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A Further Look at Zinc
A response to the Industry addendum
to the Integrated Criteria Document Zinc

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SUMMARY

This report comprises a response to the 'Industry addendum' (IA), published in 1995, in which comments are given on the 'Integrated Criteria Document Zinc' (ICDZ) published in 1992 by RIVM. The present report is focused on the main points of criticism: (i) the ecotoxicological data (NOEC values) used in deriving maximum tolerable concentrations (MTC values) in surface water and soil, (ii) the value of the MTC in surface water and soil, in relation to the background concentration in these compartments, and (iii) the estimate of the emission due to atmospheric corrosion of zinc and galvanized steel.

With respect to the ecotoxicological data (NOEC values, ecotoxicological extrapolation method, MTC values) the comments in the IA are largely rejected. Hence, the current MTC values for zinc in surface water and soil, derived in the ICDZ, are still considered to be valid. Therefore and because of the fact that the MTC values for metals, zinc included, are currently being re-evaluated in the framework of RIVM-project 'Setting Integrated Environmental Quality Objectives', this report gives no specific proposal for a revision of the current MTC values.

In the ICDZ the corrosion-related zinc emission from inland sources, 4,125 tonnes/year, was overestimated indeed. In more recent RIZA/RIVM publications the corrosion load has already been corrected downwards to approximately 1,600-1,700 tonnes/year. The current RIZA/RIVM estimates are in agreement with a recent estimate of the Dutch Central Bureau of Statistics (1,340 tonnes/year), but are still considerably higher than the industry estimates (IA: 490 tonnes/year, recently revised to 560 tonnes/year). The current RIZA/RIVM estimates are also in agreement with data on corrosion-related sewage sludge pollution with zinc, whereas the most recent industry estimate is on the low side, although near the range of estimated accuracy. In all estimation procedures a number of applications of zinc or galvanized steel is distinguished, which all add up to the total corrosion load of zinc. For each application the corrosion load is based on a combination of the corrosion rate and the exposed area; a number of the values used for these two factors greatly differ between the estimation procedures and many assumptions are underlying these values. Improving the quality of the present estimates, if needed, would require the availability of representative *in situ* corrosion measurements and reliable data on exposed areas of the different applications.

In The Netherlands only a limited number of corrosion measurements have been conducted. Comparing the data for the period '77-'81 and '87-'93, a decrease in corrosion rate over the period '80-'90 can be inferred. A decrease can indeed be expected because of the decreasing atmospheric SO_2 concentration. The data are too limited, however, to give a quantitative assessment of the decreasing trend in corrosion rate in the above period. Recent data indicate a current corrosion rate of about 10 $g/m^2/year$, on average, but this value can not straightforwardly be interpreted as representative for actual corrosion rates in practice, in contrast to the industry opinion.

SAMENVATTING

In dit rapport wordt een reactie gegeven op het in 1995 uitgebrachte 'Industrie addendum' (IA), waarin commentaar wordt geleverd op het in 1992 door het RIVM uitgebrachte 'Basisdocument Zink'. Het voorliggende rapport gaat in op de belangrijkste kritiekpunten: i) de ecotoxicologische gegevens (NOEC-waarden) die zijn gebruikt bij de afleiding van maximaal toelaatbare risiconiveaus (MTR-waarden) in oppervlaktewater en bodem, ii) de hoogte van het MTR in oppervlaktewater en bodem, in relatie tot de achtergrondconcentraties in deze compartimenten, en iii) de schatting van de emissie door atmosferische corrosie van zink en verzinkt staal.

Met betrekking tot de ecotoxicologische gegevens (NOEC-waarden, ecotoxicologische extrapolatiemethode, MTR-waarden) wordt de in het IA vermelde kritiek grotendeels verworpen. De huidige MTR-waarden, afgeleid van het basisdocument, worden daarom nog steeds geldig geacht. Om deze reden en vanwege het feit dat er momenteel in het kader van het project 'Integrale Normstelling Stoffen' een herevaluatie plaatsvindt van MTR-waarden voor metalen, waaronder zink, wordt in dit rapport geen concreet voorstel gedaan voor een herziening van de huidige MTR-waarden.

Met betrekking tot de emissies door corrosie is in het basisdocument een totale corrosievracht vanuit binnenlandse bronnen geschat van 4125 ton/jaar, hetgeen volgens de huidige inzichten inderdaad een overschatting is. In recentere RIZA/RIVM-publicaties is de corrosievracht reeds naar beneden bijgesteld, naar ca. 1600-1700 ton/jaar. De huidige RIZA/RIVM-schattingen zijn in overeenstemming met een recente schatting van het Centraal Bureau voor de Statistiek (1340 ton/jaar), maar zijn nog steeds aanzienlijk hoger dan de schattingen van de industrie (IA; 490 ton/jaar; recentelijk bijgesteld naar 560 ton/jaar). De huidige RIZA/RIVM-schattingen zijn ook in overeenstemming met de gegevens over de belasting van zuiveringsslib met zink door corrosie, terwijl de meest recente industrie-schatting aan de lage kant is, hoewel dicht bij de geschatte ondergrens. In alle schattingsprocedures wordt een aantal toepassingen van zink of verzinkt staal onderscheiden, die alle een bijdrage leveren aan de totale corrosievracht van zink. Voor elke toepassing wordt de corrosievracht bepaald door de combinatie van corrosiesnelheid en het blootgestelde oppervlak. Een aantal van de waarden die worden gebruikt voor deze twee factoren verschillen aanzienlijk in de diverse schattingsprocedures; er liggen vele aannames aan deze waarden ten grondslag. Het vergroten van de betrouwbaarheid van de huidige schattingen, indien gewenst, zou de beschikbaarheid van representatieve *in situ* corrosiemetingen en betrouwbare gegevens over blootgestelde oppervlakken van de verschillende toepassingen vereisen.

Het aantal in Nederland uitgevoerde corrosiemetingen is beperkt. Op grond van een vergelijking van gegevens over de periode '77-'81 en '87-'93 kan een afname van de corrosiesnelheid worden afgeleid voor de periode '80-'90, hetgeen in overeenstemming is met de afnemende atmosferische SO_2-concentraties. De gegevens zijn echter te beperkt voor een

kwantitatieve vaststelling van de afnemende trend in corrosiesnelheid in bovengenoemde periode. Recente corrosiemetingen wijzen op een huidige corrosiesnelheid van gemiddeld rond de 10 $g/m^2/jaar$, maar deze waarde kan niet zonder meer worden beschouwd als representatief voor de huidige corrosiesnelheid onder praktijkomstandigheden, dit in tegenstelling tot de mening van de industrie.

INTRODUCTION

At the end of 1992 RIVM published the 'Integrated Criteria Document Zinc' (Cleven et al., 1992: 'Basisdocument Zink', *in Dutch*[1]) together with the appendix 'Ecotoxicity' (Janus, 1992; *in English*). As part of the preparation of such Integrated Criteria Documents the industry is given an opportunity to comment on the draft document, via 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/NCW. This procedure was also followed in the case of the Integrated Criteria Document Zinc, subsequently referred to as the 'ICDZ'. In addition, following publication of each RIVM Integrated Criteria Document the industry has the opportunity of preparing an addendum. This procedure yielded the 'Integrated Criteria Document Zinc - Industry Addendum' (Van Tilborg & Van Assche, 1995a *(in Dutch)*, 1995b *(in English)*). The Industry addendum is subsequently referred to as the 'IA'. The criticism expressed in the IA is mainly concerned with the data on the environmental compartment water, in particular with derivation of the maximum tolerable concentration (MTC) of zinc in surface water[2] and with the estimated share of atmospheric corrosion in the zinc concentration in surface water.

In April 1995 RIVM was requested by DGM/SVS to draw up a response to the IA, in collaboration with the Institute for Inland Water Management and Waste Water Treatment (RIZA). The response had to focus on the following main points of criticism: (i) the ecotoxicological data (NOEC values) used in deriving MTC values in surface water and soil, (ii) the value of the MTC in surface water and soil, in relation to the background concentration in these compartments, and (iii) the estimate of the emission due to atmospheric corrosion of zinc and galvanized steel (DGM, 1995).

Chapter 1 (ecotoxicity) and Chapter 2 (atmospheric corrosion of zinc and galvanized steel) constitute a response to the main points of criticism raised in the IA. As far as possible, this response is limited to broad lines of argumentation, with additional, specific details being provided in Appendix 1 (ecotoxicity studies) and Appendix 2 (atmospheric corrosion). In the present report regular reference is made to the IA instead of reiterating all the comments in detail, in view of the length of the IA, its detailed comments and its wide distribution given by the zinc industry.

Chapter 3 of this report summarizes the RIVM/RIZA conclusions with respect to the main points of criticism raised in the IA.

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[1] The English-language translation of this report was published in 1993 (Cleven et al., 1993).

[2] Unless otherwise specified, the term 'surface water' refers to fresh surface water.

With respect to the assignments of tasks between RIVM and RIZA, the RIVM authors mainly prepared the sections on ecotoxicity and the RIZA authors mainly that on atmospheric corrosion of zinc and galvanized steel. On the initiative of DGM/SVS, a draft version of Chapter 2 and Appendix 2 has been discussed at a hearing on zinc corrosion (Bilthoven, 15 January 1996). Among the participants of this meeting were the authors of the IA (on behalf of the 'project group zinc' of the Dutch zinc industry), other representatives of the Dutch zinc industry, an independent TNO expert in corrosion, and representatives of DGM, RIVM and RIZA (see aforementioned list of participants). As a result of the meeting, the zinc industry was given the opportunity to provide additional data on corrosion-related emissions.

1 ECOTOXICITY

1.1 AQUATIC TOXICITY STUDIES

1.1.1 General

In the Industry addendum (IA), NOEC values[3] below 30 μg/l are considered to be outliers and the aquatic studies (used in the Integrated Criteria Document Zinc (ICDZ) for deriving the MTC for surface water) with a NOEC below 30 μg/l have been evaluated on the basis of criteria relating to the quality of the studies and the relevance of the studies. The quality criteria regard the scientific quality such as dose/response-relationships and the relevance criteria regard whether or not the test organisms and test conditions are considered relevant for the situation in the Dutch environment. Below there follows a general critique of the quality and relevance criteria employed in the IA. Part of the following statements, for example the section on quality criteria, is obviously also valid for the terrestrial toxicity studies.

The quality of the studies

It goes without saying that the studies should satisfy certain minimum standards of quality, with respect to a concentration-effect relationship, for example[4]. In this context RIVM bases itself primarily on the internationally accepted guidelines of the Organisation of Economic Cooperation and Development (OECD). In addition, use is made of internal guidelines drawn up on the basis of the expertise available at RIVM. Using these two types of guidelines, it is possible to evaluate studies with organisms for which no specific test protocols are available, or studies which have not been performed according to a standard test protocol. Moreover, the evaluation of zinc was undertaken outside a legislative framework with no requirements being set on specific test protocols and there are only test protocols available for a very limited number of aquatic organisms. There are therefore no grounds for leaving out of consideration those studies not carried out according to standard protocols.

The abovementioned quality control also holds for the derivation of NOEC values. The 'RIVM procedure' contains rules that permit a NOEC to be derived even in the absence

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[3] NOEC: 'No Observed Effect Concentration'

[4] Since a maximum of 3 concentrations were tested in many microbial soil studies, with the successive concentrations differing by a factor 10, it was not possible to establish the concentration-effect relationship or the NOEC with great accuracy. Nonetheless, the NOEC values from these qualitatively 'inferior' studies were still used in the ICDZ for deriving the MTC for soil, because otherwise scarcely any data would have remained for microbial parameters.

of statistical data or enable a NOEC to be derived from one or more effect concentrations.

The RIVM guidelines have recently been laid down in a quality system. The procedure followed in the ICDZ for deriving ecotoxicological NOEC values is described in one of the quality system manuals (Kalf & Polder, 1995).

