activity, its release can cause problems in the determination of very low background concentrations. Like lead, zinc is one of the most difficult elements to measure accurately in unpolluted waters (Martin et al., 1980). In determinations in long-term toxicity tests, loss of zinc can occur through adsorption onto the test chamber wall and onto the filter during filtrations (Mance, 1987). For a more detailed description of methods of sampling and analysis of heavy metals, the reader is referred to the corresponding sections in earlier integrated criteria documents (Slooff et al., 1989; 1990).

Draft standards (NNI, 1989a,b; 1981a,b) exist for the sampling of soil, groundwater and sludge for zinc analysis, as well as for the measurement of zinc (NNI, 1989c). NEN standards are in force for the pretreatment of various types of water samples for zinc analysis. There is a draft Dutch practical guideline (NNI, 1990a) for the sampling and analysis of airborne zinc in the particulate phase and in the gaseous phase for emission measurements, and a NEN standard (NNI, 1990b) is in force for the collection of suspended particulate matter for the determination of, among other elements, zinc in ambient air. For the measurement of zinc in water samples, detailed instructions exist for voltammetric and atomic-absorption analyses (Methods, 1988). A thorough review of various methods for the measurement of zinc in a variety of environmental samples has recently been published (ATSDR, 1989). A few analytical methods for zinc and their detection limits are presented in Table 4.1. A detection limit of 20 $\mu g.l^{-1}$ is required for zinc analyses in water under EPA contracts. Spectrometric techniques are commonly used to determine zinc in air, water and soil samples. Inductively coupled plasma-atomic emission spectroscopy (ICP-AES) is a recommended test method for measuring zinc in solid waste samples. Frequently used extracting agents in spectrometric measurements of zinc are ammonium pyrollidine dithiocarbamate (APDC) and methyl isobutyl ketone (MIBK). A very sensitive and specific method, with a detection limit of 10^{-10} to 10^{-11} moles l^{-1}, is cathodic stripping voltammetry (CSV), also known as adsorption voltammetry (van den Berg, 1986). This technique is also capable of determining zinc speciation directly in the unaltered sample.

Table 4.1. *A selection of analytical methods for zinc in biological materials and environmental samples, and the reported detection limits*

Matrix	*Sample pretreatment*	*Analytical method*)*	*detection limit*
blood or tissue	*destruction with $HNO_3/HClO_4$, measurement at 339.2 nm*	*ICP-AAS*	*0.01 µg per 100 ml of blood* *0.2 µg per g of tissue*
breath	*personal samples*	*ICP, AAS* *flame AAS*	$0.6\ \mu g.l^{-1}$ *3 µg per sample*
air	*collect air on filters*	*XRF*	$0.05\ \mu g.m^{-3}$
	collect air on filters and digest with HNO_3	*ICP-AES*	$0.015\ \mu g.m^{-3}$
water and wastewater	*acid digestion*	*AAS*	$5\ \mu g.l^{-1}$
seawater	*APDC-MIBK extraction*	*AAS*	$0.05\ \mu g.l^{-1}$
seawater	*direct in electrochemical cell, adjust pH, and complexing*	*CSV*	$7x10^{-11}$ *moles* l^{-1}
soil solid waste and sludge	*acid digestion*	*ICP-AES or flame AAS*	$100\ \mu g.kg^{-1}$
surface water	*acid digestion*	*ICP-AES*	$5\ \mu g.l^{-1}$

*) *ICP = inductively coupled plasma*
AAS = atomic absorption spectrometry
XRF = x-ray fluorescence
AES = atomic emission spectroscopy
CSV = cathodic stripping voltammetry

4.2. BACKGROUND CONCENTRATIONS

The zinc concentrations in the earth's crust range from 10 to 300 mg.kg^{-1}, with an estimated average of 70 mg.kg^{-1} (Malle, 1989). The natural background level in the Rhine-Main plain is between 3 and 30 mg.kg^{-1} (Kauder, 1987). In the Netherlands the background concentrations of zinc in natural soils lie in the broad range of 6.4 to 150 mg.kg^{-1}. For unpolluted arable land, Driel and Smilde (1981) found mean values for various soil types to range from 25 to 117 mg.kg^{-1}. For sediments, a background load of 70 mg.kg^{-1} (ZMAS, 1984a) to 95 mg.kg^{-1} (Malle, 1989) may be adopted.

The baseline concentrations of zinc in seawater and fresh surface water generally range between 0.6 and 10 μg.l^{-1} (Florence and Batley, 1977; Malle, 1989). Lower background concentrations are possible, depending on the natural conditions: Kennedy and Sebetich (1976) measured a concentration of 0.2-0.6 μg.l^{-1} in unpolluted northern California streams. Van der Weijden and Middelburg (1989) estimated the background concentration in the Rhine River to be 2.6 μg.l^{-1}. The zinc concentration in ocean water is considerably lower. In the Pacific Ocean the zinc concentration ranges between 0.01 μg.l^{-1} at the surface and 0.6 μg.l^{-1} at a depth of 3000 m (Brulant et al., 1978; Yeats, 1988), and its vertical distribution is very similar to that of silicate. Yeats (1987) measured a concentration of about 130 ng l^{-1} in the deep waters of the north Atlantic Ocean and the Sargasso Sea. The background concentration in the North Sea can be estimated to be 1 μg.l^{-1} (Hill et al., 1984). In the central North Sea, in an area with a cross section of ca 300 km, a maximum concentration of 0.5 μg.l^{-1} was found at a depth of 10 m (Kramer et al., 1985). In ambient air the concentration of zinc is usually below 1 μg.m^{-3}. In a review on atmospheric zinc concentrations, measured at various locations in the world, Milford and Davidson (1985) and Elinder (1986) give levels of 0.01-0.2 μg.m^{-3} for background areas and of 0.01-1.0 μg.m^{-3} for urban-industrial areas. Values of 0.01 to 0.34 μg.m^{-3} have been measured in rural areas in the U.S.A. and the U.K. (Schroeder, 1970; Peirson et al., 1973). The concentrations of zinc in air samples collected at the South Pole were considerably lower, less than 1 ng.m^{-3} (Zoller et al., 1974). As the background concentration in the Netherlands, the value of 0.07 μg.m^{-3} measured at Kloosterburen may be used.

4.3. OCCURRENCE IN SOIL AND GROUNDWATER

4.3.1. Soil

The occurrence of zinc in soil is strongly determined by the nature of the soil material. For sedimentary rocks, for example, Matthess (1973) gives mean values ranging from 0.6 mg.kg^{-1} for evaporites to 130 mg.kg^{-1} for shales. On the basis of literature data, Ure and Berrow (1982) reported a mean value of 60 mg.kg^{-1} for the topsoil, with a range of 15 to 2000 mg.kg^{-1}, on a dry weight basis. Dutch data on the occurrence of zinc in topsoil can be taken from five national studies as well as a few regional studies. The national studies concern investigations carried out by Edelman (1984) in a number of nature reserves, by van Driel and Smilde (1981) on agricultural soil, by the Industrial Laboratory for Soil and Plant Research in Oosterbeek (BLGG, 1990), by the RIVM concerning a processing of data from indicative soil studies (IBO data) of agricultural land intended for housing (RIVM, 1991), and by the RIVM and IB in collaboration with the RIKILT and Staring Centrum as part of the first phase of the Soil Quality Monitoring Network (RIVM/IB, 1991).

The study by Edelman (1984) clearly demonstrates the relationship between the zinc concentration and the nature of the soil material. The lowest concentrations were found in sandy nature reserves; see Table 4.2. The data refer to the upper 10 cm of the soil.

The mean zinc concentrations found by van Driel and Smilde (1981) and the BLGG (1990) for agricultural soils lie almost entirely within the ranges found for nature reserves for the corresponding soil types; Tables 4.3. and 4.4.

Table 4.2. *Ranges of mean zinc concentrations in the topsoil (mg.kg^{-1}) of nature reserves, according to Edelman (1984)*

Sand *Loam*	*Sandy loam*	*Clay*	*Peaty clay* *Clayey peat*	*Peat*
6.4-62	*28-189*	*81-153*	*62-150*	*62-150*

Table 4.3. *Mean zinc content of Dutch arable soils (mg.kg^{-1}) (van Driel and Smilde, 1981)*

clay soil	*117*	*fen peat soil*	*101*
sandy soil	*44*	*moss peat/sand mixtures*	*25*
loess	*86*		

Table 4.4. *Mean zinc content of Dutch arable soils, in relation to land use*

depth Loess (cm)	*Holocene sand*	*Pleistocene sand*	*Marine clay*	*Fluvial clay*	*Reclaimed peatland*		*Peat*
grassland							
0-5	*30*	*39*	*90*	*146*	*49*	*143*	*73*
agricultural/ horticultural land							
0-20/25	*18*	*26*	*67*	*107*	*29*	*101*	*105*

The BLGG (1990) shows that 5.9 % of the 1167 representative samples from agricultural and horticultural land exceeded the reference value, and 14.8 % of the grassland samples. The majority of the observations exceeding the reference value were made in South Limburg.

In the interpretation of the IBO data, data of almost 1100 soil samples were examined in more detail. At a mean concentration of 48 mg.kg^{-1}, 50 % of the observations exceeded the value of 32 mg.kg^{-1}. The various percentiles are presented in Table 4.5.

Table 4.5. *The mean and percentiles of the zinc concentration in dried soil (mg.kg^{-1})*

	percentile					
mean	*10*	*25*	*50*	*75*	*95*	*number*
48.1	*8.1*	*14*	*32*	*67*	*130*	*1,067*

The mean zinc concentrations, for all soil types investigated, lie within the ranges found by Edelman (1984) for the corresponding soil types. The mean concentrations per soil type are, for all sampling locations, below the reference value for a standard soil. For all sampling locations but one, the mean concentration increases in the order: sand, sandy loam, clay, peat. A statistical analysis was performed which shows that for each sampling location, the mean values differ significantly. For the various arable soils studied, a significant difference cannot be demonstrated between the different land uses. The observed mean values fall within the ranges given by Edelman, although the observed maxima are markedly higher (Table 4.6).

Table 4.6. *The mean and the maximum of the zinc concentration per soil type, in mg.kg^{-1}*

soil type	*number*	*mean*	*maximum*
clay	*387*	*81*	*1,300*
peat	*65*	*55*	*320*
sand	*545*	*25*	*400*
sandy loam	*47*	*52*	*89*
not known	*23*	*27*	*73*
total	*1,067*	*48*	*1,300*

As part of the first phase of the Soil Quality Monitoring Network, samples of different combinations of land use and soil type taken at two depths below ground level were analyzed for zinc, among other substances. A few results are presented in Table 4.7. At most of the sampling locations the zinc concentrations decrease with increasing depth. In the sandy areas, the zinc concentrations in the soil are significantly correlated with the zinc concentrations in the groundwater 10 m below ground level.

In various regional studies, zinc concentrations have sometimes been measured which, depending on the circumstances, differ greatly from the national ranges reported above. For example, significantly elevated concentrations have been observed in the water meadows of the Rivers Rhine (2,360 mg.kg^{-1}), Meuse (2,040 mg.kg^{-1}) and Scheldt (570 mg.kg^{-1}) (Rang et al., 1985; Maasoeverrapport, 1988). The same is true for polders reclaimed more recently. For example, a polder reclaimed in 1759 had a zinc level of 93 mg.kg^{-1}, one reclaimed in 1927 a level of 460 mg.kg^{-1}, and one reclaimed in 1957 contained 2,070 mg.kg^{-1}.

Table 4.7. Mean zinc concentrations in soil (in mg.kg^{-1}); level 1: 0-10 cm below GL; level 2: 10-30 cm below GL, but for farmland: 30-50 cm below GL (data from soil monitoring programme)

	sandy hydro-vague soil		*ordinary hydropodzol*		*thick earth soil*		*clay earthy peat soil*		*clay loam*	
level	*1*	*2*	*1*	*2*	*1*	*2*	*1*	*2*	*1*	*2*
grassland	-	-	*24*	*22*	*27*	*21*	*117*	*83*	-	-
arable land	-	-	*37*	*13*	*22*	*13*	-	-	*64*	*58*
orchard	-	-	-	-	*35*	*36*	-	-	*73*	*71*
forest	*5*	*4*	*6*	*3*	-	-	-	-	-	-

Besides South Limburg, areas with relatively high soil zinc concentrations are de Kempen and floodplains. In addition, elevated soil zinc concentrations occur around galvanized electricity pylons (Lexmond, 1987) and other galvanized structures.

De Kempen, South Limburg and floodplains

A serious local zinc contamination of soil and groundwater affects an area of about 35,000 hectares in de Kempen, due to emissions from the zinc smelters in Budel (the Netherlands), Overpelt (Belgium), Balen (Belgium) and Roten (Belgium). The last-mentioned plant has been closed down. The Budel smelter started operations in 1892. The thermal plant was demolished in 1973, and zinc production was continued using a hydrometallurgical process, which has considerably reduced the atmospheric zinc emission. It is estimated that at least 5 to 10 million kg of zinc has ended up on and in the soil of this region (Meeuwissen, 1989). The zinc concentration in the plough layer in the area around Budel averages 201 mg.kg^{-1} of dry soil (van Luit and Smilde, 1983). Zinc plants on Belgian territory discharged part of their wastewater to the Dommel river. On the plots inundated by the Dommel, it was noted for the first time, in the late 1950s, that crops grew poorly owing to high soil zinc levels, and that horses fell ill from eating zinc-rich grass (Meeuwissen, 1989). At present, the Budelco zinc plant produces annually 120,000 tonnes of jarosite (containing 3000 tonnes of zinc) and 12,000 tonnes of gypsum (containing 500 tonnes of zinc) as (contaminated) by-products, as well as zinc ashes and sludge. Since 1973 these waste products have been stored on the factory site in basins. At the moment they contain a total of 1.5 million tonnes of jarosite. One of the jarosite basins is leaking. The storage capacity will have been entirely utilized by 1993. Budelco has drawn up environmental impact assessments for the expansion of the storage basins and the planned processing of jarosite, and has applied for permits. The company will make a final decision in 1992 on the planned jarosite treatment, making it possible to begin operations in 1995. It will then take another 30 years before all the stored jarosite and gypsum will have been processed.

The water meadows of the Meuse River and its tributaries, such as Geul and Roer, are contaminated with zinc from old German and Belgian zinc mines, sometimes very close to the Dutch border (Moresnet, where the largest zinc producer in the world is operating). A special zinc flora (zinc pansy) has even evolved along the Geul river.

The soil around the town of Eijsden is also contaminated with zinc (Rang et al., 1987; Leenaers et al., 1989; Rang, 1990), due to the zinc white plant located there. The zinc concentration in the topsoil 4 km from this source is 106 $mg.kg^{-1}$.

High zinc concentrations also occur in the Saeftinge marsh land (Baars et al., 1989), up to 500 $mg.kg^{-1}$ in the lower-lying parts of this area, due to input via the Scheldt River.

Electricity pylons

Measurements around several electricity pylons, about 12,000 of which are made from galvanized steel, found zinc concentrations ranging from 130 to 170 $mg.kg^{-1}$ in the topsoil close to the pylons (Lexmond, 1987; Meij and Koops, 1990). Removal of zinc from soil via plants and dispersal via manure do not lead to a measurable decrease in the zinc levels. A British study (Al-Hiyaly et al., 1988) and two Canadian studies (Jones, 1983; Jones and Burgess, 1984) confirm that very high zinc concentrations (up to 6,500 $mg.kg^{-1}$) can occur in the surface soil near electricity pylons. Plants growing in soils at a short distance from the pylons had zinc concentrations 2 to 5 times higher than "control" plants. Certain plant species were adversely affected, whereas others were not affected at all. Apparently the unaffected species can rapidly evolve zinc tolerance (within thirty years). The pattern of contamination indicates that the wind direction is a contributory factor.

4.3.2. Groundwater

The zinc concentrations in groundwater can range from only a few micrograms per litre to several tens of milligrams per litre, depending on the circumstances. For the Dutch situation, data can be taken from the National Groundwater Quality Monitoring Network (van Duijvenbooden, 1989; RIVM, 1989) and from processing close on 600 chemical analyses from indicative soil studies of agricultural land intended for housing. In addition, data from a few regional studies are available.
The mean concentration in the shallow groundwater investigated in the indicative studies is 88 μg.l^{-1}: 50 % of the observations exceed 29 μg.l^{-1} (Table 4.8).

The mean zinc concentrations are below the A values for all soil types (Table 4.9). The variation in the observed values is great.

Table 4.8. The mean and percentiles of the zinc concentrations (μg.l^{-1}) in shallow groundwater

	percentile					
mean	*10*	*25*	*50*	*75*	*95*	*number*
88	*2.5*	*10*	*29*	*84*	*360*	*569*

Table 4.9. The mean and the maximum of the zinc concentration in groundwater (μg.l^{-1}) per soil type

soil type	*number*	*mean*	*maximum*
peat	*68*	*78*	*1,200*
sand	*340*	*104*	*2,900*
sandy loam	*11*	*108*	*470*
not known	*10*	*48*	*120*
total	*694*	*88*	*2,900*

Other studies have shown that very high zinc concentrations in groundwater may occur, depending on the vulnerability of the soil and the pH. For example, Bas et al. (1990) measured zinc concentrations of up to 30 $mg.l^{-1}$ in groundwater below sandy soils in North Brabant. Boumans and Meinardi (1986) found that the groundwater in nature reserves in the province of Brabant with a sandy soil and low pH had zinc levels of up to 1.4 $mg.l^{-1}$ (Figure 4.1), which can be attributed to atmospheric deposition.
For groundwater at greater depths, data can be abstracted from the National Groundwater Quality Monitoring Network. The mean of the observed concentrations is 65 $\mu g.l^{-1}$. The concentrations range from 5 $\mu g.l^{-1}$ to 16 $mg.l^{-1}$, while more than half of the observations show concentrations between 8 and 16 $\mu g.l^{-1}$. Approximately 4% of the observations exceed the reference value. Table 4.10 gives a picture of the zinc concentrations in groundwater in relation to soil type and land use. The distribution of the zinc concentrations in Dutch groundwater shows a sharp peak at 8-16 $\mu g.l^{-1}$. The available data are insufficient for deriving a statistically significant relationship between the observed zinc concentrations and land use or soil type. Elevated groundwater zinc concentrations have been observed locally, for example, up to mean values of 10 $mg.l^{-1}$ at some locations in the Strijper Aa watershed in the southern Netherlands, which were not attributed to higher leaching rates from the local soil but to lateral movement of soil zinc derived from atmospheric deposition (Pedroli and van Wijk, 1988; Pedroli et al., 1990). The normal zinc level in this region is about 0.1 $mg.l^{-1}$, which is equivalent to the zinc concentration in rainwater of on average ca 0.3 $\mu mole\ l^{-1}$ (KNMI/RIVM, 1988) multiplied by a concentration factor of 5 for evapotranspiration (Boumans and Meinardi, 1986).

<u>Table 4.10.</u> *Mean zinc concentrations ($\mu g.l^{-1}$) in Dutch groundwater*

sampling depth, in metres below ground level:	*sand*		*clay*	*peat*
	10	*25**	*10*	*10*
arable land	*73*	*41*	*23*	*25*
grassland	*79*	*20*	*11*	*11*
nature reserves	*36*	*24*	*50*	*15*
residential area	*37*	*89*	*10*	*-*

* *For sandy soils, the results of sampling at a depth of 25 metres are also presented, in connection with the good leachability of substances from sand*

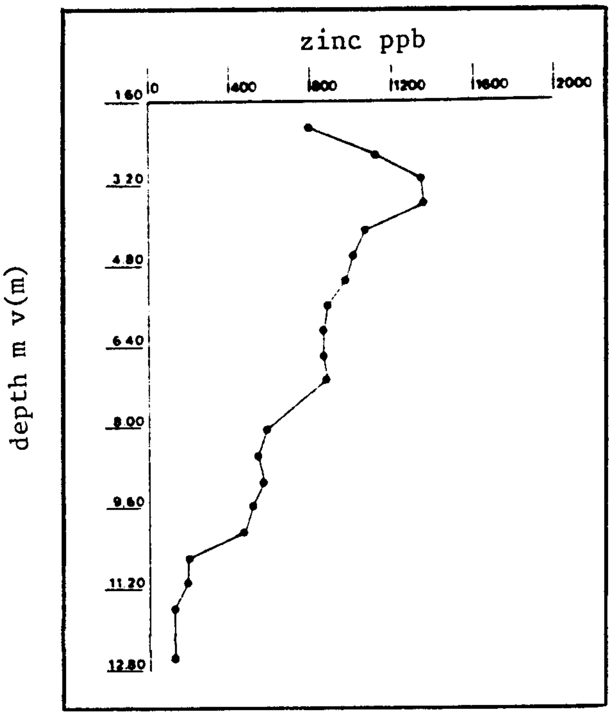

Figure 4.1. *Mean values of the zinc concentration in groundwater in de Peel, a region in the province of Brabant (Boumans and Meinardi, 1986)*

4.4. OCCURRENCE IN SURFACE WATER AND SEDIMENTS

4.4.1. Concentrations in surface water

Fresh water

State water bodies

Since 1982, the annual means of the total zinc concentrations (dissolved plus adsorbed onto suspended particles) in the Dutch State water bodies have remained below the basic quality standard which was in force until recently (200 $\mu g.l^{-1}$) (IMP-Water, 1984), but exceeds in many cases the limit value for total zinc (30 $\mu g.l^{-1}$) (VROM, 1992). The median value in the series of concentration measurements in the Rhine River at Lobith in 1988 was 32 $\mu g.l^{-1}$ (RIWA, 1988). In 1988, the yearly average total concentration was 39 $\mu g.l^{-1}$ in the Rhine River and 72 $\mu g.l^{-1}$ in the Meuse River. The concentration of dissolved zinc was less than 20 $\mu g.l^{-1}$ in both rivers. Figure 4.2 shows that the annual average concentrations in the Rhine and Meuse Rivers fell considerably between the early 1970s and the mid-1980s. The zinc load carried by these two rivers has not fallen substantially since 1985. This trend can also be observed in the yearly average concentrations in Lake IJssel and Lake Ketel (Figure 4.2). The Quarterly Reports on the Quality of Surface Waters in the Netherlands published by Rijkswaterstaat, the Dutch National Water Authority, show that over the past few years, the Meuse River at Eijsden had the highest annual mean zinc level of all State waters sampled (RIZA, 1981-1989). Table 4.11 shows a few annual average concentrations in 1987, as well as the highest and lowest concentrations measured over 1987, of total zinc for several locations in fresh waters.

Table 4.11. Annual mean concentrations and highest and lowest concentrations of total zinc in fresh waters in 1987 (DGW/DBW, 1990)

Location	*Zinc concentration ($\mu g.l^{-1}$)* *max.*	*mean*	*min.*
Lobith (Rhine)	*73*	*34*	*4*
Eijsden (Meuse)	*354*	*88*	*23*
North Sea Canal	*71*	*29*	*13*
Maassluis (Nieuwe Waterweg)	*47*	*26*	*7*
Haringvliet:			
sluices, landward side	*49*	*21*	*7*
Lake IJssel, centre	*19*	*9*	*1*
Schaar van Ouden Doel (Scheldt)	*113*	*46*	*13*

With the aid of Figure 4.2 an estimate can be made of the percentage of zinc in the water column which is associated with the suspended particulate matter. Most of the zinc is associated with the suspended solids in both the Rhine and Meuse Rivers upon entry into the Netherlands. Averaged over the last 10 years, 70 % and 75 % of the total zinc was transported in the particulate phase by the Rhine and Meuse, respectively. Based on annual mean values, about 67 % of the zinc was associated with the suspended solids in Lake Ketel and about 81 % in Lake IJssel. These proportions are somewhat lower in the Nieuwe Merwede River and IJssel River: 61 % and 46 %, respectively (ZMAS, 1984a). On the assumption that over the past 15 years the suspended solids concentration in the Rhine River averaged 37 $mg.l^{-1}$ on a dry weight basis, it can be estimated how the zinc content of suspended particulate matter has developed during this period. The zinc concentration in the suspended matter of the Rhine River has fallen from about 2,000 $mg.kg^{-1}$ to less than 700 $mg.kg^{-1}$ between 1971 and 1983 (Malle, 1985). The zinc concentration in sediments dredged from the Rotterdam harbours showed a parallel decrease (Malle, 1989a). Table 4.12 presents a few measured and calculated zinc concentrations in suspended particulate matter.

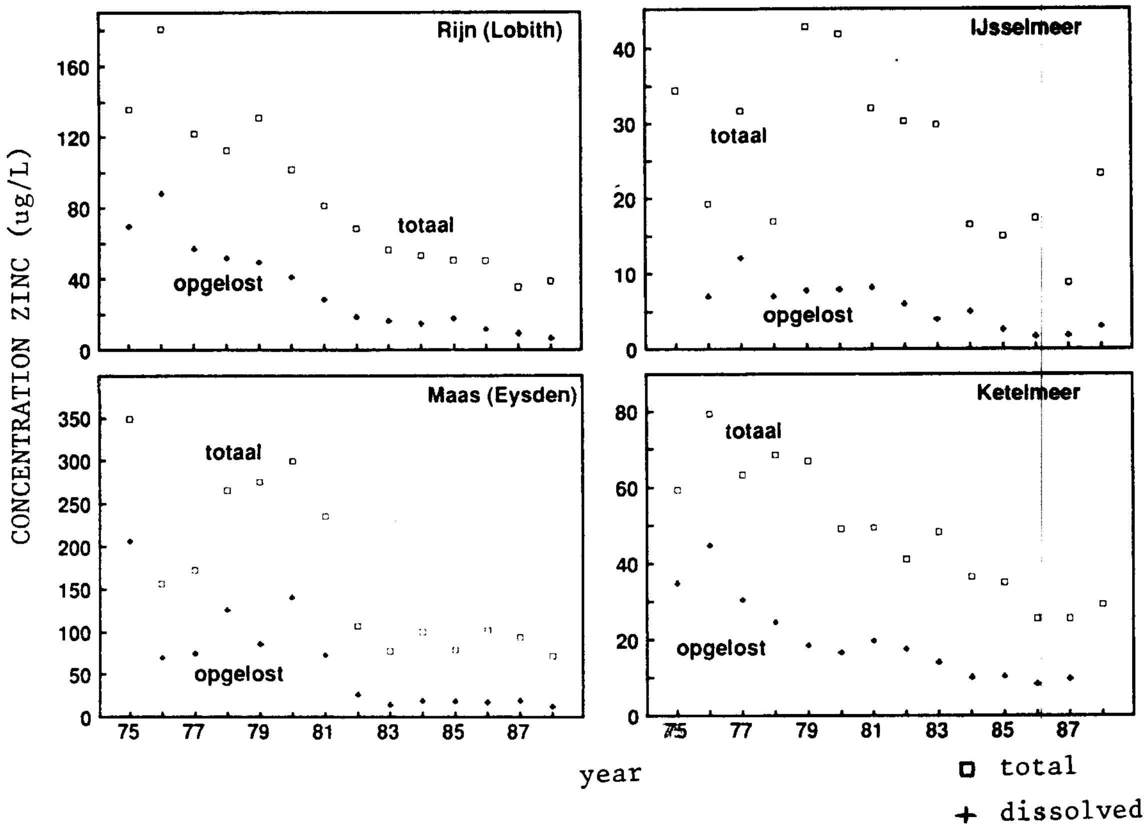

Figure 4.2. Total and dissolved zinc in a number of State water bodies (RIZA)

Table 4.12. Mean zinc concentrations in suspended particulate matter (mg.kg^{-1})

Location	*Period*	*Concentration*	*Reference*
Meuse River	*1978*	*2,745*	*ZMAS (1984b)*
Nieuwe Merwede River	*1978*	*1,592*	"
Haringvliet	*1978*	*1,828*	"
Lake Ketel	*1978*	*2,158*	"
Lake IJssel	*1978*	*583*	"
Rhine River (Lobith)	*1975-1977*	*2,020*	*calculated from Fig 4.2*
Rhine River(Lobith)	*1986-1988*	*880*	*calculated from Fig 4.2*

Non-State water bodies

In the non-State water bodies, too, the zinc concentrations are generally lower than the basic quality standard, as is evident from the frequency distribution of measurement results from 173 sampling locations in 1986 (van der Kooy, 1989). The 50th and 90th percentiles for total zinc are 50 and 182 $\mu g.l^{-1}$, respectively. In 1986, the annual mean concentrations of total and dissolved zinc measured in Lake Tjeuke were 12 and 3 $\mu g.l^{-1}$, respectively (de Haan et al., 1990).

Salt water

In salt water, about 2 % of the zinc adsorbed on suspended particles passes again into solution (Salomons and Eusink, 1981). The concentrations of **dissolved** zinc in the Wadden Sea are place- and time-dependent and in the early 1980s ranged between 2 and 10 $\mu g.l^{-1}$, and the concentrations in suspended particulate matter between 200 and 400 $mg.kg^{-1}$ (Kramer et al., 1985). The highest values were found in places where relatively much Rhine water enters, for example, the Marsdiep via the west coast.

It may be expected that, as a result of the decreasing zinc load in the Rhine River over the past decade, the zinc concentrations in the Wadden Sea have declined. The study, conducted between 1979 and 1984, also showed that the **dissolved** zinc concentration along the Dutch coast ranged between 4 and 8 $\mu g.l^{-1}$, except in the Rhine-Meuse estuary where higher values were observed (< 16 $\mu g.l^{-1}$). In the Scheldt estuary, 60 to 90 % of the dissolved zinc was organically complexed (van den Berg et al., 1987).

4.4.2. Concentrations in bottom sediments

Fresh water and estuarine environment

The zinc concentrations in bottom sediments in the Netherlands can vary considerably with location. Analysis of samples derived from the sample archives of the Institute for Soil Fertility revealed that the Rhine River was contaminated with heavy metals, including zinc, as early as the beginning of this century (Salomons and de Groot, 1978). Rhine sediment collected in 1922 contained as much as 1,000 mg $Zn.kg^{-1}$. The sediment zinc concentration increased to about 2,400 $mg.kg^{-1}$ in 1960, and then decreased to about 1,600 $mg.kg^{-1}$ in 1980. This trend can also be observed in sediments of the Nieuwe Merwede River (Nijssen, 1985). This quality development is explained by the decrease in the zinc load of the Rhine River which began about 20 years ago. The zinc concentration in dredged sediments from the tidal river area is about the same as that in suspended particulate matter in Rhine water at Lobith (corrected for the % fraction < 16 um). A downward trend can be observed in both over the period 1976-1984 (Nijssen, 1985), from about 1,600 to 1,100 mg.kg^{-1}. This trend is consistent with the estimated (uncorrected) concentrations in suspended matter presented in Table 4.12. By contrast, sediments of Lake IJssel have a lower zinc content, which is attributed to a "dilution" with locally-formed sediment as a result of precipitation of calcium carbonate and the production of organic matter during the algal bloom (Salomons and Kerdijk, 1985).

Table 4.13 presents values for a number of bottom sediments, based in part on mean concentrations and in part on a range of measured concentrations. The zinc concentration in the Rotterdam harbours decreases in a seaward direction, from 1,600 mg.kg^{-1} at Rotterdam to 250 mg.kg^{-1} at Europoort, due to admixture with relatively clean sediments of marine origin. The data of Faber (1985) in the table are the result of a study of the degree of pollution in dredged sediments from a number of South Holland waters in the early 1980s. A concentration greater than the B value (500 mg.kg^{-1}) was observed in 27 % of the results from 148 measurements.

Table 4.14 gives a picture of the distribution of zinc concentrations in sediments of the Meuse River, Rhine River and the Lake IJssel system in the past decade. In the period 1982-1989, 661 sediment samples from a number of important waters, under the management of National Water Authority directorates in Flevoland, Gelderland and Limburg, were analyzed for zinc. To permit intercomparison of concentrations in sediments, they must be corrected for the composition of the sediment. The zinc concentrations in the samples mentioned have been converted to concentrations as these would occur in a standard soil (25 % clay (< 2 μm), 10 % organic matter). For standard suspended matter (40 % clay, 20 % organic matter), values for heavy metals are a factor of 1.5 higher than for soil (V&W/VROM/L&V, 1989).

Table 4.13. Zinc concentrations in Dutch bottom sediments (mg.kg^{-1} dry weight)

Location	*Year*	*Conc.*	*Reference*
Rotterdam (Rhine Harbour)	*1980*	*1,600*	*Salomons and Kerdijk (1985)*
Botlek	*1980*	*1,000*	" "
Nieuwe Waterweg	*1980*	*400*	" "
Europoort	*1980*	*250*	" "
Haringvliet	*1980*	*1,170*	" "
Haringvliet	*1977*	*1,269*	*ZMAS (1984b)*
Hollands Diep	*1977*	*1,389*	"
Lake IJssel	*1977*	*420*	"
Lake Ketel	*1977*	*1,826*	"
Meuse River	*1977*	*2,632*	"
Delfland	*1980*	*350*	*Faber (1985)*
Rijnland	*1980*	*855*	"
Krimpenerwaard	*1980*	*1,650*	"
Nieuwe Merwede River	*1960*	*2,400*	*Nijssen (1985)*
Nieuwe Merwede River	*1980*	*1,800*	"
Amsterdam (canals)	*1983-84*	*90-2223*	*Heida (1985)*
Amsterdam (harbours)	*1983-84*	*217-645*	"
Nieuwe Meer (polder)	*1983-84*	*184-408*	"
State waters (n=3145)	*1989-90*	*<140*) (28%)* *>2,500*) (4%)*	*CUWVO (1990)*
Regional waters (n=1743)	*1989-90*	*<140*) (32%)* *>2,500*) (1%)*	*CUWVO (1990)*

**) see Table 1.2.*

Table 4.14. Normalized zinc concentrations in bottom sediments (mg.kg^{-1}) dry weight) in the period 1982-1989 (van der Mark, 1989)

Area	*mean*	*10th percentile*	*90th percentile*
Lake IJssel	*627*	*3*	*1,512*
Lakes between former coast and empoldered land	*174*	*50*	*306*
Meuse River	*1,289*	*549*	*1,665*
Rhine River	*1,389*	*392*	*3,300*

In sediments of non-State waters, the 50th and the 90th percentile of 317 samples, collected in the period 1985-1986, were 139 and 755 mg.kg^{-1}, respectively (van der Kooy, 1989). The results of a survey of the quality of bottom sediments in areas under the management of the 5 North Brabant district Water Boards gives a similar picture: of the 282 samples taken over the period 1983-1986, 47 had a concentration greater than 750 mg.kg^{-1} and 5 exceeded 2,500 mg.kg^{-1} (Noord-Brabant, 1987). Levels above 2,000 mg.kg^{-1} were found in the Beatrix Canal, two fens near Woensdrecht, and especially in the Dommel river area. Of the 74 sediment samples collected in 1989 from the Amsterdam canals, 12.2 % had a zinc concentration greater than 1,800 mg.kg^{-1}, the testing value for dumping in the Nieuwe Meer polder.

Saltwater environment

Although the marine sediments in the estuarine area of the large rivers are relatively clean compared with river sediments, the zinc concentrations are high relative to the concentrations observed elsewhere along the Belgian and Dutch coast (Figure 4.3). The source of the zinc in the Wadden Sea is the discharge of river water and sediment into the North Sea via the Haringvliet Sluices and the Nieuwe Waterweg; the Scheldt River and Ems River (Germany) are only small contributors of zinc to the Wadden Sea (Salomons and Kerdijk, 1985).

4.4.3. Input to the surface water system

Transboundary transport

The zinc load carried by the Rhine and Meuse Rivers fell dramatically between 1981 and 1989. At present the zinc input to the surface water system in the Netherlands is about 2,000 tonnes (Table 4.15).

Table 4.15. Transboundary zinc transported by the Rhine and Meuse Rivers, in tonnes per year (DBW/RIZA, 1981-1989)

	1981-1983	*1984-1986*	*1989*
Rhine River	*6,500*	*4,200*	*1,625*
Meuse River	*2,200*	*1,500*	*375*

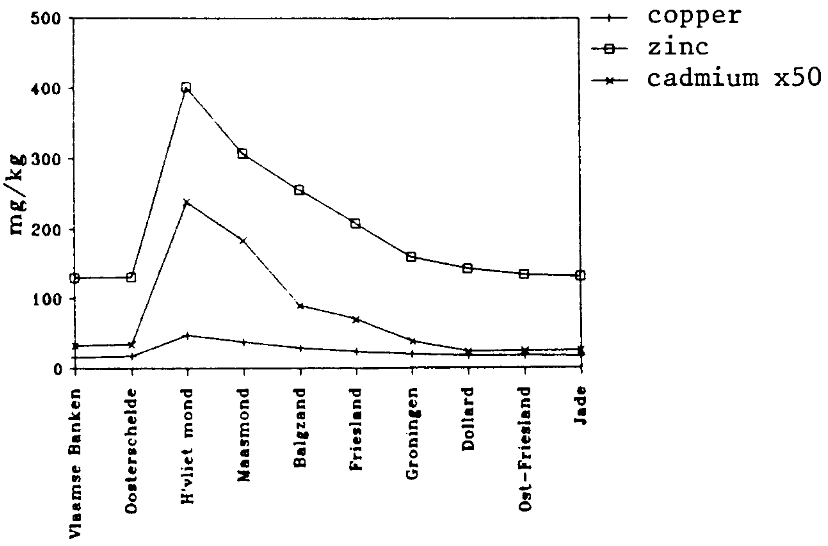

Figure 4.3. Concentrations of zinc (and copper and cadmium) in marine sediments (Salomons and Kerdijk, 1985)

Of the zinc load carried by the Rhine River, about 700 tonnes can be regarded as natural load (Malle, 1989). The North Sea receives about 60 % of the total zinc load (Salomons and Eussink, 1981). Approximately 57 tonnes enter the Netherlands annually from the Belgian zinc mining area via the Geul river (Leenaers, 1989).

4.5. OCCURRENCE IN AIR

4.5.1. Concentrations in outdoor air

Compared with situations in other countries, the airborne zinc concentrations measured in the Netherlands are not high, at least in urban-industrial areas, namely, up to about 0.250 μg Zn. m^{-3}. The national level of airborne zinc in the Netherlands (about 0.065 $\mu g.m^{-3}$) is also somewhat lower than that in Germany or Belgium (RIVM, 1986-1991). In Belgium and Germany, the annual average concentration ranges from 0.4 to 1.0 $\mu g.m^{-3}$ in large cities, and from 0.1 to 0.3 $\mu g.m^{-3}$ in rural areas (IHE, 1980; Bundesamt, 1987). The ambient zinc levels occasionally exceeded 5 $\mu g.m^{-3}$ in the vicinity of zinc (and brass)-production plants. In 1986 the highest annual average zinc concentration in Belgium was recorded at Angleur, 9.3 μg $Zn.m^{-3}$, with peaks in excess of 100 $\mu g.m^{-3}$. The annual mean zinc levels at the stations Beerse and Engis (Belgium) fluctuated around 3 $\mu g.m^{-3}$ in 1985 and 1986. The levels in North Limburg (Belgium) were around 1 to 2 μg $Zn.m^{-3}$ (IHE, 1986). The airborne zinc concentrations in the U.S. are in the 0.1-1.7 $\mu g.m^{-3}$ range, and mean zinc levels of 5 $\mu g.m^{-3}$ have been recorded in industrial areas (ATSDR, 1989).

The atmospheric zinc levels started to decline significantly in the early 1980s, and are now about 0.2 $\mu g.m^{-3}$. In the Netherlands too, the same trend is visible as in its neighbours Belgium and Germany: a significant drop in the ambient zinc levels at the end of the 1970s and in the early 1980s, followed by a gradual decline of 25-30 % between 1983 and 1988. Table 4.16. summarizes the annual average concentrations of airborne zinc determined in several series of measurements at various locations in the Netherlands (CBS, 1989). Extrapolation of these measurement results using meteorological data and dispersion models yields the spatial annual average concentration pattern over the Netherlands (Figure 4.4). According to this calculation, the national annual mean of the zinc concentration is 0.065 $\mu g.m^{-3}$ (van Jaarsveld and Onderdelinden, 1986). There is a distinct gradient from higher to lower zinc levels in a south-north direction. The high concentration levels in North Brabant can be attributed to the large contribution from foreign source areas, particularly the nonferrous metallurgical industry in the north of Belgium and the Ruhr area in Germany. The atmospheric zinc concentrations in the Netherlands are dominated (up to 85 %) by domestic sources (ca 30 %) on the one hand, and by Belgium (30 %) and German (25 %) sources on the other. In a major industrial area such as Rijnmond, the contribution from local sources has been clearly established (Keuken et al., 1987).

Table 4.16. *Zinc concentrations ($\mu g.m^{-3}$) in Dutch ambient air in the period 1971-1980*

Location	Mean conc. ($\mu g.m^{-3}$)	Period	Location	Mean conc. ($\mu g.m^{-3}$)	Period
Rijnmond	0.40-0.60	1971-72	Maastricht	0.23	1988
Vlaardingen	0.09	1983	Maastricht	0.34	1989
Vlaardingen	0.07	1986-88	Witteveen	0.08	1983
Vlaardingen	0.10	1989	Eibergen	0.05-0.06	1986-87
Vlaardingen	0.09	1990	Vredepeel	0.08-0.10	1986-87
Eindhoven	0.51	1977	Rekken	0.09	1983
Eindhoven	0.38-0.42	1978-79	Bilthoven	0.08	1983
Eindhoven	0.32	1980	Bilthoven	0.05-0.06	1986-88
Eindhoven	0.21-0.25	1985-88	Bilthoven	0.11	1989
Eindhoven	0.21	1989	Bilthoven	0.08	1990
Eindhoven	0.13	1990	Biest-Houtakker	0.10	1983
Arnhem	2.40	1977	Biest-Houtakker	0.05-0.07	1986-88
Arnhem	1.60	1979	Biest-Houtakker	0.10	1989
Nijmegen	0.40	1977	Biest-Houtakker	0.07	1990
Nijmegen	1.10	1979	Kloosterburen	0.07	1989
Biddinghuizen	0.04-0.05	1986-87	Kollumerwaard	0.06	1990

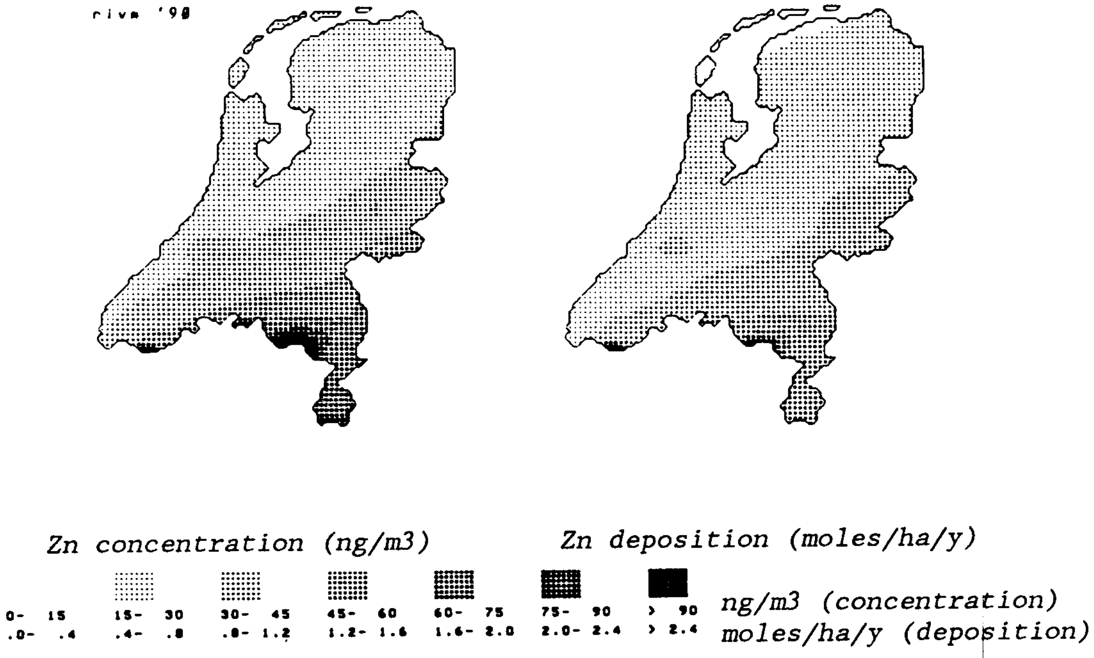

Figure 4.4. *Calculated zinc concentration in air (l) and calculated wet + dry deposition of zinc (r)*

4.5.2. Deposition

Direct measurements of the dry deposition rate are not available. The dry deposition rate is therefore estimated from the deposition velocity of the zinc-containing aerosol particles and the concentration of particulate zinc. The mean dry deposition velocity of zinc is about 0.1 $cm.s^{-1}$ (see Section 3.4). Using the national annual mean for the Netherlands of 0.065 $\mu g.m^{-3}$, the total dry deposition rate of zinc in the Netherlands can be estimated to be about 0.4 mole per ha per year, which means that a total of about 100 tonnes is deposited annually on the Netherlands (RIVM, 1986-1991).

The wet deposition rate of heavy metals is measured directly, from 1978 to 1982 as part of the then RID/VEWIN Rainwater Monitoring Network, and from 1981 within the framework of the KNMI/RIVM National Rainwater Monitoring Network. The annual average zinc concentration in rainwater ranged from 0.4 to 15 $\mu moles.l^{-1}$ (equivalent to 25-100 $\mu g.l^{-1}$) in the period 1978-1982. The mean zinc concentration in rainwater fell by a factor of 2, to 0.2-0.7 $\mu mole\ l^{-1}$ (15-45 $\mu g.l^{-1}$), from 1978 to 1988. During rainfall, the zinc concentration in rainwater in areas with higher airborne zinc levels will be elevated relative to areas with lower levels, due to washout. Consequently, wet deposition is the greatest in the south of the Netherlands (North Brabant), where the atmospheric zinc concentrations are the highest. In the latter half of the 1980s the mean wet deposition rate of zinc in the Netherlands was 1.4 moles per hectare per year, which means that a total of 370 tonnes per year was deposited on the Netherlands. It can be concluded that the wet deposition is now about 30 % lower than in the early 1980s.

From the measured dry and wet deposition reported above it follows that the annual total deposition of zinc on Dutch soil is around 470 tonnes. Via a theoretical approach, Warmenhoven et al. (1989) calculated on the basis of emission data in the Netherlands and neighbouring countries, a total deposition of about 30 tonnes of zinc annually using the so-called "OPS" (Operational Priority Substances) model (van Jaarsveld, 1989). It must be noted that the measurement results for heavy metals almost always lead to overestimation while the model results for zinc certainly lead to underestimation of the total deposition, since the corrosion term is difficult to quantify. Figure 4.4 depicts the overall annual average total (dry + wet) deposition pattern over the Netherlands. The contributions made by the Netherlands and the neighbouring countries to the total zinc deposition are presented in Table 4.17.

Table 4.17. Contributions made by several countries to the total deposition of zinc in the Netherlands

Country	*Contribution*
The Netherlands	*31 %*
Belgium	*28 %*
Germany	*24 %*
France	*11 %*
Britain	*4 %*
Others	*2 %*

The total zinc deposition fell by 25-30 % between 1983 and 1988.

4.5.3. Concentrations in the working environment and in indoor air

Data on the zinc concentrations in the workplace are not available for the Netherlands. In general, the concentrations of aerosol components in indoor air are about 30-50 % of those outdoors (Cupitt and FitzSimons, 1988), assuming that no sources emitting fine zinc particles are present indoors. Zinc-containing aerosols are generated within industrial, workplace and home environments, primarily through resuspension of street, soil or household dust. The concentrations in house dust are similar to those in street dust from urban areas (Harrison, 1979). The zinc concentrations in street dust from smaller cities are up to a few hundred $\mu g.g^{-1}$ and from larger cities up to a few thousand $\mu g.g^{-1}$ (Ferguson and Ryan, 1984; Ferguson et al., 1986). It should be noted that the resuspended zinc may be considered to be in the (super)coarse aerosol fraction, which has a very short residence time in air.

4.6. OCCURRENCE IN FOOD AND DRINKING WATER

Zinc is an essential trace element for man, and is second only to iron as a trace metal in humans, and in practically every other organism. The body of a human adult contains about 2 g zinc. The average annual zinc intake from the diet is 3.1 g. Table 4.18 gives the daily intake of zinc for a number of countries.

Table 4.18. Zinc intake (mg per day) in several countries (source: Ellen et al., 1988a; Malle, 1989; SDV, 1990)

Country	*period*	*amount*
Britain	*1978/1979*	*9.1*
USA	*1981/1982*	*18*
Finland	*1980*	*16*
Sweden	*1980*	*8.6*
Denmark	*1980*	*20*
Germany	*1986*	*10.6*
Netherlands	*1984/1985*	*8.4 *) (RIVM)*
	1984/1986	*13.6 *) (CIVO-TNO)*

**) The cause of the discrepancy must be sought in the differing design of the studies by these two institutes*

The zinc concentrations (mg.kg^{-1}) in a number of foodstuffs in the Netherlands and in animal feeds are given in Table 4.19.

Organ meat makes a substantial contribution to the total intake of zinc from food (10-20 %). A change in the zinc concentration with time was not observed over the past five years for sheep's, ox and pig's kidneys, nor for chicken livers (Ellen et al., 1989). The values mentioned in Table 4.19 for kidneys and livers are in good agreement with those from foreign literature (Ellen et al., 1989).