The use of non-endemic test organisms and test conditions

In the IA it is posited, on the basis of the relevance criteria mentioned therein, that MTC values employed in Dutch environmental policy should be derived from toxicity data that reflect the Dutch situation, with regard to both the test organisms and the test conditions (abiotic characteristics of the test medium, such as pH and hardness). This is not a position that is subscribed to nationally or internationally, however. The use of standard artificial test media is worldwide accepted in aquatic toxicity testing (e.g. in OECD guidelines), despite the wide variation in abiotic characteristics in different water types, to allow a 'generic' assessment of toxicity which is independent of the test laboratory. In the RIVM practice, tests are selected on the basis of water characteristics, especially pH and temperature, at which outliers are excluded. However, at present there are no strict guidelines available that prescribe the acceptable ranges for the relevant water characteristics. Furthermore, data on the characteristics of the (artificial) test medium used are not always reported in the published data. In the case of the aquatic toxicity studies evaluated in the ICDZ, data on test water characteristics were lacking especially in the publications on the algae toxicity tests. In the recent OECD Workshop on Aquatic Toxicity Testing of Sparingly Soluble Metals, Inorganic Metal Compounds and Minerals, it was recommended to test metals and metal compounds in natural waters or in artificial test waters with characteristics (i.e. pH, hardness, particulate matter content, etc.) that are within the ranges that are encountered in natural waters. This recommendation has to be worked out by expert groups to establish the acceptable range for the most relevant characteristics and has to be implemented in the existing guidelines (CANMET, 1995). Until that has happened, the selection of tests on the basis of test water characteristics will be arbitrary.

From a pragmatic angle, the data selection as proposed in the IA is unfeasible, because of a lack of toxicity data on endemic species. Moreover, the use of toxicity data for a variety of species, from different taxa, is considered to be of more importance in generic risk assessment for substances than the use of endemic species per se, because of the variation in sensitivity among species and especially among species of different taxa. In the ecotoxicological extrapolation method according to Aldenberg & Slob (1991)[5] employed in the ICDZ, a single, 'generic' MTC (95% protection level for ecosystems) is derived for each environmental compartment (see further 1.3). In doing so, use is made of NOEC values for as many animal and plant species (occurring in the compartment in question) as possible, so that the (wide) range in sensitivity can be used to derive a MTC having maximum reliability for a variety of ecosystems. In other words, greater importance is attached to data that are representative of species that vary widely in terms of biological structure and function than to the use of endemic test organisms and corresponding test conditions. For this reason, the Aldenberg-Slob method is only used by RIVM to derive a MTC for a substance in surface water in case there is a minimum data set of four chronic NOEC values which have to be from different taxonomic groups, including algae, crustaceans and fish (Kalf & Polder, 1995).

This said, though, in interpreting the 'generic' MTC for a substance in surface water thus derived, due allowance must be made for the differences in water characteristics of the test waters used and that of the major Dutch surface waters that are characterized by a relatively high pH (around 8) and hardness (around 200 mg/l, as $CaCO_3$). In the case of zinc this has been achieved in the ICDZ by considering the result of the extrapolation method as the MTC for dissolved zinc (although the NOEC values underlying the MTC were usually expressed as the total-zinc concentration, either nominal or analyzed) and converting this MTC for dissolved zinc to a MTC for total zinc, based on the ratio between dissolved zinc and total zinc in the main Dutch surface waters. This consideration is based on the assumption that by far the greater part of zinc present in the test waters was in the dissolved form under the conditions used in the laboratory tests, because of test conditions and/or water characteristics that favour the solubility of zinc, for example, relatively low pH and hardness in a number of test waters and the absence of particulate matter. In this way the possible overestimation of toxicity based on the results of laboratory tests was abolished. This approach is in accordance with that of the aforementioned OECD workshop on aquatic toxicity testing of metals, at which it was agreed that, for generic risk assessment, data derived from tests in standard media may be used to conduct an extrapolation to other environmental conditions, providing sufficient information is available to conduct such extrapolation (CANMET, 1995).

If the selection of data as described in the IA were indeed to be made, a large number of the available data would be rejected, including many of the data on algae and Daphnia species (which are ecologically important species) since the tests prescribed for these species in existing protocols are often conducted in artificial media differing in composition from most bodies of surface water in The Netherlands. Moreover, on this

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[5] Journal publication: Aldenberg & Slob (1993).

point the IA is self-contradictory. On the one hand the use of data from standard tests is advocated because of the quality criteria, while on the other hand many data from tests in artificial media that are in accordance with the media that are recommended in the existing test protocols are excluded on the basis of the relevance criteria, for example the results of tests conducted in soft waters.

The testing of organisms outside their 'OCEE' range

The IA describes a 'Deficiency Toxicity' (DT) model for essential elements, which, for zinc in the aquatic environment, is quantitatively elaborated in the form of a deficiency curve, a toxicity curve and 'OCEE' curves (OCEE: 'Optimal Concentration band for Essential Elements') for the water types 'ocean', 'North Sea' and 'surface water'. In this context it is posited in the IA that organisms cultured in conditions of lower zinc concentrations than those in which they occur naturally are more sensitive in the experimental situation. According to this line of reasoning the IA states that a 'jump in the effects' is observed. On this point, several remarks are pertinent. There is a paucity of data on deficiency levels of zinc (and other metals). The low to very low zinc concentrations in the culture and test media of several studies do not appear to have influenced the performance (survival, growth, reproduction) of the organisms. If the zinc concentrations in these low zinc media were truly deficient, then it would have been impossible to culture the organisms. Also given the toxicological, sub-lethal end-points focused on in most chronic studies (growth and/or reproduction), it is unlikely that the media were zinc deficient, although limiting conditions may have been present in some tests, (e.g. growth limiting amounts of bacteria as a nutritional source in the test with *Ephydatia fluviatilis*, see Appendix 1.1). However, valid ecotoxicological studies do not necessarily require optimal conditions for the (control) organisms, although the conditions must sustain the survival, development and reproduction of the organism. Any difference in sensitivity of test organisms cultured under sub-optimal conditions relative to test organisms cultured under optimal conditions might be reflected in the effects observed in the short term or at low test concentrations, for improved performance relative to the control group is then to be expected. After a sufficiently long exposure period and at higher test concentrations performance will deteriorate, because of the toxic effect of the substance. The NOEC should be derived after a sufficiently long exposure period and in the toxic concentration band. In none of the studies discussed in the IA there was a significant improvement in performance in the (low) exposure groups relative to the control group. The reason for this may lie in the sometimes small number of test concentrations and/or the magnitude of the successive concentration increments, which preclude observation of any enhancement of performance. Nevertheless, in all cases the NOEC values were determined in the toxic concentration band. The exposure periods were sufficiently long for toxic effects to be measured. If an experiment meets these criteria, there is no reason for assuming that the NOEC for test organisms kept under sub-optimal zinc concentrations should be lower than that for test organisms kept under optimal conditions.

In 1.3.1 the aforementioned DT model and its numerical elaboration for zinc, as presented in the IA, are discussed in greater detail.

1.1.2 Specific

A detailed rejoinder on each of the individual aquatic toxicity studies selected in the IA (all studies with a NOEC below 30 μg/l) is given in Appendix 1.1. In two of the nine cases this reassessment has resulted in a modification of the NOEC derived in the ICDZ. These two modifications of the NOEC (studies 3 and 5 in Appendix 1.1) were not due to the NOEC in question being 'incorrectly' derived, but to the addition of the background concentration of zinc in the test medium. In study 3 (*Ephydatia fluviatilis*) addition of the background concentration leads to only a small increase of the NOEC (from 3.2 to 3.9 μg/l), while in study 5 (*Epeorus latifolium*) the NOEC does increase substantially (from 3 to 12 μg/l) because the nominal NOEC is substantially lower than the background concentration of zinc in the medium. In general it is noted that the higher the nominal NOEC, the less effect the addition of the background concentration will have on the ultimate NOEC. Because the studies which have not been re-evaluated in this report have nominal NOEC values that are usually substantially higher than the reported or expected background concentrations, it is assumed that addition of the background concentration (when feasible on the basis of the data reported) will have little effect on the ultimate NOEC.

For the alga *Selenastrum capricornutum* an additional NOEC of 50 μg/l has become available from the IA, in addition to the two NOEC values of 15 μg/l and 5 μg/l already included in the ICDZ for this species. This leads to a revised geometric mean NOEC of 15 μg/l (the geometric mean NOEC for this species was 9 μg/l, see Appendix 1.1, studies 1 and 2).

In conclusion, it can be said that the re-evaluation of the studies that were selected in the IA does not give any cause for reassessing the remaining studies. In deriving the MTC for zinc in surface water, then, there is no reason to deviate from the NOEC values used in the ICDZ, provided the abovementioned revisions are incorporated in the set of NOEC values.

1.2 TERRESTRIAL TOXICITY STUDIES

1.2.1 General

The IA focuses mainly on the microbial soil studies, because the data in the ICDZ indicate that micro-organisms appear to be generally more sensitive to zinc than soil invertebrates and plants. The addendum comments specifically on several microbial soil studies yielding NOEC values below 200 mg/kg (see Appendix 2.1); such relatively low NOEC values for microbial processes are considered in the IA to be exceptionally low values, partly in view of the low background concentration of zinc in the soil types used in the underlying tests. This is not a correct interpretation, because these soil types may harbour zinc-sensitive micro-organisms, so that microbial processes may be affected even when the soil is supplemented with relatively small amounts of zinc. Dutch environmental policy is also obviously concerned with these (sensitive) types of soil. In Dutch soils, too, microbial populations are encountered with a relatively high sensitivity to zinc (Haanstra & Doelman, 1983; Doelman & Haanstra, 1989; Haanstra & Doelman, 1991; Van Beelen et al., 1994). In addition, many foreign studies report toxic effects of zinc at concentrations below 200 mg Zn/kg soil (Welp & Brummer, 1985; Stadelmann & Santschi-Fuhrimann, 1987; McGrath et al., 1988; Arshad & Frankenberger, 1991). In this context it should be noted that zinc-sensitive microbial populations can occur not only in soils with a low total-zinc level, but also in soils and sediments where the availability of zinc is limited by a high pH or the formation of zinc sulphide (Van Beelen et al., 1994; Van Beelen & Van Vlaardingen, 1994). When the availability of zinc increases, through acidification of the soil (because of acid deposition or the discontinuation of liming in the case of agricultural land being converted to nature reserve, for example) or a lake or river bed drying out, toxic effects are to be anticipated ('chemical time-bomb'). A reduction of the organic matter content of soils can also lead to an increase in zinc availability (see also below).

With respect to the relevance of laboratory tests with micro-organisms to predict effects in soil at the current (low) accumulation rate of zinc in soil it is stated in the IA that the tests, also those by Doelman & Haanstra (1983) that took 1.5 years, are too short for genetic adaptation of the soil (micro-)organisms. According to the addendum, genetic adaption will preclude effects at the current accumulation rate of zinc. It is noted, however, that genetic adaptation can have adverse effects on ecosystems (Bååth, 1992; Chaudri et al., 1992; Reber, 1992; Diaz-Ravin et al., 1994; Doelman et al., 1994). In general, genetic adaptation due to environmental pollution should be viewed as a trend to be prevented. In the IA it is also stated that the speciation of the soluble zinc added in the tests strongly differs from that of zinc which, in the real world, is gradually added by deposition, manure, fertilizers and other emission sources. According to the addendum the major part of emitted zinc is and stays unavailable to soil (micro-)organisms. Although the bioavailability of emitted zinc (for example zinc in manure with a high organic matter content) can be considerably lower than that of soluble zinc, it is noted that in the longer term (over several decades, for example) a gradual accumulation of zinc combined with a decrease in organic matter content can lead to serious adverse effects on soil (micro-)organisms (McGrath et al., 1988; Witter et al., 1994).

1.2.2 Specific

A detailed rejoinder on each of the individual terrestrial toxicity studies selected in the IA (some microbial soil studies with a NOEC below 200 μg/l) is given in Appendix 1.2. This re-evaluation has not resulted in any modifications of the NOEC values derived in the ICDZ. Although the number of re-evaluated studies is limited compared with the total number of microbial soil studies mentioned in the ICDZ, it is concluded that the re-evaluation of these studies does not give any cause for reassessing the remaining studies. In deriving the MTC for zinc in soil there are consequently no grounds for deviating from the NOEC values used in the ICDZ.

1.3 ECOTOXICOLOGICAL EXTRAPOLATION METHOD AND MTC VALUES

1.3.1 Ecotoxicological extrapolation method

In the ICDZ the ecotoxicological extrapolation method of Aldenberg & Slob (1991) has been used to derive MTC values. On the basis of the distribution of NOEC values, this method calculates the 'HC5', being the '95% protection level', which in principle is considered to be the MTC[6]. At the time when the ICDZ was written, RIVM considered this method to be the best ecotoxicological extrapolation method available. In the time, a

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[6] The Aldenberg-Slob method is a statistical modification of the Van Straalen method (Van Straalen, 1987; journal publication: Van Straalen & Denneman, 1989). Both methods are used to calculate the '95% protection level' (the concentration that protects 95% of the species in the ecosysteem), on the basis of the distribution of chronic NOEC values. The 95% protection level is indicated as HC5, the Hazardous Concentration for 5% of the species. The Aldenberg-Slob method can calculate both the one-sided 95% left confidence limit of the HC5 (which is lower than the 'Van Straalen'-HC5) and the one-sided 50% confidence value of the HC5 (which is higher than the 'Van Straalen'-HC5). In the ICDZ, the 50% confidence value of the HC5 (which is considered as the 'best guess' HC5), has been chosen and indicated as MTC: Maximum Tolerable Concentration. At present the MTC is usually indicated as MPC: Maximum Permissible Concentration.

group of ecotoxicological experts of the Dutch Health Council reported positively on the Aldenberg-Slob method and the underlying methodology (Gezondheidsraad 1988, 1991) and from that time the method has been used up to now by RIVM, for example in recent Criteria Documents and in the framework of the project 'Setting Integrated Environmental Quality Objectives' (the so-called 'INS'-project) and by other institutes including RIZA. With respect to the usefulness of the Aldenberg-Slob method to derive MTC values for essential and other naturally occurring substances the following remarks are made[7]:

1. The Aldenberg-Slob method assumes a logistic distribution of NOEC values for different species. In the case of essential substances there is no such distribution in the very low (essential) concentration range (Van Straalen & Verkleij, 1991). In the zinc toxicity studies, however, there are no indications of there being any deficiency involved (see also 1.1.1). Moreover, in comparisons of the Aldenberg-Slob method and the ecotoxicological extrapolation method of Wagner & Løkke (1991), the latter assuming a normal distribution of NOEC values, it was concluded that the methods result in similar extrapolation constants (Aldenberg & Slob, 1991) and similar HC5 values (Emans et al., 1992; Okkerman et al., 1993). There is therefore no reason not to apply the Aldenberg-Slob method to the available NOEC values for zinc or other essential substances.

2. In the case of naturally occurring substances such as metals, whether essential or not, the background concentration of the substances must be taken in consideration when establishing MTC values, because a MTC below the background concentration is of no practical significance. For that purpose, RIVM recently developed an 'added risk' approach, consisting of two new (linked) ecotoxicological extrapolation methods for deriving MTC values for metals, incorporating background concentrations and bioavailability (Peijnenburg et al., 1996). Both methods, the so-called 'effect-limitation' (or 'effect-addition') method and the 'concentration-limitation' (or 'concentration-addition') method, make use of the Aldenberg-Slob method. The method of effect-limitation is preferred by Peijnenburg et al. (1996) and by the advisory board of the aforementioned INS-project and applied in the draft INS-report (Crommentuijn et al., 1996) to derive new MTC values and NC values (Negligible Concentrations) for metals in surface water, ground water, sediment and soil. A short outline of the methods is given below. For additional data the reader is referred to Peijnenburg et al. (1996) which includes the English-language scientific publication on the methodology.

Effect-limitation method

In the effect-limitation method, it is assumed that at least a part of the natural background concentration is bioavailable and, hence, adds to the (adverse) effect of the total

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[7] These remarks of course also hold for the Van Straalen method.

concentration (background plus additional concentration due to anthropogenic activities, the latter assumed to be completely bioavailable). The method allowes a specified addition of effect to the natural background effect, according to the equation $\{Fu_{max} = Fu_b + (1 - Fu_b). 0.05\}$, in which Fu_{max} is the maximum permissible effect and Fu_b is the fraction of the species that is unprotected at the background concentration. Both Fu_b and the MTC, the concentration that results in Fu_{max}, are derived from the distribution of NOEC values as calculated by the Aldenberg-Slob method. The effect-limitation method needs a (default) value for the bioavailable fraction of the background concentration. For the water compartment it is usually assumed that the metals in the dissolved phase are bioavailable. Since water quality objectives are set for the dissolved phase, it is considered adequate to assume a bioavailability of 100% for the dissolved background concentration in water. For soil it is often reported that the availability of the background metal concentration is low compared to the additional (antropogenic) concentration. Therefore, it is considered adequate to assume a bioavailability of 0% for the background concentration in soil. For metals in soil (and in other cases in which there is a background concentration, but it is completely unavailable) the effect-limitation method reduces to the concentration-limitation method, see below.

Concentration-limitation method

In the concentration-limitation method, the maximum addition to the background concentration equals the HC5 and the MTC is simply derived from the equation $\{MTC = Cb + HC5\}$, in which Cb is the (unavailable) background concentration and the HC5 is the 95% protection level (at which $Fu_{max} = 0.05$) as calculated by the Aldenberg-Slob method.

It is noted that, practically, the two abovementioned new methods make up one *general* ecotoxicological extrapolation procedure that is valid for all substances, naturally occurring or not, although the procedure was originally developed for metals. For xenobiotics, that lack a background concentration, the MTC equals the HC5, as can be easily seen from the abovementioned equation, in which Cb = 0.

Although in the ICDZ the original Aldenberg-Slob method (which does not incorporates background concentrations) was used, this does not mean that the MTC values derived therein for surface water and soil are not valid (see 1.3.2 and 1.3.3. for arguments underlying this statement).

In the IA it is stated that the Aldenberg-Slob method should not be used for naturally occurring substances and certainly not for essential substances. As an alternative a 'Deficiency Toxicity' (DT) model is described for essential elements, which, for zinc in the aquatic environment, is quantitatively elaborated in the form of a deficiency curve, a toxicity curve and 'OCEE' curves (OCEE: 'Optimal Concentration band for Essential

Elements') for the water types 'ocean', 'North Sea' and 'surface water'. The basic point of departure of the DT model is accepted: namely that, in the case of essential elements such as zinc, adverse effects occur below a certain concentration, with the number of (species of) organisms with deficiency effects increasing with decreasing concentration. However, the further elaboration of the DT-model, including its quantification for zinc, leading ultimately to a "maximum tolerable concentration", cannot be subscribed to, for the following reasons:

a. The elaboration of the DT model implies a pursuit of optimal conditions for all species in a specific environment, for example fresh surface water. Environmental policy is not concerned with an overall optimization of the environment for all species, but with the protection of the biodiversity of natural ecosystems. Naturally occurring deficiencies should not therefore be considered a negative phenomenon. On the contrary, they play a natural role in maintaining the biodiversity of ecosystems. Endeavouring to eradicate such cases of deficiency is generally regarded as an undesirable human intervention in the natural situation. In this context, the example of phosphate and nitrate in surface water is illustrative. In the past the natural concentrations of these essential nutrients in surface waters were limiting for algal growth. In most surface waters today, human activities have resulted in increased concentrations of these essential nutrients, thus eliminating the limiting condition for algae when other natural factors (light, temperature) are optimal for growth. This effect (eutrophication) leads to a reduction of biodiversity in surface waters and is therefore undesirable.

   At present there are too few data available on the actual occurrence of zinc deficiency in natural ecosystems to make due allowance for this in deriving environmental quality objectives. If there are ecosystems in The Netherlands with a naturally occurring zinc deficiency, then they should be preserved and not eliminated by endeavouring to achieve optimal conditions for all species, as recommended in the IA.

b. The upper and lower boundaries of the OCEE curves for the various water types are underpinned by poor arguments:

   - For surface water the IA concluded that the OCEE lower boundary is 0.5-5 μg dissolved-Zn/l (2-15 μg total-Zn/l), based in part on OECD guidelines for aquatic toxicity tests. These guidelines prescribe a zinc concentration in the culture medium of 6 μg/l for Daphnia species (draft OECD Guideline 202, February 1994) and, according to the IA, 3 μg/l for algae (OECD Guideline 201, June

1984)[8]. However, it is debatable whether the zinc levels mentioned in these guidelines can be viewed as a deficiency limit. The artificial media in question contain a large number of essential elements besides zinc; it is therefore impossible to quantify the essential concentration level of zinc on the basis of the data on the composition of the artificial media recommended in the guidelines. In The Netherlands no habitats are known that are characterized by zinc deficiency in terms of their composition and functioning; the zinc concentrations occurring here are probably considerably higher than the actual deficiency levels, even though there is a paucity of data on deficiency levels. Given the extremely low zinc concentration in the oceans, in this water type there may well be ecosystems that are influenced (in part) by zinc deficiency.

- For surface water the IA concluded that the OCEE upper boundary is 50 μg dissolved-Zn/l (150-200 μg total-Zn/l). For zinc in surface water this OCEE upper boundary is taken in the IA to be the 'Maximum Tolerable Concentration for Essential Elements' (MTCEE). The MTCEE is set equal to twice the MTC, with the MTC taken to be 25 μg dissolved-Zn/l, the value derived in the addendum after rejection of a number of low NOEC values (see Appendix 1.1). In this IA approach, the MTC is erroneously considered to be the 'NOEC' (ecosystem) and the MTCEE to be the *'LOEC' (ecosystem) = 2x'NOEC' (ecosystem)*. With this equation, reference is made to the equation *NOEC = LOEC/2* used in the ICDZ in case of certain test results, i.e. in case, in an individual test, the lowest test concentration resulted in 10-20% effect. Based on the latter equation the IA simply posited that the LOEC is twice the NOEC. No arguments are given for this misinterpretation of the equation employed in the ICDZ which is used in the ICDZ only for data from individual tests and in case there is 10-20% effect relative to the control regarding the toxicological end-point measured. With respect to the misinterpretation of the MTC in the IA it is emphasized that the MTC is not an ecosystem NOEC, but a concentration that, in theory, results in adverse effects on 5% of the species in the ecosystem. On the basis of the above, it is concluded that the IA provides no sound scientific grounds for the cited derivation of the MTCEE.

For additional data on the DT model, including the illustrations of the deficiency, toxicity, and OCEE curves, the reader is referred to the IA.

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[8] OECD Guideline 201 prescribes a concentration of $3x10^{-3}$ $ZnCl_2$/l; this is equivalent to around 1,5 μg Zn/l. Both the concentration of 3 μg Zn/l as mentioned in the Industry addendum as the recalculated concentration of 1.5 μg/l are within the range of the lower boundary of the OCEE (0.5-5 μg Zn/l) as mentioned in the Industry addendum. So, the recalculation does not affect the OCEE lower boundary.

1.3.2 Maximum tolerable concentration of zinc in surface water

On the basis of the comments given in the IA on the aquatic toxicity studies with relatively low NOEC values, 3 of the total of 49 NOEC values used in the ICDZ as input to the Aldenberg-Slob method[9] have been revised (see 1.1.2). Recalculation of the MTR (i.e. HC5) by the Aldenberg-Slob method leads to a slight increase relative to the value calculated in the ICDZ: 7.5 μg/l (dissolved Zn) *versus* 6.3 μg/l (dissolved zinc). This slight increase is not considered to have a practical significance. For this reason, in this report no revision of the current MTC[10] is proposed. A second reason for not proposing a revised MTC in this report is the fact that the MTC values for a number of metals, zinc included, are currently being re-evaluated in the framework of the aforementioned INS-project (Crommentuijn et al., 1996). For deriving MTC values of the metals in surface water, the effect-limitation method (see 1.3.1) is used therein. Preliminary calculations of a new MTC for zinc in surface water using this method have resulted in a value of 8.4 μg/l (dissolved Zn) at bioavailability of 100% and a value of 8.8 μg/l at bioavailability of 10% (Peijnenburg et al., 1996). In these calculations a background concentration of 2.8 μg/l (dissolved Zn) has been used, based on a background concentration of 12 μg/l for total-Zn in Dutch surface water (Van den Hoop, 1995, see also below). The data set of NOEC values used by Peijnenburg et al. (1996) is that from the ICDZ, including the 3 revised values from the present report (see 1.1.2).

The current MTC (6.3 μg/l for dissolved Zn; in 'standard' Dutch surface waters equivalent to 25 μg/l for total Zn) is higher than the current target value (2 μg/l for dissolved Zn and 9 μg/l for total Zn, respectively). The target value is based on the background concentration (VROM, 1992). In a recent literature study into the background concentrations of metals in environmental compartments in The Netherlands, the background concentration for total Zn was revised to 12 μg/l (Van den Hoop, 1995). This concentration is equivalent to a dissolved-Zn concentration of 2.8 μg/l (Crommentuijn et al., 1996). The current MTC is higher than this revised background concentration, too. Furthermore, there are no indications that the current MTC implies a deficiency situation; actual deficiency levels are probably far lower. Therefore, the current MTC is considered to be valid for the time being, i.e. until a new MTC has been established in the framework of the INS-project.

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[9] In the ICDZ, one NOEC per single species was used as input to the Aldenberg-Slob method. In case several NOEC values were available for a single species, the NOEC or geometric mean NOEC for the most sensitive toxicological end-point was used as input for that single species, according to Slooff (1992).