The contribution from Dutch fishery products to the zinc intake is small, about 0.14 mg zinc per day, or 1.5 % of the total (Hagel and Vos, 1989). A clear dependence of the zinc concentration in fish on location was not demonstrated, nor were differences observed between marine fish and freshwater fish. The zinc concentration in mussels, however, did vary with location (Luten et al., 1986). The median zinc content of mussels from the Wadden Sea is 2 to 3 times lower than that of mussels from the Western

Scheldt (Luten et al., 1986). The concentrations in fish are probably the approximate natural levels, and it is believed that pollution has not had any influence on the differences between species (Hagel and Vos, 1989). The zinc levels in Dutch fish products are similar to those in products from other parts of the world. The relatively high concentrations in eel, mussels and shrimps are comparable to those in beef, mutton and pork (Vos et al., 1986).

It has been reported that zinc can accumulate in mussels, but especially in oysters (up to 4,000 $mg.kg^{-1}$) (Eisler, 1980).

The concentration of zinc, unlike that of cadmium, was found to be the same in lettuce, spinach and endive grown in the open and in greenhouses (Ellen et al., 1988b).

Drinking water generally has the same zinc concentration as the raw surface-water source. A considerably higher zinc content (up to 2 $mg.l^{-1}$) has, however, been recorded as a result of the passage of water through zinc-containing pipes (Elinder, 1986). Water containing 4 $mg.l^{-1}$ $ZnSO_4$ is found by some people to have a bitter taste (Train, 1979). In measurements in Dutch drinking water from 253 pumping stations, in 1985, the zinc content was less than 10 $\mu g.l^{-1}$ in 225 cases. The limit value of 100 $\mu g.l^{-1}$ was not exceeded at any of the stations in that year. Earlier, in 1982, a concentration of 131 $\mu g.l^{-1}$ was measured in drinking water from the pumping station located in the Dommel catchment area (Fonds et al., 1987).

Table 4.19. Zinc concentrations (mg.kg^{-1}) in a number of foodstuffs in the Netherlands and in animal feeds

Foodstuff	*Zinc conc. (median or range)*	*Foodstuff*	*Zinc conc. (median or range)*
(Staarink and Hakkenbrak, 1984):			
brown bread	*15*	*white bread*	*10*
black bread	*20*	*rusk*	*7-18*
muesli	*20-37*	*rice*	*14*
potato	*2-11*	*lettuce*	*2-11*
spinach	*5-16*	*chicory*	*1-4*
cauliflower	*2-7*	*carrot*	*1-3*
kale	*3-36*	*beetroot*	*3-28*
leek	*2-5*	*apple*	*0.2-2*
citrus juices	*0-4*	*coffee*	*5-10*
tea	*25-44*	*egg*	*11-17*
wine	*0-3*	*cheese*	*47*
milk	*3-7*	*chicken*	*6-22*
pork	*5-39*	*beef*	*31-74*
mutton	*20-48*	*liver*	*19-80*
ready-to-eat meals	*1-12*	*baby/infant food (glass)*	*2-17*
baby/infant food	*1-6*	*drinking water*	*0-0.5*
(Vaessen et al., 1983):			
cashew nuts (shelled)	*50*	*Brazil nuts (shelled)*	*49*
peanuts (shelled)	*26-33*	*walnuts (not shelled)*	*26*
nutmeg (ground)	*16-23*	*white pepper*	*7-11*
parsley	*22*	*celery*	*15*
(Ellen et al., 1989):			
*ox kidney *)*	*17*	*pig's kidney *)*	*22*
*sheep's kidney *)*	*22*	*chicken kidney *)*	*30*
(LAC, 1987):			
*eel *)*	*18*	*sole *)*	*5*
*cod *)*	*4*	*herring*	*6*
shrimps (not peeled)	*21*	*mussel *) **)*	*14*
*pike perch *)*	*4*		
(Luten, 1985):			
whiting	*4*	*roundfish (other)*	*4*
plaice	*7*	*flatfish (other)*	*6*
mackerel	*6*		
(SDV, 1990) Feeds:			
grain	*30-60*	*grass*	*30-70*
hay	*20-50*	*concentrate*	*60-250*

*) *fresh product*

**) *depending upon location, higher values are possible, up to 234 mg.kg^{-1} dry weight in mussels collected at Zuidergat (Luten et al., 1986)*

4.7. FLUXES IN THE ENVIRONMENT

Figure 4.5 depicts the zinc balance sheet for the Netherlands and the routes of the present zinc flows through the various environmental compartments. The balance sheet is based on a schematized representation of the environment, and the zinc flows as described previously in this document, particularly in Chapters 2 and 4. The different compartments are supposed to be fully mixed.

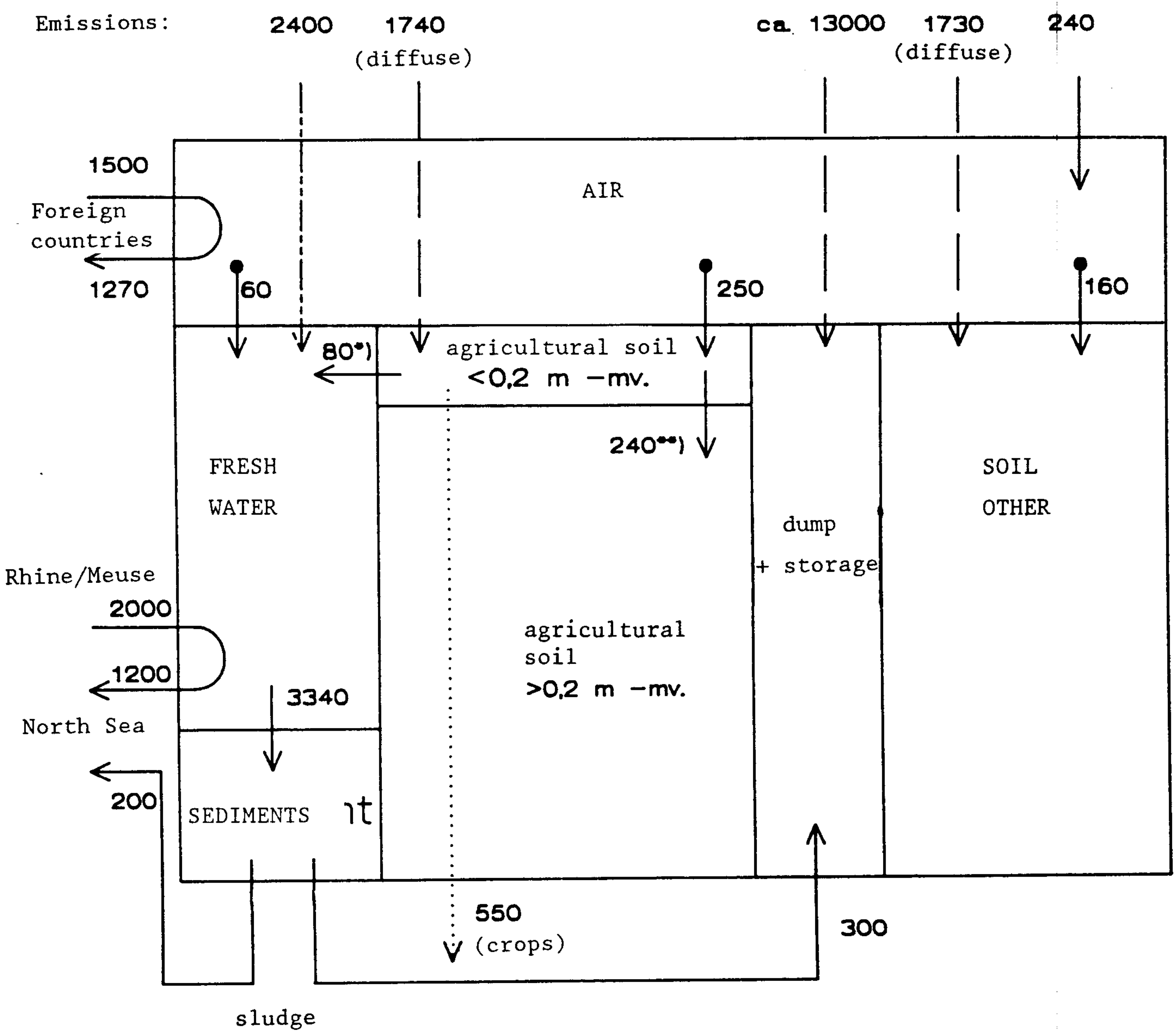

*Figure 4.5. Current zinc fluxes through the Dutch environmental compartments, in tonnes of zinc per year; *) runoff; **) leaching; ↧ deposition*

Air

The amount of 1,500 tonnes of zinc imported annually via the atmosphere was calculated from the airborne zinc concentration outside the Netherlands, 100 $ng.m^{-3}$, the mixing height (800 mg), and the residence time of air over the Netherlands (0.78 days).

Surface water

The zinc budget for this compartment was balanced by setting the export of zinc to the sea at 1,200 tonnes, corresponding to the 60 % of the total imports mentioned in Subsection 4.4.3. See also Section 4.4.

Soil

The net zinc flow to dumps and storage facilities is about 13,000 tonnes; see Chapter 2. The diffuse emission of zinc to nonagricultural soil is, in addition to the atmospheric deposition, about 1,370 tonnes, which must be largely attributed to the contribution from corrosion. Of the total input to agricultural soil (diffuse, 1,740 tonnes; deposition, 250 tonnes), about 550 tonnes are removed by crop plants. This amount represents an average over various kinds of crop.

In this schematic representation the corrosion term is entirely attributed to the nonagricultural soil. The compartment agricultural soil has been subdivided into two layers: a top layer of 0.20 m mixing depth and a layer below a depth of 0.20 m. The accumulation in the top layer has been estimated as follows: the assumed zinc concentration in soil,40 mg $Zn.kg^{-1}$ (see Subsection 4.3.1), is considerably lower than the concentration which would be in equilibrium with the concentration in the quantity of rainwater passing annually through the top layer (30 cm per year).

This concentration, 250 $\mu g.l^{-1}$, was calculated by dividing the net diffuse emission of zinc by 30 cm of net rainwater on 20,000 km^2 of agricultural land. Upon the establishment of a new equilibrium and assuming that the Kd value is 1,000 $l.kg^{-1}$, the zinc concentration in rainwater which percolates through the top layer to the deeper soil layer will equal 40.2 $\mu g.l^{-1}$. Therefore, the total amount of zinc leached is currently 240 tonnes per year. With a runoff of about 80 tonnes of zinc annually, the amount accumulated in the top layer is currently about 1,100 tonnes of zinc, or about 0.2 $mg.kg^{-1}$ of topsoil per year. It would take more than a millennium before the agricultural soils, at the present level of zinc usage, would be fully "charged" and the net zinc input would also leach largely to the groundwater. It should be noted that the compartment "dump + storage" is supposed to be leakproof, and that no estimate has been made of the runoff from "soil, other", because it will be largely included in the emissions into water. It may be mentioned that leaching through the "top layer" of "soil, other" is highly localized, since corroded zinc which reaches directly the (inhabited) soil is derived primarily from zinc or galvanized structures (crash barriers, fencing, electricity pylons, etc.).

4.8. EXPOSURE LEVELS

4.8.1. Man

The daily dietary intake of zinc averages 8-14 mg, according to Dutch studies. This range is in good agreement with that reported in foreign studies, viz. 9-20 mg per day. The mean daily intake of zinc from drinking water is < 0.01 mg and from air about 0.0007 mg. These amounts are negligible compared with the intake from food.

4.8.2. Ecosystems

With respect to aquatic organisms, the concentrations in water, particularly the levels of "dissolved" zinc, are of importance. In 1987 the mean total zinc concentrations in the various Dutch fresh State waters lay in the 9 to 88 $\mu g.l^{-1}$ range, corresponding to about 2 to 20 $\mu g.l^{-1}$ dissolved zinc. The 50th percentile for total zinc in non-State waters was 50 $\mu g.l^{-1}$. It can be seen from Figure 4.2 that these levels have remained fairly constant since 1985 and do not show a further decrease.
The levels of dissolved zinc in salt water around the year 1980 ranged from 4 to 8 $\mu g.l^{-1}$ along the North Sea coast and from 2 to 10 $\mu g.l^{-1}$ in the Wadden Sea. They were a little higher near the mouth of the Rhine/Meuse Rivers, but < 16 $\mu g.l^{-1}$.
The exposure level for terrestrial organisms varies greatly with location, soil type and soil parameters. The zinc concentration in the topsoil of nature reserves ranges from about 5 to 150 $mg.kg^{-1}$ and in that of agricultural soils from about 20 to 150 $mg.kg^{-1}$. The availability of zinc

from soils to plants is considered to be about 1 to 10 %.

4.9 SUMMARY AND CONCLUSIONS

A summary of ranges or averages of zinc levels in the Dutch environment and in food is given in Table 4.20. There are sufficient methods available for measuring zinc concentrations and for determining the chemical speciation of zinc.

Table 4.20. *Summary of ranges or averages of zinc concentrations in soil, water, air and diet in the Netherlands, as well as a few background levels*

Soil	
range of background levels	*6 - 150 mg.kg^{-1}*
agricultural soil (av)	
clay	*117 mg.kg^{-1}*
sand	*44 mg.kg^{-1}*
fen-peat	*101 mg.kg^{-1}*
moss-peat	*25 mg.kg^{-1}*
loess	*86 mg.kg^{-1}*
Water	
- fresh	
background level in River Rhine (estimated)	*2.6 µg.l^{-1}*
surface water (1988)	*9 - 88 µg.l^{-1}*
sediments	*170 - 1400 mg.kg^{-1} d.w.*
- salt	
background level	*< 1 µg.l^{-1}*
North Sea coast	*4 - 8 µg.l^{-1}*
sediments	*120 - 400 mg.kg^{-1} d.w.*
- groundwater	
10 m depth	*10 - 80 µg.l^{-1}*
Air	
national annual average	*0.065 µg.m^{-3}*
urban areas (1988)	*$\leq$ 0.25 µg.m^{-3}*
concentration in rainwater	*0.2 - 0.7 µmoles.l^{-1}*
Diet	
daily food parcel (mean values from two studies)	*8 - 14 mg*

The concentration of zinc in soils is strongly determined by the nature of the soil material, and exhibits a large variation. The mean concentration usually increases in the order: sand, sandy loam, clay, peat. In water meadows and reclaimed polders, greatly elevated zinc concentrations may be observed locally. In the Kempen and South Limburg too, higher zinc levels, determined by history, occur due to old zinc mines and discharge from zinc smelters in the past. The current accumulation of zinc in soil is small. In agricultural soil, it averages about 0.2 mg.kg^{-1} per year.

The zinc load imported into the Netherlands via the large rivers has fallen dramatically since the early 1980s, and is at present about 2,000 tonnes per year, of which 60 % enters the North Sea.

The concentration of zinc in the atmosphere is characterized by a large contribution (ca 70 %) from abroad.

5. EFFECTS

The sections on aquatic organisms (5.2) and terrestrial organisms (5.3) included in this chapter are a summary of a background report written for this integrated criteria document on the ecotoxicity of zinc, and therefore no references are cited in these sections, apart from a few exceptions. The background report has been added as a separate appendix ("Ecotoxicity").

5.1 HUMAN TOXICITY

In accordance with the wishes of the commissioning body (see introduction to this report), this section is mainly based on data taken from the report entitled "Toxicological Profile for Zinc", published by the Agency for Toxic Substances and Disease Registry (ATSDR, 1989). Certain sections have been supplemented with data from evaluations by the World Health Organization (WHO, 1972, 1973) and from the extensive review of the literature edited by Mills (1989). The latter contains chiefly data on the physiological role of zinc as an essential trace element in the diet and on the health effects associated with zinc deficiency; it contains almost no data on the toxic effects of excessive zinc.

One consequence of the use of these reviews is that in a number of cases there is uncertainty about the reported data, for example, on the exposure (single or repeated dose, the duration of exposure, the route of exposure, the size of the exposed groups), the dose administered, and the form of zinc (inorganic salt or incorporated in food). For this reason, the original literature was consulted in exceptional cases. Wherever possible, the chemical form of zinc tested and the dose of the test compound administered have been given in the text, followed by conversion to the amount of zinc (for example, a reported dose of 600 mg $ZnSO_4.7H_2O$ per day, equivalent to 140 mg Zn per day). In some cases, the dose reported in the original publication or review has been expressed in elemental zinc and taken over as such, but the test compound (if stated), has been mentioned, for example, 300 mg $Zn.kg^{-1}$ of feed (administered as ZnO). Unless otherwise stated, a dose in $mg.kg^{-1}$ should be interpreted as mg $Zn.kg^{-1}$.

The vast amount of occupational toxicity data on zinc is for the most part not considered in this section, because most data are irrelevant for the assessment of the risks of zinc to the general population (the literature on occupational toxicity relates primarily to (short-term) inhalation exposure to relatively high zinc concentrations which are not encountered outside the workplace).

5.1.1. Biological function/recommended dietary intake

Zinc is an essential trace element, and is found normally in all tissues and tissue fluids. It is a component or cofactor of more than 200 enzymes (including oxido-reductases, transferases, hydrolases, isomerases and ligases) and, as such, plays a role in the metabolism of carbohydrates, proteins and lipids. Zinc also plays a role in the absorption and cellular balances of other elements, in the synthesis of DNA and RNA, and in the stabilization of proteins, for example, in membranes. According to Sundermann and Barker (1988), the formation of zinc complexes with certain proteins results in the spatial structure required for the biological function of these proteins. For example, the binding to DNA, and thus the function, of certain proteins involved in gene expression is dependent on the presence of zinc.

In experimental animals, zinc deficiency occurs when the diet contains less than 1 mg kg^{-1}, corresponding to 0.05-0.1 mg.kg^{-1} body weight per day. However, deficiency (manifested as growth depression) has also been observed among rats fed on diets containing approximately 10 times higher levels of zinc. Growth retardation induced by zinc deficiency is largely due to reduced feed intake. Zinc deficiency symptoms in humans include loss of appetite, decreased sense of taste and smell, slow wound healing, skin lesions, and impaired immune response. In severe cases in children, too little zinc can cause growth retardation, and poorly developed sex organs in boys. The dietary levels at which these deficiency symptoms occur in humans were not reported.

The exact amount of zinc required for an adequate nutritional status cannot be determined, because absorption in the gastrointestinal tract is influenced by the composition of the diet and physiological factors. The

WHO (1973) has summarized the recommended intakes for both children and adults, taking into account age, proportion of zinc absorbed from the diet (range, 10-40 %), physiological factors (pregnancy, lactation), and excretion. Assuming 20 % absorption, the following zinc intakes (necessary for maintaining the metabolically active pool of zinc in tissues) are recommended: 3-4 mg per day for children up to 10 years of age, 11-14 mg per day for teenagers and adolescents, 11 mg per day for adults, 13-15 mg per day for pregnant women, and 27 mg per day for lactating women. At a fractional absortion of 10 %, a twofold higher zinc intake is recommended, and a twofold lower intake at 40 % absorption. The U.S. National Research Council recommends a daily intake of 15 mg for men (70 kg) and 12 mg for women (lower body weight). Extra dietary levels of zinc are recommended for women during pregnancy and lactation (not specified) and a lower zinc intake is recommended for infants and children, because of their lower body weight. A summary given by King and Turnlund (1989) for 10 countries shows similar recommendations: 8-16 mg per day for adults (men), 9-21 mg per day for pregnant women, 15-25 mg per day for lactating women, and 2-6 mg per day for young children. The recommended zinc intakes mentioned correspond to 0.10-0.35 $mg.kg^{-1}$ body weight per day for the "average" adult (body weight, 60 kg), the range most frequently reported being 0.15 to 0.20 $mg.kg^{-1}$ body weight per day. They correspond to 0.15-0.35 $mg.kg^{-1}$ body weight per day for pregnant women and 0.25-0.45 $mg.kg^{-1}$ body weight per day for lactating women, likewise assuming a body weight of 60 kg. The Netherlands Food and Nutrition Board recommends 4 mg per day for infants, increasing to 9-11 mg per day for adolescents and adults, 12-15 mg per day for pregnant women, and 16-20 mg per day for lactating women (Voorlichtingsbureau voor de Voeding, cited in Bos et al., 1991).

With regard to these data, it should be mentioned that there are indications that, under normal conditions (with a varied diet), some of the recommended quantities are probably too high, given the average daily zinc intake found in most studies. For example, there are studies indicating that a zinc intake of less than half the level recommended for pregnant women often has no discernible adverse effects on pregnancy and the development of the offspring. Various studies conducted in different countries have shown that the zinc intake of pregnant women is in many cases 10 mg per day at most; however, no information regarding any effects on reproduction associated with this intake was given.

Both the WHO (1973) and King and Turnlund (1989) have made estimates of the quantity of ingested zinc which must be absorbed daily ("true zinc requirement"), taking into account physiological requirements and endogenous zinc losses. The total zinc required by the human body is 2.2-2.5 mg per day for adults, 2.4-3.2 mg per day in pregnant women, and 3.5-5.45 mg per day in lactating women, corresponding to 0.04, 0.04-0.05 and 0.06-0.10 mg.kg^{-1} body weight per day, respectively.

5.1.2. Chemobiokinetics and metabolism

Absorption

It is estimated that 20 to 30 % of all ingested zinc is absorbed in the gastrointestinal tract (under normal conditions, at a daily intake of about 10-15 mg). The absorption of zinc is highly variable and affected by the zinc level and composition of the diet, and physiological factors such as zinc status. For example, in a study in which the zinc content of the diet of a male adult was varied from 7 to 30 mg per day, the fraction absorbed dropped from 47 % to 21 %. Of the dietary factors, phytic acid in particular plays an important role, owing to its presence in all grains and most vegetables. Phytic acid combines with zinc and other divalent cations such as calcium, cadmium, copper, magnesium and lead to form poorly soluble phytate complexes, thereby reducing absorption. According to Mills (1986), the solubility products of phytate-metal complexes are greatly reduced if calcium or magnesium are also incorporated; furthermore, calcium increases the particle size (and thus decreases the reactive surface area) of the amorphous Ca-Zn-phytate complexes, resulting in further depression of zinc absorption (Mills, 1986). Animal studies suggest that zinc from vegetable products is less available for absorption than zinc from foods of animal origin. One of the physiological factors influencing absorption is the nutritional status (e.g., zinc deficiency increases absorption). Elevated zinc concentrations in the serum and plasma of persons occupationally exposed to zinc oxide fumes suggest that there is some pulmonary absorption. In addition, there are indications that zinc can be absorbed through the skin. However, quantitative data on the absorption of zinc following inhalation or dermal exposure are not available.

Transport, distribution, metabolism

After absorption from the gastrointestinal tract, zinc is bound in plasma primarily to albumin and then transported as such to the liver and other organs. Under normal conditions, the highest zinc concentrations are found - on a fresh weight basis - in bone (100-200 mg.kg^{-1}), hair (150 mg.kg^{-1}), and prostate (100 mg.kg^{-1}). Zinc concentrations ranging from 20 to 60 mg.kg^{-1} fresh weight have been reported for other tissues, with relatively high levels in skin, gastrointestinal tract, liver, kidney, pancreas, heart, lung and brain. Because of the large bulk of muscle and bone in man, the major part of total body zinc is found in these tissues, approximately 60 % and 30 %, respectively. The zinc content of an adult ranges from 2 to 3 g; ca 95 % of this is intracellular zinc. The major proportion of the zinc within cells is "inactively" bound to metallothioneins, a group of metalloproteins which form complexes with metals, particularly zinc and copper. The most probable role of these proteins in zinc metabolism is in the control of intracellular concentrations of ionic zinc, and thereby the metabolically active fraction. Of the total body zinc approximately 0.5 % is contained in the blood, of which 80 % in the red blood cells (erythrocytes). Zinc is usually measured in blood plasma (normal level, 1 mg.l^{-1}; 0.1 % of the total body zinc) and therefore gives an unreliable picture of the zinc status. During pregnancy, the plasma zinc level falls, by about 10 % to 20 % in humans, probably due to an increase in plasma volume, changes in hormone levels, and uptake by the foetus.

To some degree, the normal distribution of zinc in some tissues is is dependent on age. Zinc concentrations increase in the prostate and decrease in the uterus with age. Levels of zinc increase after age 40 in the liver and pancreas. Levels rise to a peak in the age group 40-50 in the kidney and then decline. Heart levels of zinc decrease until age 30, rise to a peak at age 50 and then decline. Levels in the aorta decline after age 30.

Excretion

After ingestion, by far the largest part of the zinc is recovered in the faeces, due chiefly to the relatively low degree of intestinal absorption. Studies in which zinc was administered intravenously demonstrated that elimination of absorbed zinc from the circulation also takes place mainly via the gastrointestinal tract, in addition to excretion in urine, sweat and, in lactating women, in milk. The zinc concentration in human milk decreases from about 2.5 to < 1 $mg.l^{-1}$ between the 1st and 9th month of lactation; the milk zinc concentration does not appear to be related to maternal zinc status or zinc intake. In hot environments, sweat can contribute significantly to the elimination of zinc. Too little zinc in the diet or malnutrition can result in a temporary increase in the urinary excretion of zinc; this apparent inconsistency with the maintenance of whole-body zinc homeostasis (see following section) can be explained by the increase in tissue catabolism under these conditions, thereby releasing zinc to sustain normal physiological functions.

Under normal conditions, the biological half-life of absorbed zinc ranges from 150 to 500 days.

Homeostasis

Within certain limits, mammals can maintain the total body zinc and the physiologically required levels of zinc in the various tissues constant, both at low and high dietary zinc intakes. The sites of regulation of zinc metabolism are: absorption of zinc from the gastrointestinal tract, excretion of zinc in urine, exchange of zinc with erythrocytes, release of zinc from tissue (especially muscles), and secretion of zinc into the gastrointestinal tract. Regulation of gastrointestinal absorption and gastrointestinal secretion probably contributes the most to zinc homeostasis. In the depression of zinc absorption, resulting from an increased zinc intake, metallothionein plays an important role: zinc induces metallothionein production in the mucosal cells lining the gastrointestinal tract. Zinc binds to the metallothionein, which remains in the mucosal cells. The metallothionein-zinc complex is excreted from the body upon sloughing of the cells. The effectiveness of homeostatic control of zinc metabolism following exposure to high levels of zinc is demonstrated, for example, by the study of Aughey et al. (1977), in which mice received drinking water containing 500 mg $Zn.l^{-1}$. The mice showed no increase in the zinc content of liver and kidney. The plasma zinc concentration, however, increased slightly within a few days, from about 1 to 2 $mg.l^{-1}$; the zinc level declined to about 1.5 $mg.l^{-1}$ in the subsequent 4 weeks.

In spite of the mechanism for whole-body zinc homeostasis and the relatively large amounts of zinc in tissues (particularly muscle and bone), a regular exogenous supply of zinc is necessary to sustain the physiological requirements because of the limited exchange of zinc between tissues.

5.1.3. Toxicity

Short-term exposure (acute and subacute toxicity)

Experimental animals

Acute oral LD50 values for rats range from 750 to 1,375 mg zinc salt (zinc sulphate or zinc chloride) per kg body weight, equivalent to 175 to 550 mg $Zn.kg^{-1}$ body weight. In a feeding study with a small number of adult ferrets, the animals were given diets containing 0 (5 animals), 500 (3 animals), 1,500 (4 animals) or 3,000 (3 animals) mg Zn per kg (administered as ZnO). The groups fed the two highest concentrations of zinc showed signs of acute toxicity (including reduced feed intake, weight loss and, at the highest concentration, death within 2 weeks). The animals in the second highest dose group were killed after 2-3 weeks. Postmortem examination revealed both macroscopical changes (including intestinal haemorrhages, enlarged kidneys, discolouration of internal organs) and microscopical changes (including kidney lesions [diffuse nephrosis]). The ferrets also had anaemia and elevated protein, blood, glucose and bilirubin levels in the urine. Significant histopathological changes were not observed in the ferrets in the lowest dose group, nor effects on the composition of blood and urine (Staube et al., 1980).

In a study by Maita et al. (1981) mice and rats (12 rats or mice, of both sexes per group) were fed on diets containing 0, 0.30, 3.0, or 30 g $ZnSO_4.7H_2O$ per kg for 13 weeks. Five mice (4 males, 1 female) in the highest dose group died before termination of the study. Both mice and rats given the highest dose (equivalent to 1,100 mg $Zn.kg^{-1}$ body weight per day for mice and 575 mg $Zn.kg^{-1}$ body weight per day for rats) exhibited retarded growth, which was partly due to a reduction in feed consumption, lowered haematocrit values and decreased levels of haemoglobin [anaemia], and histopathological changes in the pancreas. In mice, ingestion of this dose also resulted in reduced water intake, changes in several biochemical parameters in blood (reduced levels of decrease in total protein content; elevated levels of urea and alkaline phosphatase) and macroscopical and/or microscopical changes in several organs (stomach, intestine, spleen, kidney, and thyroid). The two lower exposure levels (equivalent to 10 and 108 mg $Zn.kg^{-1}$ body weight per day for mice and 5 and 55 mg $Zn.kg^{-1}$ body weight per day for rats) had no effects (Maita et al., 1981).

Humans

The acute toxicity of zinc compounds to humans has been described chiefly in the literature on occupational toxicity. Inorganic zinc salts such as zinc chloride, zinc nitrate and zinc sulphate have a corrosive action. Symptoms resulting from ingestion of these salts include vomiting, headache, and diarrhoea. Inhalation of zinc oxide fumes resulting from heating (metallic) zinc may cause metal fume fever within a few hours, a reversible effect manifested by fever, dry cough, and muscle pains. Inhalation of zinc chloride may result in severe respiratory tract effects. In the Netherlands, MAC values (maximum acceptable concentration, applicable to the workplace) for zinc chloride and zinc oxide have been set at 1 and 5 $mg.m^{-3}$, respectively (VNCI, 1989; see also Chapter 1). For more information about the acute toxicity of zinc and its compounds, the reader is referred to the occupational toxicity literature.

The effects resulting from repeated oral exposure to zinc are examined below. The majority of the occupational toxicity data on repeated inhalation and/or dermal exposure is not considered, because of the high exposure levels, which are not encountered outside the workplace.

Ingestion of zinc as zinc sulphate at a dose rate of 2.3-4.3 mg $Zn.kg^{-1}$ body weight per day for 5-6 weeks resulted in a reduction of high-density lipoprotein (HDL)-cholesterol levels in humans; the authors did not report the material in which this HDL-cholesterol was measured. Another study observed a transient decrease in serum HDL-cholesterol levels in subjects who ingested either 50 or 75 mg Zn per day (approximately 1 mg $Zn.kg^{-1}$ body weight per day) for 6-12 weeks. Ingestion of 100 mg Zn per day (as zinc sulphate, divided into 4 doses per day; 1.7 mg $Zn.kg^{-1}$ body weight per day) for 3 to 6 months resulted in gastrointestinal disturbances in one of the 80 subjects. Another study observed gastrointestinal disturbances in 26 of the 47 subjects who ingested 150 mg Zn per day (also as zinc sulphate, 3 doses of 50 mg per day; 2.5 mg $Zn.kg^{-1}$ body weight per day). In 27 patients being orally treated with 600 mg zinc sulphate per day for 18 weeks for chronic venous leg ulcers, no effects were noted on the gastrointestinal tract, liver and kidney functions, or blood and urine. In another study, 3 of the 52 patients receiving oral treatment with 660 mg zinc sulphate per day for 10 weeks experienced a mild form of diarrhoea. The last two dosages correspond to 240-264 mg Zn per day (4-4.4 mg $Zn.kg^{-1}$ body weight per day) and 138-152 mg Zn per day (2.3-2.5 mg $Zn.kg^{-1}$ body weight per day), derived from $ZnSO_4$ and $ZnSO_4.7H_2O$ respectively.

Reproductive and developmental toxicity

Experimental animals

Severe zinc deficiency leads to infertility. Maternal zinc deficiency may result in a wide variety of foetal effects, both embryo-/foetotoxic (e.g. an increase in the number of resorptions, growth retardation and death) and teratogenic effects (chiefly skeletal deformities). The observed developmental effects are partly caused by the reduced feed intake induced by zinc deficiency (secondary effect; see also the study with monkeys below), but the teratogenic effects are very likely caused directly by the zinc deficiency (primary effect). Maternal zinc deficiency can have adverse effects on the offspring even after birth, for example, immunoincompetence and (possibly) behavioural disturbances.

Developmental effects have been reported in rats at zinc levels of < 1 $mg.kg^{-1}$ in the maternal diet (Léonard and Gerber, 1989). In a study with monkeys, embryo-/foetotoxicity was observed at a dietary zinc concentration of 4 $mg.kg^{-1}$. This study also found embryo-/foetotoxicity in offspring of the group given the same amount of feed as the zinc-deficient group.

In teratogenicity studies in which pregnant animals were exposed during the organogenesis period to maximum doses of 30 mg $Zn.kg^{-1}$ body weight per day (mice), 42 mg $Zn.kg^{-1}$ body weight per day (rats), and 88 mg $Zn.kg^{-1}$ body weight per day (hamsters), neither teratogenic effects nor effects on the implantation of the foetus or on maternal and foetal mortality were observed. The test compound was zinc sulphate. The route of administration was not reported, but given the body conducting the studies (Food and Drug Research Laboratories), it may have been by the oral route. A study in which pregnant rats were daily given 20 mg zinc sulphate (by stomach tube) during organogenesis resulted in a significantly reduced number of foetuses; the number of animals involved in this study was very small, viz. 4 in the treatment group and 4 in the control group. In a study in which mice (6-10 animals per group) were injected intraperitoneally with a single dose of 12.5, 20.5 or 25 mg $ZnCl_2$ kg^{-1} body weight (6, 10 or 12 mg $Zn.kg^{-1}$ body weight) on day 8, 9, 10, or 11 of gestation, one or more of the following effects were observed at the two highest exposure levels: increased incidence of maternal deaths, an increased number of foetal resorptions, and skeletal anomalies (delayed ossification of several parts of the skeletal system, fused sternabrae, ripple ribs). The extent and nature of the effects were dependent upon the day of administration. The lowest dose level did not result in embryo-/foetotoxicity or teratogenicity (Chang et al., 1977).

In a number of reproduction studies, female mice were orally exposed to zinc during gestation or during part of the gestation period, usually to one zinc concentration only. In a few studies the animals were also exposed before gestation or the offspring were also exposed postnatally, both during lactation (via the milk) and after the lactation period (via the diet). These studies, in which various zinc compounds were tested (including $ZnSO_4$, $ZnCl_2$, $ZnCO_3$, and ZnO), produced conflicting results when the zinc was administered at 200-250 $mg.kg^{-1}$ body weight per day in the diet. In 2 studies (mice, rats) these zinc concentrations caused embryo-/foetotoxicity (increased number of foetal resorptions, reduced foetal weight and/or, when the offspring was also exposed postnatally, reduced growth and alopecia [hair loss]). No effects were observed in the study with rats at a dose rate of 100 mg $Zn.kg^{-1}$ body weight per day. However, in most of all the reproduction studies conducted, levels of dietary zinc of 200-250 $mg.kg^{-1}$ body weight per day had no adverse effects on reproductive capacity or on the offspring, but did cause reductions in copper and iron concentrations in both the foetal body and foetal liver. Total cessation of reproduction was observed in rats ingesting 500 mg $Zn.kg^{-1}$ body weight per day. The reproduction studies also do not suggest teratogenic action, but it is not clear to what extent this was specifically investigated in these studies.

In a reproduction study with rats by Kumar (1976), a statistically significant increase in the number of foetal resorptions was seen in rats fed 180 mg $Zn.kg^{-1}$ of feed during gestation (30 mg $Zn.kg^{-1}$ in the control feed plus an additional 150 $mg.kg^{-1}$), equivalent to 9 mg $Zn.kg^{-1}$ body weight per day (standard factor, 20). This dosage is very low compared with the dosages of 200-250 mg $Zn.kg^{-1}$ body weight per day administered in the above-mentioned reproduction studies, which usually caused no embryo-/foetotoxicity. The extra zinc was given in the form of a 2 % $ZnSO_4$ solution; it is not clear from the publication whether the extra zinc was added to the diet or administered daily orally in another way. The significance of this study cannot be determined because of the mostly negative results of the other reproduction studies with much higher zinc intakes.

In conclusion, it is stated that the teratogenicity and reproduction studies provide no evidence of teratogenicity of zinc following oral exposure. Exposure to high levels of zinc in the diet can however lead to embryo-/foetotoxicity.

Humans

Numerous studies have indicated that zinc deficiency may also lead to infertility and adverse developmental effects in humans. For example, zinc influences spermatogenesis and the ability of sperm to penetrate the egg. According to Keen and Hurley (1989), there are data showing that zinc supplementation has a positive effect on the course of pregnancy in apparently healthy pregnant women; no further details were reported by these authors, either on the zinc status of these women and the supplements given, or on the nature of the positive effects. The consumption of an unbalanced diet by pregnant women in developing countries has often led to relatively low birth weights among the offspring. The intake of zinc from this diet, consisting mostly of cereal products, was about 6 mg per day; this is much lower than the recommended daily intake (Kumar, 1976). The intake of 6 mg per day mentioned gives only an indication of the zinc required by the human body because, in addition to too little dietary zinc, a deficiency of other dietary nutrients probably also played a role in this effect. Moreover, the bioavailability of zinc from diets rich in cereals is relatively low.

With the exception of a brief statement in a report by Kumar (1976), there are no indications that exposure to excessive levels of zinc has caused adverse developmental effects in humans. In the study by Kumar (1976), pregnant women, who were possibly zinc-deficient, received dietary supplements of 100 mg zinc sulphate (probably daily) during the third trimester of pregnancy. In the first 4 subjects, there were 3 premature births and one stillbirth. The study was discontinued. The significance of these results cannot be determined because of the small number of subjects and the very limited reporting by Kumar (1976).

Long-term exposure (subchronic and chronic toxicity)

Experimental animals

The effects of oral zinc supplementation on endocrine glands (pancreas, adrenal, pituitary) were investigated in a one-year study with 6 to 8-week old mice. Mice of both sexes were given zinc (as the sulphate) in drinking water at a concentration of 0.5 g l^{-1}, corresponding to 50 mg $Zn.kg^{-1}$ body weight per day (standard factor, 10). Groups of 5 test animals and 5 control animals were compared at monthly intervals. Oral zinc supplementation resulted in hypertrophy of the adrenal cortex and pancreatic islets. The histological changes in the organs examined suggested increased secretory activity. Zinc administration did not produce outwardly visible effects, or affect weight gains. Other parameters were not studied (Aughey et al., 1977).

In a 21-month feeding study in which young rats (4 males and 4 females per group) were given diets containing 100, 500, and 1000 mg $ZnSO_4.7H_2O$ kg^{-1} (equivalent to 1.1, 5.7, and 11.5 mg $Zn.kg^{-1}$ body weight per day), there were no effects on survival, feed intake, relative liver weight or on the haemogram, and no (histo)pathological changes. At the two highest dose levels, renal effects were however observed in males, namely, enlargement, granulation, and a more severe inflammation [nephritis] than in the controls. All exposure levels produced a reduction in the M/E ratio (ratio of the number of myelocytes to the number of erythrocytes) in the bone marrow. The mean values of this parameter were 1.2-1.3 in the zinc-treated group compared to 2.1 in the control group (Hagan et al., 1953).

Humans

A copper deficiency was noted in two patients being orally treated with

150 and 264 mg Zn per day (as the sulphate), respectively. These dose levels correspond to 2.5 and 4.4 mg $Zn.kg^{-1}$ body weight per day, respectively (case reports). Further data on effects of long-term exposure to zinc and its compounds are not available.

No toxic effects were recorded in workers occupationally exposed to 8-12 mg zinc oxide m^{-3} for 8 hours per day.

The above data refer to "long-term exposure", without specification of the exposure duration.

Genotoxicity

The genotoxicity data for zinc are equivocal. Conflicting results have been found particularly in **in vitro** tests, even in the same test system, for example, the Salmonella mutation assay. The conflicting results in the same test system can be explained by the differing forms of zinc tested. When zinc is added as a compound which readily ionizes (low binding constant), the availability of zinc for transport into the cell can decrease because of the strong binding of ionic zinc to medium components such as proteins, so that the intracellular zinc concentration remains low. On the other hand, when zinc is added as a compound which does not readily ionize (high binding constant), more zinc can be transported into the cell because less zinc will be bound to medium components. For example, zinc acetate (relatively low binding constant) was negative in the Salmonella mutation assay with all 5 strains tested, whereas in the same study zinc-2,4-pentanedione (relatively high binding constant) was positive in 2 out of the 5 strains (frameshift mutations). In two studies, the Salmonella assay with $ZnSO_4$ was negative, which is consistent with the above explanation. In another study, however, the Salmonella assay with ZnCl2 gave a positive result, possibly because of the presence of citrate in the growth medium; the binding constant of zinc citrate is about the same as that of zinc-2,4-pentanedione. The binding of zinc to citrate increases the availability for transport. A second example: a positive result was obtained with zinc acetate in a mutagenicity assay in mammalian cells (L5178Y TK+/- mouse lymphoma assay), but not with $ZnCl_2$ (in another study using the same test system). This disparity too can be explained by the difference in binding constant of the test compounds and, possibly, differences in the composition of the medium. Based on these data it is concluded that the final result depends upon the chemical form of zinc in the medium.

Besides gene mutations, zinc can also induce clastogenic effects (structural chromosomal aberrations such as chromatid gaps, chromatid breaks, fragments, and sister chromatid exchanges (Léonard and Gerber, 1989; Thompson et al., 1989).

The results of **in vivo** studies (bone-marrow micronucleus assay; cytogenetic effects in somatic cells) in which mammals were fed zinc in their diet, are generally negative. Only under extreme conditions (calcium-deficient diet, resulting in a 60 % weight loss) were chromosomal aberrations due to zinc observed in bone marrow cells of mice (Léonard and Gerber, 1989; Thompson et al., 1989).

In conclusion, it is stated that there is sufficient evidence that zinc is genotoxic in **in vitro** systems, with the comment that the final result is dependent upon the chemical form of zinc. However, there is no evidence of genotoxicity of zinc **in vivo** following oral exposure to zinc, which could possibly be explained by the strong binding of zinc to proteins (complex formation).

Carcinogenicity

Intratesticular injections of zinc chloride into experimental animals have produced testicular sarcomas, but there is no evidence that cancers develop after exposure by any other route. It should be noted that adequate carcinogenicity studies are lacking.

A relationship between cancer incidence and inhalation exposure to zinc could not be established in two epidemiological studies (an occupational study and a study among residents in a lead-zinc mining and smelting area). These studies were, however, very limited.

Interaction of zinc with other metals

The kinetics and effects of zinc and other divalent cations are determined by interaction processes. For example, an excess of one metal can lead to diminished absorption of another or other metals, resulting in a change in the ratio between the metals in the tissues, and substitution of one metal for another in metalloproteins. This can lead to changes in intracellular concentrations of the free metal ions, among other things. In functional proteins such as enzymes, replacement of one metal by another may result in loss of function, for example, due to a change in the spatial structure. The ultimate effect of the interaction processes depends, of course, on the nature and concentration of the metals involved. A few examples of the result of these interactions: an excess of zinc can counteract the toxic effects of metals such as copper and cadmium, because zinc impairs the absorption of these metals. For example, patients with Wilson's disease are being treated successfully by daily administration of an oral zinc supplement. Wilson's disease is a hepatolenticular degenerative disease in which high copper concentrations, caused by an inborn error of metabolism, play a role. The zinc supplement depresses the intestinal absorption of copper (increased faecal excretion of copper), thereby reducing the copper levels in the tissues. Experiments with rats have shown that zinc counteracted the hypertensive effects of cadmium. Excessive dietary zinc can also have negative effects, for example, anaemia caused by a zinc-induced deficiency of copper, and an adverse effect on calcium metabolism. According to Bos et al. (1991), the absorption of copper is depressed when the dietary zinc to copper ratio is greater than 10 to 15.

According to Sunderman and Barber (1988), the structure (and thus the function) of proteins involved in gene expression may be altered through the replacement of zinc by other divalent metal ions. This is a possible explanation for the carcinogenicity of certain nickel, cobalt and cadmium compounds.

5.2. ECOTOXICITY - AQUATIC ORGANISMS

5.2.1. Accumulation

The data reported below refer to both freshwater and saltwater organisms, and are based on laboratory and field studies.

The ability of an organism to accumulate or concentrate a substance from water is usually expressed in a "bioconcentration factor", the ratio of the concentration of the substance in the organism (fresh weight basis) to the concentration of the substance in the surrounding water: BCF = Corganism : Cwater. For naturally occurring substances, a correction is sometimes made for the concentration in the organism resulting from the background concentrations in the water, as follows:

$BCF = (C_{org}\ [exposed] - C_{org}\ [control]\ /\ C_{water}\ )$.

The BCF values reported for plants, including algae and macrophytes, range from < 100 to 50,000. The majority of BCF values for invertebrates and fish lie between 100 and 1,000, those for fish generally being lower than those for invertebrates. The highest BCFs for invertebrates, ranging between 10,000 and 100,000, have been reported for benthic organisms such as crabs, oysters and insect larvae. The highest BCF reported for fish is 2,000. It should be noted that these values were taken from reviews, which usually do not report whether the BCFs are based on fresh weight or dry weight of the organisms, and whether or not the values have been corrected for the background concentration of zinc in the organisms. Furthermore, the wide range of values observed may be partly attributable to differences in exposure duration (equilibrium state or not), and differences in exposure concentration; so caution is required when interpreting these values.

In spite of these limitations, it is concluded that zinc is concentrated by aquatic organisms from the surrounding water, and that the degree of concentration is species-dependent, varying from insignificant (fish and most invertebrates) to highly significant (algae and benthic organisms). In view of the decreasing BCF values with increasing trophic level in the food web (BCFalgae > BCFinvertebrates > BCFfish), it is further concluded that biomagnification, i.e. accumulation through food chains, is of little significance. The results of both field and laboratory studies, in which the zinc concentration was measured in a wide variety of organisms, confirm this conclusion.

5.2.2. Toxicity

A distinction has been made below between freshwater organisms and saltwater organisms. In the selection and processing of the literature on the toxicity of zinc to aquatic organisms, special attention has been paid to long-term tests (semichronic and chronic toxicity), resulting in NOEC values (no-observed-effect concentration). The reason is that these NOECs are preferably used in deriving a recommended value for the "maximum tolerable concentration". The long-term tests have therefore been evaluated on the basis of the original literature. Most of the vast amount of short-term tests have not been evaluated. The LC50 and EC50 values (lethal concentration and effect concentration, respectively, for 50 % of the exposed organisms) from short-term tests reported in this subsection are largely based on reviews. "Short-term exposure" covers tests lasting up to 96 hours and "long-term exposure" tests of more than 96 hours. However, 24/96-hour tests with bacteria and algae are also included in "long-term exposure" because of their short life-spans. Unless otherwise stated, all concentrations reported herein are expressed as <u>total zinc</u> (dissolved zinc plus particulate zinc > 45 μm). Most of the toxicity values are based on nominal (added) concentrations. All tests were conducted with readily soluble salts, most with $ZnSO_4$ or $ZnCl_2$.

Toxicity to freshwater organisms - single species tests

Short-term exposure (acute toxicity)

EC50 and LC50 values

Most tests with invertebrates have resulted in LC50 and EC50 values of between 40 and 58,000 $\mu g.l^{-1}$; occasionally values > 60,000 have been found. The 24/96-hr LC50 values reported for fish range from 90 to 41,000 $\mu g.l^{-1}$. The lowest values were reported for water fleas (belonging to the Crustacae) and salmonids such as rainbow trout, which is possibly associated with the low hardness of the test waters used (see below).

Influence of abiotic factors on acute toxicity

The toxicity of zinc, like that of other metals, is affected by abiotic (environmental) factors which determine the chemical speciation in the water. Hardness is most often mentioned as the abiotic factor having the greatest influence on the toxicity of zinc, but hard water generally also has a high alkalinity, high ionic strength and high pH, which have a modifying influence on zinc toxicity. In general, the toxicity of zinc increases with decreasing hardness, alkalinity, ionic strength and pH, because of the increase in the free (hydrated) ion concentration. Consequently, the acute toxicity of zinc is greatest in relatively soft and acidic waters.

The influence of abiotic factors on the acute toxicity of zinc varies with species of organism; the largest differences have generally been found for fish. The most extreme example of this is a study with <u>Pimephales promelus</u> (fathead minnow). The 96-hr LC50 in very hard water (hardness 360 $mg.l^{-1}$;

alkalinity 300 mg.l^{-1}; pH 8.2) was 33,000 μg.l^{-1}, while the 96-hr LC50 in very soft water (hardness 20 mg.l^{-1}; alkalinity 18 mg.l^{-1}; pH 7.5) was 780 μg.l^{-1}, approximately 40-fold lower. In most cases, less extreme differences have been found (at most a factor of 5 to 10). For example, in a number of tests with the water flea Ceriodaphnia dubia, conducted at different combinations of hardness (100-180 mg.l^{-1}) and pH (6-9), the 48-hr LC50 values differed by a factor of 4 at most.

Long-term exposure (semichronic and chronic toxicity)

NOEC values (Appendix "Ecotoxicity", Tables 1.1 and 1.2)
Long-term tests resulting in NOEC values which have been used in the derivation of a maximum tolerable concentration for zinc in fresh water (see 5.5) are summarized in Table 1.1 of the Appendix. The NOEC values in this table have been selected on the basis of the toxicological parameters investigated and of the test media used. The most important toxicological parameters are considered to be survival, growth and reproduction, and therefore most of the NOEC values selected relate to these parameters. Regarding selection on the basis of the medium, a number of tests with algae have been conducted in culture media containing EDTA (ethylene diamine tetraacetate), a chelating agent which can decrease the toxicity of zinc. The minimum EDTA concentration which will affect the toxicity of zinc cannot be determined, partly because of the widely varying concentrations of zinc and other trace elements present in the media used. Based on the available data, an upper limit of $3x10^{-3}$ mM EDTA l^{-1} has been arbitrarily chosen. Therefore the NOEC values from algal tests conducted in media containing more than $10x10^{-3}$ mM EDTA l^{-1} or unspecified amounts of EDTA have not been used in deriving a maximum tolerable concentration; these NOEC values are included in Table 1.2 of the Appendix. Tests with other organisms were usually conducted in natural waters and, occasionally, tap water. It is assumed that these waters did not contain significant levels of EDTA.