[10] As mentioned in the ICDZ, in fresh surfaces water satisfying the 'standard' conditions of Dutch surface water the MTC for dissolved Zn (6.3 μg/l) is equivalent to 25 μg total-Zn/l.

The IA proposes for zinc in surface water a 'maximum tolerable concentration' (MTCEE, see 1.3.1) of 50 μg/l, for dissolved Zn. On the basis of the distribution of the 49 NOEC values from the ICDZ, including the 3 revised values from this report, a concentration of 50 μg/l (dissolved Zn) is equivalent to a risk level of about 30%, as calculated by the Aldenberg-Slob method. In other words, at this concentration approximately 30% of the species in aquatic ecosystems will, in theory, be unprotected. This percentage is substantially higher than the 5% risk level on which current environmental policy in The Netherlands is based. On the basis of the effect-limitation method the percentage of species that will be unprotected at 50 μ/l (dissolved Zn) is expected to be somewhat lower than 30%.

In the IA it is stated that toxicity data on saltwater organisms are not relevant to the freshwater environment. In the ICDZ the MTC was calculated from the combined NOEC values for freshwater and saltwater organisms, in accordance with Slooff (1992), because there is no significant difference between the NOEC values of the freshwater data set *versus* the saltwater data set ('two-sample T test': no significant difference between the mean values). The MTC derived for dissolved zinc thus holds for freshwater as well as for saltwater[11]. The Dutch government's position, as embodied in the 'Evaluation Memorandum on Water', which lays down the most recent environmental quality objectives (such as limit and target values), is also based on equal sensitivity of freshwater and saltwater organisms for the substances (zinc included) covered by this policy paper, and thus sets one and the same set of quality objectives for freshwater and saltwater (V&W, 1994). In addition, the preliminary calculations of a new MTC for zinc in surface water (Peijnenburg et al., 1996) and the re-evaluation of the MTC in the framework of the INS-project (Crommentuijn et al., 1996) are also on the basis of the combined data set.

1.3.3 Maximum tolerable concentration of zinc in soil

In 1.2.2 it has been demonstrated that, on the basis of the comments given in the IA, there are no grounds for revising the basic data (NOEC values). For zinc in the soil, the HC5 calculated on the basis of the 'standardized' NOEC values for microbe-mediated processes and invertebrates/plants, respectively, were below the background concentration

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[11] When interpreting total-Zn concentrations in surface water, one must take into account differences in particulate matter content. This content may vary considerably, not only between fresh and salt water, but also within both environments.
In the major Dutch fresh surface waters the particulate matter content is 30 mg/l, on average.

of zinc in Dutch 'standard soil'[12]. For this reason the (lowest) HC5 was not automatically taken to be the MTC for zinc in soil, but seen as an approximation of the zinc level that may be added to the soil, taking into account the soil type-dependent background concentration. In practice, the ICDZ-interpretation of the HC5 for zinc in soil equals the concentration-limitation method that assumes a bioavailability of 0% for the background concentration of metals in soil (see 1.3.1). Therefore, the ICDZ calculation and interpretation of the HC5 is still considered to be valid.
In the IA there was also no recalculation of the MTC (i.e. HC5).

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[12] The background zinc concentration in 'standard soil' (containing 25% clay and 10% organic matter) is 140 mg/kg dw.

2 ATMOSPHERIC CORROSION OF ZINC AND GALVANIZED STEEL

2.1 EMISSIONS TO SURFACE WATER AND SOIL DUE TO CORROSION

The comments given in the Industry addendum (IA) on emissions of zinc are concerned specifically with estimation of the rate of atmospheric corrosion of zinc (roof gutters and roofing) and galvanized steel (crash barriers, electricity pylons and other objects). Zinc emissions occurring as a result of atmospheric corrosion cannot be determined on the basis of environmental monitoring. An estimate must consequently be made, determining the corrosion load as the product of three individual terms:

*corrosion load = [total area * exposure factor * corrosion rate]*

The total area of zinc or galvanized products is frequently established on the basis of production statistics and estimates of the area per unit product. The exposure factor, expressing how much of the zinc or galvanized surface is not covered by a coating, is usually estimated by specialists from the zinc/galvanizing and construction industry. As a result of aesthetic and other considerations, the exposure factor is tending to decrease. These two terms (total area and exposure factor) together determine the exposed area. The corrosion rate is determined experimentally from the weight loss of zinc or galvanized test specimens or calculated on the basis of empirically established relationships between corrosion rate and one or more atmospheric variables. The main (and often only) factor in the empirical relationships drawn up by various authors is the atmospheric SO_2 concentration (see Appendix 2.1.). The corrosion rate is influenced by other variables too, however, including the Cl^{-1} concentration in wet deposition and the duration and frequency of contact with moisture. Although the influence of the various variables is well established in a qualitative sense, there appears to be no consensus on a quantitative relationship having general validity, however.
Table 1 provides a summary of gross zinc emissions due to atmospheric corrosion[13] in The Netherlands, based on estimates of various authors. The estimation procedure used by the different authors is essentially the same. First the corrosion load is determined for each type of application (crash barriers, gutters or electricity pylons, for example). Then the corrosion load to each environmental compartment and the total corrosion load are determined. The differences in the results of the estimates for the zinc emissions as reported in Table 1 are due to differences in the corrosion rates and to differences in the exposed area of the applications which were included in the estimate. The different ratios between the emissions to the compartments surface water, sewage sludge and soil are due to differences in assumptions on the environmental fate of corroded zinc (flow-schemes of run-off water). The numbers given below are the direct results of performed calculations; their representation is not indicative of the accuracy of the calculations.

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[13] This is the total corrosion-related input to surface water/sediment and soil, with no allowance being made for output terms such as sewage treatment (water) or run-off and leaching (soil).

Table 1. Estimated gross zinc emissions due to atmospheric corrosion of zinc and galvanized steel in The Netherlands (tonnes zinc/year).

	RIVM (1992) [1]	**RIZA/ RIVM (1993)** [2]	**RIZA (1996)** [3]	**CBS (1994)** [4]	**Industry addendum (1995)** [5]	**VTBC (1996)** [6]
Reference year	**1989**	**1985**	**1993**	**1990**	**'current'**	**1995**
COMPARTMENT						
Surface water/ sediment *(of which to sewage sludge)*	2,100 *(450)*	630 *(245)*	527 *(219)*	765 *(294)*	325 *(150)*	379 *(195)*
Soil [7]	2,025	2,070	1,164	575	165	183
Total	4,125	2,700	1,691	1,340	490	562
Percentage of ICDZ estimate	100%	65%	41%	32%	12%	14%

Note: the figures given here are the direct results of model calculations. Their form may suggest an exactness not intended by their authors.

[1] Cleven et al., 1992 (ICDZ). Exposed area: 125 million m^2. Corrosion rate varying from 14 g/m^2/y in rural areas to 50 g/m^2/y along roads (weighted average: 33 g/m^2/y).

[2] Coppoolse et al., 1993 (SPEED-Document). Exposed area: 96 million m^2. Corrosion rate varying from 14 to 40 g/m^2/y (weighted average: 28 g/m^2/y). Emission to surface water and soil: calculated from table 3.21 in SPEED document. Calculation of emission to sewage sludge: 350 tonnes to sewage plant influent (table 3.21); removal percentage 70%.

[3] Van Bentum et al., 1996 (WSV-report). Exposed area: 53 million m^2. Corrosion rate (weighted average): 32 g/m^2/y. The corrosion rate was corrected for decreasing atmospheric SO_2 concentration (according to Coppoolse et al. (1993) decreasing from 15 μg/m^3 in 1985 to 3 μg/m^3 in 2010, resulting in a 20% decrease in corrosion rate over this period). Proceeding from these data Van Bentum assumes a decrease in corrosion rate (rel. to 1985) of 4% in 1990 and 6% in 1993. For these years this results in a corrosion rate varying from 13 to 37 g/m^2/y (weighted average: 32 g/m^2/y).

[4] Gorter, 1995 (CBS-report). Exposed area: 53 million m^2. Corrosion rate (weighted average): 25 g/m^2/y. On the basis of a study by Van Tongeren, this CBS study assumes an overall emission of 1,000 tonnes/year from galvanized steel objects (corrosion rate 28 g/m^2/y) and of 340 tonnes/year from gutters (De Rijke & Korenromp, 1994; corrosion rate: 20 g/m^2/y). Corrosion of zinc roofing is not included in this estimate. The various loads are calculated using the flow model of Cleven et al. (1992). The corrosion load of galvanized steel in Van Tongeren (1994) relates to the situation around the year 2010, however, and is approx. 30% higher in 1990. On the basis of this CBS study, Van Tilborg & Van Assche (1995) erroneously give a figure of 126 tonnes for the quantity of zinc ending up in sewage sludge via corrosion. The correct value is 294 tonnes.

[5] Van Tilborg & Van Assche, 1995 (Industry addendum). Exposed area approximately 70 million m^2 (of which 34 million m^2 zinc gutters/roofing and 36 million m^2 galvanized steel). Corrosion rate (weighted average): 7 g/m^2/year (average value for present atmospheric circumstances in The Netherlands).

[6] Van Tilborg (1996). Exposed area: 55 million m^2 (of which 33 million m^2 zinc gutters/roofing and 22 million m^2 galvanized steel). Corrosion rate varying from 7.2 to 14.3 g/m^2/y, (weighted average: 10.2 g/m^2/y). Van Tilborg (1996) is an elaborate version of the estimation in the IA.

[7] Affects mainly non-agricultural soils.

In the Integrated Criteria Document Zinc (ICDZ), location-specific corrosion rates of 14 to 50 g/m^2/year and a total exposed area of 125 million m^2 were used, resulting in an estimated emission of 4,125 tonnes/year (Cleven et al., 1992; reference year 1989). As additional and more recent information on corrosion rates and exposed areas has since become available, the assumptions made in the ICDZ have been adapted in more recent RIZA/RIVM publications, first in the so-called 'SPEED-document' on heavy metals (Coppoolse et al., 1993) and then in the WSV-report on emissions from building materials (Van Bentum et al., 1996), resulting in an estimated emission of 2,700 tonnes/year (reference year: 1985) and 1,691 tonnes/year (reference year: 1993), respectively[14]. The latter estimate, based on location-specific corrosion rates ranging from 13 to 37 g/m^2/year and a total exposed area of 53 million m^2, is a factor 2.5 lower than the ICDZ estimate.

The Dutch Central Bureau of Statistics, CBS, recently also presented an estimate of zinc corrosion: 1,340 tonnes/year (Gorter, 1995; reference year 1990). This estimate is close to that of Van Bentum et al. (1996). In arriving at this estimate, CBS used a total exposed area of 53 million m^2 (36 million m^2 galvanized steel objects and 17 million m^2 zinc gutters) and corrosion rates of 28 g/m^2/year for galvanized steel objects and 20 g/m^2/year for zinc gutters.

The IA (Van Tilborg & Van Assche, 1995) gives a substantially lower corrosion estimate: 490 tonnes/year. This estimate is based on an average corrosion rate of 7 g/m^2/year and a total exposed area of 70 million m^2 (36 million m^2 galvanized steel objects and 34 million m^2 zinc gutters/roofing). A more recent and elaborate version of the corrosion estimate of the IA, based on additional information, gives a somewhat higher value: 562 tonnes/year (Van Tilborg, 1996), but is still substancially lower than the most recent RIZA, RIVM and CBS estimates. The estimate of 562 tonnes/year is based on location-specific corrosion rates of 7.2 to 14.3 g/m^2/year and a total exposed area of 55 million m^2 (22 million m^2 galvanized steel objects and 33 million m^2 zinc gutters/roofing). The differences between the estimates by Van Bentum et al. (1996) and Gorter (1995) on the one hand and that by Van Tilborg & Van Assche (1995) and Van Tilborg (1996) on the other are mainly related to the differences in corrosion rates used. The considerably lower corrosion rates used in the last mentioned estimates emerge from the most recent corrosion studies and, therefore, Van Tilborg & Van Assche (1995) and Van Tilborg (1996) regard these lower values representative for the present atmospheric circumstances.

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[14] On the basis of the data in the SPEED-document and in the draft WSV-report dated July 1994, Annema et al. (1995) estimated the following corrosion loads: 509 tonnes/year to surface water (load to sewage sludge included) and 1,133 tonnes/year to soil, resulting in a total corrosion load of 1,642 tonnes/year (reference year 1990).