Finally, tests producing only one NOEC "$\geq$" (that is, no effect at the highest concentration tested) are also listed in Table 1.2; therefore these NOEC values have also not been used in deriving a maximum tolerable concentration.

The NOEC values in Table 1.1 show a wide range, from 3 μg.l^{-1} for

Ephydatia fluviatilis (sponges) and Epeorus latifolium (insects) to 1290 $\mu g.l^{-1}$ for Brachydanio rerio (fish); these values are based on the most sensitive parameter for each test. In view of the low NOEC for E. fluviatilis, it was also included in the derivation of the maximum tolerable concentration, despite the relatively high EDTA concentration of $16x10^{(-3)}$ mM l^{-1} in the test water (the justification for this is the absence of data on the influence of EDTA on the toxicity of zinc to organisms other than algae). The NOECs for the taxonomic groups for which data were available are: 5-1,000 $\mu g.l^{-1}$ for algae, 3 $\mu g.l^{-1}$ for sponges (1 test), 25 $\mu g.l^{-1}$ for molluscs (1 test), 8-150 $\mu g.l^{-1}$ for water fleas (crustaceans), 3 $\mu g.l^{-1}$ for insects (1 test), and 26-1,290 $\mu g.l^{-1}$ for fish. The data show that even within the same taxonomic group, the NOECs vary considerably. These differences are probably largely due to differences in the medium, parameters studied, and exposure duration.

EC50 and LC50 values

Tests with algae, varying in duration from 4 days to 5 weeks, have resulted in EC50 values ranging between 200 and 5,100 $\mu g.l^{-1}$.

The LC50 and EC50 values reported for invertebrates range from 26 to 32,000 $\mu g.l^{-1}$ (exposure duration: 5 days to 14 days); the LC50 values reported for fish range from 90 to 17,000 $\mu g.l^{-1}$ (exposure duration: 5 to 21 days). These L(E)C50s for invertebrates and fish are similar to those from short-term tests with these organisms.

It should be noted that the range of L(E)C50 values for each of these three groups is not related to the indicated range of exposure duration.

Additional data

Long-term tests resulting in NOEC values which have not been used in the derivation of a maximum tolerable concentration are summarized in Table 1.2 of the Appendix. Tests in which the lowest concentration tested produced an effect are also included in this table. The data in this table (and other additional data not included in this table) are not considered here.

Influence of abiotic factors on chronic toxicity

Specific data on the influence of abiotic factors on the chronic toxicity of zinc are limited and moreover equivocal. For example, conflicting results were found in two life cycle studies with the water flea Daphnia magna. In one study, the NOEC in water with a hardness of 200 mg.l^{-1} was six times higher than in water with a hardness of 50 mg.l^{-1} (zinc is less toxic at high hardness). In the other study, the NOEC in water with a hardness of 200 mg.l^{-1} was two times lower than in water with a hardness of 50 mg.l^{-1} (zinc is more toxic at high hardness). According to the authors of the first study, the conflicting results can be explained as follows: in their study, the initial hardness of soft water (50 mg.l^{-1}) was increased by the addition of calcium and magnesium, which minimizes changes in other abiotic factors (such as the low alkalinity and ionic strength). In the second study, the hardness of hard water (200 mg.l^{-1}) was decreased by dilution with deionized water, with a parallel decrease in the high alkalinity of the water. Insoluble complexes of zinc with (bi)carbonate are formed at high alkalinity, resulting in an unexpectedly high toxicity of zinc to filter feeders such as water fleas, which may be attributed to ingestion of these complexes. A study in which life cycle tests with the water flea Ceridaphnia dubia were conducted in water with different hardness values (80-170 mg.l^{-1}) and pH (6-9)) found no consistent effect of these factors on zinc toxicity.

Studies focusing on the influence of abiotic factors on the chronic toxicity of zinc are not available for organisms other than water fleas, with the exception of a study with algae which found that increasing the pH of the test water from 4.5 to 8.5 increased the NOEC from < 100 to 225 μg.l^{-1}. It can be assumed on theoretical grounds that the chronic toxicity of zinc, like its acute toxicity, will be greatest in relatively soft and acidic waters. The available NOEC values appear to confirm this assumption, but the variation in the test waters and organisms used hamper interpretation of the results.

Toxicity to freshwater organisms - field studies

Data from a large number of field studies seem to suggest that sensitive species of invertebrates and fish are adversely affected at a dissolved zinc concentration of 15-25 μg.l^{-1}. In soft, acidic waters this is about the same as the total zinc concentration. An investigation in a large number of different waters in the U.K. noted no effect on the fish status at total zinc concentrations of up to about 50 μg.l^{-1}. In the same study, the salmonid fish status was found to be unaffected at dissolved zinc concentrations up to 50 $\mu g.l^{-1}$, but coarse fish were absent from waters with dissolved zinc concentrations > 25 $\mu g.l^{-1}$. These data seem to suggest that salmonids are less sensitive to zinc than other fish species. However, a comparison of the NOECs from long-term laboratory tests with various species of fish (Appendix "Ecotoxicity", Table 1.1) does not suggest a difference in sensitivity between salmonids and other fish species. It should be noted that interpretation of the data from field studies is difficult, because of the presence of other heavy metals, among other things.

Toxicity to saltwater organisms - single species tests

Short-term exposure (acute toxicity tests)

EC50 and LC50 values
Tests with invertebrates have resulted in 24/96-hr EC50 and LC50 values of between 65 and 950,000 $\mu g.l^{-1}$. Crustaceans and molluscs are among the most sensitive invertebrates. In general, fish are less sensitive, with 26/96-hr LC50s ranging from 2,730 to 83,000 $\mu g.l^{-1}$.

Long-term exposure (semichronic and chronic toxicity)

NOEC values (Appendix "Ecotoxicity", Table 1.3)
Long-term tests resulting in NOEC values which have been used in deriving a maximum tolerable concentration for zinc in seawater (see Section 5.5) are summarized in Table 1.3 of the Appendix.
Like the NOECs for freshwater organisms, those for saltwater organisms listed in Table 1.3 vary considerably, even between different species in the same taxonomic group. The NOECs for the taxonomic groups for which data were available are: 7-10,000 $\mu g.l^{-1}$ for algae, 300 $\mu g.l^{-1}$ for coelenterates (1 test), 100-320 $\mu g.l^{-1}$ for annelids, 19-1,000 $\mu g.l^{-1}$ for molluscs, 18-440 $\mu g.l^{-1}$ for crustaceans, and 10 $\mu g.l^{-1}$ for echinoderms (1 test). NOEC values for fish are not available. A wide range of NOEC values was also found for both the alga Phaeodactylum tricornutum and the alga Skeletoma costatum, which was probably largely due to differences in medium and/or strain used of the respective species.

EC50 and LC50 values

Tests with the diatom Nitzschia closterium (alga) in a culture medium resulted in 4-d EC50s of 270 and 360 $\mu g.l^{-1}$; the latter value was found in the presence of complexing agents (citric acid and amino acids). Exposure of invertebrates and fish for 5 to 21 days resulted in EC50 and LC50 values ranging from 50 to 83,000 $\mu g.l^{-1}$. These L(E)C50s are similar to those from short-term tests with these organisms.

Additional data

Long-term tests in which the lowest concentration produced an effect are summarized in Table 1.4 of the Appendix.

Interaction of zinc with other metals

A large number of studies in which aquatic organisms were exposed to mixtures of metals, including zinc, indicate that the interaction between the metals may vary from antagonism to synergism.

The toxicity of mixtures depends, among other things, on the combination of metals, both qualitative and quantitative, and on abiotic factors which may affect the speciation of metals in water. In addition, the effects of mixtures of metals differed with species of organism. A distinction has been made below between acute and chronic toxicity, because the concentrations of the metals in a mixture may have a large influence on the combined effect. Most data are based on studies with freshwater organisms.

Interaction in acute toxicity tests

The results from acute toxicity tests with relatively high (often lethal) metal concentrations indicated that metals were generally additive in their action. This means that the toxicity of a mixture can be predicted with the concentration-addition model. In this model, the contribution of each metal is expressed as "toxic unit", this being the ratio of the aqueous concentration to the effective concentration (usually the LC50): C / L(E)C50. The toxicity of the mixture can then be predicted by simple addition of the toxic units. Although the above conclusion is mainly based on studies with fish, it is assumed that the concentration-addition model can also be applied to other aquatic organisms.

Interaction in chronic toxicity tests

Chronic toxicity tests using relatively low (sublethal) metal concentrations have been conducted with crustaceans (water fleas, crabs) and fish; the total number of chronic studies is much smaller than the number of acute toxicity studies. The chronic studies are summarized below.

In life cycle tests in which the water flea Daphnia magna was exposed to mixtures of Zn, As, Cd, Cr, Cu, Hg, Ni and Pb, the observed effect was always in good agreement with the effect predicted by the concentration-addition model. The tests were conducted in hard Lake IJssel water (hardness 200 $mg.l^{-1}$). In similar life cycle tests, exposure of D. magna to mixtures of Zn and Cd, Zn and Hg, and Cd and Hg caused significant decreases in the reproductive success of D. magna at concentrations which had no effect when presented alone. The tests were conducted in soft Lake Superior water (hardness 45 $mg.l^{-1}$). Life cycle tests in which the water flea Ceriodaphnia dubia was exposed to a mixture of As, Cd, Cr, Cu, Hg and Pb (no Zn) indicated that the metals were additive in their effect on survival and reproduction, while 3-month tests with the fathead minnow Pimephales promelas showed a less than additive action between the metals. The results of life cycle tests with P. promelas (exposed to Zn alone or to a mixture of Zn, Cd and Cu) and with the flagfish Jordanella floridae (exposed to Zn alone or to a mixture of Zn and Cd) showed that the chronic toxicity of the mixtures was little, if at all, greater than the toxicity of zinc alone on survival and/or reproduction.

Finally, in tests with the marine crab Rhithropanopeus harrisii in seawater, mixtures of Zn and Pb were generally antagonistic in their effect on larval development; the combined effect was dependent on the concentrations tested.

In conclusion, it is stated that the data for water fleas strongly suggest a (strictly) additive action of metals, whereas the data for fish strongly indicate a less than additive action on exposure to relatively low (sublethal) metal concentrations. No or insufficient data are available for other organisms. For this reason, it is assumed, mainly on the basis of the results of acute toxicity tests, that the concentration-addition model is generally also suitable for predicting the combined action of metals at relatively low exposure concentrations.

Toxicity to microbial populations in sediments

The effect of zinc on the activity of microbial populations present in freshwater sediments (including Rhine River sediment), especially the mineralization of specific substrates, has been investigated in laboratory tests with sediment slurries. The substrates were added in minute amounts (1^{-4} $\mu g.l^{-1}$ of slurry) to simulate the natural situation as accurately as possible. The results show that the effect of zinc is strongly dependent on the substrate presented, and that small amounts of added zinc are sufficient to cause effects on microbial activity (at least shortly after addition), despite high background levels of zinc in the sediment. The following examples illustrate this.

In sediment with a background level of 200 mg $Zn.kg^{-1}$ dry weight, IC50 values of > 1000, 170 and 20 $mg.kg^{-1}$ dry weight were found for the mineralization of acetate, chloroform and 4-monochlorophenol (4-MCP), respectively, based on the added concentration (IC50: the concentration which causes 50 % inhibition of the first-order mineralization rate of the substrate). The IC10s for the mineralization of chloroform and 4-MCP were 53 and 8 $mg.kg^{-1}$ dry weight (added concentration), respectively; the IC10 for acetate mineralization was not reported. In similar tests with Rhine river sediment with a background level of 800 mg $Zn.kg^{-1}$ dry weight, IC10 values of 700 and 11 $mg.kg^{-1}$ dry weight (added zinc) were found for the mineralization of chloroform. The Rhine sediments were from the same location but collected in different years. The results of the tests with Rhine sediment further show that the background zinc in the sediment also contributes to the effect of zinc, albeit much less than the added soluble zinc.

5.3. ECOTOXICITY - TERRRESTRIAL ORGANISMS

The data in this section refer to microorganisms (microbe-mediated processes in soil) and invertebrates. For data concerning agricultural crops and livestock the reader is referred to Section 5.4.

5.3.1. Accumulation

The capacity of an organism to accumulate or concentrate a substance from the soil is commonly expressed in a "concentration factor", the ratio of the concentration of the substance in the organism to its concentration in the soil: CF = Corg / Cs. (The term "bioconcentration factor" (BCF) is usually only used for accumulation from the compartment water)

Invertebrates

Earthworms

By far the most data on the accumulation of zinc in invertebrates refer to earthworms, an important group of soil organisms. The data come primarily from field studies in which earthworms and soil samples were collected from a variety of uncontaminated and contaminated soils. The CFs calculated for earthworms range from 0.01 to 100, the majority of the values being > 1. These values are based on dry weight of worms. The CFs calculated as fresh weight are about a factor of seven times lower (15 % dry matter). Based on these CFs it is concluded that zinc is concentrated from the soil by earthworms (CF > 1), even at high soil zinc levels. The concentration factor decreases with increasing soil zinc level, but only at extremely high zinc levels (> 1000 $mg.kg^{-1}$ dry weight) do earthworms not concentrate zinc.

In uncontaminated soils, the zinc levels in common earthworm species, such as Lumbricus rubellus and Allolobophora caliginosa, generally range from 400 to 700 $mg.kg^{-1}$ dry weight (equivalent to 60-100 $mg.kg^{-1}$ fresh weight), but both lower and higher values have been reported, for example, levels up to 2000 $mg.kg^{-1}$ dry weight in A. caliginosa collected from Dutch agricultural soils which had not been treated with compost (zinc content up to 209 $mg.kg^{-1}$ dry weight). Worms from contaminated soils, such as compost-or sewage sludge-treated soils or soils in industrial or mining areas, often contain > 1000 mg $Zn.kg^{-1}$ dry weight (> 150 $mg.kg^{-1}$ fresh weight). In the Netherlands, levels up to 3500 $mg.kg^{-1}$ dry weight (500 $mg.kg^{-1}$ fresh weight) have been measured in adults of the earthworm L. rubellus collected in the vicinity of the zinc-smelter complex in North Brabant (de Kempen). Several field studies have shown that the zinc concentration in earthworms is determined not only by the zinc content of the soil but also by general soil characteristics (abiotic factors), principally the pH and the CEC (cation exchange capacity). The zinc concentration in worms increases with decreasing pH and CEC. The CEC is a measure of the adsorption capacity of the soil, which is determined by its clay and organic matter (OM) contents, among other factors.

The data on the accumulation of zinc in earthworms collected from compost- or sewage sludge-amended soils indicate that the bioavailability of zinc from such "organic substrates" is low. For example, the concentration in adults of L. rubellus from a sandy soil which had been annually treated with 18 tonnes of sewage sludge per hectare for several years was only 50 % higher than the concentration in worms from the same, untreated soil (800 compared to 530 $mg.kg^{-1}$ dry weight). The mean zinc level in the top 15 cm of the treated soil was 259 $mg.kg^{-1}$ dry weight, more than 10 times higher than that in the top 15 cm of the untreated soil (20 $mg.kg^{-1}$ dry weight).

Arthropods

CF values ranging from about 0.3 to 3.0 have been reported for a wide variety of arthropods (wood lice, springtails, beetles, mites, centipedes, and spiders); these values were calculated from the zinc levels in the organisms and those in the soil or litter layer from which they were collected. Based on these data it is concluded that zinc is not or scarcely concentrated by these organisms. It should be noted that the data are very limited (except for wood lice), and that the majority of the organisms was collected from contaminated soils with a high zinc content (900 or 1,670 $mg.kg^{-1}$).

Vertebrates

A field study conducted around the zinc smelter complex in North Brabant (de Kempen) found that the zinc levels in the liver and kidneys of moles (Talpa europea) from polluted sites were somewhat higher than those in the liver and kidneys of controls, but the differences were at most a factor of 4. The zinc concentration in the moles appeared to be related to the concentration in earthworms (their main food source) rather than to that in the soil. A field study conducted in the immediate vicinity of highways in the United States found that small mammals, including both herbivorous and carnivorous species, from unpolluted locations had zinc levels ranging from 83 to 117 $mg.kg^{-1}$ dry weight, and those from polluted sites levels from 51 to 146 $mg.kg^{-1}$ dry weight. The differences were generally very small, both between the different locations and between the different species.

The slight increase in the zinc concentrations observed in these field studies is in accordance with the homeostatic mechanism in mammals for the maintenance of whole-body zinc mentioned in Section 5.1.

5.3.2. Toxicity

Data on the effect of zinc on microbe-mediated processes and invertebrates in soil are summarized in Tables 2.1. and 2.2 of the Appendix "Ecotoxicity". In the selection and processing of the literature, priority was given to long-term tests resulting in NOEC values, because these values are preferably used in the derivation of a recommended value for the "maximum tolerable concentration". However, a NOEC could not be derived from a number of microbial tests, so that a number of effect concentrations such as EC50 values have also been included in Table 2.1. In addition, tests were selected on the basis of reported soil characteristics, specifically clay content and organic matter (OM) content, to enable conversion of the experimentally determined toxicity values to normalized values, in accordance with van de Meent et al. (1990) and Denneman and Van Gestel (1990). The normalized values give an estimate of the (no-)effect concentration of zinc in a "standard soil" containing 25 % clay (particles < 2 μm) and 10 % OM. For the equation used to calculate the normalized values, the reader is referred to the Appendix. If possible, the results in the table, both the experimentally determined and the normalized toxicity values, are expressed as nominal (added) zinc concentration as well as total zinc concentration (background concentration plus added concentration). Although it is not always clear from the literature consulted, it is assumed that the values reported in both tables are based on the zinc content of dry soil (mg $Zn.kg^{-1}$ dry weight).

Only the experimentally determined NOEC and EC50 values are reported in the text below.

Micro organisms (Appendix "Ecotoxicity", Table 2.1)

The data on the effect of zinc on microbe-mediated processes in soil included in Table 2.1 of the Appendix refer to short- and long-term tests. The normalized NOEC values printed in **bold** type in this table have been used in the derivation of a maximum tolerable concentration (see 5.5). Tests in which carbon mineralization (respiration), nitrogen mineralization (including ammonification and nitrification) or mineralization of a specific substrate was determined after a single application of soluble inorganic zinc salts ($ZnSO_4$ or $ZnCl_2$) to the soil have resulted in EC50 and NOEC values of 400-8000 $mg.kg^{-1}$ and 10-3000 $mg.kg^{-1}$ (added zinc), respectively. The activity was determined one week to 1.5 years after application of zinc to the soil. The two lowest NOEC values, 10 and 12 $mg.kg^{-1}$ (added zinc) are from tests conducted in a loamy sand (pH 6.0, 1 % OM, 2 % clay; parameter: nitrification) and a silt loam (pH 6.9, 2 % OM, 44 % clay; parameter: respiration). The NOECs based on the total zinc concentration (background plus added concentration) in these soils were 17 and 19 $mg.kg^{-1}$, respectively. It should be noted that in one test, conducted in a loamy sand (pH 4.9, 4 % OM, 5 % clay), respiration was affected by the addition of as little as 10 mg $Zn.kg^{-1}$ (13 mg total $Zn.kg^{-1}$). In comparative tests conducted in a sandy loam (3 % OM, 17 % clay), the addition of $ZnCO_3$ resulted in the following NOECs for nitrogen mineralization: 1,000 $mg.kg^{-1}$ for both ammonification and nitrification at pH 7.4, and $\geq$ 10,000 $mg.kg^{-1}$ for both ammonification and nitrification at pH 8.5. Tests with $ZnSO_4$ in the same soil resulted in NOECs of 1,000 and 100 $mg.kg^{-1}$ for ammonification (at pH 6.2) and nitrification (at pH 7.0), respectively. These values are also based on added zinc.

Tests in which the activity of one or more enzymes (amylase, arylsulphatase, cellulase, phosphatase, protease, urease, xylanase) was measured 1-5 hours to 1-1.5 years after the addition of $ZnCl_2$ or $ZnSO_4$ resulted in EC50 and NOEC values of 45 -4,390 and 32 - $\geq$ 1,000 $mg.kg^{-1}$ (added zinc), respectively. The lowest NOEC is from two tests in which the urease activity was measured in unspecified soils having the same pH (9.0) and similar OM (6 % and 9 %) and clay (30 % and 42 %) content. The background levels in these two soils were not reported.

In the study by Doelman and Haanstra (1983) in which zinc was added to samples of 5 different Dutch soils (as solid $ZnCl_2$), the EC50s for enzyme activities measured shortly after addition were in most tests higher than the EC50s reported in the table, which were measured 1-1.5 years after addition. The maximum difference (for each enzyme activity in the same soil) was a factor of 20. The reason for the lower toxicity shortly after the addition of $ZnCl_2$ is probably that the $ZnCl_2$ was poorly dissolved in the soil water at that time. With regard to soil respiration, the data are contradictory. In about half the tests toxicity was also lower shortly after the addition of zinc, whereas in the other half a greater effect was observed on respiration. In the latter case, the soil had (usually partially) regained its respiratory capacity.

On the basis of the data included in Table 2.1, the effect of the soil characteristics reported therein (pH, % OM, % clay) on the toxicity of zinc cannot be even qualitatively determined. The influence of a given soil characteristic on zinc toxicity depends both on the soil concerned (in other words, on the total of soil characteristics) and on the parameter investigated. A clear example of this is the study by Doelman and Haanstra (1983), which found a different "most sensitive" soil for different parameters. The data do, however, indicate that toxicity tends to decrease with increasing pH and increasing OM and clay content of the soil, but there are clear deviations from this picture.

Additional data on microbe-mediated processes

In addition to the effects of zinc (and other metals) on microbe-mediated processes, earlier reviews (Doelman and Haanstra, 1983; Babick and Stolzky, 1985; Doelman, 1985) also considered effects on numbers and diversity of particular groups of microorganisms. Most data in these reviews concern relatively short-term tests in which effects were measured after exposure times ranging from a few hours to a few weeks. The data reviewed by Doelman (1985) indicate that zinc concentrations of the order of 10, 10-1,000, and 1,000-10,000 $mg.kg^{-1}$ "never", "sometimes" and "usually" produce effects on respiration, nitrogen mineralization and nitrification; this is generally in good agreement with the data in Table 2.1 of the Appendix.

Treatment of a sandy loam with domestic or industrial sewage sludge, which increased the soil zinc level from 24 to 26-172 $mg.kg^{-1}$ dry weight, caused a temporary decrease in nitrification. At the highest concentration (148 mg added $Zn.kg^{-1}$ dry weight), nitrification was completely inhibited during the first 3 weeks, but was unaffected 6 weeks after the sludge application. Amendment of this soil with relatively clean domestic sewage sludge to which the chlorides of Zn, Cd, Cr, Cu and Pb had been added caused greater inhibition of nitrification than treatment with industrial sewage sludge without additions. This study shows that soluble inorganic metal salts are more toxic than metals present in sludge.

The effect of zinc on the mineralization of acetate by soil microorganisms has been investigated in laboratory experiments. Mineralization was measured in soil suspensions consisting of 10 g fresh soil and 10 ml sterilized groundwater. The amount of acetate added was very small (1 $\mu g.l^{-1}$ suspension), to simulate the natural situation as accurately as possible. The soil samples were collected from the topsoil (0-20 cm) or the subsoil (below 100 cm) of different Dutch soil types. Tests with top- and subsoil of a calcareous soil (pH-KCl 7-8, OM 1-2 %, clay ca 1 %, zinc concentration 12-43 $mg.kg^{-1}$ dry weight) produced EC10 values of 303 and 59 $mg.kg^{-1}$ dry weight, respectively. The IC10 in the subsoil was 39 $mg.kg^{-1}$ dry weight; that in the topsoil could not be calculated (EC10: the toxicant concentration which causes 10 % inhibition of mineralization after a given incubation period. IC10: the toxicant concentration which causes 10 % inhibition of the first-order mineralization rate). In tests with top- and subsoil of an acid soil (pH 3-4, OM 0.3-4 %, clay ca 1 %, zinc concentration 4-6 $mg.kg^{-1}$ dry weight), both EC10 and EC10 values were much higher than in the calcareous soil (> 1,000 $mg.kg^{-1}$ dry weight), despite a lower adsorption capacity and lower pH. According to the authors, one possible explanation for this difference is the formation of ZnOH+ in the alkaline soil; this form of zinc is possibly more toxic than Zn2+. Another possible explanation is that the microbial populations present in the acid soil are less sensitive to zinc. According to the authors, this would be in accordance with the relative insensitivity of microbial populations in acidic soils reported by other authors. Additional tests with sandy subsoil samples resulted in IC10 values of between 50 and 700 $mg.kg^{-1}$ dry weight. The IC10 and EC10 values are based on total zinc concentrations.

Invertebrates (Appendix "Ecotoxicity", Table 2.2)

Tests with invertebrates, varying in duration from 2 to 20 weeks, are summarized in Table 2.2 of the Appendix. The normalized NOEC values printed in bold type in this table have been used in the derivation of a maximum tolerable concentration (see 5.5).

Tests with the earthworm Eisenia fetida have resulted in NOEC values (with regard to survival, growth and/or reproduction) of 250 to 2500 mg.kg^{-1} dry weight. In these tests, the worms were exposed in clean soil covered with an approximately equal amount of manure or sludge to which zinc had been added. The reported NOEC values are based on the zinc concentration in the manure or sludge (added zinc). A test with E. fetida in "OECD artificial soil" (10 % sphagnum peat, 20 % kaolin clay, 69 % fine sand, and 1 % CaCO3; pH 6.0 ± 0.5) resulted in an EC50 and NOEC of 660 and 200 mg.kg^{-1}, respectively. Tests with snails and crustaceans resulted in NOECs of 300 and 400 mg.kg^{-1} of feed, respectively.

In almost all these tests zinc was added to the substrate as a readily soluble inorganic salt. Two tests with E. fetida used ZnCO3 and ZnO, respectively.

Additional data on invertebrates

In an accumulation study in which adults of the earthworm L. rubellus were maintained for 4 weeks in soil samples collected from former mining areas, no effect on survival was observed despite their high to very high metal concentrations (including 417 to 183,000 mg.kg^{-1} dry weight).

In acute toxicity studies with adults of the copepod Parastenocaris germanica, a crustacean commonly found in Dutch groundwater, 96-hr LC50 values of 1,700 and 2,300 μg.l^{-1} were found in normoxic and hypoxic water, respectively. These values are within the range reported for aquatic crustaceans. The tests were conducted in buffered tap water (hardness 80 mg.l^{-1}; pH 6.8); the test compound was $ZnSO_4.7H_2O$.

5.4. TOXICITY TO AGRICULTURAL CROPS AND LIVESTOCK

5.4.1. Agricultural crops

Zinc is an essential element for plants, as it is for animals. Signs of zinc deficiency such as yellowing of leaves (chlorosis) and growth inhibition occur at soil zinc concentrations of 1 to 10 mg.kg^{-1}. The zinc concentration required to prevent zinc deficiency depends on the availability of zinc for plant uptake in soil. Zinc availability is estimated to range from about 1 % in clay soils to 5-10 % in sandy soils, related to the concentration of zinc present in the soil solution; this depends, among other things, on the pH, the adsorption capacity, and the presence of other divalent cations which influence the uptake of zinc. Zinc availability in soils is estimated on the basis of extraction experiments, for example, with dilute nitric acid (HNO_3) as the extractant. Zinc deficiency can occur particularly in soils with very high calcium carbonate and phosphorus contents (Malle, 1989; see also Chapter 3).

In the 1970s, the Institute for Soil Fertility, in the Netherlands, conducted much research into the possible consequences of the increasing agricultural use of substrates contaminated with heavy metals, such as river sediments, sewage sludge and compost. These substrates usually have a relatively high clay (mineral soil particles < 2 um) or organic matter content. In the section on "Accumulation" especially, but also in the section on "Toxicity", much attention has been paid to research with such substrates (referred to as "organic substrates" hereafter), because of their application to Dutch soils and possible effects on fodder and food crops grown on these soils. This means that this section does not give a complete survey of the available literature on the effects of zinc on agricultural crops. This is certainly true of foreign publications.

Accumulation

The zinc concentrations in plants grown in zinc-deficient soils range from 1 to 20 $mg.kg^{-1}$ dry weight. Normal values are in the range of 20 to 100 $mg.kg^{-1}$ dry weight, but certain plant species may contain up to 500 $mg.kg^{-1}$ dry weight without detrimental effects (Malle, 1989).

The accumulation of zinc (and other metals) by plants from organic substrates has been investigated in a number of Dutch studies involving a range of crops. These studies are summarized below.

In pot experiments, various food crops (potato, carrot, radish, lettuce, wheat) and English ryegrass were grown in four aged dredged-sediment soils originating from the Rotterdam harbours (700-1,660 mg $Zn.kg^{-1}$ dry weight; 6-12 % OM; texture: 19-52 % particles < 16 μm) and in two reference fluvial soils (60 and 80 mg $Zn.kg^{-1}$ dry weight; 1 and 5 % OM; 26 and 55 % particles < 16 μm, respectively).

The crops were planted as seeds or seedlings, and harvested when mature. In all cases, the edible parts of the plants grown in the dredged-sediment soils had higher zinc concentrations than did those of the crops grown in the reference soils; the maximum difference (per plant species) was a factor of 2 to 3, which is similar to the factor of 2 to 4 found for the mean zinc concentrations in the aboveground parts. Only wheat showed a 15-fold increase in the mean zinc concentration in the aboveground parts. The zinc concentrations in potato tubers, carrot roots, radish roots and lettuce tops were similar: 1.5-4.5 mg.kg^{-1} fresh weight in the crops grown on the reference soils and 3-10 mg.kg^{-1} fresh weight in those grown on the dredged-sediment soils. The corresponding concentrations in wheat grains were significantly higher, namely, 20-22 and 50-100 mg.kg^{-1} fresh weight, respectively. Grass contained 46-49 and 152-204 mg.kg^{-1} dry weight, respectively (factor for conversion from dry to fresh weight was not reported), corresponding to 7-8 and 25-34 mg.kg^{-1} fresh weight, assuming a dry matter content of 16 %. On a dry weight basis, potato tubers and carrot roots had the lowest zinc concentrations, and lettuce and grass had the highest levels (Smilde et al., 1982).

In similar pot experiments, the concentrations of zinc in lettuce, radish (roots) and wheat (grains) grown in dredged-sediment soils containing 725-1,300 mg Zn.kg^{-1} dry weight were also higher than those in the same plants grown in the reference soil (115 mg.kg^{-1} dry weight); the maximum difference (per plant species) was a factor of 2 to 5. Radish roots and lettuce had similar zinc concentrations: 1.5 and 4 mg.kg^{-1} fresh weight, respectively, in the plants grown in the reference soil, and 3.5-7.0 and 5.5-10 mg.kg^{-1} fresh weight, respectively, in those grown in the dredged-sediment soils. The corresponding concentrations in wheat grains were also significantly higher in this study: 50 and 60-100 mg.kg^{-1} fresh weight, respectively. The zinc content of four successive harvested crops of a metal-resistant variety of red fescue grass grown on these dredged-sediment soils was not increased: 33-43 mg.kg^{-1} dry weight compared to 27-46 mg.kg^{-1} dry weight in the reference soil (factor for conversion from dry to fresh weight was not reported),corresponding to 5-7 and 4-8 mg.kg^{-1} fresh weight, respectively, assuming a dry matter content of 16 %. The concentration in radish tops and roots, lettuce, and wheat straw and grains was related to the total Zn concentration in the soil and (especially) to the DTPA-extractable zinc concentration (Van Driel et al., 1985).

The accumulation of zinc by ryegrass was investigated in pot experiments with soil from grassland to which sewage sludge had been applied for 6 successive years at an annual rate of 0, 6 and 18 tonnes per hectare, as a function of pH. The zinc concentrations in the homogenized soil samples (from the top 15 cm of soil) were 17, 50 and 165 mg.kg^{-1} dry weight, respectively. The zinc levels in the grass were 30-50, 30-100 and 50-200 mg.kg^{-1} dry weight (difference at similar pH: a factor of 2 to 4), corresponding to 5-8, 5-17 and 8-33 mg.kg^{-1} fresh weight, respectively, assuming a dry matter content of 16 %. At every soil zinc level, the concentration in the plants increased with decreasing pH (Dijkshoorn et al., 1981). In an earlier experiment (Dijkshoorn et al., 1979) in which zinc was added to the soil as an inorganic salt, zinc availability was about two times higher than in the study with the sewage sludge-amended soil; the relative effect of pH was similar in the two studies (Dijkshoorn et al., 1981).

The accumulation of inorganic zinc and that of zinc present in organic substrates were also compared in pot experiments with maize plants. The zinc levels in plants grown for 7 weeks in a "Hartsells fsl, a Typic Hapludult" soil (no further details were given) to which solid ZnSO4 had been added - resulting in concentrations of 12, 60 or 240 mg Zn.kg^{-1} of soil - were 40-145, 190-1,640 and 365-3,070 mg.kg^{-1}. The concentrations in the plants decreased with increasing pH (5.5 to 7.0) and, within the same experiment, with time after the addition of zinc (lower concentration in successive crops). The latter observation indicates that zinc availability decreases with time, due to increasing adsorption of zinc onto soil particles. Plants grown for 7 weeks in soil treated with compost or sewage sludge, resulting in concentrations of 120-350 mg Zn.kg^{-1} of total substrate, contained 55-325 mg Zn.kg^{-1}. At a zinc level of 1,400 mg.kg^{-1} of total substrate, added as sewage sludge, the zinc concentration in the plants ranged from 340 to 510 mg.kg^{-1} (Mortvedt and Giordano, 1975). Given the zinc concentrations in various crops measured in the other experiments, the levels reported by Mortvedt and Giordano (1975) are probably based on dry weight, but this was not stated.

The above data clearly indicate that zinc present in organic substrates such as sludge and compost is less available for uptake by plants than inorganic (ionogenic) zinc. The zinc concentrations in edible parts of food crops grown on dredged-sediment soils having zinc levels ranging from about 700 to 1,500 mg.kg^{-1} dry weight were only slightly higher (a factor of 5 at most) than those in the same crops grown on reference soils with zinc levels of 60 to 115 mg.kg^{-1} dry weight: 3-10 compared to 1.5-4.5 mg.kg^{-1} fresh weight. Wheat grains had in both cases significantly higher zinc levels. The corresponding zinc concentrations in grass were 4-34 and 5-8 mg.kg^{-1} fresh weight, respectively (increased also by a factor of 5 at most). The data further show that the amount of zinc accumulated by crop plants decreases with increasing pH; this is true for both inorganic zinc and zinc incorporated in organic substrates. When zinc is added to soil as an inorganic salt, its availability may decrease with time, due to increasing adsorption onto soil particles.

Additional data on the accumulation of zinc and other heavy metals by plants from soil, whether or not treated with substrates such as sludge and compost, can be found in Smilde and Van Driel (1979), De Haan and Lubbers (1983) and Cottenie et al. (1983), among others.

Toxicity

NOEC values (Appendix "Ecotoxicity", Table 2.3)

Pot experiments resulting in NOEC values which have been used in the derivation of a maximum tolerable concentration for zinc in soil are summarized in Table 2.3 of the Appendix. The NOEC values in this table have been selected on the basis of the reported soil characteristics (% clay and % OM) required for the calculation of normalized NOEC values (see introduction to 5.3.2.) and on the basis of the use of soluble, inorganic zinc salts. The normalized NOECs (added Zn) printed in **bold** type in this table have been used in deriving a maximum tolerable concentration (see 5.5). Only the experimentally determined NOEC values (added Zn) are reported in the text below.

In the pot experiments included in the table, each species of crop was grown on a number of different soils, and the yield was determined after harvesting. This resulted in the following NOEC values: 50 - $\geq$ 250 mg.kg^{-1} for alfalfa, 10 -$\geq$ 250 mg.kg^{-1} for maize, 10 - $\geq$ 250 mg.kg^{-1} for lettuce (MacLean, 1974), and 100 - $\geq$ 800 mg.kg^{-1} for oats (De Haan et al., 1985).

The form of zinc added was $ZnSO_4$ or $Zn(CH_3COO)_2$. The yield of alfalfa, maize and lecttuce was usually not affected at an added zinc concentration of 250 $mg.kg^{-1}$ to soil, whether or not the soil had been pretreated with 500 mg P kg^{-1}, as $CaH_4(PO_4)_2.H_2O$. In some of the experiments a lower NOEC (higher toxicity) was observed in the absence of phosphorus, but in one of the experiments with maize the NOEC was much higher in the absence of phosphorus ($\geq$ 250 $mg.kg^{-1}$) than in its presence (10 $mg.kg^{-1}$). The lowest NOECs for alfalfa, maize and lettuce were observed in a sandy loam soil having a low pH (ca 5). All pot experiments with oats were performed in soils of relatively low pH (4.6 to 5.6); these experiments indicate that toxicity tends to decrease with increasing clay or organic matter content.

Additional data

Pot experiments with maize plants in a "Hartsells fsl, a Typic Hapludult soil (no further details were given) resulted in NOEC values of 60 $mg.kg^{-1}$ at pH 5.3-6.0 and 240 $mg.kg^{-1}$ at pH 6.5-7.0 (added zinc). The lowest effect concentrations were 240 and 1,400 $mg.kg^{-1}$, respectively. The form of zinc added was $ZnSO_4$. In a pot experiment conducted at pH 5.5, the yield reduction of the second maize crop was smaller than that of the first, indicating that zinc availability decreases with time, due to increasing adsorption of zinc onto soil particles. This is consistent with the decreasing zinc concentrations observed in successive crops. In the same study, treatment of the soil with sewage sludge or compost did not reduce the maize yield at zinc levels of up to 1,400 $mg.kg^{-1}$ of substrate, indicating that zinc present in organic substrates is less available for uptake by plants than inorganic zinc (Mortvedt and Giordano, 1975).

In a study with French beans grown in different soils to which $Zn(NO_3)_2$ had been added, the yield of beans grown in sandy soils of pH-KCl 5.0 was reduced by 20 % at a zinc concentration of 80 $mg.kg^{-1}$ dry weight, whereas the yield of beans grown in sandy soils of pH-KCl 6.0 was not reduced at zinc concentrations of up to 300 $mg.kg^{-1}$ dry weight. No yield reduction was observed at zinc concentrations of up to 500 $mg.kg^{-1}$ dry weight in calcareous clay soils having a pH-KCl of 7.4 (Lexmond, 1989).

It is apparent from a review that, in most soils, added zinc concentrations of at least 150 to 250 $mg.kg^{-1}$ are required to cause adverse effects in sensitive agricultural crops. These figures are largely based on experiments with soluble, inorganic salts of zinc. The lowest effect concentration reported in this review (50 $mg.kg^{-1}$) was obtained in the pot experiments with alfalfa and lettuce (MacLean, 1974) included in Table 2.3 of the Appendix. The effect concentration increases with increasing soil organic matter and/or clay content and with increasing pH. For example, the effect concentrations in humus-rich sandy soils and in clay soils are greater than 250 mg $Zn.kg^{-1}$ (Smilde, 1976). These data are in good agreement with the data in the review by Taylor et al. (1982). The results reported in this review show that the Swiss chard and lettuce yields started to decrease with added zinc concentrations of 65-120 $mg.kg^{-1}$ of soil, at pH values up to 6; at pH 7, yield reduction occurred only when at least 250 mg $Zn.kg^{-1}$ was added to the soil. A pH-dependent effect on the yield was also found for other species of crops. The form in which the zinc was added in these experiments was not reported (Taylor et al., 1982).

In pot and field experiments in which various crops (beans, tomato, maize, cotton and/or grass) were grown on a contaminated sandy soil from the vicinity of a zinc smelter in Belgium, plant growth was generally strongly inhibited by the zinc present in the soil. The addition of both lime and phosphorus was required for growth to return to normal. The sandy soil had a pH of 4.3, an organic matter content of 6 % and an acetic acid-extractable zinc concentration of 170 $mg.kg^{-1}$ (Smilde et al., 1974).

The toxicity of zinc (and other metals) present in organic substrates such as dredged harbour sediments and sewage sludge has been investigated in a number of Dutch studies with a wide variety of crops. These studies are summarized below.

In pot experiments, various food crops (potato, carrot, radish, lettuce, wheat) and English ryegrass were grown on four aged dredged-sediment soils originating from the Rotterdam harbours (700-1,660 mg $Zn.kg^{-1}$ dry weight; 6-14 % OM; texture: 19-52 % particles < 16 μm) and in two reference fluvial soils (60 and 80 mg $Zn.kg^{-1}$ dry weight; 1 % and 5 % OM; texture: 26 % and 55 % particles < 16 μm, respectively). The crops were planted as seeds or seedlings, and harvested when mature. No relationship was found between the dry matter yield of edible parts and the soil zinc concentration (Smilde et al., 1982).

Similar pot experiments with lettuce, radish, wheat and red fescue grass also found no clear relationship between the dry matter yield (absolute and relative) and the soil zinc level (115 $mg.kg^{-1}$ dry weight in the reference soil, and 725-1,000 $mg.kg^{-1}$ dry weight in three dredged-sediment soils). In a fourth dredged-sediment soil, however, the high zinc concentration, 1,300 mg $Zn.kg^{-1}$ dry weight, was possibly partly responsible for the yield reduction of radish roots and wheat grains, but this soil also had high levels of other metals, including cadmium and mercury. The dredged-sediment soils and the reference soil had similar percentages of OM (5-10 %) and clay (27-31 %) (Van Driel et al., 1985).
In pot experiments, the yield of maize and grass grown on domestic sewage sludge (35 % OM, 4 % clay, pH-KCl 7.3) was greater than that of the same plants grown in sandy soil or fluvial clay, despite higher metal concentrations in the sewage sludge, including 2,300 mg Zn, 900 mg Cu, and 500 mg Pb kg^{-1} dry weight. In an additional pot experiment with this sewage sludge to which zinc acetate had been added, poplar showed growth inhibition at a zinc concentration of 2,000 $mg.kg^{-1}$ dry weight in the first year after treatment (NOEC: 1,500 mg $Zn.kg^{-1}$ dry weight) and at a concentration of 1,000 mg $Zn.kg^{-1}$ dry weight in the second year (NOEC: 500 mg $Zn.kg^{-1}$ dry weight). An added zinc concentration of 3,000 $mg.kg^{-1}$ dry weight did produce chlorosis but did not reduce the yield of wheat, the crop grown after poplar on this sludge (preliminary results; Smilde, 1976).
No effect on the yield of ryegrass was observed in pot experiments with soil from grassland to which sewage sludge had been applied for 6 successive years at an annual rate of 0, 6 or 18 tonnes per hectare. The zinc concentrations in the soil samples were 17, 50 and 165 $mg.kg^{-1}$ dry weight, respectively (Dijkshoorn et al., 1981).

MacNicol and Beckett (1985) have summarized the literature data on "critical" tissue concentrations of zinc in agricultural crops at which yield was reduced by at least 10 %. In one study the critical concentration was 60 $mg.kg^{-1}$ dry weight, and $\geq$ 100 $mg.kg^{-1}$ dry weight in the others. These data are based on a large number of studies with widely differing crops and experimental conditions. The review of the literature by Smilde (1976) reports toxic effects at zinc concentrations in the aboveground parts of 300 $mg.kg^{-1}$ or more, also based on a number of studies. It is not clear whether the zinc levels in crops reported by Smilde were expressed on a fresh weight or dry weight basis.

The above data clearly indicate that zinc present in organic substrates such as sludge and compost is considerably less toxic to plants than inorganic (ionogenic) zinc. They further show that zinc toxicity generally decreases with increasing pH and increasing organic matter and clay contents. Finally, the bioavailability of inorganic zinc may decrease with time, due to increasing adsorption onto soil particles.

Interaction of zinc with other metals

Zinc and other divalent cations, including metals, are subject to interaction processes, for example, at the root surface where these interactions can affect uptake. For example, a study on the interaction between zinc and cadmium found that the cadmium concentration in spinach grown in a calcareous clay soil to which $Cd(NO_3)_2$ had been added was about ten times higher than that in spinach grown in the same soil supplemented with $Zn(NO_3)_2$ as well as $Cd(NO_3)_2$, in a Zn-Cd ratio of 100:1. This study further found that the higher the pH, the greater is the effect of zinc on the uptake (or: on the translocation to aboveground parts) of cadmium (Lexmond, 1991).

Other Dutch studies also indicate that the accumulation of cadmium depends on the Zn-Cd ratio in the soil. Conflicting literature data on the significance of this interaction point to the fact that other soil characteristics also play a role.

In pot experiments with sewage sludge supplemented with zinc and other metals (as acetate), certain combinations of metals caused growth depression of poplar at concentrations that had no effect when added alone (preliminary results; Smilde, 1976).

5.4.2. Livestock

Given the low level of accumulation of zinc in fodder crops such as grass (see 5.3) and in mammals, and in view of the low toxicity of zinc to mammals, the data concerning livestock have not been extensively treated in this section. Because of this and because of the fact that relatively many data concern cases from veterinary practice and/or are dated, considerable use has been made of reviews (Taylor et al., 1982; Hansard, 1983; Humphreys, 1988; L&V/VROM, 1987).

Recommended zinc intake

The minimum zinc requirements in animal feeds have been estimated at 20-40, 25-50 and 50-100 mg.kg^{-1} of diet for poultry, ruminants and pigs, respectively, if deficiency symptoms are to be avoided (Taylor et al., 1982; Hansard, 1983; L&V/VROM, 1987). The exact levels depend on both physiological factors such as the nutritional status, and dietary factors such as the phytic acid and calcium contents of the feed. All these factors influence the kinetics of zinc, including the degree of absorption from the gastrointestinal tract (see 5.1.1). According to Vreman (1986), ruminants, unlike pigs, can degrade zinc-phytate complexes, so increasing the availability of zinc to these animals; this is reflected in the minimum requirements mentioned above. This author mentioned a zinc requirement for farm animals (species not specified) of 10-50 mg.kg^{-1} dry weight in the total diet, provided that zinc is present in a form that can be readily absorbed.

In the Netherlands, the addition of zinc to animal feeds is permitted for all animal species, up to a maximum concentration of 250 mg.kg^{-1} dry weight (total, i.e. background plus added) (Productschap Veevoeder, 1992).

The proportion of zinc absorbed from the diet has been estimated to range from 5 % to 40 %. It has been estimated that 80 % to 95 % of the zinc present in feed is excreted by cattle and 98 % to 99 % by pigs (Vreman, 1986; L&V/VROM, 1987).

Zinc deficiency is rare under normal conditions. Signs of zinc deficiency in ruminants include reduced feed intake, languor, swollen feet, salivation, skin lesions and rough coat. In males, these symptoms are preceded by effects on the sexual organs.

Accumulation

The zinc concentrations in domesticated wild ducks (Anas platyrhynchos) fed a normal diet were found to range from 15 mg.kg^{-1} fresh weight in muscle to 90 mg.kg^{-1} fresh weight in the pancreas. Administration of diets containing lethal zinc levels (3000-12,000 mg.kg^{-1} dry weight; added as the carbonate) increased the zinc concentrations in the pancreas, liver, testes and kidneys especially (six to 30 times higher levels, depending on the dietary level and tissue). The zinc concentration in muscle was increased only about twofold, regardless of the dose level (Gasaway and Buss, 1972).

In ruminants, relatively high zinc concentrations occur in bone, liver, pancreas, muscle, kidneys, spleen and adrenal glands (Hansard, 1983). The normal values for zinc concentrations in tissues and tissue fluids of cattle and horses are 10-75 mg.kg^{-1} fresh weight in internal organs (liver, kidney, pancreas, spleen), 1-2 mg.l^{-1} in blood, and 3-5 mg.l^{-1} in milk (van Ulsen, 1973; Hansard, 1983; Humphreys, 1988; Spierenburg et al., 1988). A study of the concentrations of zinc and other metals in liver and kidneys of cattle from farms in the vicinity of the zinc smelters in North Brabant (de Kempen) found that the cadmium and lead concentrations were higher than in the control group, but the zinc levels did not differ from controls. The mean zinc concentration in liver and kidney (all animals combined) was 47 and 22 mg.kg^{-1} fresh weight, respectively (Spierenburg et al., 1988). In a study in which yearling dairy cattle received zinc in their drinking water (0.11 (control), 0.25, 0.5 and 1 mg Zn.l^{-1}, added as $ZnSO_4.7H_2O$), the highest dose level caused a 13-fold increase in the zinc concentration in the pancreas: 1834 mg.kg^{-1} dry weight compared to 139 mg.kg^{-1} dry weight in the control group. The zinc levels in liver and kidney increased by a factor of 6. The concentration of zinc in muscle was not elevated (Smith, 1980).

Severe acute zinc poisoning has been described in two yearling cattle, caused by the ingestion of zinc-containing paint. The zinc concentration in the liver (1,960 and 2,060 mg.kg^{-1} dry weight) and kidneys (625 and 720 mg.kg^{-1} dry weight) was 15 and 10 times higher than the normal value of 135 (range 70-250) and 80 (40-140) mg.kg^{-1} dry weight, respectively. The zinc level in the faeces of the poisoned animals was tens of times higher than that in clinically healthy animals: 6,000-13,000 mg.kg^{-1} dry weight compared to a mean normal concentration of 220 mg.kg^{-1} dry weight; the blood (serum) concentration increased only severalfold (van Ulsen, 1973). The liver and kidney zinc concentrations in the poisoned animals correspond to 600 and 150 mg.kg^{-1} fresh weight, respectively, assuming a dry matter content of 30 % for liver and 20 % for kidneys (Spierenburg et al., 1988). Several foals with symptoms which were ascribed to excessive dietary zinc intake (see under "Toxicity") had zinc concentrations in the liver ranging from 400 to 1,100 $mg.kg^{-1}$ dry weight, 10 to 25 times higher than the concentration in the control group (Hoskam et al., 1982).

Toxicity

Poultry maintained on diets containing up to about 1,000 mg $Zn.kg^{-1}$ showed no visual signs of zinc toxicity such as growth retardation, but histo(patho)logical changes in the pancreas were observed at a dietary level of 1,000 mg $Zn.kg^{-1}$. Dietary levels of about 1,500 and 3,000 mg $Zn.kg^{-1}$ or more caused growth depression and mortality, respectively (Gasaway and Bush, 1972; Dewar et al., 1983). Diets containing levels of zinc in the range of 750 to 1,000 $mg.kg^{-1}$ had adverse effects, including on growth and reproduction, in sheep, pigs and cattle, but ingestion of such concentrations does not, by definition, lead to visual effects, certainly not in adult animals. Exposure of poultry or mammals to zinc via drinking water or a liquid diet has resulted in effects at dose levels in the range of 50 to 500 mg $Zn.l^{-1}$ (Hansard, 1983; Humphreys, 1988). A case study by Pickup et al. (1954) suggests that the consumption of drinking water with a zinc level of 6-8 $mg.l^{-1}$ was possibly the cause of chronic constipation in dairy cattle, accompanied by a fall in milk yield, during the stable-feeding period. Elevated levels of zinc in the diet decrease the intestinal absorption of other essential elements such as copper, iron and calcium. At dietary levels of 500 mg $Zn.kg^{-1}$ or more, this can lead to secondary deficiency symptoms (Hansard, 1983; Humphreys, 1988).

Additional data concerning a few common farm animals are given below, mainly based on secondary literature sources. It has been assumed that all data relate to feeding studies, and that the exposure levels reported in these sources are expressed in mg $Zn.kg^{-1}$ of feed, although this was not always clearly stated. Some studies also do not give the exposure duration.

Poultry

Two- to six-week studies with chicks resulted in histo(patho)logical changes in the pancreas at dietary zinc levels of 1,000 $mg.kg^{-1}$ or more, in growth depression (partly due to reduced feed intake) and gizzard erosion at levels of 2,000 $mg.kg^{-1}$ or more, and in mortality at concentrations of 4,000 $mg.kg^{-1}$ and higher. Zinc was added as zinc oxide to feeds with zinc contents of 75 to 100 $mg.kg^{-1}$ (Dewar et al., 1983). In a two-month feeding study with domesticated wild ducks (Anas platyrhynchos), zinc dietary levels in the range of 3,000 to 12,000 $mg.kg^{-1}$ dry weight resulted in, among other things, a dose-related reduction in feed intake and body weight, effects on organ weights (pancreas, liver, gonads), and signs of paralysis; mortality ranged from 66 % at 3,000 mg $Zn.kg^{-1}$ to 100 % in the other dosage groups. Each group consisted of 6 mature animals (3 males and 3 females); zinc was added as zinc carbonate (Gasaway and Bush, 1972).

Sheep

In a 5-month feeding study, ewes which were 0 to 6 weeks pregnant were maintained on diets containing 0, 30, 150 or 750 mg $Zn.kg^{-1}$, added as ZnSO4. The highest dietary level significantly reduced feed consumption, efficiency of feed utilization, weight gain and the plasma copper concentration. Numerous abortions and perinatal deaths also occurred (incidence: 85 % compared to 21 % in the control group). The copper concentration in the liver of nonviable lambs (defined as a lamb which was aborted, stillborn, or died for any reason within 7 days of birth) from this zinc group was decreased about tenfold, whereas the zinc concentration was increased tenfold, compared with the concentrations in the liver of nonviable lambs from the control group. The only effect at a dietary zinc level of 150 $mg.kg^{-1}$ was a significantly increased zinc concentration in the liver of the lambs (four times higher than the control value). In a similar experiment, the pregnant ewes were maintained on diets supplemented with 750 mg $Zn.kg^{-1}$ and 2.5 or 10 mg Cu kg^{-1}. The highest copper supplement prevented the development of secondary copper deficiency in both ewes and lambs, but failed to prevent the adverse effects of high zinc on weight, feed consumption, efficiency of feed utilization and lamb viability. The incidence of non-viable lambs was 100 % and 93 %, respectively, compared to 18 % in the control group (2.5 mg Cu plus 30 mg $Zn.kg^{-1}$ of feed). The dietary zinc level of 750 $mg.kg^{-1}$ corresponds to 20 mg $Zn.kg^{-1}$ body weight per day at the start of the experiment, falling to 10 mg $Zn.kg^{-1}$ body weight per day at its end (Campbell and Mills, 1979). In other studies with nonpregnant ewes, effects were observed only at dietary zinc levels of > 1,000 $mg.kg^{-1}$ (Ott et al., 1966; cited in Campbell and Mills, 1979).

Pigs

Hoskam et al. (1982) referred to a feeding study with weanling pigs fed on a diet containing 1,000 mg $Zn.kg^{-1}$ (as zinc lactate). Appetite depression and stiffness, resulting in lameness and deaths, occurred after 2 months of exposure.

Cattle

In two studies with cattle, reduced feed intake and weight loss or reduced growth were observed at dietary zinc levels of 900 and 1,000 $mg.kg^{-1}$, respectively; the exposure duration in the latter study was 18 months. Lactating cows fed on a diet containing 1,300 mg $Zn.kg^{-1}$ only showed elevated zinc concentrations in the blood (Hansard, 1983). In a 2-month study using young cattle (steers and heifers) drinking water containing 0.11 (control), 0.25, 0.5 and 1.0 mg $Zn.l^{-1}$ (added as $ZnSO_4.7H_2O$) was given to 5 animals per group. There was a resulting dose-related decrease in water consumption, especially at the start of the period, and reduced weight gains at the 2 highest zinc levels. In addition, dose-related histopathological changes were observed in the pancreas (Smith, 1980).

Horses

In a case study near a zinc smelter in North Brabant (Budel), the symptoms noted in foals (stiffening of the leg joints and neck, and emaciation) were ascribed to the high zinc concentrations in grass. The grass fed to the afflicted animals had a mean zinc level of 1,250 (range 500-2,200) $mg.kg^{-1}$ dry weight, a factor of 3 higher than the mean reference concentration of about 400 (300-500) $mg.kg^{-1}$ dry weight (Hoskam et al., 1982). These concentrations correspond to 210 (85-365) and 65 (50-85) mg $Zn.kg^{-1}$ fresh weight. It should be noted that the reference concentration for grass mentioned here is very high compared with the reference levels in grass (5-8 $mg.kg^{-1}$ fresh weight) reported in the section on "Agricultural crops". This indicates contamination of the grass by atmospheric zinc deposition.

5.5. TOXICOLOGICAL RECOMMENDED LEVELS

5.5.1. Humans

Zinc is an essential trace element. The Netherlands Food and Nutrition Board recommends a dietary zinc intake of 4 mg per day for infants, increasing to 9-11 mg per day for adolescents and adults, 12-15 mg per day for pregnant women and 16-20 mg per day for lactating women. These recommendations are in accord with the zinc intakes recommended by other countries, the ranges usually reported being 0.15-0.20 $mg.kg^{-1}$ body weight per day for adults, 0.15-0.35 $mg.kg^{-1}$ body weight per day for pregnant women and 0.25-0.45 $mg.kg^{-1}$ body weight per day for lactating women. It should be noted that, under normal conditions (with a varied diet), these dietary recommendations are probably overestimates of the true requirement for zinc; this is true especially of the upper limits of the ranges mentioned. However, more precise estimates of the dietary zinc requirement cannot be given because the intestinal absorption of zinc depends on both nutritional and physiological factors.

In vitro tests have shown that zinc is potentially genotoxic. Whether or not this manifests itself depends on the chemical form of zinc (a determinant of the intracellular concentration) and the sensitivity of the cell population. In theory, the formation of complexes of zinc with protein will counteract a genotoxic action in vivo. This is consistent with the mostly negative results (that is, no effects) obtained in in vivo genotoxicity studies. There are no indications that zinc is carcinogenic in man following exposure by natural routes, but adequate carcinogenicity studies are lacking. Zinc **deficiency** may cause, among other things, impaired reproductive capacity and adverse effects in the offspring (both embryo- and/or foetotoxic and teratogenic effects); these effects are also known to occur in humans. In oral animal studies, exposure to excessive zinc resulted also in embryo-foetotoxic effects, but not in teratogenic effects.

Oral exposure

Both the human and experimental animal data are too limited to permit the derivation of a well-founded "maximum acceptable daily intake" (defined as that amount of a substance, expressed on a body weight basis, which may be ingested daily by humans during a lifetime without causing any harmful effects on health). In clinical studies, no ill effects on health were observed after administration of doses of up to about 600 mg $ZnSO_4$ per day (240 mg Zn per day, equivalent to 4 mg $Zn.kg^{-1}$ body weight per day) for several months. In these studies the daily dose was taken as a single dose or as 2 or 3 portions spread over the day. On the basis of these clinical studies, the Joint WHO/FAO Committee on Food Additives estimated in 1982 a "provisional maximum tolerable daily intake" for humans of 0.3-1 mg $Zn.kg^{-1}$ body weight (WHO, 1982). It should be noted that a few effects were observed in the clinical studies in subjects who received dosages of between 1 and 4 mg $Zn.kg^{-1}$ body weight per day, namely, gastrointestinal disturbances and a decrease in HDL-cholesterol levels. However, it is open to question whether these effects will also occur when similar levels of zinc are consumed through the diet, considering the difference in the chemical form of zinc (most of the zinc in the diet is incorporated in foodstuffs) and exposure regimen (more spread over the day). No data have been published since 1982 which give cause for a revision of the maximum tolerable daily intake estimated by the WHO.

Inhalation exposure

The limited data make it impossible to derive a maximum acceptable airborne concentration.

5.5.2. Aquatic and terrestrial environments

For the derivation of toxicologically maximum tolerable concentrations from single-species toxicity data, the RIVM preferably uses the Aldenberg/Slob modification of the extrapolation method according to Van Straalen. For the principle of the original method, the reader is referred to Van Straalen and Denneman (1989). For more information about the modification used in this integrated criteria document, see Aldenberg and Slob (1991). Both methods calculate the 95 % "protection level" from NOEC values. The 95 % protection level is that environmental concentration at which, theoretically, 95 % of the species in an ecosystem is fully protected (that is, the concentration at which the NOEC of 95 % of the species within an ecosystem is not exceeded). The Aldenberg/Slob modification employs a calculation method other than the original Van Straalen method. Moreover, two values are calculated for the 95 % protection level using the Aldenberg/Slob modification, namely, the 5th percentile (lower 95 % confidence limit) and the 50th percentile (lower 50 % confidence limit). The 50th percentile is taken to be the "maximum tolerable concentration" (MTC).

In the results from the Aldenberg/Slob method presented in Table 5.1 (aquatic environment) and Table 5.2 (terrestrial environment), one input datum was invariably used per species of organism or per type of microbe-mediated process, in accordance with Sloof (1992), as follows:

- If two or more NOEC values for a given species (for example, the water flea Daphnia magna) were available for the same toxicological parameter (for example, reproduction), the geometric mean has been used as input datum in the extrapolation procedure. If two or more parameters were studied, the geometric mean has been determined for each parameter, if applicable; the lowest of these values has been used as input datum.
- If two or more NOEC values for a given microbe-mediated process (for example, soil respiration) were available, the geometric mean has been used as input datum.

Fresh water (Table 5.1)

The NOEC values included in Table 1.1 of the Appendix "Ecotoxicity" have been used in the derivation of the maximum tolerable concentration for fresh water, resulting in a 5th percentile and 50th percentile for the 95 % protection level of 1.2 and 4.9 $\mu g.l^{-1}$, respectively (a total of 21 input data).

The calculated values are based on total zinc concentrations in the test waters used and would therefore in principle also have to be taken to be total zinc. However, about half the tests (algae, sponges) employed test waters prepared in the laboratory, often with deionized water. In the other tests (molluscs, crustaceans, insects, fish) natural waters were usually used, which in most cases were pretreated (filtration, sterilization, and/or mixing with filtered and deionized water), to remove suspended particles and/or organic matter. Most tests were moreover performed in flow-through systems. For these reasons, it is assumed that by far the greater part of the zinc present in the test waters was in dissolved form. Therefore, the values mentioned above are considered to be dissolved zinc.

For comparison, two additional calculations for the 95 % protection level have been performed using the Aldenberg/Slob method, one based on the lowest NOEC per species (a total of 21 input data) and one based on "all" NOECs (lowest value per test, a total of 48 input data). These calculations yielded a 5th percentile of 1.0 and 3.2 $\mu g.l^{-1}$*, respectively, and a 50th percentile of 4.0 and 6.5* $\mu g.l^{-1}$*, respectively, that is, similar to the results reported in Table 5.1. In the RIVM report "Desire for Levels" (van de Meent et al., 1990), the 50th percentile calculated for the 95 % protection level for zinc in fresh water was 1.6* $\mu g.l^{-1}$*. This value differs from the 50th percentile of 4.9* $\mu g.l^{-1}$ *mentioned above. The discrepancy between these two values is attributable to the following factors:*

- *In this integrated criteria document, the NOEC values included in "Desire for Levels" (which came partly from secondary literature sources) were re-evaluated using the original literature. This re-evaluation is based on the premises for the derivation of NOEC values currently used within the RIVM; this has led to a revision of a number of values. (These premises will be published in a RIVM report in 1993)*
- *The total number of NOEC values has been considerably increased, both for organisms for which one or more values were already available in "Desire for Levels" and for organisms for which this was not yet the case.*
- *Different extrapolation methods were employed in calculating the 95 % protection level. In "Desire for Levels", for example, the NOEC values were clustered, with only one NOEC being used as an input datum for each taxonomical group. This reduced the number of input data to 8 only. The methods also differ in the way in which the 95 % protection level is calculated.*

Salt water (Table 5.2)

The NOEC values included in Table 1.1 of the Appendix "Ecotoxicity" have been used in the derivation of the maximum tolerable concentration for salt water, resulting in a 5th percentile and 95th percentile for the 95 % protection level of 2.7 and 7.0 $\mu g.l^{-1}$, respectively (a total of 28 input data).

Approximately half of the NOEC values used come from tests with algae. The algal tests employed laboratory-prepared salt water or, in most cases, seawater which was filtered or sterilized before use. Analogous to the reasoning followed for fresh water, the above values are also considered to be **dissolved** zinc.

For comparison, two additional calculations for the 95 % protection level have been performed using the Aldenberg/Slob method, one based on the lowest NOEC per species (a total of 28 input data) and one based on "all" NOECs (lowest value per test, a total of 52 input data). These calculations yielded a 5th percentile of 1.9 and 2.2 $\mu g.l^{-1}$, respectively, and a 50th percentile of 5.2 and 4.5 $\mu g.l^{-1}$, respectively, that is, similar to the results reported in Table 5.1.

Salt water and fresh water (combined)

The individual NOEC values and the calculated values for the 95 % protection level in fresh water or salt water indicate that there is little, if any, difference between the sensitivity of freshwater organisms and salwater organisms to zinc, in other words, between the toxicity of zinc in fresh and salt water. Calculation of the 95 % protection level from the NOEC values for both fresh water and saltwater organisms (combined) as indicated in Table 5.1 results in a 5th percentile and 50th percentile of 3.1 and 6.3 $\mu g.l^{-1}$, respectively (a total of 49 input data). The latter value, rounded to 6 $\mu g.l^{-1}$, is proposed as the maximum tolerable concentration (MTC) for **dissolved** zinc in surface water, both fresh and salt.

In the principal Dutch rivers (Rhine, Meuse), approximately 75 % of the zinc present is adsorbed on suspended solids and 25 % is dissolved (Chapter 4). Therefore a concentration of 6 $\mu g.l^{-1}$ dissolved zinc in these waters corresponds to 24 $\mu g.l^{-1}$ total zinc. Converted to "standard" surface water with a suspended matter content of 30 $mg.l^{-1}$ (in accordance with Stortelder, 1989), 6 $\mu g.l^{-1}$ dissolved zinc corresponds to 26 $\mu g.l^{-1}$ total zinc (the suspended matter has been normalized to 10 % organic carbon and 40 % clay). Using these data, a concentration of 25 $\mu g.l^{-1}$ is proposed as the MTC for total zinc in Dutch surface waters (fresh water). It should be noted that these waters are characterized by high hardness (about 200 $mg.l^{-1}$, as $CaCO_3$) and high pH (about 8). In soft and acidic surface waters, most of the zinc is present in dissolved form. In such waters the MTC based on dissolved zinc (6 $\mu g.l^{-1}$) must therefore be taken as the starting point for the risk assessment.

Sediments

Ecotoxicological data for sediment are not available, with the exception of a few microbial tests in freshwater sediments. For a consideration of this environmental compartment, the reader is referred to Section 7.3 (Environmental quality objectives) in which a MTC for this compartment is proposed using an equilibrium-partitioning approach.

Soil (Table 5.2)

The derivation of a maximum tolerable concentration for soil is based on the normalized NOEC values printed in **bold** type in Table 2.1 (microbe-mediated processes), 2.2 (invertebrates) and 2.3 (plants) of the Appendix "Ecotoxicity". The Aldenberg/Slob method has been applied to the data on microbe-mediated processes on the one hand, and on invertebrates and plants (single species tests) on the other. This distinction has been made because of the possible difference in sensitivity between functional parameters (such as soil respiration involving a variety of organisms) and species-specific parameters such as growth and reproduction, in analogy with Denneman and van Gestel (1990). With regard to microbe-mediated processes, a distinction has been made in the calculation of the 95 % protection level between NOECs based on added zinc and NOECs based on total zinc. Such a distinction could not be made for the group "invertebrates/plants" because only NOECs based on added zinc are available for invertebrates. Finally, NOECs "≥" (from tests in which no effect was observed at the highest test concentration) have also been included in the calculations. This applies to a relatively small proportion of the NOECs for microbial processes, and a relatively large proportion of the NOECs for plants.

Taking the NOECs for microbe-mediated processes, the 5th percentile and 50th percentile for the 95 % protection level are found to be 4 mg and 29 mg added Zn.kg^{-1} dry weight, respectively (a total of 10 input data), and 10 mg and 70 mg total Zn.kg^{-1} dry weight, respectively (a total of 8 input data). It should be noted that the latter two values, although calculated on the basis of total zinc, are considered to be an approximation of the added zinc concentration, because the amount added was usually many times greater than the background concentration. Taking the NOEC values for invertebrates/plants, the 5th percentile and 50th percentile for the 95 % protection level are found to be 41 mg and 128 mg added Zn.kg^{-1} dry weight, respectively (a total of 7 input data).

The results indicate that if a relatively small amount of zinc is added to the "standard" soil (of the order of 30 to 70 mg.kg^{-1} dry weight), adverse effects on microbe-mediated processes can be expected. The results further show that microbial processes are more sensitive to zinc than individual species. It should be noted that the range of the input data for microbe-mediated processes is greater than that for invertebrates/plants (In the method employed, the greater the range of the input data, the greater is the extrapolation factor).

It is evident from the results that the 50th percentile for the 95 % protection level of the most sensitive "group" (microbe-mediated processes, 30-70 mg.kg^{-1} dry weight) cannot be recommended as the MTC for the standard soil (25 % clay, 10 % OM), since the reference value (at the same time desirable level) for this soil is 140 mg Zn.kg^{-1} dry weight (see also Chapter 1). This concentration has been derived from the empirical relationship between the zinc concentration and the clay and organic matter contents established in relatively unpolluted areas, as follows: reference value = [50 + 1.5 (2x % clay + % OM] mg.kg^{-1} dry weight.

The relatively low 95 % protection level for microbe-mediated processes (low relative to the reference value) can be explained as follows:

- The NOECs are based on tests with readily soluble zinc salts ($ZnCl_2$ or $ZnSO_4$). The bioavailability of dissolved zinc and exchangeable zinc (reversibly sorbed onto soil particles) is higher than that of the zinc already present "naturally" in soil (almost irreversibly included in mineral (clay) particles). It should be noted, however, that the irreversibly bound fraction is strongly dependent on soil type.

- In the correction for soil type, a formula has been employed which is based on background concentrations measured in nature reserves. It has been assumed that this formula is independent of the zinc concentration range in soil and therefore is suitable not only for normalizing background concentrations at given percentages of clay and organic matter, but also for the normalization of higher concentrations, whether or not producing an effect. However, the studies in which identical tests were performed in different soils, particularly the study of effects of zinc on microbe-mediated processes by Doelman and Haanstra (1983), show that the differences between the corresponding NOEC values are not eliminated by conversion to the standard soil. In the most extreme cases the normalized values for the corresponding NOECs differ by a factor of 5 to 15. Based on these data it is concluded that the soil-type correction formula used is in fact not suitable for the normalization of concentrations when the added zinc concentration is many times greater than the background level. This argues in favour of omitting or revising the soil-type correction in the evaluation of the risks of (greatly) elevated zinc levels in soil.
- In most studies which have investigated the effects of zinc on microbe- mediated processes, only a few concentrations of the metal were tested (3 at most), with a large difference (a factor of 10) between successive test concentrations. This means that accurate determination of NOEC values was not possible and that the variation in the observed NOEC values was possibly greater than the variation which would occur in the "true" NOEC values.

Additions or concentrations of inorganic zinc at which adverse effects on microbial processes can be expected (30-70 mg.kg^{-1} dry weight) will seldom cause yield reduction of agricultural crops, even not in acidic soils with low percentages of clay and OM (sandy soils, (silty) clay loam soils; pH < 6.0). Yield reduction will, however, occur in such (for plants) sensitive soils at additions or concentrations ranging from about 50 to 100 mg Zn.kg^{-1} dry weight, whereas in most soils this will usually occur only at zinc concentrations of about 150-250 mg.kg^{-1} dry weight or even higher. The yield of plants grown in sludge or compost or in soils amended with such substrates will be reduced only at zinc levels of at least 500 mg.kg^{-1} dry weight (Concentrations of 50, 150, 250 and 500 mg Zn.kg^{-1} dry weight correspond to 150, 450, 750 and 1,500 kg $Zn.ha^{-1}$, assuming a homogeneous distribution throughout the top 20 cm of soil and a soil density of 1,500 kg m-3). Crops grown in soils with zinc concentrations which do not reduce yields will also not accumulate zinc to levels that are harmful to farm animals.

In conclusion, it is stated that the evaluation of the risks of zinc concentrations in soil should be based on the soil type-related reference value. Relatively small increases in zinc levels in sensitive soils may cause effects, especially on microbe-mediated processes. It is not possible to identify sensitive soil types on the basis of a limited number of soil characteristics (pH, % OM, % clay), at least not with regard to effects on microbial processes. For this reason, based on the reference value for the relevant soil type, only a slight increase in the zinc concentration is considered to be toxicologically tolerable, of the order of a few tens of $mg.kg^{-1}$ dry weight.

For comparison, a few additional calculations have been performed using the Aldenberg/Slob method. For microbe-mediated processes, using the lowest NOEC for each type of process resulted in a 5th percentile of 0.5 mg added Zn and 0.5 mg total $Zn.kg^{-1}$ dry weight (in this case: the same result) and a 50th percentile of 6 mg added Zn and 10 mg total $Zn.kg^{-1}$ dry weight. Using all NOEC values printed in ***bold*** *type in Table 2.1 of the Appendix, the 5th percentile values were found to be 5 mg added Zn and 10 mg total $Zn.kg^{-1}$ dry weight, and the 50th percentile values were 15 mg added Zn and 35 mg total $Zn.kg^{-1}$ dry weight. For invertebrates/plants, using the lowest NOEC for each species and all NOEC values printed in* ***bold*** *type in Tables 2.2. and 2.3) resulted in a 5th percentile of 0.4 mg and 39 mg added $Zn.kg^{-1}$ dry weight, respectively, and a 50th percentile of 7 mg and 63 mg added $Zn.kg^{-1}$ dry weight, respectively.*

In the RIVM report "Desire for Levels" (van de Meent et al., 1990) an "indicative" MTC of 0.7 mg $Zn.kg^{-1}$ was derived using a modification of the EPA extrapolation method, as follows:

lowest normalized NOEC (7.3 $mg.kg^{-1}$) divided by 10. This normalized NOEC was based on the test with the invertebrate Arion ater, for which an experimental NOEC of 10 $mg.kg^{-1}$ was determined based on the parameter feed consumption. This test has also been included in this report (Appendix

"Ecotoxicity", Table 2.2) but, because of a different interpretation, a much higher NOEC (300 mg.kg^{-1}) was now determined, based on the parameters survival and body weight as well as feed consumption. A general discussion on the risk approach to natural substances (including essential trace elements such as zinc) has been included in "Desire for Levels", but no conclusion was reached concerning toxicologically maximum tolerable concentrations for such substances (at least no quantification for the individual substances). It was however stated that the natural background concentrations of these elements probably play a role in the natural selection of species and that for this reason a MTC below the background concentration might be undesirable. Therefore it was suggested that a soil-related approach to such substances is desirable.

Table 5.1. Calculated 95 % protection levels of zinc (μg.l^{-1}) in surface water, based on the extrapolation method according to Aldenberg and Slob (1991)

Input	*log-logistic distribution*	*Result* *5th percentile concentration*	 *50th percentile concentration*
***Freshwater organisms** [2]*			
1 NOEC per species, *incl. geometric means [1]* *(m = 21)*	*yes*	*1.2*	*4.9*
***Saltwater organisms** [3]*			
1 NOEC per species, *incl. geometric means [1]* *(m = 28)*	*no**	*2.7*	*7.0*
Fresh- and saltwater organisms (combined)			
1 NOEC per species, *incl. geometric means [1]* *(m = 49)*	*yes*	*3.1*	*6.3*

m = Number of input data

* *According to the Kolmogrov/Smirnov test, it is unlikely ($p<0.05$) that the input data used are distributed log-logistically (in other words, that the input data are a random sample from an (infinite) series of NOEC values with a log-logistic distribution). The extrapolation method, however, assumes the distribution to be log-logistic.*

[1] *If two or more NOEC values for a given species were available for the same toxicological parameter, the geometric mean has been used as input datum in the extrapolation procedure. If two or more parameters were tested, the geometric mean has been determined for each parameter, if applicable; the lowest of these values has been used as input datum.*

[2] *For a summary of all NOECs on which the input data are based, the reader is referred to Table 1.1 of the Appendix "Ecotoxicity".*

[3] *For a summary of all NOECs on which the input data are based, see Table 1.3 of the Appendix "Ecotoxicity".*

Table 5.2. *Calculated 95 % protection levels of zinc (mg.kg^{-1} dry weight) in the standard soil (25 % clay; 10 % organic matter), based on the extrapolation method according to Aldenberg and Slob (1991)*

Input	*log-logistic distribution*	*Result* *5th percentile concentration*	 *50th percentile concentration*
***Microbe-mediated processes** [2]*			
1 NOEC per process, incl. geometric means [1]	*yes* (m=10)* *yes* (m= 8)*	*4 (added Zn)* *10 (total Zn)*	*29 (added Zn)* *70 (total Zn)*
***Invertebrates/plants** [3]*			
1 NOEC per species, incl. geometric means [1]	*yes* (m= 7)*	*41 (added Zn)*	*128 (added Zn)*

m = Number of input data

* *According to the Kolmogrov/Smirnov test, it is likely ($p<0.05$) that the input data used are distributed log-logistically (in other words, that the input data are a random sample from an (infinite) series of NOEC values with a log-logistic distribution). The extrapolation method is based on this assumption.*

[1] If two or more NOEC values were available for a given microbe-mediated process or for a given species (in the latter case for the same toxicological parameter), the geometric mean has been used as input datum in the extrapolation procedure. If two or more parameters were tested for the same species, the geometric mean has been determined for each parameter, if applicable; the lowest of these values has been used as input datum.

[2] For a summary of all NOECs (including the values on which the input data are based), the reader is referred to Table 2.1 of the Appendix "Ecotoxicity".

[3] For a summary of all NOECS (including the values on which the input data are based), see Tables 2.2. and 2.3 of the Appendix "Ecotoxicity".

6. EMISSION CONTROL

This chapter describes the autonomous developments in zinc emissions, that is, developments which occur as a result of existing policy. Where, in view of the magnitude of the emissions and the state of technology, significant emission reductions can be achieved with additional specific measures to be taken, these measures are discussed. Where possible, cost estimates are given. Also, the financial consequences for the galvanizing and rayon production industries are examined in more detail.

6.1. INDUSTRIAL SOURCES

6.1.1. Zinc production

Autonomous developments

Autonomous developments in the production lead to a change in the zinc emissions to air resulting from the "plan of action for reducing acidic process emissions", water and waste. In consultation with the district Water Board concerned, a plan has been drawn up for the phased cleanup of the wastewater situation. This plan will possibly result in a reduction of the zinc input to surface water from about 15 tonnes per year, averaged over the years 1985-1990, to about 3 tonnes per year by the late 1990s. This reduction assumes a continuation of the industrial activities at the present level and a successful jarosite treatment process. The wastewater cleanup will consist of the replacement of a drainage sewer system, canalization of a rivulet, and a new wastewater treatment plant based on sulphate-reducing bacteria, in addition to the existing wastewater treatment.

For the processing of the principal waste, jarosite (a priority waste product), the intention has been declared to employ the so-called oxygen melting process with aftertreatment of the resulting slag in a SIRO oxygen-lance furnace. This oxygen melting process can also dispose of jarosite stored in the past, and stored gypsum and "cellar ashes" originating from the earlier hot-dip process. The capital investment for the jarosite processing plant (with a capacity of 200,000 tonnes of dry jarosite per year) is estimated to be at least about Dfl. 354 million (± 20 %), and the gross annual operating costs are at least Dfl. 52 million.

The estimated operating loss can be as much as Dfl. 21 million per year.

6.1.2. Zinc alloys

Autonomous developments

Besides the melting furnaces, the casting ladles and casting machines are actually the main sources of atmospheric zinc emissions in brass production. At present, these emission sources receive limited treatment. However, one of the companies has recently partly covered its melting furnaces, fitted them with an exhaust system and connected them to the Luhr filter system, thereby greatly reducing (diffuse) emissions (obligatory under the Nuisance Act). The capital cost was estimated to be about Dfl. 50,000.- per furnace. The other company has applied for a permit for a new process, in which the melt no longer needs to be transported but is poured directly, thereby greatly reducing air emissions. Current emissions from melting furnaces and casting machines will also be regulated in this permit. The company expects to have the new process in operation within five years. The total zinc emissions to air from this industrial sector will, if the new process mentioned is also implemented, be much less than 5 tonnes per year. In addition, research is currently under way into the usability of the filter cakes in the manufacturing process in the zinc- producing industry (company inf.).

Additional measures

It is clear that, in the short term, the air from the melting furnaces and casting machines can be exhausted and cleaned. Given the measured efficiency of the Luhr filter, drastic end-of-pipe measures for reducing zinc emissions seem unnecessary for the time being.

6.1.3. Zinc oxide production

Autonomous developments

In collaboration with the licensing authority, the companies involved in the zinc oxide production are currently engaged in setting up an engineering and administrative control system, which will include the checking of the quality of the cloth filters by taking continuous measurements. It is also expected that the cinders which at present are stored on site as waste will be processed abroad in the near future, at a cost of Dfl. 50.- to Dfl. 100.- per tonne (company inf.).

Additional measures

Additional measures can concentrate on the prevention of emissions during storage and packing, by exhausting the dust and, if possible, using the resulting exhaust as process air. In addition, it is advisable to examine whether cloth filters of a higher quality, or a better type of filter system, are available on the market, which can reduce the current residual emission of 10 $mg.m^{-3}$. It is known, for example, that the brass manufacturers also collect dust consisting chiefly of zinc oxide by using Luhr filters, and that the residual emissions are 0.1-4 $mg.m^{-3}$ at a comparable capacity. Such a filter system could imply a significant emission reduction.

6.1.4. Production of other zinc compounds

Autonomous developments

Given the relevance of the zinc emissions, only the manufacture of zinc-containing pesticides and zinc gluconates is considered in this subsection. One company discontinued the production of zineb in mid-1990, while the other company has installed a recovery unit (pellet reactor) to recover zinc from waste generated in the production of pesticides. It is expected that at least 90 % of the zinc will be recovered, so that the total zinc input to water from the production of zinc-containing pesticides will then be one tonne a year after mid-1990 (< 3 kg per day - a requirement for obtaining a WVO permit). In addition, a biological wastewater treatment plant (costing about f 12 million) has recently been put into operation, thereby reducing the zinc emission still further. Based on this biological treatment plant and assuming that the zinc recovery unit has an efficiency of > 90 %, it is expected that future zinc emissions will be 350 kg (3 $mg.l^{-1}$) per year at most (company inf.).

In the past few years, the zinc emissions to water from zinc gluconate production have fallen by about 50 % (to 900 kg per year), as a result of a number of internal measures and process modifications. It involved changing the rinsing procedure (blowing the drier clean so that the product is retained within the process), reducing the discharge of wet scrubber water to the sewer, installing double-coated filter cloths on both sides, and aiming for fewer production runs a year. The cost of the process modifications was about a few tens of thousands of guilders. In addition, the wastewater from the zinc gluconate production has been piped to an aerobic treatment plant since the end of 1990. It is expected that the emission to surface water will decrease further through binding of zinc to the sludge. Additional process-technical and/or -operational changes will also be implemented. On the other hand, the production of zinc gluconate will gradually be expanded. It is expected that future zinc emissions from zinc gluconate manufacturing will be about 0.6 tonne per year (company inf.).

6.1.5. Zinc-consuming industries

The principal zinc-consuming industries are discussed in alphabetical order in this subsection.

Ceramics industry

Additional measures

The atmospheric emissions from the ceramics industry can be substantially reduced by lowering the zinc concentration in glazes and frits (Beerkens, 1990). Other recommendations are the lessening of direct contact between flue gases, product improvement of the inlay, and lowering of the water content of the melt (Beerkens, 1990). Finally, air emissions can be reduced by employing cloth filters or electrostatic filters. A number of companies have already installed such filters in connection with emissions of other substances.

Metal surface treatments

Autonomous developments

Over a period of about 10 years, the metal products industry has cut its zinc discharges into water from about 130 tonnes in 1975 to 23.4 tonnes in 1985 by installing wastewater treatment systems (IMP-Water, 1984). However, reductions in zinc emissions to water have resulted in the creation of metal hydroxide sludge. This sludge must be treated as chemical waste and, since August 1989, it may no longer be exported. Since the beginning of 1990, it has been tipped on the C2 dump in the Maasvlakte. In view of the associated costs, the clean and process-integrated techniques which are currently being used on a limited scale become economically attractive. These techniques can cut both the volume of waste sludge and the emission to water.

Additional measures

For smaller establishments, relatively simple process-integrated measures suffice to reduce the emission into water to 20 kg of heavy metals per year (about 10 kg of zinc). They include curtailing the drag-out (longer drain times, tapping off drops and the like), one drag-out bath behind the process bath with direct return to the process bath, and not discharging concentrates. For medium-sized and large establishments, more drastic measures are necessary: additional drag-out and rinsing baths (direct return; cascade rinsing), recovery technology connected to a drag-out bath or treatment bath (electrolysis, reverse osmosis, electrodialysis), and treatment of the separate streams (production of processable monosludges) connected to a rinsing bath (microfiltration). The annual costs of the measures mentioned are on average about Dfl. 400.- per kg of metal removed, at a capital investment of Dfl. 1000.- per kg of metal removed. Furthermore, removal of zinc specifically from wastewater is under investigation. The annual remaining zinc emissions to water by the year 2000 are estimated at about 2.5 tonnes.

At present, most of the pickling baths are transported to Belgium, where a proportion is reprocessed to recover zinc and immobilized. Research is being carried out on alternative pickling baths which do not have to be replaced (Kroeze and Kroesen, 1990), and possibilities of extracting zinc from pickling baths are being studied.

Emissions during zinc spraying are determined especially by craftsmanship. It is therefore important that spraying on site, in particular, is done by the most experienced sprayers. However, if possible, spraying on site should be avoided. The use of isolating material (e.g. tents) and zinc collectors results in reduction in emissions. Exhaust and filter (cartridge) systems or water curtains can be installed in the booths in which zinc is sprayed. It is worth mentioning in this context that a company in Belgium recovered the cost of a filter system, about Dfl. 65,000.-within two years by selling the collected filter dust (zinc oxide).

The market situation of the galvanizing industry can be characterized as fairly good. It is a very labour-, moderately capital-, and fairly energy-intensive sector. The staying power of the sector is reasonably strong. Smaller establishments are financially more vulnerable.

Rayon production

Autonomous developments

The rayon industry is currently conducting research into the applicability of liquid membrane permeation (LMP) as a zinc removal and supply process. During the optimization phase of the process, a study was carried out to determine at which process settings an extraction efficiency of > 95 % for zinc can be achieved. The capital investment is estimated at Dfl. 9 million, and the annual costs at Dfl. 1.7 million. The capital outlay for another technique, the pellet reactor, is of the same order, but the annual costs are about Dfl. 2.6 million. However, a big disadvantage of the pellet reactor is that it does not discriminate between zinc and magnesium (of which about 200 $mg.l^{-1}$ are present in the wastewater stream) (company inf.). In addition, efforts are currently being made to modify the process operation in such a way that much less zinc is required. A pre-requisite of the zinc removal is that the recovered zinc be reused. The granting of a permit to dump the wastewater sludge from rayon production on the factory site depends upon an obligatory investigation into the possibility of bringing the zinc concentration in the wastewater sludge below the WCA (Chemical Waste Act) limit.

Additional measures

Before the formulation of any additional measures, the results of the research on the LMP process and the internal process modifications must first become available. However, it can be stated that the existing techniques are capable of reducing the zinc emission effectively (> 90 % reduction; < 2 tonnes of zinc) (company inf.).

The market situation of the rayon industry can be described as good, but vulnerable. The staying power of this sector can be characterized as strong.

Rubber production

Autonomous developments

The largest emitter is going to treat its waste water in the short term, in consultation with the government, the aim being a reduction in the zinc emission of about 95 %. This will result in a total zinc input to water of < 0.1 tonne per year in the long term.

Textile finishing

Additional measures

CUWVO has concluded that additional measures are necessary within the textile industry to reduce the latex residues, zinc, and possibly dithiocarbamates which are released when rubber backings are applied to carpets. The waste water can be treated by flocculation, sedimentation and filtration. This has already been implemented at a number of plants. The resulting effluent contains < 2 mg zinc per litre. Treatment of latex-containing waste water by flocculation, sedimentation and filtration costs approximately Dfl. 40.- to Dfl. 100.- per m^{-3} of treated water, or Dfl. 80.- to Dfl. 250.- per kg of sludge, labour and sludge transportation being the main cost items. The cost of disposing of the waste water as chemical waste varies between about Dfl. 300.- and Dfl. 600.- per m^{-3}. For the time being, complete replacement of high-zinc latex (gel type) by latex with a lower zinc content (non-gel type) in the carpet industry is not practicable from a product quality viewpoint.

6.1.6. Zinc-bearing raw materials

This subsection discusses emission control measures intended for industries which process zinc-bearing raw materials.

Phosphate ore

Autonomous developments

The source of the present input of heavy metals to the aquatic environment is the wet-chemical processing of phosphate ore. The discharges can be reduced by process modifications, by storing or reusing the phosphoric acid gypsum generated (a priority waste product) and by using phosphate ore with a lower content of heavy metals.

An improved process has recently become operational, which is expected to reduce also the zinc emissions into surface water. The covenant between the government and the fertilizer manufacturers mentions a zinc emission to surface water of 6.3 tonnes for the year 1995.

Iron and steel production

Autonomous developments

The primary iron and steel producer has committed itself to building a more effective dedusting and desulphurization plant for the sinter manufacture, which can cut the atmospheric zinc emissions by about 1.5 tonnes per year.

The costs of this measure are estimated at 200-300 million guilders, depending on the process chosen. In addition, research is being conducted into the treatment of the oxylime sludge stored in the past by an extraction process (which may create a new waste stream) (NOVEM, 1990) and of zinc-containing filtrate (van Deelen et al., 1989).

Power stations

Autonomous developments

The fitting of flue-gas desulphurization equipment to power stations is expected to cut the zinc emissions to the atmosphere by 50-90 %. The maximum air emission will be about 1.3 tonnes around the year 2000 (Meij and Koops, 1992).

The zinc contents of the by-products produced in the year 2000 are expected to be: 11 tonnes in bottom ash, 168 tonnes in fly ash, and less than 3 tonnes in gypsum. In addition, the introduction of coal gasification will produce ash with a zinc content of 34 tonnes per year.

Titanium dioxide ore

Autonomous developments
As of the beginning of 1990, titanium dioxide is produced by the so-called chlorine process, thereby reducing the zinc emission into water to about 4 tonnes per year (a reduction of about 85 % compared with the "old" situation).

6.2. NON-INDUSTRIAL SOURCES

6.2.1. Corrosion

Autonomous developments
The corrosion rate of zinc is determined by the SO_2 concentration in the atmosphere, among other factors. National Environmental Surveys II (RIVM, 1991) have estimated a reduction in the SO2 emissions from Dutch sources. However, because of uncertainty over the development of the foreign sources, it is estimated that the atmospheric SO_2 concentration will fall only slightly. The autonomous growth in galvanized surface area makes it likely that the corrosion term (4,000 tonnes a year) will change little as a result; however, a slight fall due to autonomous developments cannot be ruled out.

Additional measures
One of the main diffuse sources of zinc to the environment is the corrosion of galvanized structures which are exposed to the atmosphere. Alternatives to pure zinc as a material for protecting iron and steel from atmospheric corrosion have been marketed for several years. The driving force behind this is not concern about the diffusion of zinc to the environment so much as the demand for materials with a higher corrosion resistance (3 to 5 times the current level). The alternatives can be distinguished into zinc-containing and zinc-free materials. In any case, replacement of zinc by the latter type will lead to a reduction in the diffuse zinc pollution of the environment. However, zinc-containing alternatives will only lead to a reduction if less zinc is required for the higher (desired) corrosion resistance. It is not easy to replace zinc, because:

- zinc is a relatively cheap metal which provides good protection to ferrous metals (formation of zinc patina, i.e. sacrificial protection of iron);
- many coatings can be applied to galvanized steel (paints);
- a wide variety of substrates and surface configurations can be readily galvanized (Sharples, 1988).

In the development of alternatives, the above-mentioned advantages of zinc should be duly taken into account. In addition, the possibility of high environmental costs associated with the alternative in the form of wastewater treatment and the like must be considered. However, the alternative technology is already commercially available for a number of materials and techniques (Sharples, 1988), including:

- zinc-cobalt alloy
- zinc-nickel alloy
- phosphate/zinc-rich epoxyresin composites
- aluminium-containing coatings with an organic surface layer
- fluoropolymers

The zinc-cobalt and zinc-nickel alloys appear to offer the best prospects, especially because of the favourable cost-corrosion protection ratios. Of these two alloys, zinc-cobalt is the most attractive, because only a relatively simple process control is required, and use can be made of existing electrogalvanizing equipment (Sharples, 1989).

Research on zinc-cobalt and zinc-nickel alloys has been conducted in the Netherlands. It was found that a 10-15 μm layer of zinc-cobalt alloy (ca 1 % cobalt) can compete with a 50-80 μm hot-dipped zinc coating. Expressed in kilograms, this implies that 75 kg of zinc-cobalt alloy is equally effective in protecting a given surface area against corrosion as 500 kg of zinc applied by hot-dip galvanizing. One drawback of the zinc-cobalt alloy is that it does not lend itself to the widely used blue passivation. On the other hand, the less popular yellow passivation is possible, and provides both improved corrosion protection and a better base for paint compared with blue passivation. The use of cobalt is another negative aspect, giving rise to a (small) diffuse cobalt emission (GTO, 1989). The developers expect that, in the short term, the market acceptance of yellow passivation will increase and that 20 % at most of the hot-dip market can be taken over by zinc-cobalt alloys. This would imply a reduction in zinc emissions of about 15 to 20 %. One important consideration is that the government can accelerate and increase the market acceptance of yellow passivation through demonstration projects. The metal supports of crash barriers will be coated with zinc-cobalt alloys in the near future. The costs for zinc-cobalt coated metal are about 20 % higher than for hot-dip galvanized metal (company inf.). At present, the technique is used at Renault in France, among others.

Besides the development of alternatives to pure zinc, paint coatings on zinc layers are also increasingly used to enhance resistance to corrosion. A protective powder coating on galvanized steel adds about 100 % to the cost. Other conceivable alternatives to galvanized steel and rolled zinc are plastics, aluminium or other construction practices.

Since a large quantity of galvanized material is already exposed to the atmosphere in the Netherlands, much zinc will be lost to the environment through corrosion for decades (a few thousand tonnes per year) even when additional measures to control the corrosion are taken.

6.2.2. Agriculture

As a result of autonomous developments in **animal** manure, a reduction in the zinc emission can be expected in quantitative and qualitative terms. By adding the enzyme phytase to animal feed, resulting in enhanced absorption of minerals, the zinc concentration in manure could fall. Because of this, a decrease in the zinc content of animal feed by about 20-30 % is expected in the coming years.

Current efforts to curtail the use of **chemical fertilizers** include the giving of information, and the keeping of records on manure imposed by the government on farmers.

The use of **pesticides** is currently under great political pressure, in connection with the presence of particular residues in drinking water or drinking water collection areas, among other things. A substantial decrease in pesticide usage is expected as a result of government measures (Multi-year Plan for Crop Protection). The zinc-containing pesticides zineb, ziram and mancozeb are on provisional lists of pesticides to be eliminated in principle.

The use of **sewage sludge** as a fertilizer and organic soil conditioner in agriculture and horticulture is increasingly subject to restrictions. Because of selling problems and government policy on the dumping of waste, sewage sludge will increasingly be incinerated or dried in special furnaces. Incineration is estimated to release annually 3 tonnes of zinc to the atmosphere (RIZA, 1990). The estimation has taken into account an increase in sludge production due to growth in the volume of sewage to be treated, and to further introduction of dephosphatization. Incineration is estimated to cost Dfl. 350.- to Dfl. 550.- per tonne of dry weight.

6.2.3. Traffic

Autonomous developments

Because the number of passenger car and truck kilometres travelled annually is increasing, it is expected that the zinc emissions due to the wear of tyres will have increased by 20-50 % in the year 2000 relative to 1989. This means a total zinc emission from traffic of about 245 tonnes in 2000.

The amount of zinc contained in discarded car tyres will be about 1,700 tonnes in 2000. Of the total quantity of car tyres, the task set for the year 2000 is 25 % reuse, 25 % useful applications, and 50 % incineration in a central facility in the Netherlands (not in waste incinerators). A central plant with an annual capacity of 40,000 tonnes is required for the incineration of car tyres in the Netherlands. The capital investment for this plant is about Dfl. 25 to Dfl. 30 million, including flue-gas desulphurization scrubbers. The volume of fly ash resulting from the incineration of passenger car tyres is estimated to be 4.5 % of the total tyre volume, and will consist primarily of zinc oxide and contain about 700 tonnes of zinc per year. The amount of slag is estimated at 13-18 %, and will consist mainly of iron (de Weerd and Wieringa, 1990).

6.2.4. Other

Autonomous developments

Because of the partial softening of tap water, it is expected that the zinc emissions due to corrosion of pipes will fall by about 20 % (Riza, personal communication).

6.3. ZINC-BEARING WASTE

Zinc-bearing waste with a total zinc content of 40,000 tonnes is produced annually in the Netherlands. The present and possible future disposal methods of a number of major waste streams are presented in Table 6.1.

Shredder waste

Additional measures

A thermal system for selectively melting the nonferrous fraction from shredder waste has been developed in Germany. The recoved zinc metal is 93 % pure and can be reused. The use of zinc in automobiles shows an increase. However, since shredders produce relatively small amounts of nonferrous metals, a nonferrous-metal separation plant becomes economically viable only when the fractions from 15 to 20 shredders are collected (Rousseau and Melin, 1989). It appears important for the Dutch siutation that the problem of shredder dust (about 25 % of the input) (a priority waste) be coordinated (collection structures, capacity) and technically worked out.

Table 6.1. Summary of major zinc-bearing waste streams

Waste stream	*zinc load (tonnes)*	*present disposal method*	*possible future disposal method*
Automobile tyres	*1,000*	*recycling/dumping*	*recycling*
Batteries	*600*	*storage*	*recycling*
Pickling baths	*700*	*export*	*recycling*
Phosphoric acid gypsum	*< 100*	*discharge*	*process modification*
Blast-furnace sludge	*850*	*storage*	*reuse*
Oxylime sludge	*110*	*storage*	*reuse*
Jarosite	*3,000*	*storage*	*reuse*
Shredder dust	*1,200*	*dumping*	*incineration/dumping*
Blasting grit	*600*	*30% reuse* *70% dumping/loss to environment*	*70% reuse* *30% dumping/loss to environment*
Combustion residues from waste incinerators	*2,400*	*reuse/dumping*	*reuse/dumping*
Sewage sludge	*360*	*56% dumping/ incineration* *44% reuse*	*70% incineration* *25% reuse* *5% dumping*

Scrap

Additional measures

The sources of scrap in the Netherlands are the iron and steel industry, the car industry, the sheet-metal-processing industry and car shredders. The main scrap processors are the steel industry and iron foundries. However, the major portion of the Dutch scrap is exported, to Germany in particular, where it is used in the secondary iron and steel industry. Because of the relatively high zinc content (galvanized steel) of the scrap, the secondary production generates filter dust and filter cake containing considerable amounts of zinc (see also iron and steel production). These waste streams can be categorized according to processing possibilities as follows:

- dust or sludge with a nonferrous metal content of only a few percent by weight. These streams can be recycled back to the metallurgical process via the sinter plant;
- dust or sludge with zinc concentrations of a few percent to 20 %. These streams are currently dumped;
- dust or sludge with zinc concentrations of > 20 %. The zinc can be recovered economically from these streams.