For a limited number of applications the significance of the estimates in Table 1 can be checked. The corrosion products of zinc gutters and galvanized street furniture dominantly end up in the sewerage system, the zinc load of which can be assessed on the basis of the zinc load of the sewage sludge. This parameter belongs to the most reliable data concerning environmental pollution in The Netherlands. Using the overall zinc load found in sewage sludge (for which reliable values are available on the basis of the long-term practice of analyzing individual batches of sludge that are disposed off) and a limited number of corrections for other contributing sources, it can be calculated that 256 tonnes of zinc end up in sewage sludge annually via corrosion products (estimated accuracy: 36 tonnes/year; see also Appendix 2.2). A comparison of this value with the corresponding estimates in Table 1 shows that especially the ICDZ estimate and the IA are far off, the former being too high and the latter being too low. The other estimation procedures give results that are more or less within the range of estimated accuracy, with the recent industry estimate being somewhat too low.

As all estimates of corrosion-related zinc loads to the environmental compartments are based on a <u>combination</u> of corrosion rate and exposed area (and to some extend also on flow schemes of run-off water) the quantitative assessment of the corrosion-related zinc load in sewage sludge can not be used as a validation for the corrosion rate or the exposed area alone. Below we will deliver a discussion of the different values that are used in the estimation procedures relating to corrosion rate and exposed area, respectively.

A large number of corrosion rate values have been published in the literature[15]. Most of these values are between 7 and 70 g/m^2/year[16], with the lower range of values occurring in rural areas and the higher in areas with relatively high atmospheric SO_2 concentrations (along roads; industrialized areas) or Cl^{-1} concentrations (coastal areas). This range of values comprises data for different locations world-wide and different periods. Lower and higher corrosion rate values also occur incidentally.
A number of recent corrosion measurements (Knotkova et al., 1995; Orzessek & Van Tilborg, 1995; Lehmann, 1995) have yielded values in the range 5-15 g/m^2/y, which is relatively low compared to the wide range given above. We will discuss these results as

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[15] See for instance Knotkova et al. (1995), Repmann (1993), Van Rijn (1992), Orzessek & Van Tilborg (1995), TAUW (1987) and NACE.

[16] In a number of references the corrosion rate is expressed in μm/year; a value of 1 μm/year is equivalent to 7.14 g/m^2/year.

far as they refer to measurements in The Netherlands. Appendix 2.1 gives the underlying data of these studies.

The most extensive study on corrosion in The Netherlands is the UN/ECE study (Knotkova et al., 1995), in which corrosion rates have been measured under controlled conditions in the period '87-'93, four Dutch locations included. The results for The Netherlands lie in the range 5-13 $g/m^2/year$. Averaging over all measurements for urban (Vlaardingen) and rural (Eibergen, Vredepeel, Wijnandsrade) location(s) yields the values of 11.1 ± 1.5 and 8.7 ± 1.8 $g/m^2/year$, respectively. A study performed in the city of Arnhem in the period '90-'93 gives an average corrosion rate of 9.3 $g/m^2/year$ (Van Tilborg, 1996)[17]. As the latter study also was performed under controlled conditions the conclusion can be drawn that for these conditions the recent corrosion rate is about 10 $g/m^2/year$. It should be noted, however, that large discrepancies can exist between test conditions and conditions in practice. Therefore, this result can not straightforwardly be interpreted as representative for actual corrosion rates in practice.

There are two main reasons that limit the use of the values given above for corrosion in practice, as is relevant for estimation procedures. In the first place, the corrosion rate depends on local atmospheric conditions for which not easily a representative value can be given. Second and foremost, the corrosion rates given are the result of controlled testing, which may greatly differ from actual corrosion of zinc surfaces in practice. According to Hollander (1996), the discrepancy in corrosion rate between test conditions and practice can be as large as a factor 2 to 4, due to microclimatic and object-related effects. The most relevant of these appear to be the vertical inclination of the surface (horizontal surfaces suffering a larger corrosion rate), the cleanliness of the surface (the presence of dust and organic matter enhancing the corrosion rate), local wind flow patterns (the stronger the flow the higher the corrosion rate) and the dimensions of the object under consideration (larger objects having a lower corrosion rate). With respect to the possible discrepancy between corrosion rates under controlled testing conditions and those in practice it is noted, however, that this can act both ways, so controlled measurements can both underestimate and overestimate the actual corrosion rates in practice. Representative corrosion rate values can only be obtained by a comprehensive study that includes *in situ* measurements for a wide range of applications and locations of zinc and galvanized steel objects, so that the specific atmospheric- and object-related conditions are taken into account.

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[17] In the original publication on this study (Orzessek & Van Tilborg, 1995) an average corrosion rate of 7 $g/m^2/year$ was reported, but this value has been corrected by Van Tilborg (1996).

When a comparison is to be made with historic corrosion rates in order to determine a possible decrease in corrosion rate, as stated in the IA, comparable locations and conditions should be compared for different periods in time. For The Netherlands, only one study is available that gives corrosion rates under controlled conditions before '87: Lanting & Moree (1984) gives the result of measurements in the period '77-'81 for the locations Delft, Schiedam, Den Helder and Wezep. When averaging all measurements available for urban (Delft, Schiedam) and rural (Wezep) conditions one finds 15.7 ± 1.1 and 11.4 ± 0.4 g/m^2/year, respectively. Comparing this result with the corresponding values of the UN/ECE study a decrease in corrosion rate over the periode '80-'90 can be inferred. A decrease can indeed be expected because of the decreasing SO_2 concentration in the atmosphere and the correlation between this parameter and the corrosion rate. However, the accuracy of the data points, together with their very limited number and the difference in methodology used (see Appendix 2.1) also give space to other interpretations. A quantitative assessment of the historical trend can certainly not be given with any significance.

Apart from the corrosion rate also the values for exposed area differ greatly between the estimation procedures given in Table 1. With respect to the more recent estimates, this situation is not apparent from the given totals for exposed area (for example, 53 million m^2 in Van Bentum et al., 1996, *versus* 55 million m^2 in Van Tilborg, 1996), but the data for some (major) applications show considerable differences. In this respect the example of roof gutters can be illustrative: for this application Van Bentum et al. (1996) assumes an exposed area of 19 million m^2, whereas Van Tilborg (1996) assumes a value of 33 million m^2. The latter is almost a factor two *larger* than that used by Van Bentum et al. whereas the computed zinc load from this application is 25% *smaller*, because of a substantially lower corrosion rate adopted by Van Tilborg.

This example shows how all combinations of underlying estimates with respect to corrosion rate and exposed area add up to a total corrosion load to the environment. In addition, the estimates with respect to the run-off schemes affect the environmental fate of corroded zinc. Therefore, improving the quality of the present estimation procedures is no easy task. Only little information is really beyond doubt, so many assumptions have to be made. What would really improve this situation is the availability of representative *in situ* corrosion measurements and reliable data on exposed areas of zinc applications. However, this will probably require a large scale research project, the necessity of which one has to assess with respect to the expected benefits of improved estimates for the zinc load to the environment.

Looking into the future two effects appear to be of greatest importance for future trends in corrosion data: the increasing use of coatings on galvanized steel products and the decreasing atmospheric SO_2 concentration. The influence of the first effect has been calculated by Van Tongeren (1994) to be a decrease in the corrosion load from galvanized steel products of approximately 30% in the period up to 2010. The decreasing atmospheric SO_2 concentration will certainly also lead to a decrease in corrosion. Because of the differences in statistical models for the influence of SO_2 on corrosion and the fact that these models are only valid for the historically higher concentration range the magnitude of this decrease is uncertain. According to most of the available empirical relationships between the corrosion rate and atmospheric SO_2 concentration (see Appendix 2.1), a corrosion rate around 5 $g/m^2/year$ can be expected in the ultimate situation of absence of SO_2.

2.2 SHARE OF CORROSION IN ZINC POLLUTION OF SURFACE WATER

Of the corrosion-related gross zinc emission to surface water, about one half ends up in surface waters (sediments included), either directly or via sewage plant effluent, and the other half in sewage sludge (see Table 1 and Appendix 2.2). Van Bentum et al. (1996) reports a net corrosion-related zinc emission to surface water of 308 tonnes/year (see Table 1: 527 minus 219 tonnes/year). This reference does not include detailed data on all zinc sources, because the onderlying study is aimed on emissions to surface water due to the use of building materials. With respect to other zinc sources to surface water, the following data can be derived from Annema et al. (1995): 2,000 tonnes/year originating from transboundary input via the major Dutch rivers (Rhine and Meuse), 54 tonnes/year from atmospheric deposition which is largely (90%) transboundary input and approximately 450 tonnes/year from inland sources other than corrosion[18]. Based on these data, atmospheric corrosion of zinc has a share of 40% in surface water zinc pollution due to inland sources and a share of 11% in overall surface water zinc pollution. These percentages can be somewhat higher or lower, depending on the underlying data. For example, RIZA (1995) mentions a transboundary input of 2,450 tonnes for the reference year 1990 (2,100 tonnes via the Rhine *[this value is used by the International Rhine Committee]* and 350 tonnes via the Meuse). Using this transboundary load, the atmospheric corrosion of zinc has a share of 9% in overall zinc water pollution.

According to the original (Dutch) version of the IA, the atmospheric corrosion of zinc has a share of 3% in overall surface water zinc pollution. This share was calculated on the basis of a corrosion load of 175 tonnes/year (see Table 1: 325 minus 150 tonnes/year) and a transboundary zinc load of 6,600 tonnes/year (Rhine and Meuse: 5,700 and 950

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[18] The other inland sources include a large number of industrial sources and further mainly run-off and traffic.

tonnes/year, respectively, around 1990). The load in the Rhine was calculated erroneously from a load of 77 g Zn/s. In the translated (English) version of the IA, a corrected value of 2,450 tonnes/year was reported for the zinc load in the Rhine, resulting in a transboundary load of 3,400 tonnes/year and a value of 5% for the share of atmospheric corrosion in overall surface water zinc pollution. The share of 5% is somewhat lower than that calculated on the basis of the RIVM and RIZA data.

Much of Dutch surface water is fed by Rhine and Meuse water; for The Netherlands as a whole the relatively small share of corrosion in overall surface water zinc pollution will therefore be of only limited influence on the concentration in this compartment. On a local scale, however, zinc emissions due to corrosion may contribute significantly to surface water levels. In the Westland region, for example, relatively high zinc concentrations are encountered in surface water, probably due to corrosion of greenhouse structures, which are very numerous in that region (PIMM, 1995).

2.3 SHARE OF CORROSION IN ZINC POLLUTION OF (NON-AGRICULTURAL) SOILS

Van Bentum et al. (1996) reports a corrosion load to soil of 1,164 tonnes/year. Zinc pollution due to corrosion affects mainly non-agricultural soils, so it is assumed that practically the total corrosion load ends up in non-agricultural soils. With respect to other zinc sources to non-agricultural soils, the following data can be derived from Annema et al. (1995): 163 tonnes/year originating from atmospheric deposition which is largely (90%) transboundary input and 221 tonnes/year from inland sources other than corrosion (mainly traffic and compost). Based on these data, atmospheric corrosion of zinc has a share of 83% in non-agricultural soil zinc pollution due to inland sources and a share of 75% in overall non-agricultural soil zinc pollution. In the case of agricultural soils, atmospheric corrosion is of much less relevance for zinc pollution than the emission by fertilizers (manure and artificial fertilizers), on average at least. As with non-agricultural soils, around zinc or galvanized steel objects highly elevated zinc levels may occur locally, however, since only the direct vicinity of the objects becomes polluted as a result of corrosion.

3 CONCLUSIONS

3.1 ECOTOXICITY

The re-evaluation of the ecotoxicity studies selected in the Industry addendum provides no grounds for a reassessment of the remaining ecotoxicity studies in the Integrated Criteria Document Zinc. This holds both for the aquatic toxicity studies and the terrestrial toxicity studies. In the re-evaluation of the ecotoxicity studies, due allowance has been made for the fact that zinc is an essential element and to the other points of criticism, either with respect to the quality or the relevance of the study, mentioned in the IA. In deriving the MTC values for zinc there is therefore no reason to deviate from the NOEC values used in the ICDZ. An exception here is formed by a small number of NOEC values (3 of the total of 49 NOEC values used in the ICDZ for deriving the MTC of zinc in surface water) that have been revised on the basis of the comments given in the IA. These revisions have virtually no impact on the overall set of NOEC values.

In the ICDZ the Aldenberg-Slob ecotoxicological extrapolation method was used to derive maximum tolerable concentrations (MTC values) for zinc. With respect to the usefulness of this method to derive MTC values for essential and other naturally occurring substances this method has short-comings, as stated in the IA. The major short-coming of the Aldenberg-Slob method is the fact that background concentrations of naturally occurring substances are not taken into account. For that reason, preference is given at present to the 'added risk' approach recently developed by RIVM, consisting of two new (linked) ecotoxicological extrapolation methods, incorporating background concentrations and bioavailability. Both methods, the so-called 'effect-limitation' (or 'effect-addition') method and the 'concentration-limitation' (or 'concentration-addition') method, make use of the Aldenberg-Slob method.