Further research into reuse of the second category of filter dust is being conducted in Germany, among other countries. The collected dust is blown into the furnace through the bottom. An estimated 70 to 100 % of this dust is subsequently found back in the newly formed dust. As a result, zinc enrichment occurs whereby concentration levels can be reached at which zinc (> 20 %) (and lead) can be profitably recovered.

Blasting grit

Additional measures

The task set for the year 2000 is 70 % reuse and less than 30 % dumping (including diffuse emissions). It is not yet possible to indicate the actual percentage that will be reused. The dispersion of blasting grit to the environment can be reduced by employing enclosing systems fitted with exhaust equipment and filters and, for repairs to ships, the so-called "dock-floor discipline" (VROM, 1986). Other measures, which at the same time have a preventive effect, are application of more durable coats of paint, alternative paint application techniques, and the use of other blasting agents, such as ice and cryogenic carbon dioxide or nitrogen (Voorter, 1989).

Household waste

Additional measures

The volume of household waste to be incinerated will increase considerably in the future. It is expected that 120 % more waste will be incinerated in 2000 than in 1986 (Nagelhout et al., 1989). However, the anticipated emissions to the atmosphere will fall substantially because the future incinerators, as well as the existing ones, will have to comply with the Incineration Guideline 1989, which limits the dust emission concentration to 5 $mg.m^{-3}$. It is expected that the guideline will result in a reduction of the zinc emission per m-3 of air of about 90 %. In combination with the anticipated increase in waste incineration, the total atmospheric zinc emission from incineration will be 60-80 % lower in 2000 than the present input. The cost of modifying an existing plant is estimated at f 20 million. The cost of building a new incinerator with a relatively large annual capacity is about f 200 million per tonne of capacity. As a result of the policy outlined, the total volume of residues from waste incinerators (a priority waste stream), mostly slag and fly ash, will increase to more than 1,250 ktonnes a year by 2000. The task set for the year 2000 is that about 80 % of this is to be reused (VROM, 1988).

6.4. SUMMARY AND CONCLUSIONS

Table 6.2 summarizes the zinc emissions to the environmental compartments air, water and soil, which could possibly be expected in the year 2000 with the autonomous emission-control measures described in this chapter. It can be seen that autonomous developments will lead to a reduction in the atmospheric zinc emission by about 35 %, chiefly because it has been estimated that the zinc emissions from waste incineration will fall by 90 %.

The autonomous developments will result in only a slight decrease in the zinc input to water and soil; the uncertainty in the autonomous development of the corrosion term precludes a reliable estimate of this decrease. Under the Rhine Action Plan and the North Sea Plan, the emissions of priority substances (including zinc) should have been cut by 50 % of their 1985 levels by 1995. The reduction resulting from autonomous developments will in all probability be well below this target.

The emission from agricultural activities is expected to decrease by about 23 %. As a result, the minimum zinc accumulation in agricultural soil will fall to about 90-100 tonnes per year in 2000.

It is expected that by the year 2000 a number of specific zinc-bearing waste streams, which are dumped or stored at present, will be entirely or partly processed and possibly reused. They include jarosite (3,000 tonnes of zinc per year), batteries (600 tonnes per year), pickling baths (700 tonnes per year) and blasting grit (600 tonnes per year). It is expected that a larger proportion of the household waste and sewage sludge will be incinerated in the future. Because of the adoption of stringent emission standards for waste incinerators, this will not lead to a larger zinc input to the atmosphere.

Table 6.2. *Estimate of the zinc emission developments for the various sources, based on autonomous developments*

Source	*air*		*water*		*soil*	
	1989	*2000*	*1989*	*2000*	*1989*	*2000*
Industry	*167*	*150*	*130*	*85*	-	-
Power stations	*2*	*0.5*	-	-	-	-
Waste incineration	*70*	*7-10*	-	-	-	-
Agriculture	-	-	-	-	*1,740*	*1,300*
Traffic	-	-	*75*	*90*	*127*	*155*
Corrosion	-	-	*1,650*	*1,600*	*2,025*	*2,000*
Total	*239*	*160*	*1,855*	*1,775*	*3,467*	*3,455*

7. EVALUATION

7.1. EXCEEDING OF CURRENT STANDARDS AND GUIDELINES

7.1.1. Soil and groundwater

The data presented in Section 4.3 show that about 6 % of the arable land samples and about 15 % of the grassland samples exceed the relevant reference value. Most of the observations exceeding the reference values occur in the south, particularly in the water meadows along the Geul, Roer and Meuse rivers, and have largely a "historical" character. In the water meadows along the Geul river, the C value for zinc of 3,000 mg.kg^{-1} is often exceeded (Rang, 1990).

Zinc concentrations above the reference value also occur around zinc-emitting sources (de Kempen). Systematic exceeding of the reference value can also occur in highly localized areas, such as in the immediate vicinity of electricy pylons and, according to calculations, also near other galvanized semi-permanent structures, such as crash barriers. In risk areas, a historical zinc contamination of soil in conjunction with other sources such as deposition, and factors such as soil composition (low-humus soil) can constitute a threat to the quality of groundwater; see Figure 4.1. The mean concentration of zinc in shallow groundwater and in deeper groundwater is about 88 and 65 μg.l^{-1}, respectively. The 50th percentile is below 30 and 16 μg.l^{-1}, respectively. In most cases, therefore, the desirable level of 65 μg.l^{-1} (VROM, 1992) is not exceeded. Zinc levels in excess of the C value of 800 μg.l^{-1} have been reported to occur locally, particularly in de Peel, a region in the province of Brabant (Rang, 1990).

7.1.2. Surface water and sediments

All large rivers exceed the limit value for surface water (VROM, 1992: 30 μg.l^{-1} total zinc).

With regard to sediments too, the limit value for newly formed sediment (480 mg.kg^{-1} dry weight) and the desirable level (140 mg.kg^{-1} dry weight) are often exceeded.

7.1.3. Air

Standards, guidelines and MTC have not yet been formulated for the compartment air. It should be noted that the ambient air zinc concentrations in the Netherlands are slightly lower than those in Germany and Belgium.

7.2. RISKS AND RISK GROUPS

7.2.1. Risks to man

Oral exposure

The average zinc intake in the Netherlands ranges from 8 to 14 mg per day (0.13-0.23 $mg.kg^{-1}$ body weight per day); this range is based on two studies; see Chapter 4. This intake is approximately the same as the daily requirement for zinc, estimated to be 0.15-0.25 $mg.kg^{-1}$ body weight per day for adults. For lactating women, the average intake is at most a factor of 2 to 3 lower than the estimated dietary zinc requirement, so that the occurrence of a (marginal) zinc deficiency in this group cannot be ruled out with certainty. The two values for the average daily zinc intake are a factor of 2-8 and 1-4, respectively, lower than the estimated "maximum tolerable intake" (0.3-1 $mg.kg^{-1}$ body weight per day; see 5.5.4). Based on these data, harmful effects are not expected at the current exposure levels. It should be noted that the possibility of too low a zinc intake seems to be greater than that of excessive intake.

Inhalation exposure

Given the large margin between (no-)effect concentrations in experimental animals and occupational toxicity studies on the one hand (of the order of $mg.m^{-3}$), and the current ambient air concentrations (ca 0.2 $\mu g.m^{-3}$) on the other, it is very unlikely that inhalation exposure to zinc constitutes a hazard to the general population.

7.2.2. Risks to ecosystems

Aquatic environment

A "maximum tolerable concentration" (MTC, 95 % protection level) for **dissolved** zinc in surface water, both fresh and salt, of 6 $\mu g.l^{-1}$ has been derived in Subsection 5.5.2. This concentration in Dutch surface waters (Rhine and Meuse River systems) corresponds to 25 $\mu g.l^{-1}$ **total** zinc. The current average concentrations in the large rivers are higher than the MTC, particularly in the Meuse River and probably also in the Scheldt. Higher concentrations may also occur locally in the smaller non-State waters. Based on the distribution of the NOEC values used in the derivation of the MTC, it has been calculated what percentage of the species in a community is, theoretically, still protected at lifetime exposure to concentrations which currently exceed the MTC. Using concentrations of, for instance, 35, 50 and 90 $\mu g.l^{-1}$ total zinc results in "protection levels" of approximately 93 %, 90 % and 82 %, respectively. This means that at these concentrations the NOECs of about 7 %, 10 % and 18 %, respectively, of the species in a community are exceeded, (probably) resulting in adverse effects on parameters such as survival, growth and reproduction. The lowest (35 $\mu g.l^{-1}$) and highest (90 $\mu g.l^{-1}$) values used in the above example refer to the annual mean zinc concentrations in 1987 in the Rhine and Meuse Rivers, respectively.

A MTC for sediment cannot be derived from the available ecotoxicological data. Based on a limited study, partial inhibition of the mineralization of poorly degradable substances is expected at the current zinc levels in freshwater sediments.

Terrestrial environment

Because of the widely varying soil type-related background concentrations, one MTC for zinc in soil cannot be derived in a straightforward manner. For this reason, it has been proposed in Subsection 5.5.2 to base the evaluation of the risks of zinc concentrations in soil on the soil type-specific reference value. The current zinc levels in a variety of agricultural soils generally lie within the ranges found in similar soils in nature reserves. The mean concentrations measured in various studies (18-44 $mg.kg^{-1}$ in sandy soils, 67-146 $mg.kg^{-1}$ in clay soils, and 55-143 $mg.kg^{-1}$ in peat soils) are usually lower than the reference values calculated for comparable soil types (66 $mg.kg^{-1}$ for sandy soil [3 % clay; 5 % OM], 228 $mg.kg^{-1}$ for clay soil [57 % clay; 5 % OM], and 143 $mg.kg^{-1}$ for peat soil [3 % clay; 59 % OM]). These three reference values (arbitrarily chosen examples) have been calculated on the basis of percentages clay and OM which are mentioned for the above soil types in the Working Paper on Soil Quality (VROM, 1986). If the zinc concentrations in sensitive soils are increased by a few tens of $mg.kg^{-1}$ (of the order of 30-70 $mg.kg^{-1}$ dry weight), microbe-mediated soil processes are the first to be affected, certainly when the increase is the result of a single application of soluble inorganic zinc. The probability of such effects occurring decreases when the zinc application is spread over a long period of time. The same is true when the zinc is present in organic substrates, because the bioavailability of zinc in such substrates is lower than that of soluble inorganic zinc. Additions of the order of magnitude mentioned will seldom cause yield reduction of agricultural crops, not even in acidic soils with low organic matter and clay content. Such soils are generally considered to be the most sensitive because of their low adsorption capacity. Although this is certainly true for effects on plants, such a clear relationship does not seem to apply to effects on microbe-mediated processes. Based on these data, unacceptable risks are not expected nationally at the current soil zinc levels, or not on a large scale. Regional risk areas with greatly elevated zinc levels at which possibly effects occur on plants and microbe-mediated processes are de Kempen in North Brabant and floodplains of the Geul and Dommel rivers, due to (largely historical) mining and processing of zinc ore. Effects on plants have been demonstrated in crops growing on plots flooded by the Dommel river. An estimate of the risks in these areas is not possible without detailed data on zinc concentrations, associated soil types, and the speciation of zinc. In these areas, the high soil cadmium levels caused by the processing of cadmium-containing zinc ore in the past are an additional risk factor. Finally, on a local scale, greatly elevated zinc concentrations can occur in soils around galvanized objects such as electricity pylons.

7.3. ENVIRONMENTAL QUALITY OBJECTIVES

In 1991, the Ministry of VROM made a proposal for desirable levels and limit values for a large number of substances (including zinc) in soil and water (VROM, 1991). This proposal, also based on the RIVM report "Desire for Levels" (van de Meent et al., 1990), implies in a number of cases a tightening of the standards as formulated in the Third Water Management Memorandum (V&W/VROM/L&V, 1989). A summary of the relevant standards and guidelines has previously been given in Table 1.2. The values proposed in "Desire for Levels" are based on ecotoxicological risks (MTC) (van de Meent et al., 1990). The environmental quality objectives are restricted to surface water, sediment, soil and groundwater; environmental policy has not formulated quality objectives for the compartment air, while the toxicological information is insufficient for deriving a MTC. Possible differences between MTC values in "Desire for Levels" and those proposed in this Integrated Criteria Document are the consequence of an updating of the available literature and the resultant NOECs on the one hand, and the use of an improved extrapolation method on the other. The extrapolation procedure currently used by the RIVM in deriving MTCs is described in Slooff (1992). Based in part on this procedure, which has already been implemented in the Draft Document Zinc preceding this Integrated Criteria Document Zinc, it has been decided in the preparatory interdepartmental consultations on the policy document on the memorandum "Environmental Quality Objectives for Soil and Water" not to adjust the zinc standards in accordance with "Desire for Levels" (de Brijn, pers. comm.). The standards from the Third Water Management Memorandum for zinc in surface water and newly formed sediment are therefore retained, and have been adopted as limit values in the policy document (VROM, 1992).

7.3.1. Soil and groundwater

Since zinc is a naturally occurring element and also an essential trace element, it is obvious that a desirable level will be based on the "natural occurrence" of zinc and will not be derived from a limit value based on risks. It is not realistic for environmental policy to aim at a completely natural situation; therefore, the Ministry of VROM (1991) has chosen a level as measured in relatively unpolluted areas as a starting point. The formulation of one desirable level for soil and groundwater within the context of the general environmental quality can however be called into question, considering the natural variations in zinc concentrations. Background concentrations of zinc in relatively unpolluted areas can vary from 6 to 150 $mg.kg^{-1}$ for soil, and from 1 to 1,000 $\mu g.l^{-1}$ for groundwater. Possibly, it would be more appropriate to elaborate the desirable level within the framework of the special environmental quality, so that different areas are distinguished. The current proposal for zinc in soil, 140 $mg.kg^{-1}$ dry weight, regardless of the soil type, is possibly too high for one area and too low for another. The information compiled in this Integrated Criteria Document raises the question as to whether it is possible to derive ecotoxicologially one MTC and a limited value possibly based on it. The bioavailability of zinc in soil appears to be low: there exists no relationship between the total zinc content of soil and the occurrence of adverse effects on soil-inhabiting animals and microbe-mediated soil processes. It is the amount of zinc applied, the form in which it is added, and the way in which it is applied (spread over a period of time) which determine its toxicity. Looked at in this light, it is perhaps advisable to pay more attention to emission objectives (use of sewage sludge and animal manure). The discrepancy between the MTC for soil as proposed in "Desire for Levels" (0.7 $mg.kg^{-1}$ dry weight) and the limit value for added zinc (30-70 $mg.kg^{-1}$ dry weight) put forward in this Integrated Criterial Document arises from the availability of data, their interpretation, and the use of the Aldenberg-Slob method (more data) instead of the EPA method (see Slooff, 1992).

Based on the statement in "Desire for Levels" that there is at present insufficient scientific knowledge for establishing a clear relationship between heavy metal concentrations in soil and groundwater, as well as between concentrations in groundwater and surface water, the Ministry of VROM (1992) has not derived a soil- or surface water-related limit value for groundwater. Ecotoxicity data for groundwater are lacking (in the process of development), while human toxicity data do not give cause for taking measures to reduce zinc concentrations.

7.3.2. Water and sediments

With regard to the desirable level for zinc in water, the question arises as to whether this should be set at the level of the concentrations measured in surface waters, which in the Netherlands are little influenced by human activities (proposal of the Ministry of VROM: 2 and 9 $\mu g.l^{-1}$, dissolved and total zinc respectively) or actually at a natural level, partly because of the greater mobility of zinc in this compartment.

In the setting of standards for sediments (VROM, 1992), a distinction has been made between old sediment (below a depth of 10 cm) and new sediment (the top 5-10 cm). The desirable level for old sediment is 140 $mg.kg^{-1}$ dry weight, based on "Desire for Levels" (van de Meent et al., 1990). However, on the basis of the new insights resulting from the realization of the Draft Document Zinc and which have subsequently been elaborated in the policy document on the memorandum "Environmental Quality Objectives for Soil and Water" (VROM, 1991), it has been decided to retain the old limit value from the Third Water Management Memorandum (480 $mg.kg^{-1}$ dry weight) (VROM/V&W/L&V, 1989).

7.4. MEASURING STRATEGIES

It is advisable to determine the soil zinc concentrations in those locations where systematic exceeding of the reference values can be expected, for example, near zinc structures such as electricity pylons. The accumulation of zinc in problem areas also deserves continuing attention, such as de Peel, a region which not only is affected by a historical zinc contamination, but where also much animal manure is spread on the land and the soil has a low humus content.

With regard to surface water, sampling points in the non-State waters are desirable.

The bioavailability of zinc in soil is influenced by many factors. More insight is needed into the speciation characteristics of zinc, and into the quantification of these factors, which determine the soil-plant relationships of zinc. Also, the Kd values of zinc in polluted areas should be determined.

7.5. CONCLUSIONS AND RECOMMENDATIONS

The risks associated with the current concentrations of zinc in the environment appear to be nil for man, and limited and localized for animals and plants.

For humans, especially lactating women, the possibility of too low a zinc intake is greater than that of excessive intake.

The "protection levels" for the aquatic environment are on average greater than 85 %. With regard to the terrestrial environment, effects on microbe-mediated processes can be expected at present on a local scale only.

For the long term, it is important to know where significant zinc accumulation occurs regularly. One problem in the identification of these areas is that the main contributions to the zinc emission come from diffuse sources. The industrial sources are relatively unimportant compared with these diffuse releases. Emission of zinc through metal corrosion and emission from agriculture should be investigated more specifically.

With respect to corrosion, there is a lack of information on soil concentrations in localized areas, particularly near galvanized structures. A reduction of the emissions from atmospheric corrosion could be brought about by coating these structures or by using zinc alloys.

As regards agricultural soil, it was noted that some accumulation of zinc occurs, indicating that the input is greater than the output.

The zinc budget for arable land has two output terms: harvested crops, and leaching and runoff; and two input terms: precipitation, and application of organic and chemical fertilizers. The leaching and runoff of zinc of about 80 g per ha per year is the least controversial. The precipitation term is taken to be about 150 g zinc per ha per year in this document, while others have used values of up to 930 g per ha per year. Values for addition of zinc with various fertilization scenarios, and for removal by crop plants vary widely in the literature, chiefly because of uncertainties in the concentrations of zinc in animal feeds and grass. Nevertheless, every known calculation shows a net accumulation. In this document the accumulation in agricultural soil is at least 1,100 tonnes of zinc per year, or >530 g per ha per year. This results in an average increase in the zinc concentration in the topsoil (the upper 20 cm) of about 0.2 $mg.kg^{-1}$ per year. Grassland can accumulate zinc at a rate which is more than twice that in agricultural soil. It should be noted that the calculated accumulation strongly depends on the Kd value used, which can vary greatly from one soil type to another. The use of zinc as an animal feed supplement began around the year 1965, and so also the "loading" of soils with zinc through manure application. The use of zinc-containing pesticides to combat various fungous diseases in fruits, vegetables, bulbs and ornamental plants adds 800-2,800 g zinc per ha per year to the soils on which they are grown.

The average annual zinc accumulation in agricultural soil is no cause for concern. Assuming an unchanged accumulation pattern, it will take a millennium before the soil is saturated with zinc. However, with a view to effects on groundwater in the longer term, particularly in the vulnerable sandy soils, and with a view to reduced copper uptake by crop plants at elevated soil zinc levels, the developments in the processes contributing to zinc accumulation should be followed. A better understanding of the relationships between zinc concentrations in soil and groundwater, as well as between the concentrations in ground- and surface water, will be helpful.

Where the reference values for soil and water are exceeded, it is usually the consequence of a historical, at any rate more than a century-old, contamination from zinc production plants and zinc mines, which are or were situated in the south of the Netherlands and the neighbouring region of Belgium. Although both the transboundary inputs of zinc and the amounts of zinc emitted in the Netherlands to soil and water have fallen dramatically in the past decade, the existing distribution pattern will change very little in the future.

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NATIONAL INSTITUTE OF PUBLIC HEALTH AND ENVIRONMENTAL PROTECTION
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THE NETHERLANDS

Appendix to Report no. 710401028

INTEGRATED CRITERIA DOCUMENT ZINC:

ECOTOXICITY

J.A. Janus August 1993

Advisers: P. van Beelen, J.H. Canton, C.J. Roghair,
M.A. Vaal

(Reprint; published in November 1992 as Appendix to RIVM-report no. 710401019)

RIJKSINSTITUUT VOOR VOLKSGEZONDHEID EN MILIEUHYGIENE

CONTENTS

../ii

INTRODUCTION

Data in the present Appendix are underlying the sections on ecotoxicity in the "Basisdocument Zink" ("Integrated Criteria Document Zinc"). The Criteria Document (Cleven et al., 1992), also prepared by the Dutch National Institute of Public Health and Environmental Protection, comprises a systematical survey and a critical evaluation of relevant data on zinc, as much as possible with regard to the specific situation in the Netherlands. The information in the Criteria Document will serve as a scientific basis for an effect-oriented policy that is aiming to achieve environmental levels at which the risks to humans and other organisms are "acceptable" and, preferably, "negligible", according to the definitions used by the Dutch government.
The Criteria Document, including the present Appendix, has been written by order of the Dutch Ministry for Housing, Physical Planning and Environment, Directorate Substances and Risk-management.

The Appendix comprises data on aquatic organisms (chapter 1) and terrestial organisms (chapter 2). Both chapters contain data on accumulation and, especially, on the toxicity of zinc. Based on the toxicity data, "Maximum Tolerable Concentrations" (MTCs) for surface water and soil are proposed in chapter 3 (ecotoxicological effect assessment).

A substantial number of publications on the toxicity of zinc was provided by two recent RIVM reports, namely, Van de Meent et al. (1990) and Denneman and Van Gestel (1990). These reviews were assumed to cover the period up to May 1989. Additional publications originate from earlier reviews and from an on-line literature search in BIOSIS and TOXALL; this search covered the period from May 1989 up to November 1990, half a year before the draft for comment was published in May 1991. Some data published from November 1990 and onwards have been included in the document, but further updating was not exhaustive.

1 AQUATIC ORGANISMS

1.1 ACCUMULATION

The accumulation of zinc, an essential trace element for plant and animal life, is regulated in species of several taxonomical groups, for example, in molluscs (Fernandez and Jones, 1990), crustaceans (Price and Uglow, 1979, Memmert, 1987), fish (Winner and Gauss, 1986) and in mammals (Cleven et al., 1992). Within taxonomical groups there can be differences with respect to this ability. Excess zinc may either be stored as metabolically inactive zinc-protein complexes (metallothioneins) or excreted. Storage of zinc may be concentrated locally, for example, in lysosomal granules in the kidney (molluscs) or in the hepatopancreas (crustaceans).

The ability of an organism to accumulate or concentrate a compound from the water is usually expressed as "bioconcentration factor", the ratio of the compound concentration in the organism to the compound concentration in the ambient water ($BCF = C_{organism} : C_{water}$). The term "bioconcentration" is used in this document in case the BCF exceeds unity (BCF >1); the term "bioaccumulation" is used in case the BCF does not exceed unity (BCF <1). The BCF values reported below are based on laboratory and field studies reviewed by U.S. EPA (1979, 1980) and Mance and Yates (1984), and refer to both freshwater and saltwater organisms. It is noted that it is often not clear whether the BCF values reported in these reviews are based on dry weight or on fresh weight of the organisms, and whether or not these values have been corrected for the background level of zinc in the organisms. It is assumed that all values are whole-body BCF values. The wide range of values observed, sometimes even for species within the same taxonomical group, may be partly the result of differences in exposure level and exposure time. So, the BCF values reported below must be interpreted with reservation.

For plants, including both unicellular algae and macrophytes, BCF values in the wide range of <100 to 50,000 have been reported. The majority of BCF values for invertebrates and fish is in the lower range of 100-1,000, those for fish usually being lower than those for invertebrates. The higher range of BCF values for invertebrates is 10,000-100,000, reported for sediment-dwelling species such as crabs, oysters and insect larvae. The highest BCF reported for fish is 2,000 (U.S. EPA, 1979, 1980; Mance and Yates, 1984). These values show that zinc is concentrated from the water, regardless of the organisms studied, but that the accumulation potential varies from insignificant (BCF <100) to highly significant (BCF >1,000), depending on

the species studied. According to the definitions used by Taylor (1983), compounds showing BCF values >1,000 are considered to represent compounds with potentially serious accumulation problems.
Laboratory tests using organisms of different taxonomical groups (polychaete worms, mussels and fish) did not indicate biomagnification. *["Biomagnification" is defined as the occurence of a substance at successively higher concentrations with increasing trophic levels in food chains; Taylor, 1983]*. This is in accordance with the above-mentioned BCF values (which are decreasing with increasing trophic level) and with the results of microcosm and field studies. For example, in a field study in German waters, the concentrations of zinc (and other metals) decreased along the food chain, with the lowest concentration measured in fish (Mance et al., 1980).

In daphnids *(Daphnia magna*, crustaceans) exposed for 7 weeks in a renewal system to a zinc concentration of 250 $\mu g.l^{-1}$, the zinc concentration clearly followed a similar trend as the total zinc concentration in the water ("dissolved" plus "particulate"), indicating that uptake from food particles substantially contributes to the bioaccumulation of zinc in these filter-feeding organisms. In similar tests with the zebra fish *Brachidanio rerio* exposed for 5 weeks to 250 $\mu g.l^{-1}$ in the water in combination with unpolluted and polluted daphnids, the zinc concentration in the fish was independent of their food source. This indicates that fish do not accumulate additional zinc from their food. In fish the zinc concentration hardly increased during the exposure time in the artificial freshwater (total hardness 250 $mg.l^{-1}$, as $CaCO_3$; pH 7.8; "background" zinc concentration 30 $\mu g.l^{-1}$) used (Memmert et al., 1987). The result of this study is in accordance with the conclusion of Skidmore (cited in Alabaster and Lloyd, 1980) that zinc is taken up by fish directly from the water, especially by the mucus and gills.

1.2 TOXICITY

Introduction

In this section a distinction has been made between freshwater organisms and saltwater organisms (the latter including estuarine organisms and truly marine organisms), and between "short-term" and "long-term" exposure. Short-term exposure usually covers data on experiments with exposure times up to 96 hours; the most relevant endpoint of "acute toxicity" studied in these experiments is lethality, or immobilization in case of organisms such as water fleas (e.g. *Daphnia* species). Long-term exposure preferably covers data on experiments in which organisms are exposed during a significant part of their lifetime or, at least, during a sensitive life stage. The most relevant endpoints of "chronic toxicity" studied in these latter experiments are (beside lethality) growth and reproduction, at sublethal concentrations. The section on long-term exposure includes ≤96-hr data on organisms (such as algae and bacteria) which have very short lifetimes, in case the exposure time covers one or more generations.

The data available on zinc include a large number of long-term toxicity tests, resulting in a "no-observed-effect-concentration" (NOEC*) with regard to survival, growth and reproduction. Because long-term NOEC values with respect to these toxicological endpoinds are used preferably to derive a "maximum tolerable concentration" (MTC), this section has been focused on long-term toxicity tests. In most cases, these tests are "single species" laboratory tests. The vast amount of short-term toxicity tests resulting in LC50 or EC50 values ("median lethal concentration" or "median effect concentration") has not been evaluated. The results of the short-term tests are summarized only briefly on the basis of reviews selected and some additional publications.

Unless stated otherwise, the results in this section are expressed as *zinc* (not as the compound tested) and represent nominal (added) *total zinc* concentrations, i.e. dissolved plus particulate zinc. From the few data available on background zinc concentrations in the test waters used it can be concluded that the added concentrations usually were (much) higher than the background zinc concentration in the test waters. So, it is assumed that the background zinc levels will contribute little to actual exposure levels. In some cases, however, toxicity values based on nominal concentrations (especially NOEC values for sensitive species) may underestimate the actual exposure level, and therefore overestimate the risk. For example, in the long-term test with *Epeorus latifolium* larvae (Hatakeyama, 1989; table 1.1), the nominal NOEC was 3 $\mu g.l^{-1}$, while the background zinc concentration was 9 $\mu g.l^{-1}$.

* *In publications in which a statistical analysis of the test results was reported, the NOEC was derived in accordance with the result of this analysis, i.e. the NOEC was chosen as the highest concentration in the series of test concentrations that did not result in a statistically significant (adverse) effect.*

In many publications, especially on algal tests, a statistical analysis of the test results was not reported. In those cases, the NOEC was chosen arbitrarily as the highest concentration in the series of test concentrations that resulted in ≤10% effect, compared to the control concentration. Concentrations that resulted in more than 10% effect were considered to be effect concentrations.

1.2.1 Freshwater organisms

Short-term exposure (acute toxicity tests)

LC50 and EC50 values

Skidmore and Firth (1983) reviewed the results of lethal toxicity tests with invertebrates and fish from the Northern Hemisphere. For invertebrates (13 tests), 24/96-hr LC50 values range from 40 to 32,000 $\mu g.l^{-1}$; those for fish range from 140 to 40,000 $\mu g.l^{-1}$. Thirteen out of the 52 tests (25%) resulted in LC50 values <1,000 $\mu g.l^{-1}$; the majority of the tests resulted in values ranging from 1,000 to 10,000 $\mu g.l^{-1}$. In this review information on the test compounds used is not reported.

The majority of the acute EC50 and LC50 values reported by U.S. EPA (1980) and Mance (1987) are in the same range. For example, the in U.S. EPA (1980) reported values range from 100 to 58,100 $\mu g.l^{-1}$ for invertebrates and from 90 to 40,900 $\mu g.l^{-1}$ for fish. The lowest acute LC50, 90 $\mu g.l^{-1}$, was reported for the cutthroat trout *Salmo clarki* (Rabe and Sappington, 1970; cited in U.S. EPA, 1980). Some values for invertebrates (worm and insect species) are higher than 60,000 $\mu g.l^{-1}$. Test compounds used in the studies reviewed in these publications usually were zinc sulphate or zinc chloride which have a high aqueous solubility. Occasionally zinc nitrate or zinc acetate was used. Additional reviews on acute L(E)C50 values and other toxicity data on zinc have been written by Train (1979), Alabaster and Lloyd (1980) and Mance (1984).

The data reviewed indicate that salmonid species of fish are more sensitive than non-salmonid ("coarse") species, and that the former species of fish are amongst the most sensitive groups, together with crustaceans such as water fleas. However, this may have been related to the relatively soft waters used in the tests with these organisms. For example, lethal toxicity tests with swim-up alevins of the chinook salmon *Oncorhynchus tshawytscha* and the steelhead *Salmo gairdneri* in soft water resulted in 96-hr LC50 values of 93 and 97 $\mu g.l^{-1}$, respectively (actual concentrations). Newly hatched alevins, 5-8 mo old parr and smolts of these two fish species were found to be less sensitive. Water quality of the waters (well or river water) used in these tests was relatively uniform throughout the series of tests, with median values for hardness and pH of 23 mg.l^{-1} (as $CaCO_3$) and 7.1, respectively (Chapman, 1978a).

Abiotic factors influencing acute toxicity

The acute toxicity of zinc -and that of other metals- is dependent on abiotic (environmental) factors such as hardness, alkalinity, pH, ionic strength, and the presence of chelating (complexing) agents such as humic acids, amino acids and EDTA. The data reviewed, especially those on fish, generally show that the acute toxicity is greatest in relatively soft and acid waters, i.e. under environmental conditions favouring the presence of the simple hydrated metal-ion. Two examples of studies on the influence of abiotic factors on zinc toxicity are described below.

An extreme example of the influence of abiotic factors on zinc toxicity has been reported for the fathead minnow *Pimephales promelas:* tests with this fish species in "very hard" and "very soft" water resulted in 96-hr LC50 values of 33,000 and 780-960 μg.l^{-1}, respectively. In the same study a less extreme difference was found for the fish *Lepomis macrochirus* (bluegill): 40,900 *versus* 4,850-5,820 μg.l^{-1}. The hard water was natural limestone spring water, with the following characteristics (before adding zinc as hydrated zinc sulphate): hardness and alkalinity 360 and 300 mg.l^{-1}, respectively; pH 8.2. The soft water was prepared by mixing the spring water with distilled, demineralized water, resulting in a hardness and alkalinity of 20 and 18 mg.l^{-1}, respectively, and in a pH of 7.5 (Pickering and Henderson, 1966). In a large number of tests with neonates of the water flea *Ceriodaphnia dubia* tested in 3 different surface waters (range hardness 100 to 180 mg.l^{-1}, as $CaCO_3$) at fixed pH values of 6, 7 and 8, the 48-hr LC50 values decreased both with hardness (at fixed pH) and pH (at fixed hardness), but the maximum difference was within a factor of 4: 41 *versus* 164 μg.l^{-1} (Belanger and Cherry, 1990).

Water hardness (determined by the calcium and magnesium concentration; usually expressed as mg.l^{-1} $CaCO_3$) is generally mentioned as the abiotic factor having the greatest influence on the acute toxicity of zinc. However, hard waters generally also have higher alkalinities, higher ionic strengths and higher pH values, which makes it very difficult, if not impossible, to estimate the contribution of the different abiotic factors to the variation in zinc toxicity (for specific species or groups of species). Moreover, according to Winner and Gauss (1986), there are only a few studies in which the influence of hardness on acute toxicity has been studied in the absence of concurrent changes in other abiotic factors such as alkaliny. An example of the concurrent changes in hardness and other abiotic factors is shown in the afore-mentioned study by Pickering and Henderson (1966) in which hard water was diluted with distilled water.

Long-term exposure (chronic toxicity tests)

NOEC values (tables 1.1 and 1.2)

Long-term "single species" toxicity tests resulting in NOEC values which have been used in the ecotoxicological effect assessment to derive a maximum tolerable concentration in fresh water are summarized in table 1.1. The NOEC values listed in this table have been selected on the basis of the (biological) relevance of the toxicological endpoints studied and on the basis of test waters used. With respect to the latter, a number of the algal tests have been conducted in artificial nutrient media containing EDTA (ethylenediaminetetraacetate), a chelating agent which can decrease the toxicity of zinc. The EDTA concentration that will affect the toxicity of zinc depends, on amongst other things, on the concentration of zinc and that of other trace elements present in the medium. Hence, an exact figure for the amount of EDTA that will not affect the toxicity of zinc under the variable conditions used in the different algal tests cannot be mentioned. Based on the available data, for example, the studies with the alga *Chlorella vulgaris*, a "limit" EDTA concentration of $10x10^{-3}$ $mMol.1^{-1}$ (10 times higher than the chelator concentration of $\leq 1x10^{-3}$ $mMol.1^{-1}$ mentioned in the OECD guidelines for algal growth tests), has been choosen arbitrarily. The NOEC values from algal tests conducted in test waters containing EDTA concentrations higher than $10x10^{-3}$ $mMol.1^{-1}$ have not been used in the effect assessment. In addition, NOEC values from tests conducted in artificial media containing unspecified amounts of EDTA also have been excluded from the effect assesment. The NOEC values which have not been used in the effect assessment are listed in table 1.2 together with effect concentrations.

Toxicity tests with organisms other than algae were usually conducted in natural waters or, occasionally, in tap water. It is assumed that these waters did not contain significant amounts of EDTA. In the test with the poriferan *Ephydatia fluviatilis* (Francis and Harrison, 1988; table 1.1.), the artificial test water contained a relatively high EDTA concentration of $16x10^{-3}$ $mMol.1^{-1}$, but the NOEC of 3.2 $\mu g.1^{-1}$ was one of the two lowest

NOEC values derived for zinc. Therefore, this NOEC was included in the effect assessment.

LC50 and EC50 values

Two studies with the unicellular alga *C. vulgaris* resulted in a 4-d and 5-w EC50 (growth) of 2,400 and 5,100 $\mu g.l^{-1}$, respectively (Rachlin and Farran, 1974; Rosko and Rachlin, 1977). For the unicellular alga *Senedesmus quadricauda* 5-d EC50 values (growth) of 680, 560 and 201 $\mu g.l^{-1}$, total zinc, were found at fixed copper concentrations of 0.06, 6 and 127 $\mu g.l^{-1}$, respectively. The EC50 values based on computed zinc ion concentrations were 481, 214 and 10 $\mu g.l^{-1}$, respectively (Petersen, 1982).
Two similar "life-table" renewal tests with the water flea *Daphnia magna* resulted in 21-d LC50 values of 158 and 840 $\mu g.l^{-1}$, respectively, using $ZnCl_2$ as the test compound (Biesinger et al., 1972; Enserink et al., 1991). Both studies were conducted in lake water, the former study in Lake Superior water (hardness 45 $mg.l^{-1}$,as $CaCO_3$; pH 7.7) and the latter study in Lake IJssel water (hardness 225 $mg.l^{-1}$, as $CaCO_3$; pH 8.1). In the former study, the EC50 for reproduction was 102 $\mu g.l^{-1}$. Enserink et al. (1991) also exposed exponentially growing populations of *D. magna* in the Lake IJssel water (flow-through test), resulting in a 17-d EC50 (yield: mean maximum number of daphnids) of 570 $\mu g.l^{-1}$. Tests with *Erpobdella octulasta* (annelids) and *Ancylus fluviatilis* (molluscs) resulted in a 10-w LC50 and a 14-w LC50 of 60 and 80 $\mu g.l^{-1}$, respectively (Willis, 1988, 1989, table 1.2). Very low 10-d LC50 values were reported for the chironomid insect *Tanytarsus dissimilis:* 26-53 $\mu g.l^{-1}$ (mean value of 3 static tests: 37 $\mu g.l^{-1}$). The 10-d exposure time included embryogenesis, hatching and molting (two-third life cycle). The tests were conducted in unfiltered Lake Superior water (hardness 45 $mg.l^{-1}$, as $CaCO_3$; pH 7.5); the test compound was $ZnCl_2$ (Anderson et al., 1980). According to these authors these LC50 values are 43 to 16,000 times lower than LC50 values reported for other insect species.
Skidmore and Firth (1983) reviewed the results of long-term lethal toxicity tests with freshwater animals from the Northern Hemisphere; the exposure time ranged from 5 to 21 days. For invertebrates (6 tests) the LC50 values range from 160 to 32,000 $\mu g.l^{-1}$ and for fish (13 tests) from 90 to 17,000 $\mu g.l^{-1}$. These values are similar to the 24/96-hr L(E)C50 values derived for these organisms (see "short-term exposure"). Eight out of the 19 tests (40%) resulted in LC50 values <1,000 $\mu g.l^{-1}$.
Chapman (1978a) reported 8-d LC50 and LC10 values for different life stages of two species of salmonids, chinook salmon *O. tshawytscha* and steelhead

S. gairdneri, the LC50 values (range 93 to >661 $\mu g.l^{-1}$) being 1.5-3 times higher than the LC10 values (range 54 to 364-661 $\mu g.l^{-1}$). For more details on the study by Chapman (1978a) the reader is referred to the section on short-term exposure.

With the exception of the tests by Willis (1988, 1989), the above-mentioned tests resulting in L(E)C50 values are not summarized in table 1.2.

Additional data on long-term exposure (miscellaneous data)

Long-term "single species" toxicity tests resulting in NOEC values which have not been used in the effect assessment are summarized in table 1.2, together with tests in which the lowest test concentration resulted in an effect. Some additional data which are not listed in this table are summarized below.

* In a large number of "single species" tests with a variety of green algae *(Chlorophyta)* collected from natural waters it was found that algae of the same species or genus may show considerable differences in sensitivity to zinc and other heavy metals (copper, lead), but that these differences largely disappeared after cultering for some time in the laboratory. This study indicates that populations from polluted waters usually are more resistent than those from unpolluted waters, and that differences in sensitivity are not related to genetic factors (Whitton, 1970).

* Growth of the alga *Selenastrum capricornutum*, exposed in the laboratory to surface waters collected in a mining area, was completely inhibited. The lowest zinc concentration in these waters was 550 $\mu g.l^{-1}$; in the water in question, copper and cadmium concentrations were 1.5 and 5 $\mu g.l^{-1}$, respectively. Based on laboratory tests with *S. capricornutum* in a nutrient medium it appears that the growth inhibition could be attributed completely to zinc (Bartlett et al., 1974).

* An early life stage test with the chinook salmon *O. tshawytscha* in water with a hardness of 25 $mg.l^{-1}$ (as $CaCO_3$) resulted in an NOEC of 270 $\mu g.l^{-1}$; the lowest effect-concentration was 510 $\mu g.l^{-1}$. The test substance was zinc chloride (Chapman et al., manuscript; cited in U.S. EPA, 1980).

* Exposure of underyearling minnow *Phoxinus phoxinus* to a concentration of 60 $\mu g.l^{-1}$ (added as zinc nitrate) for 3 months resulted in a reduced ability to compensate for rotation of the water current. Yearling and adult fish were less sensitive (Bengtsson, 1974a).

Abiotic factors influencing chronic toxicity

In life cycle tests with the water flea *C. dubia* (Belanger and Cherry, 1990, table 1.1), the animals were exposed to zinc in three different river waters (hardness about 80, 120 and 170 mg.l^{-1}, as $CaCO_3$) at three different pH values (parent pH 8; adapted pH values 6 and 9). This study showed no consistent effect of pH and hardness on zinc toxicity; the maximum difference between the NOEC values for reproduction (including those estimated from the lowest effect-concentration) was a factor of 6.

In two life cycle studies with the water flea *D. magna* the effect of hardness on zinc toxicity was studied by increasing the hardness of the original soft water by adding both $CaSO_4$ and $MgSO_4$. In this way other factors such as alkalinity are affected as little as possible. In addition the influence of humic acid on zinc toxicity was studied. In the one study (Paulauskis and Winner, 1988, table 1.1), increasing the hardness of the test water from 50 to 200 mg.l^{-1} (as $CaCO_3$) resulted in a 6-fold increase in the NOEC for reproduction (decrease in toxicity); the NOEC for survival was less affected. These authors also studied the interactive effects of hardness and humic acid (HA, range 0 to 1.5 mg.l^{-1}). In tests in soft water (hardness 50 mg.l^{-1}), addition of 1.5 mg HA.l^{-1} resulted in a 2- to 3-fold increase in the NOEC (from 25 to 50-75 μg.l^{-1}). In tests in hard water (hardness 200 mg.l^{-1}), addition of 1.5 mg HA.l^{-1} resulted in a 1.3- to 1.5-fold increase in the NOEC (from 150 to 200-225 μg.l^{-1}). These data show that (under the conditions of this study) the combined effect of increasing hardness and humic acid content resulted in a decrease in toxicity of approximately one order of magnitude. In the other study (Winner and Gauss, 1986), increasing the hardness from 50 to 100 mg.l^{-1} (as $CaCO_3$) resulted in a significant ($p \leq 0.05$) decrease in mortality at 125 μg.l^{-1}, the only zinc concentration tested. The decrease in toxicity was not accompanied by a reduction in zinc bioaccumulation. The chronic toxicity of 125 μg.l^{-1} in soft water (hardness 50 mg.l^{-1}) was also significantly reduced by adding 1.5 mg HA.l^{-1}; the effect of humic acid on zinc toxicity was not studied in medium hard water (hardness 100 mg.l^{-1}).

Besides these two studies there appear to be no other studies on the "independent" effect of water hardness on zinc toxicity. In life cycle tests with *D. magna*, Chapman et al. (unpublished, cited in U.S. EPA, 1980 and in Paulaskis and Winner, 1988, table 1.2) studied the influence of hardness on zinc toxicity by diluting the original hard water from about 200 to 50 mg.l^{-1}, as $CaCO_3$), resulting in a 2-fold increase in the NOEC (decrease in toxicity). The (unexpected) result of this study is contradictory to the results of the studies by Winner and Gauss (1986) and by Paulauskis and Winner (1988) conducted with the same test organism. According to the latter authors, the high toxicity in the hard (hardness 200 $mg.l^{-1}$) and medium-hard (hardness 100 $mg.l^{-1}$) test waters used by Chapman et al. can be explained by the high alkalinity of these waters, as follows: a high alkalinity results in the formation of insoluble complexes of zinc with the carbonates determining alkalinity, increasing the toxicity to filter-feeding organisms such as daphnids by increasing oral exposure (see also section 1.1).

The effect of pH on zinc toxicity was studied in tests with alga *Senedesmus quadricauda* (Starodub and Wong, 1978., table 1.1 and 1.2). Increasing the pH of the test water from 4.5 to 8.5 resulted in an increase in the NOEC from <100 to 225 μgl^{-1}.

Based on the above-mentioned studies with water fleas it is concluded that an increase in water hardness without significant changes in other abiotic factors results in a decrease in the toxicity of zinc, but that the ultimate effect at a certain hardness appears to depend also on other factors such as alkalinity. Natural hard waters also have high alkalinities which may counteract the protective effect of hardness against zinc toxicity to filter-feeders that bioaccumulate substantial amounts of zinc from food particles. For organisms other than water fleas there are no controlled studies on the influence of abiotic factors on chronic toxicity, with the exception of the algal study which showed decreasing toxicity with increasing pH. On a theoretical basis it can be assumed that the chronic toxicity, just as acute toxicity, will be greatest in soft and relatively acid waters, i.e. under environmental conditions favouring the presence of the simple hydrated metal-ion.

Field and (micro-)ecosystem studies ("multiple species" tests)

The effect of zinc on the community structure of natural phytoplankton populations (green and blue-green algae, diatoms, and other species of algae) was studied in 3-w tests using tanks filled with natural water. At the lowest concentration tested (100 $\mu g.l^{-1}$, added as $ZnCl_2$) the growth of some species was stimulated, while that of other species was delayed or inhibited. The results show species-dependent differences in sensitivity, resulting in changes in community structure. Growth of all groups of algae was reduced at 1,000 $\mu g.l^{-1}$ (Nosov et al., 1981). Changes in community structure were also observed in an earlier, 14-w study in which periphytic communities (bacteria, fungi, algae and ciliate protozoa) were collected at

2-w intervals from 4 outdoor channels supplied with running pond water containing average zinc concentrations of 130 (control), 1,100, 2,800 and 6,500 $\mu g.l^{-1}$. The diversity of primary producers (algal species) decreased and the percentage of decomposers and consumers increased in all three treated streams; this effect increased with increasing zinc concentration. Hardness of the pond water averaged 170 $mg.l^{-1}$ (as $CaCO_3$); the pH was highest (8-9) at 130 $\mu g.l^{-1}$ and lowest (7-8) at 6,500 $\mu g.l^{-1}$ (Williams and Mount, 1965).

Field studies have been reviewed by Alabaster and Lloyd (1980) and Mance (1987). It is noted that it is difficult to interpret the results of these studies, because of the wide range of zinc concentrations reported and because of the presence of other pollutants. The data indicate that sensitive invertebrate and fish species may be adversely affected at dissolved zinc concentrations of 15-25 $\mu g.l^{-1}$; in soft, acid waters these concentrations are similar to total zinc concentrations. A comparison of zinc concentrations and biota status in a wide range of waters in the United Kingdom usually showed no relationship between fish status and total zinc concentrations up to about 50 $\mu g.l^{-1}$. Regarding dissolved zinc concentrations, similar concentrations (up to 50 $\mu g.l^{-1}$) were not related to salmonid fish status in the U.K. waters, but non-salmonid ("coarse") fish were not observed in waters with dissolved zinc concentrations >25 $\mu g.l^{-1}$. The data from these field studies generally are in agreement with those of the laboratory studies.

Emans et al. (1992) derived NOEC values of 1.7 and 4.3 $\mu g.l^{-1}$, on the basis of multiple species tests reported by Marshall et al. (1983) and Gächter (1976). The former test included both algae and invertebrates, while the latter was limited to algae. Emans et al. noted that the tests had severe shortcomings, so, the NOEC values were considered unreliable.

1.2.2 Saltwater organisms

Short-term exposure (acute toxicity tests)

LC50 and EC50 values

Tests with invertebrates resulted in 24/96-hr LC50-values of 170 to 950,000 $\mu g.l^{-1}$. Most of these LC50 values range from about 1,000 to 10,000 $\mu g.l^{-1}$, but a considerable number of these values is <1,000 $\mu g.l^{-1}$. Molluscs and crustaceans are (among) the most sensitive species. A test with larvae of the oyster *Crassostrea gigas* resulted in a 48-hr EC50 of 120 $\mu g.l^{-1}$

(parameter: (ab)normal development). Fish generally are less sensitive, with 24/96-hr LC50 values of 2,730 to 83,000 $\mu g.l^{-1}$, the majority of the values being >10,000 $\mu g.l^{-1}$ (Mance, 1987). In a second review (U.S. EPA, 1980) acute LC50 and EC50 values of 165-55,000 $\mu g.l^{-1}$ and 2,730-83,000 $\mu g.l^{-1}$ were reported for invertebrates and fish, respectively. Test compounds used in the studies reviewed in these publications usually were $ZnSO_4$ or $ZnCl_2$ which have a high aqueous solubility.
Static tests with the mysid crustacean *Holmesimysis costata* resulted in 96-hr LC50 values of 74-97 $\mu g.l^{-1}$ for 1-d to 9-d old juveniles, based on actual concentrations. The tests were conducted in natural seawater with a salinity of 34 $^{o}/oo$; the test compound was $ZnSO_4.7H_2O$ (Martin et al., 1989). MacRae and Pandey (1991) estimated an 72-hr "LC50" of about 65 $\mu g.l^{-1}$ for the crustacean *Artemia francisca* (brine shrimp), based on emergence and hatching; 65 $\mu g.l^{-1}$ was one of the nominal test concentrations used. The cysts were exposed in hatching medium (no further data on the medium reported).