With respect to the MTC of zinc in surface water, the use of the revised data set of NOEC values and/or the use of the added risk approach (more specific: the 'effect-limitation' method which is considered to be most appropriate for deriving MTC values for metals in surface water) do not result in a substantial change of the MTC. Both the MTC as derived in the ICDZ and the MTC values derived with the effect-limitation method (preliminary calculations) are higher than the background concentration of zinc in the major Dutch surface waters and there are no indications for deficiency at the MTC level.

With respect to the MTC of zinc in soil, the interpretation of the HC5 as an approximation of the zinc level that may be added to the soil, taking into account the soil type-dependent background concentration, equals in practice the added risk approach (more specific: the 'concentration-limitation' method which is considered to be most appropriate for deriving MTC values for metals in soil), in both cases assuming 0% bioavailability for the background concentration.

On the basis of the above conclusions with respect to the re-evaluation of the ecotoxicity studies and the ecotoxicological extrapolation method, the MTC values for zinc in surface water and soil that were derived in the ICDZ are still considered to be valid. Therefore and because of the fact that the MTC values for metals, zinc included, are currently being re-evaluated in the framework of RIVM-project 'Setting Integrated Environmental Quality Objectives', no revision of the current MTC values is proposed in this report.

In the IA a 'Deficiency Toxicity' (DT) model is presented for deriving 'Maximum Tolerable Concentrations for Essential Elements' (MTCEE), as an alternative for the Aldenberg-Slob method that was rejected therein. The basic point of departure of the DT model is accepted, namely that, in the case of essential elements such as zinc, adverse effects occur below a certain concentration. However, the further elaboration of the model, including its quantification for zinc in the aquatic environment, leading ultimately to a MTCEE of 50 μg/l for dissolved zinc in surface water, is rejected, for the following reasons:

- The elaboration of the DT-model implies a pursuit of optimal conditions for all species in a specific environment, for example fresh surface water. However, an overall optimization of concentrations of zinc and other essential elements in natural environments is not possible because of species-specific differences in nutritional needs and sensitivity. Besides of this, optimization is not wanted because it can easily result in a reduction of biodiversity of natural ecosystems.
- The upper and lower boundaries of the 'Optimal concentration band for essential Elements' (OCEE) for zinc in the various water types are underpinned by poor arguments. In deriving the MTCEE for zinc in surface water, the MTCEE being the upper limit of the OCEE, several misinterpretations are included. In addition to the misinterpretations, the 'MTC' underlying the MTCEE was calculated in the IA after an arbitrary selection and rejection of studies resulting in low NOEC values that were included in the ICDZ. It is concluded that the IA provides no sound scientific grounds for the cited derivation of the MTCEE.

In 1995 the Steering Party on Public Housing Experiments (SEV) issued an update of the 'Guidelines for Sustainable Housing Construction', in which it is recommended to avoid using zinc in outdoor applications such as roofing, gutters and drainpipes, above all because of the major contribution (through corrosion) to the zinc pollution of soils and surface waters and the associated ecotoxicological aspects (SEV, 1995). Because of the criticism on the ICDZ given in the IA, the SEV applied to TNO for advice. In this *framework TNO's Environmental Sciences Division prepared an ecotoxicological assessment of zinc on the basis of the ICDZ and the IA. This assessment (Hooftman & Hanstveist, 1995) does not include a re-evaluation of the ecotoxicity studies, but is concerned more with commenting on the general issues raised in the IA. TNO, too, largely rejects the criticism on the ICDZ given in the IA.*

3.2 ATMOSPHERIC CORROSION OF ZINC AND GALVANIZED STEEL

In the Integrated Criteria Document Zinc the emission due to atmospheric corrosion (4,125 tonnes/year) was overestimated indeed. In more recent RIZA/RIVM publications the estimated corrosion-related emission has already been corrected downwards to approximately 1,600-1,700 tonnes/year. The current RIZA/RIVM estimates are in agreement with the CBS estimate (1,340 tonnes/year), but are considerably higher than the industry estimate (Industry addendum: 490 tonnes/year, recently revised to 560 tonnes/year).
For that part of the corrosion load that flushes into the sewerage system the recent RIZA/RIVM estimates and CBS estimate are in agreement (i.e. within the range of estimated accuracy) with the data on corrosion-related sewage sludge pollution with zinc. The most recent industry estimate is on the low side, although near the range of estimated accuracy (the original IA estimate is considerably below the range of estimated accuracy). As all estimates of corrosion-related zinc loads to the environmental compartments are based on a combination of corrosion rate and exposed area (and to some extend also on flow schemes of run-off water) the quantitative assessment of the corrosion-related zinc load in sewage sludge can not be used as a validation for the corrosion rate or the exposed area alone.

In The Netherlands only a limited number of corrosion measurements have been conducted; the studies were performed under controlled conditions. Two of the three available studies were conducted recently, one in the period '87-'93 (four locations) and one in the period '90-'93 (one location). It can be concluded that, under similar conditions as were present in these studies, the current corrosion rate is about 10 $g/m^2/year$, on average. It should be noted, however, that large discrepancies can exist between test conditions and conditions in practice. Therefore, this value can not straightforwardly be interpreted as representative for actual corrosion rates in practice. Representative corrosion rate values can only be obtained by a comprehensive study that includes *in situ* measurements for a wide range of applications and locations of zinc and galvanized steel objects, so that the specific atmospheric- and object-related conditions are taken into account.

Comparing the above series of corrosion rate measurements for the period '87-'93 with the corresponding values of the series of measurements (four locations) for the period '77-'81, a decrease in corrosion rate over the period '80-'90 can be inferred. A decrease can indeed be expected because of the decreasing SO_2 concentration in the atmosphere. The data are too limited, however, to give a quantitative assessment of the historical trend in corrosion rate in the above period.

Apart from the corrosion rate also the values for exposed area greatly differ between the estimations procedures. With respect to the more recent estimates this situation is not apparent from the given totals for exposed area, but the data for some (major) applications show considerable differences.

In conclusion: all combinations of underlying estimates (corrosion rate, exposed area, run-off schemes) add up to the corrosion load of zinc to the environmental compartments. Therefore, improving the quality of the present estimation procedures is no easy task. Only little information is really beyond doubt, so many assumptions have to be made. What would really improve this situation is the availability of representative *in situ* corrosion measurements and reliable data on exposed areas of zinc applications. However, this will probably require a large scale research project, the necessity of which one has to assess with respect to the expected benefits of improved estimates for the zinc load to the environment.

Atmospheric corrosion is the main inland emission source for non-agricultural soils and surface water, with a share of approximately 85% (non-agricultural soils) and 40% (surface water) in the zinc pollution by inland sources. Corrosion also makes the greatest contribution to the overall zinc pollution of non-agricultural soils: 75%. Locally (i.e. in the direct vicinity of zinc or galvanized steel objects) highly elevated zinc concentrations may occur in the soil; this holds both for non-agricultural and agricultural soils. In the case of agricultural soil, atmospheric corrosion is of much less relevance for zinc pollution than the emission by fertilizers (manure and artificial fertilizers), on average at least. In the case of surface water corrosion makes only a minor contribution to the overall pollution (on average) and thus to the zinc concentration in this compartment, owing to the high zinc load in the major rivers (transboundary input). However, the share of corrosion in the overall zinc load of surface waters is greater than assumed in the Industry addendum (approximately 10% *versus* 5%) and on a local scale corrosion may make a major contribution to the zinc concentration in surface water.

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APPENDIX 1: ECOTOXICITY STUDIES

(Selected in Industry Addendum)

1.1 Aquatic toxicity studies

In Appendix I of the IA, the aquatic toxicity studies (used in the ICDZ for deriving the MTC for surface water) with a NOEC below 30 μg/l are evaluated on the basis of criteria relating to quality and relevance. The comments on these studies given in the IA are discussed in detail below.

1. Bartlett et al., 1974 (*Selenastrum capricornutum*; NOEC = 15 μg/l, *nominal*)
* The test conditions are largely in accordance with OECD Guideline 201 (algae): the prescribed culture media contain EDTA, in order to keep the metals required for algal growth (such as poorly soluble iron) in a soluble form that is available to algae, and have a low hardness. The media described in this international guideline are designed not to mimic the Dutch situation, but to create conditions guaranteeing a certain growth (rate), as specified in the guideline.
With respect to the EDTA content in algal test media, a upper limit concentration of $10x10^{-3}$ mMol/l (10 times higher than the maximum chelator concentration of $1x10^{-3}$ mMol/l mentioned in the OECD guideline for algal growth test) had been arbitrarily choosen in the ICDZ, because EDTA can decrease the toxicity of zinc by reducing the free, available Zn-ion concentration. It is noted that the effect of EDTA on zinc toxicity for algae is not quite clear, because EDTA can bring metal ions and other cations into a suitable form for uptake by algae (Van Donk, 1983). In a recent OECD workshop on aquatic toxicity testing of sparingly soluble metals, inorganic metal compounds and minerals (SIMMs) it was stated that strong chelators such as EDTA will change the solubility and possibly bioavailability of SIMMs. Therefore it was recommended not to use EDTA in test media when assessing the toxicity of SIMMs or to use test media with a complexing capacity that reflect that of the natural environment (CANMET, 1995).
* The 'irregular pattern of the slopes' in Figure 2 of the article (the figure from which the NOEC is derived) does not suggest a 'large variation' but indicates that the growth rate decreases with increasing zinc concentration. Although it is true that the article gives no statistical data on these slopes, there is nothing unusual in deriving a LOEC or NOEC from a graph. In this study, the lowest test concentration (30 μg/l) resulted in 20% inhibition of the growth rate compared to the control on day 4 (no date on control growth rate at prolonged exposure). Based on the assumptions made in the ICDZ with respect to deriving a NOEC from a LOEC, this results in a NOEC of 15 μg/l (NOEC = LOEC/2).

Inhibition of growth rate is a generally accepted and ecologically relevant parameter for determining effects on algae (cf. OECD Guideline).

* In itself it is correct to state that the amount of zinc present in the culture medium should be added to the nominal test concentration. However, the background concentration was not reported in the publication and could not be derived from supplementary literature; for this reason the nominal (added) concentration was taken.

* With respect to the NOEC of 50 $\mu g.l^{-1}$ dissolved zinc mentioned in the addendum for *Selenastrum capricornutum* (determined in accordance with OECD Guideline 201, Janssen Pharmaceutica, 1994; test substance: zinc powder), it should be remarked that this confirms the result of the study by Barlett et al.: a factor three difference between the results of corresponding tests is normal, certainly in view of the fact that the NOEC of 15 μg/l is merely the nominal, added concentration. It should also be remarked that the NOEC of 50 μg/l was determined in an artificial culture medium with a low hardness (24 mg/l), so that this NOEC, too, is irrelevant to the Dutch situation according to the criteria used in the addendum.

* Conclusion: The NOEC of 15 μg/l has been correctly derived and justifiably used to derive the MTC. The NOEC of 50 μg/l reported in the IA (from a more recent study with *Selenastrum capricornutum* that was not available at the time the ICDZ was prepared) has also been correctly derived and can likewise be used to derive the MTC, supplementing the other two NOEC values for this organism (study 1: 15 μg/l and following study: 5 μg/l). For *Selenastrum capricornutum* this leads to a revised geometric mean NOEC of 15 μg/l (was 9 μg/l).

2. Kuwabara, 1985 (*Selenastrum capricornutum*; NOEC = 5 μg/l, *nominal*)

* In the IA it is stated that the enlargement of the cells during exposure to zinc is due to an excessive uptake of zinc. This effect is held to be due to the algae being cultured in a medium containing virtually no zinc (less than 0.065 μg/l) or other cations (Ca, Mg) and the subsequent exposure to zinc concentrations 'far outside the OCEE-range'. In the culture medium, the zinc uptake mechanisms of the algae would have been been stimulated as much as possible to satisfy their essential zinc requirements, resulting in an accumulation of too much zinc when the algae are subsequently exposed to 'normal' zinc concentrations, since the algae are unable to addapt sufficiently fast. Furthermore, this effect would be aggrivated by the fact that the bivalent cation pumps will import extra zinc from the Ca- and Mg-depleted medium, to satisfy the cation requirement. It is unlikely, however, that more zinc ions can be absorbed than the number of binding sites for bivalent cations. This would not lead to an enlargement of the cells. After 14 days, moreover, the cells return to their normal size: this would then suggest that zinc has been excreted. A more plausible explanation for the transient increase in cell size is that the cells became 'stressed' during the transition from a zinc-free medium to zinc exposure

and increased their production of macromolecules such as lipds, polysaccharides and proteins as a metabolic adaptation to the stress. This phenomenon, an increased synthesis of macromolecules as an acclimatory response to chemical stresses, has been observed in several algal toxicity studies. For further information on this phenomenon the reader is refered to Thompson & Couture (1991). At the end of the experiment (14 days) the swelling of the cells was no longer observed and the NOEC was derived from the growth rate (daily increase in number of cells).