Long-term exposure (chronic toxicity tests)

NOEC values (table 1.3)
Long-term "single species" toxicity tests resulting in NOEC values which have been used in the ecotoxicological effect assessment to derive a maximum tolerable concentration in seawater are summarized in table 1.3.

LC50 and EC50 values
Tests with the diatom *Nitzschia closterium* (Algae) resulted in 4-d EC50 values (growth) of 270 and 360 $\mu g.l^{-1}$ in a non-chelating and a chelating artificial test medium (the latter containing citric acid and amino acids), respectively. The initial pH of the former medium was higher than that of the latter: about 8 *versus* 7 (Rosko and Rachlin (1975).
Long-term lethal toxicity tests (exposure time 5-14 days) resulted in LC50 values of 100 to 83,000 $\mu g.l^{-1}$ for invertebrates and fish (Mance, 1987). These values are similar to the 24/96-hr L(E)C50 values derived for these organisms (see "short-term exposure"). A flow-through test with the mussel *Mytilus edulis* resulted in a 21-d EC50 (growth) of 60 $\mu g.l^{-1}$, based on nominal concentrations. The test was conducted in natural seawater with a salinity of 33 $^{o}/oo$; the test compound was $ZnCl_2$ (Strömgren, 1982; see also table 1.4). A renewal test with the mysid crustacean *H. costata* resulted in a 7-d LC50 of 46 $\mu g.l^{-1}$, based on actual concentrations. The test was

conducted in natural seawater with a salinity of 35 $^{o}/oo$; the test compound was $ZnSO_4.7H_2O$ (Martin et al., 1989; see also table 1.3).

Additional data on long-term exposure (miscellaneous data)

Long-term "single species" toxicity tests in which the lowest test concentration resulted in an effect are summarized in table 1.4. An additional study which is not listed in this table is summarized below. Tests with both mono- and multispecies cultures of marine unicellular algae (dinoflagellates and diatoms) in seawater indicate that the sensitivity to zinc increased with increasing number of species in one culture, especially with respect to maximum cell densities. For example, maximum cell density of the diatom *Thalassiosira rotula* was not affected at 50 $\mu g.l^{-1}$ in a monospecies culture, while this growth parameter was reduced by 30% at 5 $\mu g.l^{-1}$ in a five-species test. According to the author these results indicate that the sensitivity of natural phytoplankton communities to zinc (and other compounds) may be higher than predicted on the basis of single species laboratory tests, due to complex interactions such as interspecific nutrient competition (Kayser, 1977).

1.2.3 Metal interactions

There are numerous laboratory studies on the combined action (also called joint action) of metals, zinc included. The combined action of metals may vary from an antagonistic action (less than additive) to a synergistic action (more than additive), even for mixtures of the same metals. For example, tests with algae indicated a antagonistic effect of zinc and cadmium with respect to growth inhibition (Dragos et al., 1988), while tests with floating weeds indicated a synergistic effect of zinc and cadmium with respect to growth inhibition (Hutchinson and Czyrska, 1975). The differences observed with respect to the combined action of metals appear to be related to test species, to abiotic factors (such as water hardness) that may alter the speciation of metals, and to the combination of metals, both qualitative and quantitative. Because there are strong indications that the concentrations of the metals in mixtures are amongst the factors determining the ultimate combined effect, a distinction between acute toxicity studies (conducted at "high" concentrations) and chronic toxicity studies (conducted at "low" concentrations) has been made below.

Acute toxicity studies

Short-term studies which were conducted at lethal or nearly lethal concentrations have been reviewed by Alabaster and Lloyd (1980) and EIFAC (1987). The former review is limited to studies in which zinc was one of the compounds tested, while the latter review also contains a large number of studies in which zinc was not included. The studies reviewed and additional studies show several types of combined action, but an additive action of metals (zinc included) is most commonly observed. It is noted that this statement is largely based on tests with fish, especially freshwater species, but the limited data on invertebrates and plants are generally in agreement with those for fish.

In the case of a strictly additive action, the toxicity of the mixture can be predicted by concentration addition, as follows:

$$TU_{\text{mixture}} = TU_{\text{compound 1}} + TU_{\text{compound 2}} + \ldots\ldots + TU_{\text{compound n}}$$

$TU_{compound}$ = the ratio of the concentration to the effective concentration (e.g. C / LC50). In the case of a strictly additive action it is assumed that there is no interaction, but that the compounds act in a qualitatively similar way, i.e. affect the same toxicological endpoint.

The review by EIFAC (1987) also indicates that the concentration-addition model is appropiate for the prediction of the combined lethal toxicity of mixtures of compounds commonly found in sewage and industrial effluents (including both metals and compounds such as ammonia, phenol and cyanide).

Chronic toxicity studies

Long-term studies that were conducted at concentrations that were usually sublethal are limited. The available data, focused on studies including zinc, are summarized below.

* Van Leeuwen et al. (1987) and Enserink et al. (1991) studied the combined action of Zn, As, Cd, Cr, Cu, Hg, Ni and Pb on survival and reproduction of water flea *D. magna*. Two types of tests were conducted: 3-w renewal life-table tests starting with neonates (endpoint: survival) and 2-w flow-through population tests starting with exponentially growing populations (endpoint: yield, i.e. mean maximum number of daphnids). Both in tests with equitoxic mixtures (based on LC50 and EC50 values for the individual metals) and in tests with non-equitoxic mixtures (based on (former) Dutch water quality criteria), the observed LC50 and EC50 values of the mixtures were closely to the expected (calculated) values based on concentration addition: 1.0-2.5 TU observed *versus* 1.0 TU expected. *[The observed L(E)C50*

values of these mixtures of eight metals may range theoretically from 1 TU (addition) to 8 TU (no addition)] The concentrations in the mixtures tested ranged from about 0.1 to 10 TU (all metals combined), i.e from 0.1 to 10 times the concentration that would result in 50% effect. The tests were conducted in Lake IJssel water (hardness 225 $mg.l^{-1}$, as $CaCO_3$; pH 8.1).

* Life-table tests with *D. magna* were also conducted by Biesinger et al. (1986), to study the combined action of binary mixtures of Zn and Cd, Zn and Hg, and Cd and Hg. The metals were tested at one-half, once and twice the 16% reproduction impairment concentrations reported in Biesinger and Christensen (1972). The tests with binary mixtures resulted in significant ($p \leq 0.05$) decreases in reproductive success when metals were combined at concentrations which did not significantly decrease reproduction when the metals were tested individually. The tests were conducted in Lake Superior water (hardness 45 $mg.l^{-1}$, as $CaCO_2$; pH 7.4-8.2).

* In tests with the estuarine mud crab *Rhithropanopeus harrisii*, concentrations of 25 or 50 $\mu g.l^{-1}$ of either zinc or lead in seawater usually resulted in a 1-d delay in larval development, while combinations of these metals usually did not. The ultimate effect was dependent on the concentrations used. For example, the combination of 25 μg $Zn.l^{-1}$ and 50 μg $Pb.l^{-1}$ resulted in an developmental time of 15.8 days, while the combination of 50 μg $Zn.l^{-1}$ and 50 μg $Pb.l^{-1}$ resulted in a developmental time of 14.7 days; the latter development time is very similar to that for controls (14.3 days). So, in this study most combinations of these two metals showed an antagonistic effect (Benijts-Claus and Benijts, 1975).

* Eaton (1973) compared the numbers of embryos produced per female fathead minnow *P. promelas* exposed to either zinc alone (life cycle test by Brungs, 1969) or to trimetal mixtures of Zn, Cd and Cu (life cycle test by Eaton, 1973). This comparison shows that the results of the two studies can be described fairly well by a single concentration-response curve, indicating that the toxicity of the trimetal mixtures was little if any more toxic than its zinc component alone (no additive or otherwise combined action). For more details on these two studies, conducted in the same pond water (hardness 200 $mg.l^{-1}$, as $CaCO_3$; pH 7.7) see table 1.2.

* Spehar et al (1978) compared the results of life cycle tests with the flagfish *Jordanella floridae*, exposed to either zinc or cadmium alone (Spehar, 1976) or to binary mixtures of these two metals (Spehar et al., 1978). Based on survival of larvae not previously exposed as embryos it was concluded that the toxicity of the mixtures was little if any greater than that of zinc alone; data on survival of larvae previously exposed as embryos even suggested that the metals acted antagonistically. With respect

to reproductive parameters, the metal mixtures may have caused greater reductions in the number of spawnings per female and embryo production than corresponding individual metal concentrations, but a statistically significant additive action could not be shown. The tests were performed in Lake Superior water (hardness 45 mg.l^{-1}, as $CaCO_3$; pH 7.1-7.9; see also table 1.1.

* Spehar and Fiandt (1986) studied the joint effects of As, Cd, Cr, Cu, Hg and Pb (zinc <u>not</u> included) in chronic tests with the daphnid *C. dubia* and in semi-chronic tests with the fathead minnow *P. promelas*. The tests showed that the combined action was nearly strictly additive for daphnids (test parameters: survival and reproduction), but less than additive for fathead minnows (paramaters: survival and growth). According to these autors the reason for this species-dependent difference in the combined action of metals is not clear, but may be related to differences in metabolic defence mechanisms (such as the binding to metallothioneins) that are more specialized in fish than in daphnids. This may allow fish to become more tolerant during long-term exposure. The authors also refer to a review by the European Inland Fisheries Advisory Commission (EIFAC, 1980; not available) which states that the concentration-addition model is adequate for describing the acutely lethal joint action of commonly occurring constituents of sewage and industrial wastes (not specifically metals), but that toxicity based on concentrations approaching no effect levels are less than additive and probably do not contribute to the chronic toxicity of mixtures.

The above-mentioned chronic toxicity tests conducted at sublethal metal concentrations consistently show that the combined action of metals to daphnids is strictly or nearly additive, in conformity with lethal toxicity tests. The chronic tests with fish, however, generally show no additive or a less than strictly additive action, which is in contrast to lethal toxicity tests. Chronic toxicity tests with other organisms are not available or too limited for evaluation. Therefore, mainly on the basis of acute toxicity tests, it is assumed that concentration addition will generally be appropriate to estimate the chronic toxicity of low concentration metal mixtures to organisms other than fish.

1.2.4 Water-sediment systems

Van Beelen and co-workers studied the effect of zinc (added as $ZnCl_2$) on the mineralization of acetate, chloroform or 4-monochlorophenol (4-MCP) by microbial populations present in the freshwater sediments used (sediment characteristics not reported; "background" zinc concentration about 200 mg.kg^{-1} dry weight). Test slurries, containing 10 g fresh sediment and 10 ml filter-sterilized groundwater, were incubated under anaerobic conditions for 1 hour. The substrates were added in minute amounts (1 to 4 μg.l^{-1} slurry) to simulate environmental conditions and to prevent unnatural rapid growth of resistent microbes which could obscure the effect of zinc. The results of the tests were expressed as IC10 or IC50, defined as the toxicant concentration that causes 10% or 50% inhibition of the first-order mineralization rate of the substrate. IC50 values were >1,000, 170 and 20 mg.kg^{-1} dw (added concentrations). IC10 values for chloroform and 4-MCP mineralization were 53 and 8 mg.kg^{-1} dw (added concentration), respectively; that for acetate mineralization was not reported (Van Beelen et al., 1990). In similar tests in slurries containing River Rhine sediment from the same location but collected in different years, the IC50 and IC10 in the 1987 sample were 2,100 and 700 mg.kg^{-1} dw (added concentrations), respectively, while these values were 150 and 11 mg.kg^{-1} dw (added concentration) in the 1990 sample. The EC50 and EC10 (the toxicant concentration that causes 50% or 10% inhibition of the mineralization of the substrate after a certain incubation time) with respect to chloroform mineralization in the 1990 sediment were 320 and 25 mg.kg^{-1} dw (added concentration), respectively, after 7 days of incubation. Based on the total zinc concentration, the EC50 and EC10 were 955 and 452 mg.kg^{-1} dw. The concentration-response curves indicate that the background concentration of zinc also contributes to the effect of zinc, although less than added zinc. Therefore a partial inhibition of mineralization of substrates such as chloroform at zinc concentrations present in Dutch sediments is expected. The characteristics of the sediment samples were similar, although the 1987 sample contained more organic matter than the 1990 sample: 8.5% *versus* 5.3%; the background zinc concentration was 800 mg.kg^{-1} dw in both samples (Van Beelen et al., 1991a). IC10 values for other microbial activities tested in this sediment, viz., methane formation, mineralization of acetate and mineralization of 4-MCP were 1,800, 130 and 5 mg.kg^{-1} dw (added concentration), respectively (Van Beelen, unpublished data). These studies show that the effect of zinc depends on the specific substrate used in the test, and thus on the sensitivity of the microbial subpopulation which is able to mineralize this substrate, and further that only small amounts of added soluble zinc may result in significant effects on microbial activity (at least, shortly after addition), despite high background concentrations. The latter can be explained by differences in sorption and speciation of background zinc and newly added soluble zinc.

Table 1.1 Freshwater organisms - long-term toxicity tests used to derive a maximum tolerable concentration (MTC) in fresh water (NOEC and MATC values)

Organism & life stage	A	Test-type	Test-comp.	Test-water	pH	Hardness	Exp.-time	Criterion	Result µg Zn/l	Reference [& footnote]
Algae (unicellular)										
Chlorella vulgaris	-	S	$ZnSO_4$	art.	-	150	2-w	$NOEC_g$ $MATC_g$	400 1,265	 {√ (400 x 4,000)} Ahluwalia & Kaur '88 [1]
Chlorella vulgaris	-	S	$ZnCl_2$	art.	7-9	55	5-w	$NOEC_g$ $MATC_g$	560 1,160	 {√ (560 x 2,400)} Rosko & Rachlin '77 [2]
Chroococcus paris	-	S	$ZnSO_4.7H_2O$	art.	7.8	54	10-d	$NOEC_g$ $MATC_g$	200 280	 {√ (200 x 400)} Les & Walker '84 [3]
Kirchneriella subcapitata	-	-	$Zn(NO_3)_2$	art.	-	-	2-w	$NOEC_g$	95^{ϵ}	[4] Dragos et al.'88 [5]
Monoraphidium contortum	-	-	$Zn(NO_3)_2$	art.	-	-	2-w	$NOEC_g$ $MATC_g$	190 375	[6] {√ (190 x 750) Dragos et al.'88 [5]
Navicula incerta	-	S	$ZnCl_2$	art.	8.5	-	4-d	$NOEC_g$ $MATC_g$	1,000 2,370	 {√ (1,000 x 5,600)} Rachlin et al. '83 [7]
Scenedesmus quadricauda	-	S	$ZnSO_4$	art.	6.5	-	2-w	$NOEC_g$ $MATC_g$	100 150	 {√ (100 x 225)}
	-	S	$ZnSO_4$	art.	8.5	-	2-w	$NOEC_g$ $MATC_g$	225 335	 {√ (225 x 500)} Starodub & Wong '87 [8]
Scenedesmus quadricauda	-	S	$ZnSO_4.7H_2O$	river	7.5	200	4-d	$NOEC_g$	700^{ϵ}	 Bringmann & Kühn '59 [9]
Selenastrum capricornutum	-	S	$ZnCl_2$	art.	7	15	4-d	$NOEC_g$	15^{ϵ}	 Bartlett et al. '74 [10]
Selenastrum capricornutum	-	S	-	art.	-	"very soft"	2-w	$NOEC_g$ $MATC_g$	5 7	 {√ (5 x 10)} Kuwabara '85 [11]
Synechococcus 6301	-	S	$ZnSO_4$	art.	-	-	14-d	$NOEC_g$ $MATC_g$	390 475	 {√ (390 x 585)} Mohanty '89 [12]
Algae (multicellular)										
Cladophora glomerata 1 cm fragments	-	S	-	art.	8.4	≥35	3-d	$NOEC_g$	60 69	 {√ (60 x 80)} Whitton '67 [13]
Hormidium rivulare	-	S	$ZnSO_4/ZnCl_2$	art.	6	≥35	1-w	$NOEC_g$ $MATC_g$	1,000 3,150	 {√ (1,000 x 10,000)} Hargreaves & Whitton '76a [14]

(to be continued)

Table 1.1 Freshwater organisms - long-term toxicity tests used to derive a maximum tolerable concentration (MTC) in fresh water (NOEC and MATC values) [continued]

Organism & life stage	A	Test-type	Test-comp.	Test-water	pH	Hardness	Exp.-time	Criterion	Result µg Zn/l	Reference [& footnote]
Poriferans										
Ephydatia fluviatilis	-	F	$ZnCl_2$	art.	7	150	10-d	$NOEC_{g,t-d}$ $MATC_{g,t-d}$	3.2 4.5	 (√ (3.2 x 6.5)) Francis & Harrison '88 [15]
Molluscs										
Corbicula sp. adult	+	F	$ZnSO_4$	river	8.2	68	4-w	$NOEC_{g,s}$ $MATC_{g,s}$	25 35	 (√ (25 x 50)) Belanger et al. '86 [16]
Crustaceans										
Ceriodaphnia dubia P < 1 d --> F_1 [lc]	+	R	-	New river	6	81	1-w	$NOEC_r$ $MATC_r$	25 35	 (√ (25 x 50))
Ceriodaphnia dubia P < 1 d --> F_1 [lc]	+	R	-	New river	8	81	1-w	$NOEC_r$	8^{ϵ}	[17]
Ceriodaphnia dubia P < 1 d --> F_1 [lc]	+	R	-	New river	9	81	1-w	$NOEC_r$ $MATC_r$	25 35	 (√ (25 x 50))
Ceriodaphnia dubia P < 1 d --> F_1 [lc]	+	R	-	Amy Bayou	6	118	1-w	$NOEC_r$	25^{ϵ}	[18]
Ceriodaphnia dubia P < 1 d --> F_1 [lc]	+	R	-	Amy Bayou	8	118	1-w	$NOEC_r$ $MATC_r$	50 70	 (√ (50 x 100))
Ceriodaphnia dubia P < 1 d --> F_1 [lc]	+	R	-	Amy Bayou	9	118	1-w	$NOEC_r$	25^{ϵ}	[19]
Ceriodaphnia dubia P < 1 d --> F_1 [lc]	+	R	-	Clinch river	6	168	1-w	$NOEC_r$	25^{ϵ}	[20]
Ceriodaphnia dubia P < 1 d --> F_1 [lc]	+	R	-	Clinch river	8	168	1-w	$NOEC_r$ $MATC_r$	50 70	 (√ (50 x 100))
Ceriodaphnia dubia P < 1 d --> F_1 [lc]	+	R	-	Clinch river	9	168	1-w	$NOEC_r$	17^{ϵ}	[21] Belanger & Cherry '90 [22]
Daphnia magna P < 1 d --> F_1 [lc]	-	R	$ZnSO_4.7H_2O$	pond	8.3	50	7-w	$NOEC_r$ $MATC_r$ $NOEC_s$	25 35 75	 (√ (25 x 50))
Daphnia magna P < 1 d --> F_1 [lc]	-	R	$ZnSO_4.7H_2O$	pond	8.3	100	7-w	$NOEC_r$ $MATC_r$ $NOEC_s$	75 85 100	 (√ (75 x 100))
Daphnia magna P < 1 d --> F_1 [lc]	-	R	$ZnSO_4.7H_2O$	pond	8.3	200	7-w	$NOEC_{r,s}$ $MATC_{r,s}$	150 160	 (√ (150 x 175)) Paulauskis & Winner '88 [23]
Daphnia magna P < 1 d --> F_1 [lc]	+	R	$ZnCl_2$	lake	7.7	45	3-w	$NOEC_r$	35^{ϵ}	Biesinger & Christensen '72 [24]
Daphnia magna P < 1 d --> F_1 [lc]	+	R	$ZnCl_2$	lake	7.7	45	3-w	$NOEC_r$ $MATC_r$	74 α 100	 (√ (74 x 140)) Biesinger et al. '86 [25]

(to be continued)

Table 1.1 Freshwater organisms - long-term toxicity tests used to derive a maximum tolerable concentration (MTC) in fresh water (NOEC and MATC values)
[continued]

Organism & life stage	A	Test-type	Test-comp.	Test-water	pH	Hardness	Exp.-time	Criterion	Result µg Zn/l	Reference [& footnote]
Crustaceans (continued)										
Daphnia magna	+	R	$ZnCl_2$	lake	8.1	225	21-d	NOEC_g	37	[26]
P < 1 d --> F [lc]								MATC_g	67	(√ (37 x 120))
								$\text{NOEC}_{s,r}$	310	[26]
Daphnia magna	+	F	$ZnCl_2$	lake	8.1	225	17-d	$\text{NOEC}_{s,r}$	420^{ϵ}	[27]
									Enserink et al.'91	[28]
Daphnia magna	+	R	-	lake	7.7	65	21-d	$\text{NOEC}_{s,r}$	100	
P < 2 d --> F_1 [lc]								$\text{MATC}_{s,r}$	120	(√ (100 x 150))
(population "I" and "L")										
Daphnia magna	+	R	-	lake	7.7	65	21-d	NOEC_r	25^{ϵ}	[29]
P < 2 d --> F_1 [lc]								NOEC_s	100	
(population "P")									Münzinger & Monicelli '91	[30]
Insects										
Epeorus latifolium	-	F	$ZnSO_4$	ground	7.9	83	4-w	NOEC_e	3	
larvae, length 6 mm								MATC_e	5	(√ (3 x 10))
								NOEC_g	30	
									Hatakeyama '89	[31]
Fish										
Brachydanio rerio	-	R	$ZnSO_4.7H_2O$	art.	7.5	100	2-w	NOEC_h	1,290	
eggs < 4 hr --> larvae [els]							2-w	NOEC_s	6,095	
									Dave et al. '87	[32]
Jordanella floridae	+	F	$ZnSO_4.7H_2O$	lake	7.5	44	>3-m	NOEC_g	26	α
P (larvae) --> F_1 (larvae) [lc]								MATC_g	36	(√ (26 x 51))
1-d (from unexposed eggs)								$\text{NOEC}_{s,r,h}$	51	α
Jordanella floridae	+	F	$ZnSO_4.7H_2O$	lake	7.5	44	>3-m	$\text{NOEC}_{s,g,r,h}$	75	α [33]
P (larvae) --> F_1 (larvae) [lc]								$\text{MATC}_{s.g.r,h}$	102	(√ (75 x 139)
1-d (from exposed eggs)									Spehar '76	[34]
Phoxinus phoxinus	+	F	$ZnNO_3.4H_2O$	tap	7.5	70	5-m	$\text{NOEC}_{s,g}$	50	α
yearlings								$\text{MATC}_{s,g}$	80	(√ (50 x 130))
									Bengtsson '74b	[31]
Pimephales promelas	+	R	$ZnSO_4.7H_2O$	art.	7.0	100	1-w	NOEC_d	120	
embryos --> larvae [els]								MATC_d	225	(√ (120 x 430))
									Dawson et al.'88	[35]
Pimephales promelas	+	R	-	lake	7.5	48	1-w	NOEC_s	85	α
larvae < 1 d								MATC_s	125	(√ (85 x 184))
								NOEC_g	184	
									Norberg & Mount '85	[36]

(to be continued)

Table 1.1 Freshwater organisms - long-term toxicity tests used to derive a maximum tolerable concentration (MTC) in fresh water (NOEC and MATC values) [continued]

Organism & life stage	A	Test-type	Test-comp.	Test-water	pH	Hard-ness	Exp.-time	Criterion	Result µg Zn/l	Reference [& footnote]
Fish (continued)										
Pimephales promelas	+	F	$ZnSO_4.7H_2O$	lake	7.5	46	>8-m	NOEC$_{s,h}$	145	α
P --> F_1 [lc]								MATC$_{s,h}$	205	{√ (145 x 295)}
(eggs < 1 d) (larvea 2 m)								NOEC$_{m,r}$	295	α
								NOEC$_g$	≥ 575	α
									Benoit & Holcombe '78	[37]
Pimephales promelas	+	F	$ZnSO_4.7H_2O$	well	-	220	4-w	NOEC$_g$	300	
larvae 1 d --> fry								MATC$_g$	370	{√ (300 x 450)}
								NOEC$_s$	700	
									Broderius & Smith jr. '79	[38]
Salmo gairdneri	+	F	$ZnSO_4$	well	7.8	330	2-yr	NOEC$_s$	320	α [39,40]
fingerlings --> adults								MATC$_s$	450	{√ (320 x 640)}
								NOEC$_g$	≥ 2,200	α
Salmo gairdneri	+	F	$ZnSO_4$	tap	6.8	26	2-yr?	NOEC$_s$	140	α [41]
eyed eggs --> sexual maturity								MATC$_s$	190	{√ (140 x 260)}
								NOEC$_g$	≥ 545	
Salmo gairdneri	+	F	$ZnSO_4$	tap	6.8	26	3-w	NOEC$_s$	36	α [42,40]
"fish" (unexposed as eggs)								MATC$_s$	50	{√ (36 x 71}
									Sinley et al. '74	[31]
Salvelinus fontinalis	+	F	$ZnSO_4.7H_2O$	lake	7.5	45	3-yr	NOEC$_h$	535	α [43]
P --> F_2 [lc]								MATC$_h$	850	{√ (535 x 1,360)}
(yearlings) (larvae 3 m)								NOEC$_{s,g,r}$	≥ 1,360	
Salvelinus fontinalis	+	F	$ZnSO_4.7H_2O$	lake	7.5	45	>3-m	NOEC$_s$	715	α [31]
eggs 6 hr --> larvae 3 m [ELS]								MATC$_s$	990	{√ (715 x 1,370)}
								NOEC$_g$	2,060	α
									Holcombe et al.'79	[44]

Parameters:
d = developmental effects (deformities); e = emergence; g = growth; h = hatchability;
m = maturation (sexual development); r = reproduction; s = survival; t-d = tissue-deterioration.

lc: life cycle test; **els:** early life stage test (egg-larval test)

For footnotes see next pages; for further information see the "list of abbreviations tables 1.1 to 1.4".

Footnotes table 1.1

[1] Test medium according to Allen and Arnon (1955); the medium contained 4 mg/l EDTA-complex (10x10^{-3} mMol/l), and macro- and micro-elements including 0.05 mg Zn/l. According to the authors, growth was significantly reduced at 4,000 µg/l, but statistical data were not reported.

[2] No statistics reported. Test medium: sterile Bristol's medium containing macro- and micro-elements (assumed to be chelator free, see [7]). Chlorophyll a content per cell was reduced 15% at 560 µg/l, but the number of cells was increased 10%. At 2,400 µg/l both parameters were reduced at least 20%.

[3] No statistics reported. Test medium according to Allen (1968); the medium contained EDTA (3x10^{-3} mMol/l), and macro- and micro-elements including 0.05 mg Zn/l. Growth parameter: optical density, measured by spectrometry.

[4] Growth parameter: generation time. The NOEC was estimated from the lowest effect concentration (15% increase in generation time at 190 µg/l) using a factor of 2.

[5] No statistics reported. Test medium: modified Zehnder et al. (1960) no. 11 medium; EDTA omitted. Test concentrations reported: <u>0.187</u>, 0.750, 1.5, 3 and 4 mg/l, without data on analysis.

[6] Growth parameters: cell number, chlorophyll a content (in medium and per cell), optical density and generation time. Chlorophyll content per cell increased with increasing zinc concentration.

[7] No statistics reported. Test medium: sterile, chelator free LDM medium (100 ml/l Bristol's solution and 900 ml/l seawater). Bristol's solution contains macro- and microelements. Growth parameter: number of cells.

[8] Statistics: $p \leq 0.05$. Test medium: CHU-10 medium; this EDTA-free medium represents a relatively unpolluted lake water (Wong et al., 1982, 1978; Chu, 1942). Growth rate (increase in optical density) measured by spectrometry.

[9] Test water: filtered river water. "Toxic threshold" for growth (number of cells) 1,400 µg/l. The NOEC was estimated from the toxic threshold using a factor of 2.

[10] Test medium: AAPBT-medium (EPA, 1971) containing 300 µg/l Na$_2$-EDTA (equivalent to 0.9x10^{-3} mMol/l). The NOEC was estimated from the lowest effect concentration (20% decrease in dry weight at 30 µg/l) using a factor of 2. Zinc was completely inhibitory and algicidal at 100 and 700 µg/l, respectively.

[11] No statistics reported. Test medium: nutrient medium eluted through Chelex-100 to remove cationic impurities. Test media (S-3) were finally filter sterilized (0.45 µm). Computed free Zn-ion concentrations were equal to total-zinc concentrations. Growth parameters: lag phase, growth rate, and stationary phase cell density.

[12] No statistics reported. Test medium: BG-11 medium, containing 1 µg/ml Fe-EDTA (3x10^{-3} mMol/l). After about 2 weeks of growth, a known quantity of cells were transferred to fresh medium for repeated culture for 7 to 10 times. During each trasfer growth parameters were measured. At the NOEC indicated (390 µg/l) the increase in cell number was marginal untill the end of day 7, after which a sharp increase up to day 14 was seen, while in control cultures (65 µg/l) the lag phase was only 2 days followed by a progresssive increase in the number of cells up to day 11. Due to the increased lag phase at 390 µg/l, the growth parameters chlorophyll a content, phycocyanin content, protein content (all expressed as µg/ml medium), total CO$_2$-fixation capacity and total dry mass of algae were reduced. However, on a per cell basis there was no adverse effect on these parameters. Furthermore, exponential growth rate after the lag phase and the total number of cells after the growth phase were not adversely affected, while total inhibition of cell growth was observed at 585 µg/l.

[13] No statistics reported. Test medium: EDTA-free modified no. 10 medium of CHU (1942), enriched with 10% river water and trace elements. Hardness calculated from original Chu (1942) medium.

[14] No statistics reported. Test medium according to Hargreaves and Whitton (1976b); the medium contained 6x10^{-3} mMOl/l EDTA, and macro-and micro-elements. A series of tests was conducted, at different hardness (range 35-500). In a second series of tests, conducted at a calcium level of 0 mg/l (hardness 10 mg/l, due to the presence of 0.1 mMol Mg/l), growth was reduced at 1,000 µg/l, within the range of pH-values of 3 to 7. Because control growth in the absence of calcium was poor, the results of the second series of tests were not used to derive a NOEC.

[15] Test medium contained 6 mg/l Na$_2$EDTA.2H$_2$O (16x10^{-3} mMol/l), and macro- and microelements. At 1x10^{-7} Mol Zn/l and higher concentrations, a "pronounced toxicity" existed (progresssive deterioration of of interior tisues, although growth continued. Required for normal growth: 1x10^{-9} to 1x10^{-8} Mol Zn/l (0.065 to 0.65 µg/l).

[16] Statistics ($p \leq 0.05$) on growth data only (shell length and total weight). At 25 µg.l^{-1} mortality was 5%. Tests were conducted in field-located artificial streams containing coarse sand sediment (diameter 2-9 mm); the cages with clams were buried in the sand.

[17] The NOEC was estimated from the lowest effect concentration (28% inhibition at 25 µg/l) using a factor of 3.

[18] The NOEC was estimated from the lowest effect concentration (16% inhibition at 50 µg/l) using a factor of 2.

[19] The NOEC was estimated from the lowest effect concentration (13% inhibition at 50 µg/l) using a factor of 2.

[20] The NOEC was estimated from the lowest effect concentration (20% inhibition at 50 µg/l) using a factor of 2.

[21] The NOEC was estimated from the lowest effect concentration (30% inhibition at 50 µg/l) using a factor of 3.

[22] Reproductive parameter: number of young per female. The NOEC-values listed in the table sometimes differ from the NOEC-values reported by Belanger and Cherry (1990), because in their statistical analysis of the reproduction data, the pH = 8 and 0 µg/l Zn treatment in each test water was considered to be the control value. The NOEC-values in table 1.1 are based on comparisons (per test water) with the 0 µg/l Zn control at

Footnotes table 1.1 (continued)

corresponding pH. Data on survival reported incompletely, but it appears that survival was not affected at the test concentrations used (0, 25 and 50 µg/l in New river water; 0, 50 and 100 µg/l in Amy Bayou and Clinch river water). The parent pH of the test water was approximately 8.

[23] Statistics: $p \leq 0.05$. Soft test water (hardness 50) was prepared by diluting pond water with distilled, deionized, carbon-filtered, Organex-Q-filtered water; this dilution of water contains essentially no trace organic compounds. Medium (hardness 100) and hard (hardness 200) test waters were prepared from soft water by adding $CaSO_4$ and $MgSO_4$ in quantities that would maintain the approximate 2:1 ratio of calcium to magnesium in the pond water. Reproductive parameter: brood size.

[24] Test medium: Lake Superior water, strained through # 20 bolting cloth. Reproductive parameter: total number of young. A 16% reproductive impairment concentration representing "the minimal reproducible value below which the variability in reproduction could not be detected from controls" was reported at 70 µg/l. The NOEC was estimated from the lowest effect concentration (16% impairment at 70 µg/l) using a factor of 2.
Survival and growth of initial animals were reported to be less sensitive than reproduction, without further details.

[25] Statistics: $p \leq 0.05$. Test water: Lake Superior water, strained through # 20 bolting cloth. In one out of two test performed, reproduction was considerably reduced (40-50%) at 74 µg/l, but this effect was not statistically significant. Tests were conducted at sublethal concentrations (see also Biesinger & Christensen, 1972). Reproductive parameter: total number of young.

[26] Statistics: $p \leq 0.01$. Because only the lowest effect concentrations with respect to growth (120 µg/l) and survival and reproduction (1,000 µg/l) were reported, the NOEC-values were derived from these concentrations using a factor of 3.2, i.e. the ratio used between test concentrations.

[27] Tests were started with exponentially growing populations. The NOEC is the EC10 for yield (mean maximum number of daphnids) reported by Enserink et al. (1991).

[28] Test water: Lake Ijssel water filtered through a 25 µm mesh and UV-treated.

[29] No statistics reported. The NOEC has been estimated from the lowest concentration (14% inhibition at 50 µg/l) using a factor of 2.

[30] Test water: 40 µm filtered lake water. Three different populations were tested separately. Reproductive parameter: number of young. In additional 3-w tests under the same test conditions, brood size (eggs/animal) and body length of primiparous animals of all three populations were significantly ($p \leq 0.05$) affected ($p \leq 0.05$) at 150 µg/l, the only test concentration used in these additional tests.

[31] Statistics ($p \leq 0.05$) reported on growth data only. Background zinc concentration in test water 9 µg/l.

[32] Parameter h: hatching time. The NOEC-values indicated for hatching and survival are the reported arithmetic mean values from 10 ring tests conducted in 5 laboratories. The lowest NOEC-values for hatching and survival were 180 and 2,875 µg/l, respectively.

[33] At 139 µg/l, only growth of male fish was significantly ($p \leq 0.05$) reduced. However, reproductive parameters were also strongly reduced, although not statistically significant due to the variable response.

[34] Statistics: $p \leq 0.05$. Test medium: untreated Lake Superior water.

[35] Statistics ($p \leq 0.05$) on growth data only. Concentrations were analysed in stock solutions, not in test waters. Survival and growth were affected at higher concentrations than that resulting in larval deformities; NOEC-values for survival and growth could not be derived from the data reported.

[36] Statistics: $p \leq 0.05$. Test medium: Lake Superior water; pH based on Lake Superior water characteristics reported by Spehar (1976). No data on pretreatment of Lake Superior test water.

[37] Statistics: $p \leq 0.05$. Test medium: Lake Superior water, passed through an ultraviolet sterilizer. Total number of spawnings found on substrates, adhesiveness to spawning substrate and egg fragility (chorion rupture during removal from substrate) were affected at 145 µg/l. However, maturation and the total number of spawnings were not affected up to 295 µg/l. Eight-week survival was determined for both parental fish and offspring.

[38] No statistics reported. NOEC for growth (dry weight) derived from figure. Control survival was low, about 60%.

[39] Mortality 6.4% at 640 µg/l, versus 0% at concentrations up to 320 µg/l. The investigators reported a MATC between 320 and 640 µg/l. The test did not yield valid reproduction data, but male and female fertility appeared to be unaffected up to the highest concentration tested (2,200 µg/l)

[40] In this study the NOEC and EC were derived in accordance with the view of the authors, although mortality at the effect concentration indicated was less than 10% (versus 0% in the control groups).

[41] Mortality at 260 µg/l was 13.1% for yolk-sac fry and 6.9% for feeding fry, versus 5.5% and 2.6%, respectively, in the experimental control group. The investigators reported a MATC between 140 and 260 µg/l. At lower concentrations mortality was very similar to both experimental controls and hatchery controls.

[42] Mortality 8% at 71 µg/l versus 0% in the control group; the investigators reported a MATC between 36 and 71 µg/l.

[43] Egg fragility (force required to rupture egg chorions) was reduced at 266 µg/l, but hatchability was not affected at 535 µg/l.

[44] Statistics: $p \leq 0.05$. Test medium: Lake Superior water, passed through an ultraviolet sterilizer.

Table 1.2 Freshwater organisms - long-term toxicity tests: additional data (miscellaneous toxicity values)

Organism & life stage	A	Test-type	Test-comp.	Test-water	pH	Hardness	Exp.-time	Criterion	Result µg Zn/l	Reference [& footnote]
Bacteria										
Zoogloea ramigera	-	S	$ZnCl_2$	art.	7	80	1-d	EC_g	1,000	Norberg & Molin '83 [1]
Algae										
Anabaena variabilis	-	S	$ZnSO_4$	art.	-	-	2-w	EC_g	400	Ahluwalia & Kaur '88 [2]
Chlorella fusca	-	S	$ZnCl_2$	art.	-	220	1-d	$NOEC_g$ $MATC_g$	6,500 20,550 (√ (6,500 x 65,000))	Hofner et al.'87 [3]
Chlorella vulgaris	-	S	$ZnCl_2$	art.	-	-	18-d	$NOEC_g$ $MATC_g$	20,000 34,640 (√ (20,000 x 60,000))	Maeda et al. '90 [4]
Chlorella vulgaris	-	S	$ZnSO_4$	art.	6	55	4-d	EC_g	1,000	Rachlin & Farran '74 [5]
Chlorella vulgaris	-	S	$ZnSO_4.7H_2O$	art.	5.5	-	5-d	EC_g	50,000	Skowronski & Rzeczycka '80 [6]
Chlorella vulgaris	-	S	$ZnSO_4.7H_2O$	art.	-	-	3-d	$NOEC_g$ $MATC_g$	60,000 64,800 (√ (60,000 x 70,000))	Wren & McCarrol '90 [7]
Chlorella vulgaris	A	S	$ZnSO_4.7H_2O$	art.	-	-	3-w	$NOEC_g$	≥ 35,500 α [8]	Coleman et al.'71 [9]
Chlorella sp.	-	-	$ZnCl_2$	art.	-	-	10-d	EC_g	65,000	De Fillippis & Pallaghy '76 [10]
Cladophora glomarata 1 cm fragments	-	S	-	art.	8.4	≥35	3-d	$NOEC_g$ $MATC_g$	300 345 (√ (300 x 400))	Whitton '67 [11]
Pediastrum tetras (4-cell colonies)	A	S	$ZnSO_4.7H_2O$	art.	-	-	3-w	$NOEC_g$	8,070 α [12] 12,060 (√ (8,070 x 18,030))	Coleman et al.'71 [9]
Scenedesmus quadricauda	-	S	$ZnSO_4$	art.	4.5	35	2-w	EC_g	100	Starodub & Wong '87 [13]
Spiruluni maxima	-	S	$ZnCl_2$	art.	-	220	10-d	$NOEC_g$ $NOEC_g$	6,500 20,550 (√ (6,500 x 65,000))	Hofner et al.'87 [3]
Stichococcus bacillaris	-	S	$ZnSO_4.7H_2O$	art.	5.5	-	5-d	EC_g	50,000	Skowronski & Rceczycka '80 [14]

(to be continued)

Table 1.2 Freshwater organisms - long-term toxicity tests: additional data (miscellaneous toxicity values) [continued]

Organism & life stage	A	Test-type	Test-comp.	Test-water	pH	Hardness	Exp.-time	Criterion	Result µg Zn/l	Reference [& footnote]
Macrophytes										
Lemna paucicostata "6746"	-	S	$ZnSO_4.7H_2O$	art.	4/5	620	1-w	$NOEC_g$ $MATC_g$	5,000 7,000	[15a] (√ (5,000 x 10,000))
	-	S	$ZnSO_4.7H_2)$	art.	6/7	110	1-w	EC_g	1,000	[15b] Nasu & Kugimoto '81 [15]
Protozoans										
Euglena gracilis	-	S	$"Zn^{2+}"$	art.	-	-	2-w	$NOEC_g$ $MATC_g$	0.75 2	 (√ (0.75 x 7.5)) Mills, 1976 [16]
Euglena gracilis	-	S	$ZnCl_2$	art.	3.5	175	1-w	$NOEC_g$	≥ 1,000	Gingrich et al.'84 [17]
Euglena gracilis	-	S	$ZnSO_4$	art.	-	175	1-w	$NOEC_g$	≥ 1,950	Price & Vallee '62 [18]
Euglena viridis	A	S	$ZnSO_4.7H_2O$	art.	-	-	3-w	$NOEC_g$ $MATC_g$	4,200 α 6,040	[19] (√ (4,200 x 8,700)) Coleman et al.'71 [9]
Tetrahymena pyriformis	-	S	$ZnSO_4$	art.	-	"0"	4-d	NOLC	1,330	Carter & Cameron '73 [20]
Annelids										
Erpobdella octulasta newly hatched	+	R	$ZnSO_4$	river	-	15	10-w	LC50	60	Willis '89 [21]
Molluscs										
Ancylus fluviatilis shell lenght < 2 mm	+	R	$ZnSO_4$	river	-	15	14-w	LC50	80	Willis '88 [22]
Corbicula sp. adults (13-16 mm)	+	F	$ZnSO_4$	river	8.4	71	4-w	$EC_{s,g,b}$	34 α	Farris et al.'89 [23]
Corbicula sp. adults (13-16 mm)	+	F	$ZnSO_4$	tap	7.9	56	4-w	$NOEC_b$	≥ 1,100 α	Farris et al.'89 [24]
Crustaceans										
Dapnia magna P (<1-d) --> F_1 [lc]	-	R	$ZnSO_4.7H_2O$	pond	8.8	145	>4-m	$EC_{s,g}$	100	Winner '81 [25]

(to be continued)

Table 1.2 Freshwater organisms - long-term toxicity tests: additional data (miscellaneous toxicity values) [continued]

Organism & life stage	A	Test-type	Test-comp.	Test-water	pH	Hardness	Exp.-time	Criterion	Result µg Zn/l	Reference [& footnote]
Crustaceans (continued)										
Daphnia magna [lc]	-	-	$ZnCl_2$	-	-	52	-	NOEC	97	
Daphnia magna [lc]	-	-	$ZnCl_2$	-	-	104	-	NOEC	43	
Daphnia magna [lc]	-	-	$ZnCl_2$	-	-	211	-	NOEC	42	Paulauskis & Winner '88 (from Chapman et al., unp.)
Gammarus pulex P brooding females --> F_1	-	-	$ZnSO_4.7H_2O$	art.	-	-	3-w	EC_r $NOEC_s$	100 300	Maltby & Naylor '90 [26]
Macrobrachium hendersodyanum adults	-	R?	-	tap	7.2	65	2-w	NOLC EC_l	3,000 3,000	Patil & Kaliwal '87
Insects										
Clistoronia magnifica P (3th instar larvae) --> F_2 [lc]	+	F	$ZnCl_2$	well	7	31	>5-m	$NOEC_{s,a-e,r}$	≥ 5,240	Nebeker et al.'84 [27]
Fish										
Lebistes reticulatus newborn fish (< 2-d)	-	R	$ZnSO_4.7H_2O$	-	8	80	3-m	$EC_{s,g}$	1,150	Crandall & Goodnight '62 [28]
Phoxinus phoxinus mature	+	F	$ZnNO_3.4H_2O$	tap	7.5	70	5-m	$NOEC_{s,g}$ $MATC_{s,g}$	130 α 160 (√ (130 x 200))	Bengtsson '74b [29]
Pimephales promelas P fish (2 m) --> F1 (fry 3 w) [lc]	+	F	$ZnSO_4.7H_2O$	pond	7.7	200	10-m	$NOEC_r$ $MATC_r$ $NOEC_{h,s}$ $NOEC_{g,m}$	≥ 30 α ≥ 75 (√ (30 x 180)) 180 α 1,300 α	Brungs '69 [30]
Pimephales promelas P fish (2 w) --> F_1 (larvae 1 m) [lc]	+	F	$ZnSO_4.7H_2O$	pond	7.7	200	12-m	$NOEC_r$ $MATC_r$ $NOEC_{g,m}$ $NOEC_{s,h}$	≥ 27 α 34 (√ (27 x 42)) 148 α 303 α	Eaton '73 [31]
Oncorhynchus nerka	+	F	$ZnCl_2$	well	7.2	20-90				
adults							3-m	$NOEC_{s,g,m,r}$	≥ 120 α	
eggs --> smolts							21-m	$NOEC_{s,g}$	≥ 240 α	Chapman, '78a [32]

(to be continued)

Table 1.2 Freshwater organisms - long-term toxicity tests: additional data (miscellaneous toxicity values) [continued]

Organism & life stage	A	Test-type	Test-comp.	Test-water	pH	Hardness	Exp.-time	Criterion	Result µg Zn/l	Reference [& footnote]
Fish (continued)										
Salmo gairdneri yearlings	+	F	$ZnSO_4.7H_2O$	well	7.3	374 (EDTA)	12-w	$NOEC_g$	520 α	
								$MATC_g$	765	(√ (520 x 1.120)
								$NOEC_s$	≥ 1,120 α	
										Watson & McKeown '76 [33]
Salmo trutta yolk-sac fry	+	F	$Zn(NO_3)_2$	art.	4.5	4	4-w	LC	20 α	
					6.5	4	4-w	$NOEC_{s,g}$	≥ 18 α	
										Reader et al.'89 [34]
Salmo trutta yolk-sac fry	+	F	$Zn(NO_3)_2$	art.	4.5	4	4-w	LC	4 α	
					4.5	22	4-w	$NOEC_{s,g}$	≥ 21 α	
										Sayer et al.'89 [35]
Amphibians										
Bufo arenarum larvae	-	S	-	art.	-	-	5-d	NOLC	16,000	Herkovits & Pérez-Coll '91 [36]
Bufo arenarum embryos --> stage 25	-	S	-	art.	-	-	-	$NOEC_{s,d}$	≥ 2,000 [37]	Herkovits et al.'89 [36]
Bufo arenarum embryos --> stage 20	-	S	-	art.	-	-	-	$NOEC_{s,d}$	≥ 4,000	Herkovits & Pérez-Coll '90 [36]

Parameters:
a-e = adult emergence; b = biochemistry; d = developmental effects (deformities); g = growth; h = hatchability; l = lesions (gill); m = maturation (sexual development); r = reproduction; s = survival.

lc: life cycle test.

For footnotes see next pages; for further information see "list of abbreviations tables 1.1 to 1.4"

Footnotes table 1.2

[1] No statistics reported. Growth parameter: optical density.

[2] No statistics reported. Test medium according to Allen and Arnon (1955); the medium contained 4 mg/l EDTA-complex ($10x10^{-3}$ mMol), and macro- and micro-elements including 0.05 mg Zn/l. Growth parameter: chlorophyll a content.

[3] No statistics reported (exception: protein content data, which were left outside consideration). Test medium: Kubl (1962) nutrient medium containing macro- and micro-elements including 6.95 mg/l $FeSO_4$-EDTA ($20x10^{-3}$ mMol/l). Growth parameter: biomass (dry weight).

[4] No statistics reported. Test medium: 6N-U-Bold medium (containing EDTA?, see [7]). Algae collected from arsenic polluted environment. Both growth rate during exponential phase and the maximum number of cells were reduced at 60,000 µg/l.

[5] No statistics reported. Test medium: Bristol's medium (modification Bold, 1949). Growth parameter: number of cells.

[6] No statistics reported. Growth parameter: chlorophyll a content based on dry weight of cells. The pH (readjusted daily) ranged from 5.5 to 7.0.

[7] Test medium: Bold's basal medium (Stein, 1973) containing micro-elements (including 1,900 µg Zn/l) and an unspecified amount of EDTA (Coleman et al., 1971; Wren & Carrol, 1990). Growth parameter: total chlorophyll content per vial.

[8] Optimum growth was achieved at 18.030 µg/l. Growth was reduced more than 10% at 35,500 compared to the optimum groth concentration, but was not reduced compared to the control concentration (1,880 µg/l).

[9] No detailed statistical data reported (i.e. a comparison between each treatment group and the control group was not made). Test medium: Bold's (1967) basal medium, containing micro-elements (including 1,900 µg Zn/l) and an unspecified amount of EDTA (Coleman et al., 1971; Wren & Carrol, 1990). Growth parameter: dry weight.

[10] No statistics reported. Test medium: modified inorganic medium according to De Filippis and Pallaghy 1976. Total pigment concentration and composion affected at 65,000 µg/l. Respiration (µl O_2 /hr/ml medium) and photosynthesis (µg/l O_2 hr/ml medium) were initially reduced, but recovered completely from day 6 and onwards. Photosynthesis per unit mass of total chlorophyll was not inhibited. Only one test concentration.