* It is true that Ca- and Mg-free conditions do not occur in nature, but the availability of these elements can still be limiting for growth and development. For this reason, these results are certainly relevant.

* Given the low background concentration of zinc in the medium (less than 0.065 μg/l) the actual NOEC will be practically equal to the nominal NOEC.

* Conclusion: The NOEC has been correctly derived and justifiably used to derive the MTC.

3. Francis, 1988 (*Ephidatia fluviatilis*; NOEC = 3.2 μg/l, *nominal*)

* The sponge was grown under growth-limiting conditions (by limiting the quantity of bacteria, the source of nutrition for this species); in other words, there was growth, but not maximum growth as under optimum conditions. It is unclear whether this led to the sponge being stressed. Growth-limiting conditions may certainly be relevant, because growth-limiting quantities of nutritional sources also occur in the natural situation. It is not unusual to test organisms under conditions whereby performance is not maximum: in the revised draft guideline for testing daphnias (OECD 202) a quantity of food is prescribed that does not quite lead to maximum reproduction, but does ensure sufficient reproduction for toxic effects to be measured. The background concentrations of zinc (0.65 μg/l) and other micro- and macro-elements in the culture and test medium corresponded to those in a natural body of water where this sponge is common. According to the authors of the article, this sponge requires zinc concentrations of 0.065 and 0.65 μg/l, respectively, for minimum and normal growth; the medium was therefore not deficient in zinc.

* The aforementioned NOEC was established on the basis of the occurrence of tissue deterioration, despite the fact that no effect on growth rate was observed at a concentration 10 times higher. However, the text of the article indicates that after further exposure this tissue deterioration results in mortality. For this reason the NOEC was determined on the basis of tissue deterioration, despite this effect not being quantitatively described.

* The EDTA content in the medium was indeed high, higher than the EDTA upper limit for *algae* studies mentioned in the ICDZ (see study 1). Despite the high EDTA content in the test water (which is assumed to obscure the toxicity of zinc) a very low NOEC was

found, indicating that this organism is very sensitive to zinc.

* The NOEC ($5x10^{-8}$ M/l = 3.25 µg/l) is the nominal (added) concentration, with a background zinc concentration of 0.65 µg/l in the medium. The best possible approximation of the actual exposure concentrations is obtained by adding the background concentration to the nominal concentrations. This leads to a revised NOEC of 3.9 µg/l.

* Conclusion: The NOEC of 3.2 µg/l has been correctly derived, but has, erroneously, not been corrected for the background concentration of 0.65 µg/l. The revised NOEC is 3.9 µg/l (in this case, practically the same as the nominal NOEC).

4. Belanger, 1990 (*Ceriodaphnia dubia*; NOEC = 8 µg/l, *nominal*)

* The article reports that the actual (measured) concentrations deviated from the nominal concentrations by no more (up or down) than 15%, without further information being given on the actual test concentrations; for this reason nominal concentrations were assumed. Although it is preferable to employ actual levels, if there is less than 20% deviation from the nominal concentration it is standard practice to employ the latter value (see also study 6). The NOEC value does not therefore have to be corrected for the zinc present in the medium.

* In this study 9 tests were performed (3 different river waters; 3 pH levels per water type tested). At a concentration of 25 µg/l one of the tests at pH 8 resulted in a 30% decrease in reproduction, significantly lower than in the corresponding control. Proceeding from the assumptions used in the ICDZ, this results in a NOEC of 8 µg/l (NOEC = LOEC/3). However, the fact that in the same water type no effect was found at pH 6 or pH 9 at 25 µg/l (although there was an effect at 50 µg/l) does not imply that there was a 'pH anomaly' or 'measurement error' in the former test; the difference is by no more than a factor 2 and within this pH range there may be an effect on speciation and consequently on the toxicity of zinc. It is emphasized that the other 6 NOEC values (varying from 17 to 50 µg/l) have also been used in the ICDZ for deriving the MTC.

* Conclusion: The NOEC has been correctly derived and justifiably used to derive the MTC.

5. Hatakeyama, 1989 (*Epeorus latifolium*; NOEC = 3 µg/l, *nominal*)

* Mortality in the controls was indeed fairly high (mortality: 25%, 33%, 50%, 75%, 100% and 100% at nominal zinc concentrations of, respectively, 0, 3, 10, 30, 100 and 300 µg/l), but still clearly dependent on concentration. The effect on the parameter emergence was also clearly concentration-dependent (75%, 67%, 42%, 17%, 0% and 0% at, respectively, 0, 3, 10, 30, 100 and 30 µg/l).

* The measured background zinc concentration in the test medium was 8.8 ± 2.3 µg/l. This should indeed be added to the nominal concentrations, resulting in a revised NOEC of 12 µg/l.

* Conclusion: The NOEC of 3 µg/l has been correctly derived, but should have been corrected for the background concentration of 9 µg/l. The revised NOEC is 12 µg/l, substantially higher than the nominal NOEC (by a factor 4).

6. Belanger, 1986 (*Corbicula sp.*; NOEC = 25 µg/l, *nominal*)
* According to the IA, the NOEC of 25 µg/l is correct, but is valid for soft water only. In the ICDZ the result of the ecotoxicological extrapolation method is considered to be the MTC for dissolved zinc, being subsequently 'translated' to yield the MTC for total zinc (see also Chapter 2).
* The NOEC is the nominal concentration; the actual concentration was 20% lower.
* Conclusion: the NOEC has been correctly derived and justifiably used to derive the MTC. In the IA this value was ultimately accepted (although under proviso) as 'reliable' and used in deriving the MTC.

7. Palauskis, 1988 (*Daphnia magna*; NOEC = 25 µg/l, *nominal*)
* The NOEC of 25 µg/l is derived from 2 tests in soft water (hardness: 50 mg/l), with a statistically significant effect on reproduction (parameter: brood size) being found in one test at 25 µg/l, but not in the duplicate test (although it was found at 50 µg/l and higher). If the entire range of test concentrations is taken into account, there is clearly a concentration-dependent effect in both tests. Although in the former test at 50 µg/l a slightly less pronounced effect on reproduction may have been observed than at 25 µg/l (average brood size: 12.06 at 25 µg/l versus 12.26 at 50 µg/l), in both cases this was significantly lower than in the control and the difference from the control increases further with increasing concentration. There is therefore no 'anomaly in the measurements which disturbs the dose-response relationship'.
* It is stated correctly in the IA that the presence of humic acids has a major impact on toxicity, but at present there is not a single (OECD) guideline for aquatic toxicity testing that prescribes addition of humic acids or similar complexing agents occurring naturally in surface water. In the aforementioned OECD workshop on aquatic toxicity testing of metals (see study 1) it was stated, however, that artificial test waters should have characteristics (i.e. pH, hardness, complexing capacity, etc.) that are within the ranges that are encountered in natural waters. This recommendation has to be worked out by expert groups to establish the acceptable range for the most relevant parameters and has to be implemented in the existing guidelines (CANMET, 1995).
* The statement that Palauskis' study is aimed at determining the limits of an organism's niche is incorrect, viewed *inter alia* against the background of current test guidelines. All the types of test waters used in the study (soft water: pond water diluted with 'pure' water; medium-hard water; and hard water: prepared by adding calcium and magnesium to the aforementioned soft water) were of sufficient quality for survival, development and

reproduction, with virtually no water type-dependent differences being found in the control groups.
* The background zinc concentration in the pond water used to prepare the classes of water used in this study by dilution with "pure" water was 3.5-4.6 μg/l, so that the background concentrations in the test media used were at any rate lower than 3.5-4.6 μg/l. The actual concentrations will therefore have been practically equal to the nominal concentrations.
* <u>Conclusion</u>: The NOEC has been correctly derived and justifiably used to derive the MTC.

8. Spehar, 1976 (*Jordanella floridae*; NOEC = 26 μg/l, *actual*)
* The above NOEC is based on a test in which the fish were exposed for almost their entire life cycle, except for the egg phase. This NOEC is lower than that of the fish exposed throughout the life cycle, i.e. including the egg phase (75 μg/l; this NOEC has <u>also</u> been used in the ICDZ for deriving the MTC). According to the IA, the 'zinc deficiency' condition in the egg phase (zinc concentration < 1 μg/l, i.e. 'outside the OCEE') combined with zinc exposure in the fish phase normally does not occur in nature. It is perfectly feasible for such a situation to occur in nature, however, as a result of fish larvae and fish migrating to other areas or pollution occurring in a formerly unpolluted environment. Exposure of fish in the egg phase may lead to a lower sensitivity during later phases of the life cycle, i.e. to acclimatization. In toxicity tests, non-acclimatized organisms are preferably used.
* Malachite green was used in the experiments to prevent fungal infection of the embryos. In the addendum it is assumed that this treatment may have aggravated the impact of zinc, as a result of an increase in the zinc permeability of the embryos' vitelline membrane (according to the article this effect has been demonstrated at higher malachite green concentrations than those employed in this study). If this effect indeed occurred in the study by Spehar et al. (1976), then it did so only in the test in which the fish were also exposed during the egg phase (resulting in a NOEC of 75 μg/l) and not in the test in which this was not the case (resulting in the NOEC of 26 μg/l).
* In the test that resulted in the actual NOEC of 26 μg/l the average background zinc concentration in the test medium was < 1 μg/l. In the test that yielded the actual NOEC of 75 μg/l the average background zinc concentration in the test medium was 10 μg/l. Both tests were conducted in untreated Lake Superior water; the article gives no explanation for this difference in background concentration. It is noted that there appear to be no differences in performance (as measured bij survival, growth and reproduction) in the < 1 μg/l control group and the 10 μg/l control group. Therefore it is concluded that this study does not indicate zinc deficiency at 1 μg/l.

* Conclusion: The NOEC (26 μg/l) has been correctly derived and justifiably used to derive the MTC.

9. Münzinger, 1991 (*Daphnia magna*; NOEC = 25 μg/l)
The above NOEC (LOEC: 50 μg/l, divided by 2) is based on the test results for the strain that showed the lowest reproductive success of the three strains tested, even in the control situation. The fact that this strain shows a lower reproductive success is no reason to label as less reliable the NOEC for this strain, which was also found to be the most sensitive to zinc. It is emphasized that the NOEC for the other two strains (100 μg/l) has also been used in the ICDZ for deriving the MTC.
* It is unclear what is meant in the addendum by the remark that the NOEC of 25 μg/l is based on 'one single measurement'. Although no duplicate tests were conducted for each strain, the article gives no reason for disregarding this test.
* The background zinc concentration in the test medium was less than 6 μg/l. The actual concentrations (50 μg/l or more) will therefore have been practically equal to the nominal concentrations.
* Conclusion: The NOEC (25 μg/l) has been correctly derived and justifiably used to derive the MTC. In the IA this value was ultimately accepted (although under proviso) as "reliable" and used in derivation of the MTC.

1.2 Terrestrial toxicity studies

In Appendix II of the IA some of the terrestrial toxicity studies used in the ICDZ to derive the MTC for soil have been evaluated on the basis of criteria relating to quality and relevance. These are the microbial studies which yield a (substantially) lower NOEC than most NOEC values for microbial processes. The comments on these studies given in the IA are discussed in detail below.

1. Chang, 1981 (microbial parameter: respiration)
Test result: NOEC = 12 mg/kg (added Zn); standardized NOEC = 9 mg/kg (added Zn)
* It is indeed possible that the microflora of this soil, with an very low background zinc concentration (7 mg/kg), is adapted to a relatively low level of zinc. The fact that most soils contain substantially higher zinc levels does not mean that the test is irrelevant: even in soils with high zinc levels, but with low zinc bioavailability, the microflora can be sensitive to zinc.
*Conclusion: The NOEC has been correctly derived and justifiably used to derive the MTC.