[11] No statistics reported. Test medium: modified no. 10 medium of CHU (1942), enriched with 10% river water and trace elements; the test medium contained $8x10^{-3}$ mMol EDTA/l. Hardness calculated from original Chu (1942) medium.

[12] Optimum growth was achieved at 4,200 µg/l. Growth was reduced more than 10% at 18,030 µg/l, compared to both control (1,880 µg/l) and optimum growth concentration.

[13] Statistics: $p \leq 0.05$. Test medium: CHU-10 medium; this medium represents a relatively unpolluted lake water (Wong et al., 1982, 1978; Chu, 1942). Parameter: growth rate (increase in optical density measured by spectrometry).

[14] No statistics reported. Growth parameter: dry weight of cells. The pH (readjusted daily) ranged from 3.5 to 5.5.

[15] No statistics reported. Growth paramater: number of fronds.
  [15a] Test medium: Hoagland type M medium.
  [15b] Test medium: Bonner-Devirian's medium.

[16] Test medium: Chalkley's medium (Kudo, 1954); no further data on test medium reported.
Growth (mean number of cells per ml) significantly ($p < 0.05$) reduced at 7.5 µg/l. At all concentrations tested, including the control, cell counts were very low and variable, depending on point in time of measurement. Furthermore, there was no continuous increase in cell numbers as time went on, not even in the controls. The result of this test is in strong contrast with the results of a number of other studies, e.g. those reported by Price and Valley (1962) and Gingrich et al. (1984), see [17] and [18].

[17] Test medium: modified medium of Hutner et al. (Price and Vallee, 1962). The modified medium contained (amongst other) $2x10^{-3}$ M phosphate (60 mg P/l), 270 mg/l malic acid, 3 g/l glutamic acid, 15 g/l sucrose or 3 g/l ethanol, and 60 mg/l thiamine, HCl, and sulphates of iron, copper and manganese.
E. glacilis (Klebs), 'z' strain, no. LB 753 is normally cultured in a nutrient medium containing 1,000 µg Zn/l. Without this zinc concentration in the medium (< 10 µ/l) the cells continu to proliferate as rapidly as those cultured at 1,000 µg/l, but zinc-deficient cells begin to plataeu after 3 days, whereas zinc-sufficient cells continue log phase growth (parameter: cell numbers).

[18] Test medium: see [17]. E. glacilis, strain 'z'. Growth parameter: cell numbers. Without zinc added to the zinc deficient medium (< 0.2 µg/l), zinc-deficient cells started to plateau between day 4 and 5, while zinc-sufficient cells (grown at 650 µg/l) started to plateau between day 7 and 8, resulting in much higher final cell numbers. Exponential growth rate was independent of zinc concentrations between 65 and 1,950 µg/l.

Footnotes table 1.2 (continued)

[19] Optimum growth was achieved at 4,200 µg/l. Growth was reduced more than 10% at 8,700 µg/l, compared to both control (1,880 µg/l) and optimum growth concentration.

[20] No statistics reported. Test medium: distilled water. Survival was reduced almost completely at 2,670 µg/l.

[21] In two additional tests (3-m flow-through tests), reproduction was significantly ($p \leq 0.05$) reduced at 100 µg/l, the lowest concentration tested.

[22] In an additional test (4-m flow-through test), reproduction was significantly reduced at 180 µ/l, while a concentration of 100 µg/l (higher than the 14-w LC50 for newly-hatched animals) was without effect.

[23] Tests conducted in outdoor experimental streams containing coarse sand sediment. Lenght gain was significantly ($p \leq 0.05$) reduced at 34 µg/l; weight gain was reduced about 50% (not statistically significant). Both growth parameters were significantly reduced at the next higher concentration tested (1,100 µg/l). Biochemistry parameter: cellulolytic activity, measured by endo- and exocellulase activity.

[24] Laboratory tests conducted in dechlorinated charcoal-filtered tap water. Parameters other than cellulolytic activity (see [23]) were not measured.

[25] Longevity, and body length of primiparous animals significantly ($p \leq 0.05$) reduced at 100 µg/l. Brood size not affected at 200 µg/l.

[26] Statistics $p \leq 0.05$. Test medium: artificial pond water. Reproductive parameters: number of offspring per brood, measured both in current broods (exposed into the brood pouch) and in subsequent broods (broods that were produced after transfer of the females to clean water; brooding females were exposed for one complete instar, i.e. 3-4 weeks). The number of offspring per brood was not affected at 100 µg/l, but the percentage of broods aborted was increased from about 10% in controls to about 20% (no statistical analysis of the abortion data).

[27] Statistics: $p \leq 0.05$. Exposure of aquatic stages (1st and 2nd generation larvae and pupae).

[28] No statistics reported.

[29] Statistics ($p \leq 0.05$) reported on growth data only.

[30] No statistics reported. Test water: pond water originating from a spring mixed with carbon-filtered, demineralized tap water. The number of spawnings/female, the number of eggs/female and the total number of eggs produced were strongly reduced (at least 65%) at 180 µg/l, the lowest concentration tested; the indicated NOEC for reproduction (30 µg/l) is the analyzed concentration in the control water.
Hatching succes and 3-w survival of fry from exposed eggs were not affected at 180 µg/l.
In parallel tests, hatching succes and 3-w survival of fry from eggs produced by the controls were not affected at 660 µg/l; but fry survival was reduced 60% at 1,300 µg/l). Survival, growth and maturation of the initial fish were not affected at 1,300 µg/l.

[31] No statistics reported. Test water: pond water originating from a spring mixed with carbon-filtered, demineralized tap water. Trimetal test (simultaneous ecxposure to Zn, Cu and Cd). Reproductive parameters (no. of spawnings/female, no. of embryos/female) were reduced 20%-30% at the lowest concentration tested (27 µg Zn/l, 5 µg Cu/l, 4 µg Cd/l). This effect was not considered biologically relevant, because similar variations have been observed in duplicates in other tests with this species. At the next higher concentration (42 µg Zn/l, 7 µg Cu/l, 7 µg Cd/l) reproductive parameters were reduced about 80%.

[32] Statistics: $p \leq 0.05$. Well water passed through an ultraviolet sterilizer. Eggs from zinc-exposed fish (exposed to concentrations of 30 to 120 µg/l).

[33] Statistics $p \leq 0.05$. Growth parameter: weight. Hardness measured by the EDTA tritimetric method.

[34] Test medium: filtered and deionized water. Only one test concentration (19.5 µg/l nominal), "typical" for soft, acid waters). At pH 4.5: 90% mortality versus 10% in the control group. At pH 6.5: survival and growth were not significantly ($p \leq 0.05$) affected. At both pH-values, zinc probably existed entirely as simple hydrated ion; the toxicity at pH 4.5 is therefore likely to be a joint effect of H^+ and the zinc ion.

[35] Statistics on growth data only. At a hardness of 4 mg/l: at least 70% mortality at 4, 9 and 18 µg/l (inversely related to zinc level !) versus 25% mortality in controls. At a hardness of 22 mg/l: no mortality in control or zinc-treated groups. See also [34]; same group of investigators; same test conditions.

[36] Test medium: Holtfreter's solution (HS)

[37] Embryos from (i) parent animals producing <5% abnormal embryos and (ii) parent animals producing >25% abnormal embryos. At 1,000 µg/l, zinc showed a significant ($p < 0.01$) protective effect against abnormal development and mortality of embryos from the latter group. At 2,000 µg/l there was no difference compared to control animals.

Table 1.3 Saltwater organisms - long-term toxicity tests used to derive a maximum tolerable concentration (MTC) in seawater (NOEC and MATC values)

Organism & life stage	A	Test-type	Test-comp.	Test water	Salinity °/oo	Exp.-time	Criterion	Result µg Zn/l	Reference [& footnote]
Algae (unicellular)									
Amphidinium carteri	-	S	ZnSO$_4$	asw	-	9-d	NOEC$_g$	100	
							MATC$_g$	140	√ (100 x 200)
									Braek et al.'76 [1]
Asterionella japonica	-	S	ZnSO$_4$	nsw	35	3-d	NOEC$_g$	30	[2]
clone AST N1.1				(BS)			MATC$_g$	42	√ (30 x 60)
									Fisher & Jones '81
Asterionella japonica	-	S	ZnSO$_4$	nsw	35	3-d	NOEC$_g$	7^{ϵ}	[2,3]
clone AST C2 or N1.1				(BS)					
Asterionella japonica	-	S	ZnSO$_4$	nsw	35	3-d	NOEC$_g$	20^{ϵ}	[2,4]
clone AST C2 or N1.1				(CB)					
Asterionella japonica	-	S	ZnSO$_4$	nsw	35	3-d	NOEC$_g$	7^{ϵ}	[5,6]
clone AST N1.1				(BS)					
Asterionella japonica	-	S	ZnSO$_4$	nsw	35	3-d	NOEC$_g$	7^{ϵ}	[5,7]
clone AST N1.1				(CB)					
Asterionella japonica	-	S	ZnSO$_4$	nsw	35	3-d	NOEC$_g$	20	[2]
clone AST C4				(BS)			MATC$_g$	28	√ (20 x 40)
Asterionella japonica	-	S	ZnSO$_4$	nsw	35	3-d	NOEC$_g$	40	[2]
clone AST C4				(CB)			MATC$_g$	49	√ (40 x 60)
									Fisher & Frood '80
Chaetoceros compressum	-	S	ZnSO$_4$	nsw	35	3-d	NOEC$_g$	10^{ϵ}	[2,8]
clone Chaet C2				(BS)					
Chaetoceros compressum	-	S	ZnSO$_4$	nsw	35	3-d	NOEC$_g$	≥ 60	[2]
clone Chaet C2				(CB)					Fisher & Frood '80
Gymnodinium splendens	-	S	ZnSO$_4$	nsw	32	5-w	NOEC$_g$	500	[9]
							MATC$_g$	700	√ (500 x 1,000)
									Kayser '77 [10]
Nitzschia closterium	-	S	ZnSO$_4$	nsw	35	3-d	NOEC$_g$	40	[2]
clone Nitz C.1				(BS)			MATC$_g$	49	√ (40 x 60)
Nitzschia closterium	-	S	ZnSO$_4$	nsw	35	3-d	NOEC$_g$	≥ 60	[2]
clone Nitz C.1				(CB)					
Nitzschia closterium	-	S	ZnSO$_4$	nsw	35	3-d	NOEC$_g$	10^{ϵ}	[2,11]
clone Flag 8.4				(BS)					
Nitzschia closterium	-	S	ZnSO$_4$	nsw	35	3-d	NOEC$_g$	≥ 60	[2]
clone Flag 8.4				(CB)					Fisher & Frood '80
Phaeodactylum	+	F	ZnCl$_2$	nsw	-	2-w	NOEC$_g$	10,000	
tricornutum							MATC$_g$	16,000	√ (10,000 x 25,000)
									Jensen et al.'74 [12]
Phaeodactylum	-	S	ZnSO$_4$	asw	-	10-d	NOEC$_g$	4,000	[13]
tricornutum							MATC$_g$	4,470	√ (4,000 x 5,000)
Phaeodactylum	-	S	ZnSO$_4$	asw	-	10-d	NOEC$_g$	500	[14]
tricornutum							MATC$_g$	705	√ (500 x 1,000)
									Braek et al.'76 [1]

(to be continued)

Table 1.3 Saltwater organisms - long-term toxicity tests used to derive a maximum tolerable concentration (MTC) in seawater (NOEC and MATC values)
[continued]

Organism & life stage	A	Test-type	Test-comp.	Test water	Salinity $^o/oo$	Exp.-time	Criterion	Result µg Zn/l	Reference [& footnote]
Algae (unicellular) (continued)									
Prorocentrum micans	-	S	$ZnSO_4.2H_2O$	nsw	32	5-w	$NOEC_g$	100	
							$MATC_g$	225	√ (100 x 500) Kayser '77 [10]
Rhizosolenia spp.	+	S	-	nsw	-	12/24-hr	$NOEC_g$	15	
							$MATC_g$	19	√ (15 x 25) Davies & Sleep '79 [15]
Schroederella schroederi	-	S	$ZnSO_4.2H_2O$	nsw	32	11-d	$NOEC_g$	10	[9]
							$MATC_g$	22	√ (10 x 50) Kayser '77 [10]
Scrippsiella faeroense	-	S	$ZnSO_4.7H_2O$	nsw	32	7-w	$NOEC_g$	100	[9]
							$MATC_g$	315	√ (100 x 1,000) Kayser '77 [10]
Skeletonema costatum clone Skel-5	+	F	$ZnCl_2$	nsw	-	2-w	$NOEC_g$	25	[9]
							$MATC_g$	35	√ (25 x 50) Jensen et al.'74 [12]
Skeletonema costatum Clone Skel-5	-	S	$ZnSO_4$	asw	-	10-d	$NOEC_g$	50	
							$MATC_g$	70	√ (50 x 100)
Skeletonema costatum clone Skel-0	-	S	$ZnSO_4$	asw	-	10-d	$NOEC_g$	100	
							$MATC_g$	140	√ (100 x 200) Break et al.'76 [1]
Skeletonema costatum clone Skel C7	-	S	$ZnSO_4$	nsw (BS)	35	3-d	$NOEC_g$	20	[2]
							$MATC_g$	28	√ (20 x 40)
Skeletonema costatum clone Skel C7	-	S	$ZnSO_4$	nsw (CB)	35	3-d	$NOEC_g$	≥ 60	[2]
Skeletonema costatum clone Skel C7	-	S	$ZnSO_4$	nsw (BS)	35	3-d	$NOEC_g$	7^{ϵ}	[5,16]
Skeletonema costatum clone Skel C7	-	S	$ZnSO_4$	nsw (CB)	35	3-d	$NOEC_g$	7^{ϵ}	[5,17]
Skeletonema costatum clone Skel C6	-	S	$ZnSO_4$	nsw (BS)	35	3-d	$NOEC_g$	30^{ϵ}	[2,18] Fisher & Frood '80
Skeletonema costatum	-	-	-	-	-	10/14-d	$NOEC_g$	200	MARITOX $9761^{\int}$ [19]
Skeletonema costatum	-	-	-	-	-	10/14-d	$NOEC_g$	50	MARITOX $9761^{\int}$ [19]
Thalassiosira pseudonana	+	F	$ZnCl_2$	nsw	-	2-w	$NOEC_g$	100	[9]
							$MATC_g$	160	√ (100 x 250) Jensen et al.'74 [12]
Thalassiosira pseudonana	-	S	$ZnSO_4$	asw	-	9-d	$NOEC_g$	200	
							$MATC_g$	280	√ (200 x 400) Break et al.'76 [1]
Thalassiosira rotula	-	S	$ZnSO_4.7H_2O$	nsw	32	14-d	$NOEC_g$	10	[20]
							$MATC_g$	22	√ (10 x 50) Kayser '77 [10]
Thalassiosira guillardii	-	-	-	-	-	10/14-d	$NOEC_g$	200	MARITOX $9761^{\int}$ [19]

(to be continued)

Table 1.3 Saltwater organisms - long-term toxicity tests used to derive a maximum tolerable concentration (MTC) in seawater (NOEC and MATC values)
[continued]

Organism & life stage	A	Test-type	Test-comp.	Test water	Salinity $^{o}/oo$	Exp.-time	Criterion	Result µg Zn/l	Reference [& footnote]
Algae (multicellular)									
Laminaria hyperborea	-	R	$ZnSO_4$	nsw	-	4-w	$NOEC_g$	100	
zoospores --> sporophytes							$MATC_g$	160	√ (100 x 250)
									Hopkins & Kain '71
									[21]
Coelentarates									
Eirene viridula	-	R	$ZnSO_4$	nsw	30	3-m	$NOEC_{mc}$	300	
							$MATC_{mc}$	550	√ (300 x 1,000)
									Karbe, '72 [22]
Annelids									
Capitella capitata	-	-	-	-	-	25/40-d ?	$NOEC_r$	320	MARITOX 51618$^{\int}$ [19]
Ctenodrilus serratus	-	S	$ZnSO_4.7H_2O$	nsw	-	3-w	$NOEC_{r,s}$	100	
P --> F [lc]							$MATC_{r,s}$	225	√ (100 x 500)
									Reish & Carr '78 [23]
Ctenodrilus serratus	-	-	-	-	-	28/31-d	$NOEC_r$	100	MARITOX 51618$^{\int}$ [19]
Nereis arenaceodentata	-	-	-	-	-	4-m?	$NOEC_r$	100	MARITOX 51618$^{\int}$ [19]
Ophryotrocha diadema	-	S	$ZnSO_4.7H_2O$	nsw	-	3-w	$NOEC_{r,s}$	100	
P --> F [lc]							$MATC_{r,s}$	225	√ (100 x 500)
									Reish & Carr '78 [23]
Ophryotrocha diadema	-	-	-	-	-	4-w	$NOEC_r$	100	MARITOX 51618$^{\int}$ [19]
Molluscs									
Crassostrea gigas	+	R	$ZnSO_4$	nsw	29	5-d	$NOEC_{d,g}$	50	
eggs --> larvae							$MATC_{d,g}$	70	√ (50 x 100)
									Brereton et al.'73
									[24]
Haliotis refescens	-	-	-	-	-	9-d	$NOEC_r$	19	MARITOX 50173$^{\int}$ [19]
Mercenaria mercenaria	-	R	$ZnCl_2$	nsw	24	8-d	$NOEC_{s,g}$	50	
2-d old larvae									
									Calabrese et al. '77
									[25]
Scrobicularia plana	+	R	$Zn(NO_3)_2$	nsw	31	2-w	NOLC	1,000	
length 4-5 cm							$MATC_s$	2,235	
									Akberali et al '81
									[26]

(to be continued)

Table 1.3 Saltwater organisms - long-term toxicity tests used to derive a maximum tolerable concentration (MTC) in seawater (NOEC and MATC values)
[continued]

Organism & life stage	A	Test-type	Test-comp.	Test water	Salinity $^{o}/oo$	Exp.-time	Criterion	Result µg Zn/l	Reference [& footnote]
Crustaceans									
Callianassa australiensis	-	-	-	-	-	14-d	NOLC	440	MARITOX 15338[∫] [19]
Holmesimysis costata 9-d old juveniles	+	R	$ZnSO_4.7H_2O$	nsw	35	1-w	$NOEC_{s,g}$ $MATC_{s,g}$	18 [α] 24	 √ (18 x 32) Martin et al., '89 [27]
Mysidopsis bahia	-	-	-	-	-	lc	$NOEC_r$	120	MARITOX 51549[∫] [19] (from U.S. EPA)
Tigriopus brevicornis	-	-	-	-	-	-	$NOEC_r$	297	MARITOX 51537[∫] [19]
Echinoderms									
Arbacia lixula	-	-	-	-	-	20-d	NOLC	1,000	MARITOX 51385[∫] [19]
	-	-	-	-	-	4-d	$NOEC_r$	10	MARITOX 51385[∫] [19]

Parameters:
d = developmental effects (deformities); g = growth; mc = morphological changes; r = reproduction; s = survival

lc: life cycle test.

For footnotes see next page; for further information see the "list of abbreviations tables 1.1 to 1.4".

Footnotes table 1.3

[1] No statistics reported. Test medium sterilized either by autoclaving or by filter sterilization (0.2 μm filter) ; no further data on test medium reported. Growth parameter: maximum growth rate (divisions/day), calculated on the basis of cell counts.

[2] No statistics reported. Test water (seawater enriched with nutrients minus Cu, Zn or EDTA) was sterilized by 0.22 μm filter. BS and CB: seawater from 2 different locations. (BS usually contained somewhat less dissolved organic carbon and lower background levels of Zn (1.5 versus 5.2 μg/l total-Zn) and Cu. Growth parameter: relative growth rate (divisions/day) during log-linear growth phase.

[3] The NOEC was estimated from the lowest effect concentration (35% inhibition at 20 μg/l) using a factor of 3.

[4] The NOEC was estimated from the lowest effect concentration (18% inhibition at 40 μg/l) using a factor of 2.

[5] No statistics reported. Test water sterilized by uv-irradiation. BS and CB: seawater from 2 different locations (see [2]); the seawater was not enriched with nutrients. Growth parameter: relative growth rate (divisions/day) during log-linear growth phase.

[6] The NOEC was estimated from the lowest effect concentration (26% inhibition at 20 μg/l) using a factor of 3.

[7] The NOEC was estimated from the lowest effect concentration (21% inhibition at 20 μg/l) using a factor of 3.

[8] The NOEC was estimated from the lowest effect concentration (19% inhibition at 20 μg/l) using a factor of 2.

[9] At the NOEC indicated, growth rate was not (or hardly) affected in the exponential growth phase, but the maximum and/or final cell densities were lower than control values when the test was continued beyond this phase.

[10] No statistics reported. Test water: seawater, enriched with nitrate, phospate and silicate; test water sterilized by 0.22 μm filter. Growth parameter: number of cells.

[11] The NOEC was estimated from the lowest effect concentration (14% inhibition at 20 μg/l) using a factor of 2.

[12] No statistics reported. Only stock solutions and highest test concentration were analysed for zinc. Growth parameter: relative growth rate, calculated on the basis of cell counts.

[13] No statistics reported. Test medium sterilized either by autoclaving or by filter sterilization (0.2 μm filter); EDTA-free. Growth parameter: maximum growth rate (divisions/day), calculated on the basis of cell counts.

[14] No statistics reported. Test medium sterilized either by autoclaving or by filter sterilization (0.2 μm filter); test medium contained 2.3 μM EDTA (which can chelate 76 μg Zn/l) and a trace mineral mixture. Growth parameter: maximum growth rate (divisions/day), calculated on the basis of cell counts.

[15] No statistics reported. Growth parameter: carbon fixation rate ($\mu g\ C.l^{-1}.hr^{-1}$). Test population: natural phytoplankton, being almost exclusively diatoms of the genus Rzizosolenia.

[16] The NOEC was estimated from the lowest effect concentration (32% inhibition at 20 μg/l) using a factor of 3.

[17] The NOEC was estimated from the lowest effect concentration (23% inhibition at 20 μg/l) using a factor of 3.

[18] The NOEC was estimated from the lowest effect concentration (20% inhibition at 60 μg/l) using a factor of 2.

[19] MARITOX: TNO/DGW ecotoxicological data base on marine organisms; the NOEC values indicated in the table have been reported by Scholten et al. (1991). The number following MARITOX refers to the TNO literature system. Data in MARITOX have been evaluated for reliability, in accordance with the system used in AQUIRE; all NOEC values indicated in the table were considered to be reliable.

[20] During the exponential growth phase, growth rate was reduced at 50 μg/l, but the maximum and final cell numbers were not adversely affected at this concentration.

[21] No statistics reported. Growth parameter: number of sporophytes.

[22] No statistics reported. Parameter: macroscopic morphological changes.

[23] Statistics ($p \leq 0.05$) reported for reproduction. Reproductive parameter: number of worms. Based on the number of initial worms that survived the first 4 days of exposure, reproduction was affected at much lower concentrations than survival.

[24] No statistics reported. Test medium: UV-sterilized seawater. The 5-d exposure period was followed by a 5-d depuration period; growth was measured up to day 10.

[25] The NOEC indicated is the LC5 reported by Calabrese et al. (1977). The estimated percent growth at this concentration was 100%. Background zinc level in seawater: 18 μg/l.

[26] No statistics reported.

[27] Statistics: $p \leq 0.05$. Growth parameter: carapace length. Abotts correction used for control mortality (22%).

Table 1.4 Saltwater organisms - long-term toxicity tests: additional data (miscellaneous toxicity values)

Organism & life stage	A	Test-type	Test-comp.	Test water	Salinity °/oo	Exp.-time	Criterion	Result µg Zn/l	Reference [& footnote]
Algae									
Nitzschia closterium	-	S	$ZnSO_4$	asw	-	4-d	EC_g	180	[1a]
						4-d	EC_g	240	[1b]
									Rosko & Rachlin '75 [1]
Molluscs									
Crassostrea gigas eggs --> larvae	+	R	$ZnSO_4$	nsw	29	5-d	$EC_{s,g}$	125	Brereton et al.'73 [2]
Crassostrea virginica length 100 mm	-	F	$Zn(NO_3)_2$	nsw	31	20-w	$NOEC_{s\ (g)}$	≥ 200	Shuster & Pringle '69 [3]
Mytilus edulis length 2-3 cm	-	F	$ZnCl_2$	nsw	33	3-w	EC_g	10	Strömgren '82 [4]

Parameters:
g = growth; s = survival

Footnotes table 1.4

[1] No statistics reported. Zinc was analyzed in stock solutions.
[1a] Test medium: non-chelating seawater.
[1b] test medium: chelating seawater.

[2] No statistics reported. The 5-d exposure period was followed by a 5-d depuration period; growth was measured up to day 10.
In a short-term study with this species (Nelson et al., 1972), a concentration of 700 µg/l resulted in a significant ($p \leq 0.05$) increase in the number of deformed larvae, after a 2-d exposure of eggs; a concentration of 70 µg/l was without effect.

[3] No statistics reported. The oysters showed shell growth throughout the experiment, but due to poor growth of control animals, a sound evaluation of this parameter was not possible.

[4] Statistics: $p \leq 0.05$. Background zinc concentration in seawater 5 $\mu g.l^{-1}$.

For further information see the "list of abbreviations tables 1.1 to 1.4".

List of abbreviations tables 1.1 to 1.4

A	+:	Test substance analyzed in test solution;
	-:	Test substance not analyzed in test solution, or: no data.
α		Value based on actual (analyzed) concentrations in test solutions, as mentioned explicitly in the literature source. Values <u>not</u> indicated by "α" are considered to be nominal concentrations.
∫		Secundary literature source; primary source not available.
≥		Value indicated is highest concentration used in the test.
Test type		S: static; R: renewal; F: flow-through (continuous flow).
Exposure time:		d: day(s); hr: hour(s); w: week(s); m: month(s); yr: year(s).
Criterion	LC:	Lethal concentration (indicated if the lowest concentration tested resulted in significant mortality).
	LC50:	Median lethal concentration, i.e. that concentration which is calculated (from a series of test concentrations) to cause mortality of 50% of the number of organisms exposed to that concentration.
	EC:	Effect concentration (indicated if the lowest concentration tested resulted in a significant effect).
	EC50:	Median effect concentration, i.e. that concentration which is calculated (from a series of test concentrations) to cause a particular response in 50% of the number of organisms exposed to that concentration.
	NOLC:	No observed lethal concentration. If also sublethal parameters (toxicological endpoints) were studied in a test, the abbreviation $NOEC_s$ (survival) was used, next to NOEC values for the sublethal parameters studied, e.g. $NOEC_g$ (growth).
	NOEC:	No observed effect concentration, i.e. the highest concentration (in a series of test concentrations) without effect. For general information on deriving NOEC values the reader is referred to the text (section 1.2, introduction).
	$NOEC^{\epsilon}$:	NOEC values marked by "ε" have been estimated from the LOEC (lowest observed effect concentration) in case the real NOEC could not be derived from the data reported (e.g. if only a "toxic treshold" was reported) or in case the lowest concentration tested resulted in a marginal effect. NOEC values have been estimated mainly if more than one test was available for one test species, resulting in both NOEC and LOEC values for the same toxicological endpoint, to allow the calculation of the geometric mean NOEC relating to this endpoint (which is required in the extrapolation method which has been used in the ecotoxicological effect assessment. The following application factors have been used arbitrarily to derive a $NOEC^{\epsilon}$: - in case the LOEC resulted in 10%-20% effect: factor of 2; - in case the LOEC resulted in 20%-50% effect: factor of 3.
	MATC:	Maximum acceptable toxicant concentration, i.e. the theoretical threshold concentration between the highest concentration without effect (NOEC) and the lowest concentration with effect (LOEC) The MATC is calculated as follows: MATC = $(\sqrt{(NOEC \times LOEC)})$, i.e. the MATC is the geometric mean value of the NOEC and the LOEC.

The NOEC values (including the estimated NOEC values) listed in the tables 1.1 and 1.3 have been used in the ecotoxicological effect assessment. The MATC values listed in these tables were not used in the effect assessment, but have been listed in accordance with publications from the United States, e.g. U.S. EPA (1980), in which a MATC (also called "chronic value") is reported.

Hardness:	Expressed as mg/l $CaCO_3$, unless stated otherwise. In a number of cases the hardness was not reported in the publication, but calculated from the calcium and magnesium concentration in the test water.

2 TERRESTRIAL ORGANISMS

2.1 ACCUMULATION

The data in this section have been limited to data on the accumulation of zinc in wildlife animals; most data refer to field studies. For data on the accumulation in agricultural crops and livestock the reader is referred to section 5.4 in the Integrated Criteria Document Zinc (Cleven et al., 1992).

2.1.1 Invertebrates

Earthworms

Data on the accumulation of zinc in invertebrates mainly refer to polychaete earthworms (annelids), an important group of terrestrial invertebrates. Soil earthworm biomass can amount up to 1,000 $kg.ha^{-1}$, accounting for up to 80% of the total soil fauna biomass. Furthermore, earthworms are important for the cycling of nutrients, for the improvement of soil structure, and as a food source for wildlife animals, especially birds and small mammals such as moles (Ma, 1983a; Denneman, 1985). In the Netherlands, investigators at the Research Institute for Nature Management have conducted a number of field studies on the accumulation of heavy metals in earthworms, in relation to soil zinc concentrations and/or soil-related (abiotic) factors such as pH and organic matter content (Ma, 1983; Ma et al., 1983, Ma, 1987). In these studies the earthworms (whole body) were analyzed with their guts voided, to prevent overestimation of the amount actually accumulated. Four of these field studies, which included zinc, will be discussed here in detail. Concentration factors (CF = $C_{organism} : C_{soil}$, i.e. the ratio of the compound concentration in the organism to the compound concentration in soil) were not reported by Ma and co-workers, but calculated from their data.

1. Metal concentrations were analyzed in adults of *Lumbricus rubellus* collected from a sandy soil (pH-KCl 5.9; 5% organic matter) that had been treated for several years with sewage sludge (0, 6, 12 or 18 $tonnes.ha^{-1}.yr^{-1}$). Mean zinc concentrations in worms were 530 (control), 632, 734 and 793 $mg.kg^{-1}$ dry weight (dw), respectively, equivalent to 81, 97, 113 and 122 $mg.kg^{-1}$ fresh weight (dry matter content of adult *L. rubellus* equals 15-16%). Mean zinc concentrations in the top 15 cm soil layer were 20 (control), 96, 174 and 259 $mg.kg^{-1}$ dw; below this top layer

zinc concentrations were not increased. These data result in CF values of 26, 7, 4 and 3 on the basis of dry weight zinc concentrations in worms, and of 4, 1, 0.6 and 0.5 on the basis of fresh weight zinc concentrations in worms (Ma et al., 1983).

2. Metal concentrations were analyzed in *Allolobophora caliginosa* collected from 6 different agricultural soils (3 loamy soils and 3 sandy soils) treated with municipal waste compost for several years (3 treatment concentrations per soil, viz., 0, 20 and 40 tonnes.yr^{-1}, so a total of 18 plots were included in the study). The different soils were chosen to study the influence of soil related factors on the accumulation. Soil pH-KCl, organic matter (OM) content and cation exchange capacity (CEC) were 4.7-7.1, 3-14%, and 5-29 meq. 100 g^{-1} soil, respectively. In each soil, the zinc concentration in adult worms and, especially, that in soil increased with increasing treatment concentration; per soil the treatment-related increase in zinc concentration in worms was ranging from <10% to 300%. The zinc concentration in subadult worms also generally increased with increasing treatment concentration, but the results were less consistent. "Background" zinc concentrations in worms from untreated spots were 426-1,965 and 499-1,797 mg.kg^{-1} dw for adults and subadults, respectively; concentrations in worms from treated spots were 913-2,255 and 729-1,969 mg.kg^{-1} dw for adults and subadults, respectively. The concentration in adult worms usually was higher than that in subadult worms, but the differences were always within a factor of 2. Zinc concentrations in soils were 24-209 mg.kg^{-1} dw in untreated soils and 154-472 mg.kg^{-1} dw in treated soils. The data from this study result in CF values ranging from 3 to 82 for adult worms; those for subadult worms generally were somewhat lower. Dry matter content of this worm species was not reported, so CF values on the basis of fresh weight zinc concentrations in worms could not be calculated. Multiple regression analyses showed that zinc concentrations in adult worms increased with increasing soil zinc concentrations (top 20 cm soil layer) and decreasing CEC and pH; the %OM did not exert a significant influence. The best fit equation including zinc concentration, CEC and pH as independent soil variables could account for 80% of the variation in zinc concentrations in adult worms. (Ma, 1983).

3. Metal concentrations were analyzed in *L. rubellus* collected at different distances from a zinc-smelting complex in the Kempen (Southern Netherlands). Regression analysis showed that the zinc concentration in adult worms and, especially, that in soil decreased with increasing distance from the nearest zinc smelter. Zinc concentrations in worms were 717-3,500 mg.kg^{-1} dw (equivalent to 110-540 mg.kg^{-1} fresh weight); those in

soils (sandy podzolic soils, pH-KCl 3.5-6.1; OM 2.2-8.6%) were 10-1,220 $mg.kg^{-1}$ dw. The data from this study result in CF values ranging from 2 to 126, on the basis of dry weight zinc concentrations in adult worms (0.3 to 19 on the basis of fresh weight zinc concentrations in adult worms) Multiple regression analyses showed that zinc concentrations in worms increased with increasing soil zinc concentrations (mineral top 10 cm soil layer) and decreasing pH and %OM, although the influence of the organic matter content was not statistically significant. The best fit equation including zinc concentration, pH and %OM as soil variables could account for 50% of the variation of zinc concentrations in worms. A comparison of the zinc concentration in adult and subadult *L. rubellus* showed that, on the average, the concentration in subadults was about 25% lower than that in adults collected from the same plot (Ma, 1983; Ma et al., 1983).

It is noted that the regression equations of the relationships between zinc concentration in worms and various soil variables including soil zinc concentration (studies 2 and 3) show regression coefficients that are significantly <1, which means that the concentration factor decreases with increasing zinc concentration in soil.

4. Metal concentrations were analyzed in adult *L. rubellus* collected in the vicinity of a zinc-smelting complex in the Kempen (Southern Netherlands; sites 1 to 4) and in a control site (site 5). Soil zinc concentrations in the polluted area were 60-1,015 $mg.kg^{-1}$ dw, that in the control site was 35 $mg.kg^{-1}$ dw. Mean measured zinc concentrations in worms were 1,474, 1,789 and 730 $mg.kg^{-1}$ dw at site 2, 3 and 5, respectively (equivalent to 227, 275, and 112 $mg.kg^{-1}$ fresh weight). Predicted values of zinc concentrations in worms (calculated from Ma et al., 1983) were 1,164-1,525 $mg.kg^{-1}$ dw (equivalent to 179-235 $mg.kg^{-1}$ fresh weight) for sites 1 to 4, and 837 $mg.kg^{-1}$ dw (equivalent to 129 $mg.kg^{-1}$ fresh weight) at site 5; these calculated values are within 35% of the measured values. The data from this study result in CF values of 2-21 based on measured dry weight zinc concentrations in worms and in CF values of 1-24 based on calculated dry weight zinc concentrations in worms (Ma, 1987). In accordance with the above-mentioned studies by Ma and co-workers, it was observed that the concentration factor decreased with increasing soil zinc concentration.

Additional data on the accumulation of zinc in earthworms collected from diverse sites or on the accumulation of zinc in laboratory studies are summarized below.

* Wright and Stringer (1980; cited in Ma et al., 1983) reported concentrations for several earthworm species collected in the vicinity of

the Avonmouth smelter in England, ranging from 634 to 1,398 mg.kg^{-1} dw. These concentrations are similar to those reported by Ma and co-workers for *L. rubellus* collected in the vicinity of a zinc-smelting complex in the Netherlands.

* Scanlon (1987) reported concentrations of 222-361 and 227-1,475 mg.kg^{-1} dw in earthworms collected in control sites and polluted sites in the immediate environments of highways with various traffic densities, respectively. Soil zinc concentrations ranged from 15 mg.kg^{-1} in the control sites to 151 mg.kg^{-1} in the polluted sites.

* Hartenstein et al. (1980a) exposed the earthworm *Eisenia foetida* for 5 weeks in aerobic sludge (background zinc concentration 1,634 mg.kg^{-1}) to which zinc acetate was added to obtain zinc concentrations of 2,500, 5,000 or 10,000 mg.kg^{-1}. Zinc concentrations in worms (guts voided) were 133-177 mg.kg^{-1} dw at the lowest exposure concentration and 111-248 mg.kg^{-1} dw at the highest exposure concentration, resulting in CF values of 0.06, 0.03 and 0.02 at the three exposure concentrations, respectively. A similar concentration (211 mg.kg^{-1} dw) was found in manure-sludge fed earthworms of this species. These concentrations are up to 10-20 times higher than background concentrations (12-32 mg.kg^{-1} dw) in this species. Exposure of *E. foetida* collected at different time intervals (2-28 weeks) from outdoor sludge containing zinc concentrations of 875-2,100 mg.kg^{-1} dw resulted in concentrations in worms of 68-210 mg.kg^{-1} dw. The zinc concentrations reported in this species were lower than those reported for other earthworm species (data reviewed by Hartenstein et al. (1980a)

* Beyer and Cromartie (1987) analyzed metal concentrations in soils and different species of earthworms collected from 20 diverse soils, from both "natural" and "polluted" (mining, industrial) sites. Zinc concentrations in worms from natural sites (soil zinc concentrations 23-220 mg.kg^{-1} dw) were 120-650 mg.kg^{-1} dw; those in worms from industrial sites (soil zinc concentrations 52-2,500 mg.kg^{-1} dw) were 200-1,600 mg.kg^{-1} dw. The data result in CF values of 2-26 and 0.1-25 at natural and industrial sites, respectively. CF-values <1 were only observed in two industrial sites containing very high zinc concentrations (2,100 and 2,500 mg.kg^{-1} dw). It was noted that the concentrations of zinc were very poorly correlated with those in soils (correlation coefficient +0.01). Species differences between earthworm species collected at the same site were observed, but the differences in zinc concentration were within a factor of 2 or, occasionally, a factor of 3.

* Corp and Morgan (1991) conducted a laboratory study in which adults of the earthworm *L. rubellus* were exposed to samples of soils from former

mining areas in Wales (U.K.), containing high concentrations of heavy metals. In samples of each soil, both "native" worms (collected in the respective soil) and "introduced" worms (collected in a control soil) were kept for 4 weeks. Zinc concentrations in control worms and soil were 498 and 416 $mg.kg^{-1}$ dw, respectively. Zinc concentrations in exposed worms were 609-5,270 $mg.kg^{-1}$ dw, at soil zinc concentrations of 417-183,000 $mg.kg^{-1}$ dw, resulting in CF values ranging from 0.01 to 3. concentrations in earthworms increased with increasing concentrations in soil samples, but CF values decreased with increasing soil zinc concentrations. In general, exposed native worms contained significantly more zinc than exposed introduced worms, especially at high soil zinc concentrations. Multiple regression analyses showed that zinc concentrations in worms increased with increasing soil zinc concentrations and decreasing pH. The best fit equation including zinc concentration and pH as soil variables could account for 74% of the variation in zinc concentrations in worms.
* Denneman et al. (1985) reported CF values for a variety of earthworm species collected from control and polluted sites; the values reported below were derived from a number of older publications (1970-1980), which have not been reviewed in the present document. The CF values for worms from control sites were 0.5-18 while those for worms from polluted sites were 0.02-7.3. Per individual species, the highest CF values were generally observed at control sites. It was not reported whether the CF values are based on dry weight or fresh weight of worms.

Based on the above-mentioned CF values (total range about 0.01-100, the majority of the values being >1) it is concluded that zinc is concentrated from the soil by earthworms. These CF values are based on dry weight zinc concentrations in worms. On the basis of the dry matter content reported for adult *L. rubellus* (15%), CF values based on fresh weight of worms are about 7 times lower. The concentration factor decreases with increasing zinc concentration in soil. Besides the zinc concentration in soil, major soil-related factors that influence the accumulation of zinc in earthworms are pH and CEC; the zinc concentration in worms is inversely related to these two factors. The CEC, "cation exchange capacity", is largely determined by the clay and organic matter content of the soil. In worms collected from "unpolluted" sites, zinc concentrations in common earthworm species such as *L. rubellus* and *A. caliginosa* are generally in the range from 400 to 700 $mg.kg^{-1}$ dw (60-100 $mg.kg^{-1}$ fresh weight, based on the dry matter content of *L. rubellus)* but both lower and higher concentrations have been reported, for example concentrations up to about 2,000 $mg.kg^{-1}$ dw

(300 mg.kg^{-1} fresh weight) in *A. caliginosa* collected in agricultural soils that were not treated with compost. In worms collected from "polluted" sites such as agricultural soils treated with compost or slugde or industrial or mining areas, zinc concentrations in worms can easily exceed 1,000 mg.kg^{-1} dw (150 mg.kg^{-1} fresh weight). For example, concentrations up to 3,500 mg.kg^{-1} dw (500 mg.kg^{-1} fresh weight) were found in adult *L. rubellus* collected in the vicinity of a zinc-smelting complex in the Netherlands. Higher concentrations are not known from field studies conducted in the Netherlands.
The data on the accumulation of zinc from soil treated with "organic" substrates such as compost and sludge show that the bioavailability of zinc from these substrates is rather low.

Arthropods

Data on the accumulation of zinc in invertebrates other than earthworms appear to be scarce. In a review by Denneman et al. (1985) the following data were reported. For woodlouse species *Porcellio scaber*, *Oniscus asellus* and *Philoscia muscorum* (crustaceans), CF values ranged from 0.3 to 2.7; about half of these values was >1. The values were calculated on the basis of the zinc concentration in litter. For the springtail *Orchesella cincta* (insects), the CF based on the zinc concentration in soil (A-horizon of forest soil) was 2.1 at a control site (soil zinc concentration 68 mg.kg^{-1}) and 0.2 at a polluted site (soil zinc concentration 904 mg.kg^{-1}). Both woodlice and springtails are litter decomposers, especially woodlice. For *O. cincta* and other springtail species, CF values were 0.03-0.04 at a polluted forest site with a zinc soil concentration (A-horizon) of 1,670 mg.kg^{-1}. For other soil arthropods (including beetles, centipedes, spiders and mites) collected from this forest site, CF values were ranging from 0.03 to 0.24. The concentrations in these arthopods appeared to be independent of trophic level or feeding habits (Denneman et al., 1985). On the basis of these data it appears that zinc usually is not concentrated from the soil by arthropods. It is noted that is not reported whether the above-mentioned CF values are based on dry weight or fresh weight of the organisms.

2.1.2 Vertebrates

In the in 2.1.1 mentioned study by Ma (1987), zinc concentrations in liver and kidneys of moles, *Talpa europea*, were compared to those in earthworms collected at the same sites. Mean concentrations in liver (137-232 mg.kg^{-1} dw) and kidneys (191-373 mg.kg^{-1} dw) of moles from the polluted sites in the Kempen were somewhat increased compared to those in liver (115 mg.kg^{-1} dw) and kidneys (131 mg.kg^{-1} dw) of moles from the control site, but the differences between minimum and maximum concentration per organ were within a factor of 4. The zinc concentrations in moles appeared to be more related to zinc concentrations in earthworms, their main food source, than to those in soil (Ma, 1987). The results of this study and a comparison with normal zinc concentrations in liver and kidneys of mammals (Cleven et al., 1992) indicate that the zinc concentrations observed in the moles are unlikely to cause adverse effects.

In a similar study, metal concentrations were measured in soil, vegetation, earthworms and several species of small mammals *(Microtus pennsylvanicus, Peromymyscus leucopus, Blerina brevicauda, Mus musculus, Rattus norvegicus, Cryptotis parva, Sorex cinereus)* collected in two control sites and in polluted sites in the immediate environments of highways with different traffic densities (United States). The mammalian species collected included both herbivorous and carnivorous species. Zinc concentrations in soil and vegetation ranged from 15-151 and 54-219 mg.kg^{-1} dw, respectively. Whole-body zinc concentrations in mammals were 83-117 mg.kg^{-1} dw at control sites and 51-146 mg.kg^{-1} dw at polluted sites. Although there was a tendency of increasing concentrations in mammals with increasing pollution concentrations, the differences were usually very limited, both between sites (considering concentrations regardless of species) and between species (considering all sites) (Scanlon, 1987).

2.2 TOXICITY

Introduction

Data on the effects of zinc soil concentrations on microorganisms (microbe-mediated processes), invertebrates, and plants (agricultural crops) are summarized in tables 2.1 to 2.3. The data listed in these tables have been selected on the basis of 1) the toxicity value(s) that could be derived from the studies, 2) exposure time and 3) data on soil-related factors.

With respect to item 1, "no-observed-effect-concentrations" (NOEC* values) were given priority over effect-concentrations (EC values), because NOEC values are used preferably to derive a "maximum tolerable concentration" (MTC). With respect to item 2, long-term data were given priority over short-term data. With respect to item 3, studies which included data on soil-related factors, specifically clay content and organic matter content, were given priority over studies which did not include these data, because data on clay and organic matter content were used to calculate toxicity values in a "standard soil", in accordance with Van der Meent et al. (1990) and Denneman and Van Gestel (1990). Hence, two values have been listed for each test result. Firstly, the experimentally determined toxicity value in the soil or substrate in question and secondly, a calculated value which is an estimate of the corresponding toxicity value in a standard soil containing 10% organic matter (OM) and 25% clay (particles <2 μm). The calculated value is based on the assumption that the bioavailability, and hence the toxicity, is proportional to these soil-related factors. For the equation used to calculate the standardized values, see "list of abbreviations tables 2.1 to 2.3". Furthermore it is indicated whether the toxicity values are expressed as "added concentration" (ω) or as "total concentration" (ψ), the latter including the background zinc concentration in soil.

The standardized NOEC values which have been used in the ecotoxicological effect assessment have been printed **bold** in tables 2.1 to 2.3. It is noted that a number of these values for microbe-mediated processes and, especially, for plants are "≥" values (i.e. the highest concentration did not result in an effect) which may overestimate the risk, because the real NOEC may be higher. Nevertheless, because of the limited number of NOEC values, these values have been included in the effect assessment.

* *In publications in which a statistical analysis of the test results was reported, the NOEC was derived in accordance with the result of this analysis, i.e. the NOEC was chosen as the highest concentration in the series of test concentrations that did not result in a statistically significant (adverse) effect.*

In a number of publications a statistical analysis of the test results was not reported. In those cases, the NOEC was chosen arbitrarily as the highest concentration in the series of test concentrations that resulted in ≤10% effect, compared to the control concentration. Concentrations that resulted in more than 10% effect were considered to be effect concentrations.

2.2.1 Microorganisms (table 2.1)

Data on microbe-mediated processes (C-mineralization, N-mineralization, mineralization of specific substrates, and enzyme activities are summarized in table 2.1. The data refer to both short-term and long-term toxicity tests in which soil samples received a single application of inorganic zinc (laboratory tests). The data include both NOEC values and effect concentrations. Some of these studies are discussed below.

In the study by Doelman and Haanstra (1983) in which zinc was added to different soil samples as solid $ZnCl_2$, EC50 values for enzyme activities measured 1-1.5 years after the application usuallly were lower (higher toxicity; factor of 1 to 20) than those measured shortly after the application. This can be explained by the fact that $ZnCl_2$ was not yet dissolved in soil solution shortly after application. With respect to respiration, data were not consistent: in one half of the tests the results were similar to those with respect to enzyme activities, while in the other tests respiration was more strongly inhibited after short-term exposure than after long-term exposure.

In the study by Liang and Tabatabai (1978), a concentration of 5 mMol $ZnSO_4.kg^{-1}$ soil resulted in an effect on N-mineralization in different test soils. At this concentration the sulphate concentration in soil is 480 $mg.kg^{-1}$ (0.048 %). These authors refer to a study by Sindhu and Cornfield (1967) which showed that Na, K, Ca an Mg salts of sulphate or chloride did not affect N-mineralization at amounts up to 1%, equivalent to 7,000-8,000 $mg.kg^{-1}$ of sulphate (0.7-0.8%) or 5,000-7,000 $mg.kg^{-1}$ of chloride (0.5-0.7%). These data show that zinc was the causative agent in the above-mentioned study by Liang and Tabatabai.

Additional data on microorganisms

* Earlier reviews on the effects of zinc -and other heavy metals- on microbes (microbial numbers and species diversity) and microbe-mediated processes, and on physicochemical soil-related factors influencing toxicity, have been written by Doelman and Haanstra (1983), Babich and Stotzky (1985) and Doelman (1985). Most data reviewed are on relatively short-term tests in which effects were measured after exposure times ranging from a few hours to a few weeks. The data reviewed by Doelman (1985) show that zinc concentrations that "never", "sometimes" and "mostly" result in effects on soil respiration, nitrogen mineralization and/or

nitrification are 10, 10-1,000 and 1,000-10,000 mg.kg^{-1}, respectively; these data are generally consistent with those in table 2.1.

* Addition of increasing amounts of domestic or industrial sludge to a sandy loam resulting in an increase in soil zinc concentration from 24 to 26-172 mg.kg^{-1} dw (increase of 2-148 mg.kg^{-1} dw), resulted in a temporarily reduced nitrification. At concentrations of 26-61 mg.kg^{-1} dw, the effect on nitrification was only observed 1-2 weeks after addition. At the highest concentration tested, 172 mg.kg^{-1} dw, nitrification was totally restored after 6 weeks, although it was totally inhibited during the first 3 weeks. It is noted that the sludges, especially the industrial sludge, also contained relatively high concentrations of other metals including Cd, Cr, Cu and Pb, but Zn was particularly high. Additions of domestic sludge amended with the chlorides of Cd, Cr, Cu, Mn, Pb and Zn resulted -at the highest rate of application- in a greater inhibition of nitrification than a similar treatment with unamended industrial sludge, although the final total metal concentrations were similar. This comparison shows that the inorganic metal salts are more effective than those forms associated with sludge. In preliminary experiments with the soil used in this study, nitrification was temporarily inhibited at 100 mg.kg^{-1} and totally inhibited at 1,000 mg.kg^{-1} (Wilson, 1977b). It is noted that the form of zinc used in the preliminary experiments is not reported.

* Van Beelen and co-workers studied the effect of zinc (added as $ZnCl_2$) on the mineralization of acetate by microbial populations present in soils (collected at 0-20 cm) or subsoils (collected below 100 cm). Test slurries contained 10 g fresh soil or subsoil and 10 ml filter-sterilized groundwater. Only a minute amount of acetate (1 μg.l^{-1} slurry) was used, because this readily degradable compound is also present in natural environments at low concentrations. In calcareous soil and subsoil from a polder location (OM 1-2%, clay ±1%, pH KCl 7-8; background zinc concentration 12-43 mg.kg^{-1} dw), EC10 values were 303 and 59 mg.kg^{-1} dw (total concentrations), respectively, after an exposure time of 0.75 and 4 days, respectively. The IC10 in the subsoil sample was 39 mg.kg^{-1} dw (total concentration); that in the soil sample could not be calculated wich sufficient accuracy since the incubation time of 0.75 days was much too long for the rapid mineralization rate (half-life 0.017 days) in this soil sample *[The EC10 is defined here as the toxicant concentration that causes 10% inhibition of the mineralization of acetate after a certain incubation time, while the IC10 is defined as the toxicant concentration that causes 10% inhibition of the first-order mineralization rate of acetate. The IC10 is not time-dependent, in contrast to the EC10, and therefore considered by*

the authors to be a more suitable effect value than the EC10]. In acid soil and subsoil from a second location (OM 0.3-4%, clay ± 1%, pH KCl 3-4, background zinc concentration 4-6 mg.kg^{-1} dw), both EC10 and IC10 values were (much) higher, above 1,000 mg.kg^{-1} dw, despite a lower sorption capacity (K_f-value) and lower pH compared to the alkaline soil and subsoil. According to the authors one possible explanation of this difference is the formation of $ZnOH^+$ in the alkaline samples; this zinc species may be more toxic than Zn^{2+}. Another explanation is a lower sensitivity of the microbial populations present in the acid soils; this would be in accordance with the relative insensitivity of the microbial population in acid soils reported earlier by authors other than Van Beelen et al. (Van Beelen, 1991b). In similar tests with anaerobic incubation of sandy subsoil samples, IC10 values for acetate mineralization ranged from about 50 to 700 mg.kg^{-1} (Van Beelen et al., 1990, 1991c).

2.2.2 Invertebrates (table 2.2)

Data on invertebrates, especially toxicity tests resulting in NOEC values with respect to survival, growth and reproduction, are summarized in table 2.2. The data refer to tests with exposure times varying from 2 to 20 weeks.

In the study by Neuhauser et al. (1984) the 6-w exposure period was followed by a 6-w recovery period in which the soil was covered with uncontaminated manure. In the recovery period, worms showed compensatory growth (higher growth rate than control animals) resulting in recovery to approximately the control weight value, even of worms exposed to the highest concentration tested (10,000 mg Zn.kg^{-1} manure). Reproduction rate of worms exposed to the higher concentrations recovered to the control rate value, but a compensatory mechanism with regard to this parameter was not observed.

Additional data on invertebrates

* Corp and Morgan (1991) conducted an accumulation study in which adults of the earthworm *L. rubellus* were kept in samples of soils from former mining areas in Wales (U.K.) containing high levels of heavy metals. In samples of each soil, both "native" worms (collected in the respective soil) and "introduced" worms (collected in a control soil) were kept for 4 weeks.

Survival of native and introduced worms was reported to be fairly similar in each case (no further details reported). In one soil all worms died within 14 days, possibly due to the very high lead concentration of almost 40,000 mg.kg^{-1} dw. In the other soil samples, worms survived despite high to very high zinc concentrations (417 to 183,000 mg.kg^{-1} dw) and high to very high concentrations of other metals such as lead, copper and cadmium.
* Data on groundwater organisms are limited to an acute lethal toxicity study with adults of the copepod *Parastenocaris germanica*, a crustacean with a rather large distribution in the Netherlands, especially in sandy phreatic aquifer communities. Static tests under normoxic and hypoxic conditions resulted in 96-hr LC50 values of 1,700 and 2,300 μg.l^{-1}, respectively; 96-hr LC5 values (approaching no effect) were 400 and 600 μg.l^{-1}, respectively. The differences between corresponding values derived under normoxic and hypoxic conditions were not statistically significant. The LC50 values are within the range reported for aquatic crustaceans. The tests were conducted in buffered tap water (pH 6.8, total hardness 80 mg.l^{-1}) originating from groundwater; the test compound was $ZnSO_4.7H_2O$ (Notenboom et al., 1992).

2.2.3 Plants (table 2.3)

Pot experiments with plants (agricultural crops), resulting in NOEC values with respect to yield, are summarized in table 2.3.
For a large number of additional data on the effects of zinc on agricultural crops the reader is referred to section 5.4.1 in the "Integrated Criteria Document Zinc" (Cleven et al., 1992).
Data on plants other than agricultural crops are not available.

Table 2.1 Microbe-mediated processes - toxicity tests: miscellaneous toxicity values

Parameter	Test-comp.	Soil	pH	OM %	Clay %	Temp. ^0C	Exp.-time	Criterion	Result in test soil (mg Zn/kg)(dw)	Calculated value in standard soil*
C-mineralization										
Respiration	$ZnCl_2$	loamy sand (95%) and 5% oak litter	4.8	$7^{\simeq}$	$3^{\simeq}$	22	3-w	NOEC	48^{ω}	**89^{ω}**
									Chaney et al. '78 [1]	
Respiration	$ZnCl_2$	litter (fir needles)	-	$77^{\simeq}$	$0^{\simeq}$	22	4-w	NOEC	100^{ω} 111^{ψ}	**127^{ω}** **141^{ψ}**
									Spalding '79 [2]	
Respiration	$ZnSO_4$	loamy sand	4.9	4	5	30	8-w	EC (21%)	10^{ω} 13^{ψ}	20^{ω} 26^{ψ}
	$ZnSO_4$	loamy sand	4.9	4	5	30	8-w	EC (45%)	100^{ω} 103^{ψ}	197^{ω} 203^{ψ}
									Cornfield '77 [3]	
Respiration	$ZnSO_4$	silt loam	6.9	2	$44^{\simeq}$	25	3-m	NOEC	12^{ω} 19^{ψ}	**9^{ω}** **14^{ψ}**
									Chang & Broadbent '81 [4]	
Respiration	ZnO	Bagshot sand	6.0	4	5	30	5-m	EC (14%)	$1,000^{\omega}$ $1,074^{\psi}$	$1,972^{\omega}$ $2,118^{\omega}$
									Bhuiya & Cornfield '72 [5]	
Respiration	$ZnCl_2$	sand (low %OM)	7.7	2	2	20	8-w	EC50	500^{ω} 514^{ψ}	$1,029^{\omega}$ $1,058^{\psi}$
							15-m	NOEC	150^{ω} 164^{ψ}	**309^{ω}** **338^{ψ}**
	$ZnCl_2$	sand (high %OM)	5.1	6	9	20	10-m	EC50	$1,250^{\omega}$ $1,267^{\psi}$	$2,035^{\omega}$ $2,062^{\psi}$
							10-m	NOEC	150^{ω} 167^{ψ}	**244^{ω}** **272^{ψ}**
	$ZnCl_2$	sandy loam	7.4	3	19	20	20-m	NOEC	$3,000^{\omega}$ $3,103^{\psi}$	**$3,769^{\omega}$** **$3,896^{\psi}$**
	$ZnCl_2$	clay	6.8	3	60	20	18-m	NOEC	400^{ω} 626^{ψ}	**274^{ω}** **428^{ψ}**
	$ZnCl_2$	sandy peat	4.3	13	5	20	8-w	EC50	$8,000^{\omega}$ $8,038^{\psi}$	$13,254^{\omega}$ $13,317^{\psi}$
							18-m	EC (9%)	150^{ω} 188^{ψ}	248^{ω} 311^{ψ}
									Doelman & Haanstra '83 [6]	

(to be continued)

Table 2.1 Microbe-mediated processes - toxicity tests: miscellaneous toxicity values [continued]

Parameter	Test-comp.	Soil	pH	OM %	Clay %	Temp. °C	Exp.-time	Criterion	Result in test soil (mg Zn/kg)(dw)	Calculated value in standard soil* (mg Zn/kg)(dw)
N-mineralisation										
N-mineralization	$ZnSO_4$	-	5.8	4	23	30	3-w	EC (14%)	325^{ω}	364^{ω}
	$ZnSO_4$	-	6.6	5	45	30	3-w	EC (12%)	325^{ω}	236^{ω}
	$ZnSO_4$	-	7.8	6	30	30	3-w	EC (15%)	325^{ω}	305^{ω}
	$ZnSO_4$	-	7.4	9	34	30	3-w	EC (14%)	325^{ω}	275^{ω}
									Liang & Tabatabai '77 [7]	
N-mineralization	$ZnSO_4$	silt loam	6.9	2	$44^{\approx}$	25	3-m	NOEC	100^{ω}	**75**$^{\omega}$
									107^{ψ}	**81**$^{\psi}$
									Chang & Broadbent '82 [8]	
Ammonification	ZnO	sand	6.0	2	-	20	2-w	NOEC	$1,000^{\phi}$	
	ZnO	sand	7.0	2	-	20	2-w	EC (mod.)	$1,000^{\phi}$	
	ZnO	sand	7.7	2	-	20	2-w	EC (great)	$1,000^{\phi}$	
									Doelman & Haanstra '83$^{\int}$	
Ammonification	$ZnSO_4$	sandy loam	6.2	3	17	30	3-w	NOEC	$1,000^{\omega}$	**1,327**$^{\omega}$
									$1,057^{\psi}$	**1,403**$^{\psi}$
	$ZnCO_3$	sandy loam	7.4	3	17	30	3-w	NOEC	$1,000^{\omega}$	$1,327^{\omega}$
									$1,057^{\psi}$	$1,403^{\psi}$
			8.5	3	17	30	3-w	NOEC	$\geq 10,000^{\omega}$	$13,270^{\omega}$
									$\geq 10,057^{\psi}$	$13,345^{\psi}$
									Premi & Cornfield '69 [9]	
Ammonification	$ZnSO_4$	sand	-	-	-	30	4-w	EC (20%)	$2,500^{\phi}$	
									Doelman & Haanstra '83$^{\int}$	
Nitrification	$ZnSO_4$	-	5.8	4	23	30	10-d	EC (58%)	325^{ω}	364^{ω}
	$ZnSO_4$	-	7.8	6	30	30	10-d	EC (24%)	325^{ω}	305^{ω}
	$ZnSO_4$	-	7.4	9	34	30	10-d	EC (39%)	325^{ω}	275^{ω}
									Liang & Tabatabai '78 [10]	
Nitrification	$ZnSO_4$	sandy loam	7.0	3	17	30	3-w	NOEC	100^{ω}	**133**$^{\omega}$
									157^{ψ}	**208**$^{\psi}$
	$ZnCO_3$	sandy loam	7.4	3	17	30	3-w	NOEC	$1,000^{\omega}$	$1,327^{\omega}$
									$1,057^{\psi}$	$1,403^{\psi}$
			8.5	3	17	30	3-w	NOEC	$\geq 10,000^{\omega}$	$13,270^{\omega}$
									$\geq 10,057^{\psi}$	$13,345^{\psi}$
									Premi & Cornfield '69 [9]	
Nitrification	$ZnSO_4$	clay loam	5.6	2	28	30	7-w	NOEC	100^{ω}	**102**$^{\omega}$
									236^{ψ}	**241**$^{\psi}$
	$ZnSO_4$	sandy loam	5.3	2	8	30	7-w	NOEC	100^{ω}	**182**$^{\omega}$
									124^{ψ}	**225**$^{\psi}$
	$ZnSO_4$	loamy sand	6.0	1	2	30	7-w	NOEC	10^{ω}	**21**$^{\omega}$
							7-w	NOEC	17^{ψ}	**35**$^{\psi}$
									Wilson '77a [11]	

(to be continued)

Table 2.1 Microbe-mediated processes - toxicity tests: miscellaneous toxicity values [continued]

Parameter	Test-comp.	Soil	pH	OM %	Clay %	Temp. ^0C	Exp.-time	Criterion	Result in test soil (mg Zn/kg)(dw)	Calculated* value in standard soil
Mineralization of specific substrates										
Glucose	$ZnSO_4$	-	5.0	6	9	25	2-w	NOEC	5,000$^{\phi}$	8,139$^{\phi}$
									Denneman & van Gestel '90$^{\int}$	
Glutamic acid (max. CO_2 prod.)	$ZnCl_2$	sand (low %OM)	7.7	2	2	20	1.5-yr	EC50	400$^{\omega}$ 414$^{\psi}$	823$^{\omega}$ 852$^{\psi}$
	$ZnCl_2$	sand (high %OM)	5.1	6	9	20	1.5-yr	NOEC	≥ 1,000$^{\omega}$ ≥ 1,017$^{\psi}$	**1,628**$^{\omega}$ **1,656**$^{\psi}$
		sandy loam	7.4	3	19	20	1.5-yr	NOEC	400$^{\omega}$ 503$^{\psi}$	**502**$^{\omega}$ **631**$^{\psi}$
		clay	6.8	3	60	20	1.5-yr	NOEC	400$^{\omega}$ 626$^{\psi}$	**274**$^{\omega}$ **428**$^{\psi}$
								EC50	1,500$^{\omega}$ 1,726$^{\psi}$	1,027$^{\omega}$ 1,182$^{\psi}$
		sandy peat	4.3	13	5	20	1.5-yr	NOEC	≥ 1,000$^{\omega}$ ≥ 1,038$^{\psi}$	**1,657**$^{\omega}$ **1,720**$^{\psi}$
									Doelman & Haanstra '83 [6]	
Enzyme activities										
Amylase	$ZnCl_2$	litter (fir needles)	-	≅77	≅0	-	4-w	NOEC	≥ 1,000$^{\omega}$ ≥ 1,111$^{\psi}$	**1,273**$^{\omega}$ **1,414**$^{\psi}$
									Spalding '79 [2]	
Arylsulphatase	$ZnCl_2$	sand (low %OM)	7.7	2	2	20	< 1-w ?	EC50	900$^{\omega}$ [12] 914$^{\psi}$	1,853$^{\omega}$ 1,882$^{\psi}$
	$ZnCl_2$	sand (high %OM)	5.1	6	9	20	< 1-w ?	EC50	2,180$^{\omega}$ [12] 2,197$^{\psi}$	3,549$^{\omega}$ 3,576$^{\psi}$
	$ZnCl_2$	sandy loam	7.4	3	19	20	1-1,5-yr	EC50	4,390$^{\omega}$ 4,493$^{\psi}$	5,512$^{\omega}$ 5,641$^{\psi}$
	$ZnCl_2$	clay	6.8	3	60	20	1-1.5-yr	EC50	2,860$^{\omega}$ 3,086$^{\psi}$	1,958$^{\omega}$ 2,113$^{\psi}$
									Doelman & Haanstra '83 [6]	
Cellulase	$ZnCl_2$	litter (fir needles)	-	≅77	≅0	-	4-w	NOEC	≥ 1,000$^{\omega}$ ≥ 1,111$^{\psi}$	**1,273**$^{\omega}$ **1,414**$^{\psi}$
									Spalding '79 [2]	
Phosphatase	$ZnCl_2$	sand (low %OM)	7.7	2	2	20	1-1.5-yr	EC50	150$^{\omega}$ 164$^{\psi}$	309$^{\omega}$ 338$^{\psi}$
	$ZnCl_2$	sand (high %OM)	5.1	6	9	20	1-1.5-yr	EC50	2,970$^{\omega}$ 2,987$^{\psi}$	4,835$^{\omega}$ 4,862$^{\psi}$
	$ZnCl_2$	sandy loam	7.4	3	19	20	< 1-w ?	EC50	2,760$^{\omega}$ [12] 2,863$^{\psi}$	3,465$^{\omega}$ 3,595$^{\psi}$
	$ZnCl_2$	clay	6.8	3	60	20	1-1.5-yr	EC50	2,710$^{\omega}$ 2,936$^{\psi}$	1,855$^{\omega}$ 2,010$^{\psi}$
									Doelman & Haanstra '83 [6]	

(to be continued)

Table 2.1 Microbe-mediated processes - toxicity tests: miscellaneous toxicity values (continued)

Parameter	Test-comp.	Soil	pH	OM %	Clay %	Temp. °C	Exp.-time	Criterion	Result in test soil (mg Zn/kg)(dw)	Calculated value in standard soil* (mg Zn/kg)(dw)
Enzyme activities (continued)										
Phosphatase (acid -)	$ZnSO_4$	-	7.0	6	30	37	1-hr	EC (32%)	1,625$^{\omega}$	1,527$^{\omega}$
	$ZnSO_4$	-	7.0	9	34	37	1-hr	EC (33%)	1,625$^{\omega}$	1,375$^{\omega}$
	$ZnSO_4$	-	6.5	4	23	37	1-hr	EC (30%)	1,625$^{\omega}$	1,820$^{\omega}$
							1-hr	NOEC	162$^{\omega}$	**181**$^{\omega}$
									Juma & Tabatabai '77 [13]	
Phosphatase (alkaline-)	$ZnSO_4$	-	10.0	6	30	37	1-hr	EC (59%)	1,625$^{\omega}$	1,527$^{\omega}$
	$ZnSO_4$	-	10.0	9	34	37	1-hr	EC (28%)	1,625$^{\omega}$	1,375$^{\omega}$
							1-hr	NOEC	162$^{\omega}$	**137**$^{\omega}$
									Juma & Tabatabai '77 [13]	
Protease	$ZnCl_2$	sandy loam	7.4	3	19	20	1-1.5-yr	EC50	3,250$^{\omega}$ 3,303$^{\psi}$	4,081$^{\omega}$ 4,147$^{\psi}$
									Doelman & Haanstra '83 [6]	
Urease	$ZnSO_4$	-	9.0	3	17	37	2-hr	EC (61%)	325$^{\omega}$	431$^{\omega}$
	$ZnSO_4$	-	9.0	6	30	37	2-hr	EC (33%)	325$^{\omega}$	305$^{\omega}$
	$ZnSO_4$	-	9.0	4	23	37	2-hr	EC (23%)	325$^{\omega}$	364$^{\omega}$
	$ZnSO_4$	-	9.0	6	30	37	2-hr	NOEC	32$^{\omega}$	**30**$^{\omega}$
	$ZnSO_4$	-	9.0	7	42	37	2-hr	EC (51%)	325$^{\omega}$	244$^{\omega}$
	$ZnSO_4$	-	9.0	9	34	37	2-hr	NOEC	32$^{\omega}$	**27**$^{\omega}$
									Tabatabai '77 [14]	
Urease	$ZnSO_4$	-	6.5	4	31	37	5-hr	NOEC	≥ 50$^{\omega}$	**48**$^{\omega}$
	$ZnSO_4$	-	7.3	5	31	37	5-hr	NOEC	≥ 50$^{\omega}$	**47**$^{\omega}$
									Bremner & Douglas '71 [15]	
Urease	$ZnCl_2$	sand (low %OM)	7.7	2	2	20	1-1.5-yr	EC50	290$^{\omega}$ 304$^{\psi}$	597$^{\omega}$ 626$^{\psi}$
	$ZnCl_2$	sand (high %OM)	5.1	6	9	20	1-1.5-yr	EC50	45$^{\omega}$ 62$^{\psi}$	73$^{\omega}$ 101$^{\psi}$
	$ZnCl_2$	sandy loam	7.4	3	19	20	1-1.5-yr	EC50	3,200$^{\omega}$ 3,353$^{\psi}$	4,018$^{\omega}$ 4,210$^{\psi}$
	$ZnCl_2$	clay	6.8	3	60	20	1-1.5-yr	EC50	85$^{\omega}$ 311$^{\psi}$	58$^{\omega}$ 213$^{\psi}$
	$ZnCl_2$	sandy peat	4.3	13	5	20	1-1.5-yr	EC50	60$^{\omega}$ 98$^{\psi}$	99$^{\omega}$ 162$^{\psi}$
									Doelman Haanstra '83 [6]	
Xylanase	$ZnCl_2$	litter (fir needles)	-	$77^{\cong}$	$0^{\cong}$	-	4-w	NOEC	≥ 1,000$^{\omega}$ ≥ 1,111$^{\psi}$	**1,273**$^{\omega}$ **1,414**$^{\psi}$
									Spalding '79 [2]	

For footnotes see next page; for further information see the "list of abbreviations tables 2.1 to 2.3".

Footnotes table 2.1

[1] Statistics: $p \leq 0.05$. Substrate: microcosm (soil and litter) collected in the field. CEC soil: 6.3 meq/100 g. Organic matter content in soil: 1.9%; estimated organic matter content in litter: 95%. The %OM in the substrate was calculated from ((0.95 x %OM in soil) + (0.05 x %OM in litter)). The clay content in the substrate was calculated from 0.95 x %clay in soil. Test compound added in aqueous solution.

[2] Statistics: $p \leq 0.05$. Test compound added in aqueous solution.

[3] Statistics: $p \leq 0.05$. Test compound added as a solid.

[4] No statistics reported. Parameter: cumulative CO_2 production. CEC (27.5 meq/100 g) used to calculate the clay content. The NOEC indicated is the threshold concentration (i.e. the concentration that would cause an inhibition of 10%) estimated by Chang & Broadbent (1981) on the basis of the extractable concentration-effect relationship and the total concentration in soil to reach this extractable concentration. Test compound added in solution.

[5] Statistics: $p \leq 0.05$. Respiration (CO_2 release) measured during the last 3 months of the incubation period. Treatment did not alter soil pH by more than 0.3 units. Test compound added as a solid. In a similar test in which the soil was mixed with 0.5% of finely-ground oat straw, respiration was not adversely affected at 1,000 mg Zn/kg soil.

[6] Statistics $p \leq 0.05$. The pH (KCl) indicated is the initial value before exposure. In the C-mineralization study, respiration was measured for 8-10 weeks, starting "directly" (short-term exposure) and 8-18 months (long-term exposure), respectively, after addition of zinc to the soil.

[7] Statistics: $p \leq 0.05$. The percentage inhibition is based on all three N-mineralization parameters studied (ammonium-N, nitrite-N and nitrate-N). Test compound added in solution.

[8] No statistics reported. CEC (27.5 meq/100 g) used to calculate the clay content. N-mineralization parameters: organic-N, inorganic-N, and nitrate-N. Test compound added in solution.

[9] Statistics: $p \leq 0.05$. The pH indicated is the value measured after exposure to the concentration of zinc indicated; the initial pH was 7.1.

[10] Statistics: $p \leq 0.05$. Test compound added in solution. After treatment the pH was within 0.1 units.

[11] Statistics: $p \leq 0.05$. The pH values indicated are the values measured after exposure to the concentration of zinc indicated. The initial pH values were 6.8, 6.2 and 7.4 in the clay loam, sandy loam and loamy soil, respectively. Nitrogen was added to all soil samples. The N-mineralization parameters studied were (i) ammonium-N and (ii) nitrite-N + nitrate-N. Test compound added in solution.

[12] Enzyme activity was measured "directly" after addition of zinc to the soil.

[13] No statistics reported. Soils were selected on the basis of characteristics including background acid and alkaline phosphatae activity. The pH indicated is the buffered value; initial pH values ranged from 5.8 to 7.8. Test compound added in solution.

[14] No statistics reported. Soils were selected on the basis of characteristics including background urease activity. The pH indicated is the buffered value; initial pH values ranged from 5.1 to 7.8. Test compound added in solution.

[15] No statistics reported. Test compound added in aqueous solution.

Table 2.2 Invertebrates - toxicity tests: miscellaneous toxicity values

Organism	Test-comp.	Substrate	Substrate characteristics			Temp. °C	Exp.-time	Criterion	Result in test soil	Calculated value in standard soil*
			pH	OM %	clay %				mg Zn/kg (dw)	
Oligochaetes (Annelids)										
Eisenia fetida adults	$Zn(NO_3)_2$	art. soil (OECD)	6	8	8	20	2-w	LC50	660^{ω}	$1{,}074^{\omega}$
							2-w	$\text{NOEC}_{\mathbf{w}}$	200^{ω}	$\mathbf{326}^{\omega}$
									Neuhauser et al.'85 [1]	
Eisenia fetida < 2-w old	sol. salts	soil+<u>manure</u>	-	$50^{\simeq}$	$0^{\simeq}$	25	6-w	$\text{NOEC}_{g,\mathbf{r}}$	$1{,}000^{\omega}$	$\mathbf{1{,}273}^{\omega}$
									Neuhauser et al.'84 [2]	
Eisenia fetida hatchlings	$ZnSO_4.7H_2O$	soil+<u>sludge</u>	6.5	-	-	24	8-w	$\text{NOEC}_{s,\mathbf{g}}$	$1{,}500^{\omega}$	-
									Hartenstein et al.'81 [3]	
Eisenia fetida		soil+<u>manure</u>	-	$50^{\simeq}$	$0^{\simeq}$	22				
	ZnO						8-w	$\text{NOEC}_{s,\mathbf{g},\mathbf{r}}$	$^{\epsilon}2{,}000^{\omega}$	$\mathbf{2{,}545}^{\omega}$
	$Zn(C_2H_3O_2)_2$						8-w	$\text{NOEC}_{s,g,\mathbf{r}}$	$1{,}000^{\omega}$	$\mathbf{1{,}273}^{\omega}$
	$ZnCl_2$ or $Zn(NO_3)_2$						8-w	$\text{NOEC}_{s,\mathbf{g},\mathbf{r}}$	$^{\epsilon}1{,}000^{\omega}$	$\mathbf{1{,}273}^{\omega}$
	$ZnSO_4$ or $ZnCO_3$						8-w	$\text{NOEC}_{s,g,\mathbf{r}}$	$^{\epsilon}250^{\omega}$	$\mathbf{318}^{\omega}$
									Malecki et al.'82 [4]	
Eisenia fetida	$Zn(C_2H_3O_2)_2$	soil+<u>manure</u>	-	$50^{\simeq}$	$0^{\simeq}$	22	20-w	$\text{NOEC}_{s,g,\mathbf{r}}$	$2{,}500^{\omega}$	$\mathbf{3{,}182}^{\omega}$
									Malecki et al.'82 [5]	
Gastropods (Molluscs)										
Arion ater 5-7 g	$ZnCl_2$	feed	-	$95^{\simeq}$	$0^{\simeq}$	20	4-w	$\text{NOEC}_{\mathbf{f},\mathbf{s},\mathbf{w}}$	300^{ω}	$\mathbf{382}^{\omega}$
									Marigomez et al.'86 [6]	
Crustaceans (Arthropods)										
Porcellio scaber	$Zn(NO_3)_2$	feed	-	$95^{\simeq}$	$0^{\simeq}$	-	10-w	$\text{NOEC}_{f,\mathbf{g},r}$	400^{ω} [7]	$\mathbf{509}^{\omega}$
									Denneman & van Gestel ,90	

Parameters:

f = feeding activity (consumption); g = growth; r = reproduction (cocoon production); s = survival; w = weight.
The most sensitive parameters have been printed **bold.**

Footnotes table 2.2; for further information see the "list of abbreviations tables 2.1 to 2.3".

[1] No statistics reported. The NOEC was estimated from plotted data. Test compound added to the soil in aqueous solution.

[2] Statistics: $p \leq 0.05$. Worms were exposed to 30 g soil covered with 20 g contaminated manure. The NOEC indicated is the average result of 4 tests using the acetate, chloride, nitrate and sulphate salt; the average value was reported by Neuhauser (1984). The experimental result is expressed as mg Zn/kg dry manure. No data on soil characteristics.

[3] Statistics applied ("p" not reported). Worms were exposed to 50 g soil (dry weight basis) covered with 50 g contaminated wet sludge (Zn salt added as a solid). After 4 weeks of exposure the remaining sludge was removed and a fresh supply of Zn-treated sludge was added. Soil and sludge pH ranged from 6.5 to 7, independent of treatment. Soil: silt loam; no further soil characteristics reported.

[4] Statistics: $p \leq 0.05$. Worms were exposed to 30 g soil covered with 20 g contaminated manure. The zinc-manure mixture was removed and replenished at 4 and 6 weeks. The experimental results are expressed as mg Zn/kg dry manure. The NOEC values marked by "ϵ" were estimated from the lowest effect concentration, using a factor of 2.

[5] Statistics: $p \leq 0.05$. Worms were exposed to 90 g soil covered with 100 g contaminated manure. The experimental result is expressed as mg Zn/kg dry manure. No data on soil characteristics.

[6] Statistics: regression analysis. Feed (natural diet): equiproportional, grinded mixture of letttuce, apple, carrot and pumpkin with a 1.5% agar aqueous solution mixed with $ZnCl_2$. Feeding activity tended to decrease at 300 mg/kg during the last week of exposure, but body weight and survival were not affected.

[7] Feed: mixture of carrots and potatoes.

Table 2.3 Plants - toxicity tests: NOEC values

Species	Test-comp.	Soil type	pH	OM %	Clay %	Temp. ^0C	Exp.-time	Criterion	Result in test soil (mg Zn/kg)(dw)	Calculated value in standard soil* (mg Zn/kg)(dw)
Medicago sativa (Alfalfa)	$ZnSO_4.7H_2O$	sandy loam (A) [2]	7.5	4	16	-	8-w	NOEC$_y$	≥ 250$^{\omega}$ ≥ 329$^{\psi}$	**337**$^{\omega}$ 444$^{\psi}$
	$ZnSO_4.7H_2O$	sandy loam (B) [2]	7.4	4	16	-	8-w	NOEC$_y$	≥ 250$^{\omega}$ ≥ 330$^{\psi}$	**337**$^{\omega}$ 445$^{\psi}$
	$ZnSO_4.7H_2O$	sandy loam (C) [2]	7.4	8	16	-	8-w	NOEC$_y$	≥ 250$^{\omega}$ ≥ 327$^{\psi}$	**317**$^{\omega}$ 415$^{\psi}$
	$ZnSO_4.7H_2O$	sandy loam (D) [2]	7.3	7	16	-	8-w	NOEC$_y$	≥ 250$^{\omega}$ ≥ 327$^{\psi}$	**322**$^{\omega}$ 421$^{\psi}$
	$ZnSO_4.7H_2O$	mixed loam (E) [2]	7.4	3	23	-	8-w	NOEC$_y$	≥ 250$^{\omega}$ ≥ 356$^{\psi}$	**282**$^{\omega}$ 402$^{\psi}$
	$ZnSO_4.7H_2O$	sandy loam [F) [2]	7.5	3	14	-	8-w	NOEC$_y$	≥ 250$^{\omega}$ ≥ 322$^{\psi}$	**362**$^{\omega}$ 466$^{\psi}$
	$ZnSO_4.7H_2O$	sandy loam (G) [2]	7.2	10	13	-	8-w	NOEC$_y$	≥ 250$^{\omega}$ ≥ 328$^{\psi}$	**337**$^{\omega}$ 442$^{\psi}$
	$ZnSO_4.7H_2O$	sandy loam [H) [2]	4.9	3	16	-	8-w	NOEC$_y$	50$^{\omega}$ 103$^{\psi}$	**68**$^{\omega}$ 140$^{\psi}$
	$ZnSO_4.7H_2O$	sandy loam (I) [2]	6.8	3	16	-	8-w	NOEC$_y$	≥ 250$^{\omega}$ ≥ 302$^{\psi}$	**340**$^{\omega}$ 410$^{\psi}$
	$ZnSO_4.7H_2O$	sandy loam (J) [2]	7.5	3	16	-	8-w	NOEC$_y$	≥ 250$^{\omega}$ ≥ 301$^{\psi}$	**340**$^{\omega}$ 409$^{\psi}$
									MacLean '74 [1]	
Zea mays (Corn)	$ZnSO_4.7H_2O$	sandy loam (A) [2]	7.5	4	16	-	6-w	NOEC$_y$	≥ 250$^{\omega}$ ≥ 329$^{\psi}$	**337**$^{\omega}$ 444$^{\psi}$
	$ZnSO_4.7H_2O$	sandy loam (B) [2]	7.4	4	16	-	6-w	NOEC$_y$	≥ 250$^{\omega}$ ≥ 330$^{\psi}$	**337**$^{\omega}$ 445$^{\psi}$
	$ZnSO_4.7H_2O$	sandy loam (C) [2]	7.4	8	16	-	6-w	NOEC$_y$	≥ 250$^{\omega}$ ≥ 327$^{\psi}$	**317**$^{\omega}$ 415$^{\psi}$
	$ZnSO_4.7H_2O$	sandy loam (D) [2]	7.3	7	16	-	6-w	NOEC$_y$	≥ 250$^{\omega}$ ≥ 327$^{\psi}$	**322**$^{\omega}$ 421$^{\psi}$
	$ZnSO_4.7H_2O$	mixed loam (E) [2]	7.4	3	23	-	6-w	NOEC$_y$	≥ 250$^{\omega}$ ≥ 356$^{\psi}$	**282**$^{\omega}$ 402$^{\psi}$
	$ZnSO_4.7H_2O$	sandy loam (F) [2]	7.5	3	14	-	6-w	NOEC$_y$	≥ 250$^{\omega}$ ≥ 322$^{\psi}$	**362**$^{\omega}$ 466$^{\psi}$
	$ZnSO_4.7H_2O$	sandy loam (G) [2]	7.2	10	13	-	6-w	NOEC$_y$	≥ 250$^{\omega}$ ≥ 328$^{\psi}$	**337**$^{\omega}$ 442$^{\psi}$
	$ZnSO_4.7H_2O$	sandy loam (H) [without P]	4.9	3	16	-	6-w	NOEC$_y$	50$^{\omega}$ 103$^{\psi}$	**68**$^{\omega}$ 140$^{\psi}$
	$ZnSO_4.7H_2O$	sandy loam (H) [with P]	5.0	3	16	-	6-w	NOEC$_y$	≥ 250$^{\omega}$ ≥ 303$^{\psi}$	**340**$^{\omega}$ 412$^{\psi}$
	$ZnSO_4.7H_2O$	sandy loam (I) [2]	6.8	3	16	-	6-w	NOEC$_y$	≥ 250$^{\omega}$ ≥ 302$^{\psi}$	**340**$^{\omega}$ 410$^{\psi}$
	$ZnSO_4.7H_2O$	sandy loam (J) [without P]	7.5	3	16	-	6-w	NOEC$_y$	≥ 250$^{\omega}$ ≥ 301$^{\psi}$	**340**$^{\omega}$ 409$^{\psi}$
	$ZnSO_4.7H_2O$	sandy loam (J) [with P]	6.7	3	16	-	6-w	NOEC$_y$	10$^{\omega}$ 61$^{\psi}$	**14**$^{\omega}$ 82$^{\psi}$
									MacLean '74 [1]	

(to be continued)

Table 2.3 Plants - toxicity tests: NOEC values
[continued]

Species	Test-comp.	Soil type	pH	OM %	Clay %	Temp. ^{0}C	Exp.-time	Criterion	Result in test soil	Calculated value in standard soil*
									(mg Zn/kg)(dw)	
Lactuca sativa (Lettuce)	$ZnSO_4.7H_2O$	sandy loam (A) [2]	7.5	4	16	-	5-w	$NOEC_y$	≥ 250$^{\omega}$ ≥ 329$^{\psi}$	**337**$^{\omega}$ 444$^{\psi}$
	$ZnSO_4.7H_2O$	sandy loam (B) [2]	7.4	4	16	-	5-w	$NOEC_y$	≥ 250$^{\omega}$ ≥ 330$^{\psi}$	**337**$^{\omega}$ 445$^{\psi}$
	$ZnSO_4.7H_2O$	sandy loam (C) [2]	7.4	8	16	-	5-w	$NOEC_y$	≥ 250$^{\omega}$ ≥ 327$^{\psi}$	**317**$^{\omega}$ 415$^{\psi}$
	$ZnSO_4.7H_2O$	sandy loam (D) [2]	7.3	7	16	-	5-w	$NOEC_y$	≥ 250$^{\omega}$ ≥ 327$^{\psi}$	**322**$^{\omega}$ 421$^{\psi}$
	$ZnSO_4.7H_2O$	mixed loam (E) [2]	7.4	3	23	-	5-w	$NOEC_y$	≥ 250$^{\omega}$ ≥ 356$^{\psi}$	**282**$^{\omega}$ 402$^{\psi}$
	$ZnSO_4.7H_2O$	sandy loam (F) [2]	7.5	3	14	-	5-w	$NOEC_y$	≥ 250$^{\omega}$ ≥ 322$^{\psi}$	**362**$^{\omega}$ 466$^{\psi}$
	$ZnSO_4.7H_2O$	sandy loam (G) [2]	7.2	10	13	-	5-w	$NOEC_y$	≥ 250$^{\omega}$ ≥ 328$^{\psi}$	**337**$^{\omega}$ 442$^{\psi}$
	$ZnSO_4.7H_2O$	sandy loam (H) [without P]	4.9	3	16	-	5-w	$NOEC_y$	10$^{\omega}$ 63$^{\psi}$	**14**$^{\omega}$ 85$^{\psi}$
	$ZnSO_4.7H_2O$	sandy loam (H) [with P]	5.0	3	16	-	5-w	$NOEC_y$	50$^{\omega}$ 103$^{\psi}$	**68**$^{\omega}$ 140$^{\psi}$
	$ZnSO_4.7H_2O$	sandy loam (I) [2]	6.8	3	16	-	5-w	$NOEC_y$	≥ 250$^{\omega}$ ≥ 302$^{\psi}$	**340**$^{\omega}$ 410$^{\psi}$
	$ZnSO_4.7H_2O$	sandy loam (J) [2]	7.5	3	16	-	5-w	$NOEC_y$	≥ 250$^{\omega}$ ≥ 301$^{\psi}$	**340**$^{\omega}$ 409$^{\psi}$
									MacLean '74 [1]	
Avena sativa (Oat)	$Zn(Ac)_2$	loamy soil	5.6	2	12	-	5-m	$NOEC_y$	100$^{\omega}$ 147$^{\psi}$	**157**$^{\omega}$ 231$^{\psi}$
	$Zn(Ac)_2$	loamy soil	5.4	2	40	-	5-m	$NOEC_y$	200$^{\omega}$ 257$^{\psi}$	**162**$^{\omega}$ 208$^{\psi}$
	$Zn(Ac)_2$	loamy soil	5.2	3	58	-	5-m	$NOEC_y$	≥ 800$^{\omega}$ ≥ 936$^{\psi}$	**548**$^{\omega}$ 641$^{\psi}$
	$Zn(Ac)_2$	sandy loam	5.0	3	4	-	5-m	$NOEC_y$	200$^{\omega}$ 215$^{\psi}$	**421**$^{\omega}$ 453$^{\psi}$
	$Zn(Ac)_2$	sandy loam	5.4	7	5	-	5-m	$NOEC_y$	400$^{\omega}$ 428$^{\psi}$	**742**$^{\omega}$ 794$^{\psi}$
	$Zn(Ac)_2$	sandy loam	4.6	19	4	-	5-m	$NOEC_y$	≥ 800$^{\omega}$ ≥ 824$^{\psi}$	**1,237**$^{\omega}$ 1,275$^{\psi}$
									De Haan et al. '85 [3]	

Parameter: y = yield.

For footnotes see next page; for further information see the "list of abbreviations tables 2.1 to 2.3".

Footnotes table 2.3

[1] Statistics: $p \leq 0.01$). Test range 0-2-10-50-250 mg Zn/kg.
After zinc treatment of the soils, corn was grown during a 6-w period, followed by lettuce for 5 weeks and two successive crops of alfalfa in a 16-w period.
Soil types used:
(A): Grenville sandy loam, unmanured and unfertilized since 1921;
(B): "A" plus 2.2.% (w/w) dry alfalfa;
(C): "A" plus 2.2% (w/w) dry muck;
(D): "A" plus 2.2% (w/w) dry peat;
(E): "A" mixed with an equal quantity of a clay loam;
(F): "A" treated with a total amount of 257 metric tonnes of farmyard manure and chemical fertilizer containing a total of 584 kg N, 498 kg P, and 489 kg K/ha since 1909;
(G): Granby sandy loam unmanured and unfertilized since 1909;
(H): Bainsvile fine sandy loam;
(I): "H" plus 2,000 ppm $CaCO_3$;
(J): "H" plus 6,000 ppm $CaCO_3$.

[2] Test were conducted both with and without pretreatment of the soil with 500 ppm P (added as $Ca(H_2PO_4)_2.H_2O$; both conditions resulted in the same NOEC.

[3] Statistics: Student-Newman-Keuls multiple range test; "p" not reported.
pH = pH-KCl. Test range 0-50-100-200-400-800 mg Zn/kg dw.
Yield parameters: grain and straw dry weight. Yield depression at the highest test concentration was significantly correlated with soil CEC (r = 0.9).

List of abbreviations tables 2.1 to 2.3

$\geq$ Value indicated is highest concentration used in the test.

$\int$ Secundary literature source; primary source not available.

Exposure time: day(s); hr: hour(s); w: week(s); m: month(s); yr: year(s).

Criterion

LC50: Median lethal concentration, i.e. that concentration which is calculated (from a series of test concentrations) to cause mortality of 50% of the number of organisms exposed to that concentration.

EC50: Median effect concentration, i.e. that concentration which is calculated (from a series of test concentrations) to cause a particular response in 50% of the organisms exposed to that concentration.

NOEC: No observed effect concentration, i.e. the highest concentration (in a series of test concentrations) without effect. For general information on deriving NOEC values the reader is referred to the text (section 2.2, introduction).

EC(..%): At the concentration indicated (usually the only concentration tested), the toxicological parameter was inhibited by ..%. Example: EC (21%).

So, LC50 and EC50 values are theoretical concentrations which have been calculated on the basis of a concentration-response relationship, while NOEC- and EC(..%)-values are concentrations which were actually included in the test series.

Result:

ω: added (nominal) concentration;

ψ: total concentration (background plus added)

φ: "unknown" (value from review)

Abbreviations:

OM: organic matter

dw: dry weight

ww: wet weight

* Calculated value in "standard soil" containing 25% clay (particles <2 μm) and 10% organic matter (OM):

$$\mathbf{Value}_{\mathbf{st}} = \text{Value}_{\text{exp}} \times \frac{140}{50 + 1.5\ (2 \times \%\text{clay} + \%\text{OM})}$$

The calculated values which have been printed **bold** have been used in the ecotoxicological effect assessment.

Upper and lower limits for OM and clay levels used in the calculations:

OM: 2-30%

clay: 5-50%

≈ Actual value not reported, but calculated or estimated from the data reported, using the following equations (unless stated otherwise):

% Organic carbon x 1.7 = %OM (Denneman and Van Gestel, 1990)

CEC (meq/100 g) = (2.5 x %OM) + (0.5 x %clay) (Doelman and Haanstra, 1983)

OECD artificial soil:

10% sphagnum peat, 20% kaolin clay, 69% fine sand, 1% calcium carbonate to adjust pH (dry weight basis).

The soil characteristics indicated in the tables are based on measurements conducted at the RIVM.

Unless stated otherwise, the pH indicated in the tables is the initial value measured before treatment of the soil.

3 ECOTOXICOLOGICAL EFFECT ASSSESSMENT

Introduction

In recent years there has been a rapid development of extrapolation procedures that are aiming to derive acceptable concentrations in environmental compartments (specifically surface water and soil) from "single-species" toxicity data such as LC50, EC50 and NOEC values. The discussion on these extrapolation procedures and modifications thereof, both in national and international expert groups (for example in the Dutch Health Council and in OECD workshops), has led to several adaptations of the effect assessment procedure used in advisory reports of the National Institute of Public Health and Environmental Protection (RIVM). For an overview of the existing extrapolation procedures the reader is referred to the "RIVM Guidance Document" (Slooff, 1992). This document also describes the effect assessment procedure which is used by RIVM at present. The effect assessment procedure describes the extrapolation methods that are used to derive "Maximum Tolerable Concentrations" (MTCs), in dependence of the available data.

With respect to zinc, the "refined effect assessment procedure" has been used below, both for surface water and soil. The refined effect assessment procedure is used if the data set for the compartment in question comprises chronic NOEC values for at least four different species. The species must be different in anatomical design and ecological function, in order to meet the species diversity in ecosystems to some extend. Within this effect assessment procedure, a "95%-protection level" (also called HC_5, the Hazardous Concentration for 5% of the species) is derived on the basis of the distribution of the experimentally derived NOEC values, using the extrapolation procedure by Aldenberg and Slob (1991). This method assumes a log-logistic distribution of species susceptabilities. The 95%-protection level is defined as the concentration at which the NOEC of 95% of the species within an ecosystem is not exceeded. This level is chosen as the median estimate (50% confidence limit value). For more details on this and other extrapolation procedures the reader is referred to Slooff (1992) and to the primary publications on the procedures (for references, see Slooff, 1992).

The text below comprises a summary of the ecotoxicological effect assessment procedure for zinc. For more data on this effect assessment procedure and the results thereof the reader is referred to section 5.2.2 in the "Integrated Criteria Document Zinc" (Cleven et al., 1992). That section also contains an extensive discussion with respect to this effect assessment.

3.1 SURFACE WATER

3.1.1 Fresh water

Based on the NOEC values for freshwater organisms (table 1.1), a 95%-protection level of 4.9 $\mu g.l^{-1}$ has been calculated. Based on the conditions used in the tests with freshwater organisms (amongste other things, the characteristics of the test waters), this concentration is considered to be "dissolved" zinc (<0.45 μm fraction).

3.1.2 Sea water

Based on the NOEC values for saltwater organisms (table 1.3), a 95%-protection level of 7.0 $\mu g.l^{-1}$ has been calculated. Analogous to section 3.1.1, this concentration is considered to be dissolved zinc.

3.1.3 Fresh water and sea water (combined)

There appears to be no significant difference in sensitivity to zinc between freshwater and saltwater organisms. In other words, there appears to be no significant difference in zinc toxicity in fresh water and sea water. Therefore, in accordance with Slooff (1992), NOEC values for freshwater and saltwater organisms have been combined to one data set, resulting in a 95%-protection level of 6.3 $\mu g.l^{-1}$ (dissolved zinc). This concentration, rounded to 6 $\mu g.l^{-1}$ is recommended as maximum tolerable concentration (MTC) for dissolved zinc in surface water.
Based on data on the concentrations of dissolved zinc *versus* particulate zinc in the major Dutch surface waters (Cleven et al., 1992), a concentration of 6 $\mu g.l^{-1}$ dissolved zinc corresponds with approximately 25 $\mu g.l^{-1}$ total zinc (dissolved plus particulate) in these waters. It is noted that Dutch surface waters are characterized by, amongst other things, high values for hardness (200 $mg.l^{-1}$, as $CaCO_3$) and pH (8). In soft and acid surface waters the fraction of dissolved zinc is much higher, and, therefore, the total zinc concentration is similar to the dissolved

concentration. So, in soft and acid waters the MTR for total zinc will be approximated by the MTR for dissolved zinc (6 $\mu g.l^{-1}$).

3.2 SOIL

For soil a distinction has been made between data on micro-mediated processes on the one hand, and data on invertebrates and plants (combined) on the other, because of possible differences in sensitivity between functional parameters (such as C-mineralization which involve microbial populations consisting of different species) and species-dependent parameters (such as growth and reproduction capacity of single species). Based on the NOEC values for microbe-mediated processes, table 2.1), 95%-protection levels of 29 and 70 $mg.kg^{-1}$ dw have been calculated for added zinc (ω) and total zinc (ψ), respectively. Although the latter value is based on total zinc concentrations used in the tests, this concentration is considered to be an approximation of the added zinc concentration, because the added concentrations usually were much higher than the background zinc concentrations present in the test soils. Based on the combined data set of NOEC values for invertebrates (table 2.2) and plants (table 2.3), a 95%-protection level of 128 $mg.kg^{-1}$ dw has been caluculated for added zinc (ω). A 95%-protection level for total zinc could not be calculated because of the lack of data on background zinc levels in the tests with invertebrates and plants. It is noted that only standardized NOEC values were used in the calculations (see section 2.2, introduction). The above-mentioned results indicate that additions of relatively small amounts of zinc, in the order of magnitude of 30 to 70 $mg.kg^{-1}$ dw, to a "standard soil" (10% organic matter; 25% clay) may result in effects on microbial populations. Invertebrates and plants appear to be less sensitive than microbial populations. Based on the empirical relationship between the zinc concentrations in relatively unpolluted Dutch soils (natural reserves) and the clay and organic matter content in the corresponding soils, the reference value for zinc in the standard soil is 140 $mg.kg^{-1}$ dw ({50 + 1.5 (2 x %clay + %OM} $mg.kg^{-1}$ dw). Therefore, the calculated 95%-protection level for the most sensitive "group" (microorganisms, 30-70 $mg.kg^{-1}$) cannot be recommended as maximum tolerable concentration for zinc in the standard soil.

Based on all available data it is concluded that the soil-dependent reference value (which increases with increasing clay and organic matter content) should be used as a starting-point for the risk assessment of zinc concentrations in soil. Increases in zinc content above the reference value should be limited (up to about 30 $mg.kg^{-1}$ dw), to prevent effects on microbial populations. Based on the limited number of soil-related factors reported in most studies (pH, %OM, %clay) and the variable responses with respect to effects on microbe-mediated processes, it is not possible to predict the sensitivity of soils on the basis of these factors.

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