2. Tabatabai, 1977 (microbial parameter: urease activity)
Test results: NOEC = 32 mg/kg (added Zn); standardized NOEC in the 2 soil samples = 27 and 30 mg/kg (added Zn)
* Urease is an enzyme involved in the nitrogen cycle. The enzyme can best be measured under artificial standard conditions in the presence of toluene, a Tris buffer and an excess of urea, for urease activity is simply more difficult to measure under natural conditions. The urease test has been accepted for years as a test for the sensitivity of the soil microflora to metals. It is inconsistent to accept the urease tests of Doelman & Haanstra (see study 4) but not the urease tests of Tabatabai. Conversion of two EC50 values for urease activity obtained in the Doelman & Haanstra study to NOEC values would result in standardized NOEC values of 20 and 25 mg/kg. These values are comparable with the standardized NOEC values of Tabatabai's study.
* Conclusion: The NOEC values have been correctly derived and justifiably used to derive the MTC.

3. Wilson, 1977 (microbial parameter: nitrification)
Test results: NOEC = 10 and 100 mg/kg (added Zn), in Leefield soil and in Decatur and Cecil soils, respectively; standardized NOEC in the three soil types in question: 21, 102 and 182 mg/kg (added Zn)
* In the 'Leefield' and 'Cecil' soil types (with background concentrations of, respectively, 7 and 24 mg/kg) the microflora may have indeed adapted to a low zinc concentration, but this does not imply that the tests in these soils are irrelevant (see also study 1). After addition of 100 mg Zn/kg a very clear, statistically significant inhibition of nitrification was observed in both soils. In the Leefield soil this effect remained observable throughout the 7-week test duration, resulting in a NOEC of 10 mg/kg. In the Cecil soil there was a significant effect in weeks 2 and 3 only; on this basis a NOEC of 100 mg/kg was derived. At coser look a value of 10 mg/kg represents a better estimate of the NOEC for this soil, since the disappearance of the effect is probably an artefact of the test. After three weeks the ammonium supplement was completely converted to nitrate, halting nitrification in the control. Towards the end of the test the zinc-inhibited microflora in the 100 mg Zn/kg group has ultimately nitrified the added ammonium, too. If more ammonium had been added, or if there had been continual addition of ammonium, then nitrification would not have been halted in the control and the zinc-inhibited microflora would probably not have been able to catch up with the control. In nature there is continuous production of ammonium, which can be converted to nitrate by nitrification.
* There is indeed a large difference between the tested zinc concentrations (10, 100 and 1,000 mg/kg), so that the NOEC could not be determined with any degree of accuracy. However, it would be unwise to reject the NOEC values from this study solely for this reason, because a similar test range was used in many of the other studies. Rejection of all

NOEC values having less accuracy because of the limited test range would lead to a substantial loss of data.

* Conclusion: The NOEC values have been correctly derived (although the toxicity of zinc in the Cecil soil was most probably underestimated) and justifiably used to derive the MTC.

4. Doelman, 1983 (various microbial parameters)

* This report reviews a variety of studies (respiration, ammonification, glutamate mineralization and enzymatic tests). The results that have not been used to derive the MTC are effect concentrations obtained in tests that could not be used to derive a NOEC directly. Because of the relatively large number of microbial soil tests with zinc, the ICDZ uses 'direct' NOEC values only, not 'indirect' values derived from effect concentrations (NOEC = calculated EC10 or NOEC = LOEC divided by a given factor, the magnitude of which depends on the percentage effect at the LOEC). At this moment the RIVM is making more use of indirectly derived NOEC values, in order to make maximum use of the available data.

* Conclusion: The results that have not been used are effect concentrations and not NOEC values.

APPENDIX 2: ATMOSPHERIC CORROSION

2.1 Corrosion rate of zinc

General

The atmospheric corrosion of zinc is a complex process which is known to be governed by various different factors. In a review article Porter (1994) gives the following factors of influence:

- duration and frequency of moisture contact
- pH of rainwater
- SO_2 deposition on zinc surface
- chloride content of rainwater
- dirt
- surface orientation
- duration of atmospheric contact.

Because of the complexity of the corrosion process, Porter (1994) gives merely guideline values rather than generally valid formulae. His review shows that not one of the variables has been systematically studied, that is by varying only that parameter while keeping the others constant. Moreover, a variety of different methods are used to measure corrosion (weight loss, layer thickness, collection and analysis of rainwater), which maybe relevant for interpretation of the results. For this reason the various publications on zinc corrosion are difficult to compare.

Various literature studies, for example TAUW (1987) and Haskoning (1990), indicate that the corrosion rate of zinc (and hot-dip galvanized steel) lies in the range of 7 to 70 $g/m^2/year$, with a subdivision according to environment (rural, urban, industrial and coastal) being given in most cases. The corrosion rate is lowest in rural areas and highest in industrial areas. Lower and higher values are reported incidentally.

Measurements in the Netherlands

For the Netherlands only two series of zinc corrosion measurements in different locations (Lanting & Moree, 1984: period '77-'81; Knotkova et al., 1995: period '87-'93) are available. In addition, measurements were performed in the city of Arnhem in the period '90-'93 (Orzessek & Van Tilborg, 1995). The three studies refer to measurements under controlled conditions, performed in open atmosphere.

Lanting & Moree, 1984

This study gives results of weight loss measurements of four locations in the period '77-'81. Weight loss during three months was measured followed by extrapolation to one-year weight loss by use of the model function $R=ct^{0.8}$ (with R the corrosion rate, c a constant and t being time). The results for four years are available, yielding as average for the period '77-'81:

Den Helder	(sea)	33.6±1.8 g/m^2/y
Delft	(urban)	15.2±0.9 g/m^2/y
Schiedam	(urban)	16.4±0.8 g/m^2/y
Wezep	(rural)	11.4±0.4 g/m^2/y

Combination of measurements of Delft with those of Schiedam yields as average for urban locations: 15.7±1.1 g/m^2/y.

NOTE: The given accuracy is an estimate by the authors based on a statistical analysis of the distribution of the one-year values.

UN/ECE study (Knotkova et al, 1995, additional data by Hollander, 1996)

In this study the corrosion loss in 36 locations throughout Europe was measured, during several time intervals in the period '87-'93. The values for the four locations in The Netherland are:

	location	87/89	87/91	90/91	92/93	all values: g/m^2/year
Vlaardingen	urban	13.0	9.3	11.3	10.6	average : 11.1±1.5
Eibergen	rural	6.3	5.5	8.1	7.8	average rural locations: 8.7±1.8
Vredepeel	rural	9.2	7.5	9.0	11.0	
Wijnandsrade	rural	10.0	7.9	10.2	11.3	

Strictly speaking the results of Lanting and Moree (1984) can not easily be compared with the results of the UN/ECE studies because of the different methodologies used: three-months weight loss extrapolated to a one-year weight loss *versus* weight loss measured over two-year or four-year intervals. So, when comparing the results of the two studies to make an analysis of the difference in corrosion rate in the period '80-'90 care has to be taken in drawing conclusions.

However, the problem of different methodologies used is due to arise when any set of corrosion rate measurements are to be compared. Except for the UN/ECE study for a smaller period of time, not any single study has had the objective of analysing the time dependence of the corrosion rate over long time intervals.

Orzessek & Van Tilborg, 1995; additional data by Van Tilborg, 1996
This study gives the result of corrosion measurements performed in Arnhem in the period '90-'93. The average value reported on beforehand, 7±2 g/m^2/year (Orzessek & Van Tilborg, 1995), was later corrected to 9.3 g/m^2/year because of the dependence on the time of exposition (Van Tilborg, 1986).

Dependence on atmospheric SO2 concentration

Recent examples of empirically established relationships between the zinc corrosion rate and the atmospheric SO_2 concentration are:

- *Corrosion rate (g/m^2/year) = [2.1 + 0,28*SO_2 (μg/m^3)]*
  (from Kucera, 1990, published as: Corrosion rate (μm/year) = [0.29 + 0.039*SO2], cited in the Industry addendum);
- *Corrosion rate (g/m^2/year) = [4,9 + 0,101*SO2 (μg/m^3)]*
  (from Hollander, 1996; based on measurements in the period 1987-1991).

The basic corrosion rate according to the equation as given by Hollander (4.9 g/m^2/year), is within the range of 4 to 6 g/m^2/year that is based on equations given by a number of other authors[19]. The basic value according to the equation given by Kucera (2.1 g/m^2/year) is relatively low compared to the other values. The current environmental policy in The Netherlands aims at an average atmospheric SO_2 concentration of 3 μg/m^3 in the year 2010; in 1985 the average concentration was around 15 μg/m^3 (Coppoolse et al., 1993).

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[19] *Corrosion rate (g/m^2/year) = [4.6 + 0.34 Cl^- + 0.2 SO_2]*
Cl^- = mg/l (in deposition); SO_2 = μg/m^3. The equation is based on corrosion measurements in The Netherlands in the period 1977-1981 (Boers & Tiemens, 1984, cited in Annema, 1995 and in Hollander, 1996).

Corrosion rate (g/m^2/year) = [6.05 + 0.22 SO_2]
SO_2 = μg/m^3. The equation was first published in 1982 (NAPAP, 1990, cited in Annema, 1995).

Corrosion rate (g/m^2/year) = [3.8 + 0.16 SO_2 + 0.08 Cl^-]
SO_2 = μg/m^3; Cl^- = mg/m^2/day (deposition).
From: Corrosion rate (μg/year) = [0.53 + 0,023 SO_2 + 0.011 Cl^-], first published in 1987 (NAPAP, 1990, cited in Annema, 1995).

2.2 Corrosion-related zinc load in sewage sludge

Since 1980 the heavy-metal content of each batch of sewage sludge leaving Dutch sewage treatment plants has been measured. Since there are some 470 sewage treatment plants in the Netherlands, from each of which about 4 batches of sludge are removed each year on average, a good impression is obtained of the total quantity of zinc ending up in sewage sludge. In its Environmental Statistics CBS publishes an annual review of these data. The following table summarizes the data for a 6-year period ending 1993 (most recent information available):

year	**zinc load in sludge (tonnes/year)**
1988	359
1989	384
1990	358
1991	337
1992	361
1993	366
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average	**361 ± 15**

By subtracting the contribution from all known sources (households, industry, traffic) from this load, the sludge zinc load due to corrosion can be determined.

household grey-water sewerage

In a study carried out by STORA in 1984 (STORA, 1985) the composition of household grey-water sewerage was measured in seven residential estates spread over the Netherlands. (Grey-water sewerage contains no rainwater run-off and consequently no corrosion products from gutters, roofing or street furniture.) The study yields an emission factor of 8.1 g/inhabitant/year. This value is in good agreement with the estimate of De Waal Malefijt (1982), who calculated a value of 8.9 g/inhabitant/year on the basis of literature values for foodstuffs, composition of tapwater and piping corrosion. Based on a national population of 15.2 million in 1993, a mass flow percentage of 96% of the household effluent ending up in water treatment plant (Coppoolse et al., 1993) and 70% sewage plant removal efficiency (CBS, 1994), this means that 83 tonnes of zinc from household grey-water sewerage end up in sewage sludge each year.

industry

According to Coppoolse et al. (1993), industrial discharges to the sewer totalled 24 tonnes in 1993. This value is based on inventories of industrial emissions. Of this figure, 16 tonnes end up in sewage sludge.

road traffic run-off

For this item Coppoolse et al. (1993) give a value of 9 tonnes/year. This value is based on measurements on run-off in 1989, and includes tyre wear, exhaust gas and atmospheric deposition. Of this figure, 6 tonnes end up in sewage sludge.

	gross load to sewer (tonnes/year)	**% of water flow to sewage water treatment***	**load to sludge (tonnes/year)**
households ('grey water')	123	96	83
industry	24	96	16
run-off	11	76	6
SUBTOTAL			105±32**
TOTAL IN SLUDGE			361±15
ALLOCATED TO CORROSION			**256±36**

* Percentage of input flow into the sewerage system that enters the sewage plant. Deviations from 100% occur because of malfunctioning sewers, presence of stormwater sewers and sewer overflows.

** Accuracy of contributing factors estimated at 30%

From these data it is calculated that (in 1993) 256 tonnes of zinc ended up in sewage sludge as a result of the corrosion of zinc gutters, roofing and galvanized street furniture. Because of the reliability of the data on sludge composition and the relatively limited corrections for known sources, this value may be considered reliable. This is expressed in the estimated accuracy of 36 tonnes/year, i.e. 14% of the absolute value. In principle, the value of ± 260 tonnes/year can be considered an upper estimate as contributions of possible unknown source would yield lower values. However, no such sources can be conceived of at present.

From the given value it can be concluded that a load of approximately 480 tonnes/year of corrosion products flushes into the sewerage system in The Netherlands.