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SCIENTIFIC / TECHNICAL REPORT submitted to EFSA

Pre-Assessment of Environmental Impact of Zinc and Copper Used in Animal Nutrition[1]

Prepared by Sara C Monteiro, Steve Lofts, Alistair B A Boxall

Abstract

Copper and zinc are routinely used as additives in feed for livestock and aquaculture farming. During their use as feed additives, it is inevitable that Cu and Zn will be released to the environment. This project therefore assessed the environmental impact of Cu and Zn arising from use as additives in feed for livestock and aquaculture animals.

The environmental risks of Cu and Zn arising from aquaculture were assessed using simple exposure models recommended by EFSA. Predicted concentrations were below predicted no effect concentrations (PNEC), indicating that the use of both metals in feed additives for fish poses an acceptable risk to the environment where these types of facility exist.

A more complex modelling approach was used for assessing the risks of inputs of Cu and Zn from livestock treatments using the Intermediate Dynamic Model for Metals and soil/agriculture and water chemistry scenarios relevant for a range of European Member States. Overall, the livestock evaluations indicated that environmental risks for Cu and Zn are acceptable at the current time but in the future risks could occur in some systems. The systems most vulnerable to metal input in manure were acid sandy soils. The distribution of these scenarios within Europe is largely in Flanders, the Netherlands, northwestern Germany and Denmark. There is a clear need to better establish whether such soils are as sensitive to metal inputs as is predicted here. Since problems of high metal concentrations in drainflow and runoff, once established, would be difficult to remediate, it is important to proactively assess soil sensitivity before setting policy on manure application.

[1] **NP/FEEDAP/2008/01. Accepted for Publication on 26th October 2010**

Summary

Copper and zinc are routinely used as additives in feed for livestock and aquaculture farming. During their use as feed additives, it is inevitable that Cu and Zn will be released to the environment. Under Regulation (EC) 1831/3003 (EC, 2003), in order to protect human health, animal health and the environment, feed additives should undergo a safety assessment through a Community procedure before being placed on the market, used or processed within the Community. This project therefore assessed the environmental impact of Cu and Zn arising from use as additives in feed for livestock and aquaculture animals.

The environmental risks of Cu and Zn arising from aquaculture were assessed using simple exposure models recommended by EFSA. Concentrations of Cu and Zn in marine sediments, arising from the use of feed additives in sea cage aquaculture, were 21.3 mg/kg and 182 mg/kg respectively. Concentrations, estimated for different fish types farmed in raceways/ponds/tanks and recirculation systems, ranged from 12.1 – 12.5 µg/l for Zn and 1.13 – 2.96 µg/l for Cu. For all fish species in the cage, raceway/pond/tank and recirculating systems, predicted concentrations were below predicted no effect concentrations (PNEC), indicating that the use of both metals in feed additives for fish poses an acceptable risk to the environment where these types of facility exist. It is important to recognise that exposure concentrations used for this assessment are likely to be highly conservative.

A more complex modelling approach was used for assessing the risks of inputs of Cu and Zn from livestock treatments. The assessment utilised the Intermediate Dynamic Model for Metals (IDMM) and soil/agriculture and water chemistry scenarios that were selected to represent the agri-environment conditions that are likely to be experienced across European Member States.

For copper, a risk of exceeding the soil PNEC was only found for the long term exposure simulations (50 years) for manure derived from piglet rearing, in seven scenarios. In only two of these scenarios is swine rearing locally significant. Risks of exceeding the soil zinc PNEC were predicted at fewer sites than for copper, but the number of manure types whose continuous application presents a risk of exceedence was larger. This is particularly so in the most sensitive scenario where the application of most manure types for 50 years was predicted to result in PNEC exceedence. This is largely due to the ecological sensitivity of this acidic sandy soil to zinc accumulation, as indicated by the low PNEC of 31 mg Zn/kg soil.

Risks of exceeding the freshwater PNECs were fewer than those for soil, particularly for copper where only one potential exceedence was identified. This is due to the relatively strong retention of copper by soils, resulting in only small predicted increases in average surface water concentrations in response to manure application. In contrast, leaching of zinc in drainage and runoff was more pronounced in response to increasing manure application. In the extreme case of an acidic sandy soil, the surface water

PNEC was predicted to be exceeded after 10 years by the continuous application of any manure type. Apart from this scenario, zinc concentrations in surface waters tended to be more sensitive to application rate in the runoff scenarios rather than the drainage scenarios, although this does not necessarily lead to potential risks within the considered timeframe.

Overall, the livestock evaluations indicated that environmental risks are acceptable at the current time but in the future risks could occur in some systems. The systems most vulnerable to metal input in manure were clearly acid sandy soils, represented in the scenarios. The distribution of these scenarios within Europe is largely in Flanders, the Netherlands, northwestern Germany and Denmark. There is a clear need to better establish whether such soils are as sensitive to metal inputs as is predicted here, for example by field surveys of copper and zinc concentrations in drainflow from fields with known histories of metal input rates. Since problems of high metal concentrations in drainflow and runoff, once established, would be difficult to remediate, it is important to proactively assess soil sensitivity before setting policy on manure application.

Key words: copper, zinc, feed additives, environmental risk, livestock, aquaculture

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Background

Copper and zinc are routinely used as additives in feed for livestock and aquaculture farming. Copper is an essential trace element that plays a vital role in the physiology of animals e.g foetal growth and early post-natal development, haemoglobin synthesis, connective tissue maturation, nerve function and bone development, and inflammatory processes. It is involved in different biochemical processes of animal metabolism such as enzyme-coenzyme catalytic reactions. Copper deficiency leads a range of symptoms including depression of growth, anaemia, bowing of the legs, spontaneous fractures, ataxia of newborns, cardiac and vascular disorders and depigmentation, decrease in some organs weight, depressed reproductive performance including egg production. Several investigations have shown that the addition of copper to the diets of pigs increases their growth performance and the positive effect on growth seems to be dependent on a simultaneous increase in feed intake. Zinc is an essential trace element in all living systems from bacteria, plants and animals to humans. Zinc deficiency causes lesions of the skin of pigs and results in poor growth, feathering and skeletal development of poultry. Both copper and zinc were initially authorised for all species under Directive 70/524/EEC concerning additives in feeding stuffs. In 2003, SCAN issued two opinions on the use of elements in feed additives and considered that there may be a risk associated with Cu and Zn. Consequently maximum limits of Cu and Zn in feed additives were reduced (Commission Regulation (EC) N0 1334/2003) these are:

- Cu: pigs = 25 mg/day; bovine and ovine = 25 mg/d; fish = 25 mg/d; others = 25 mg/d
- Zn: milk replacers = 200 mg/d; fish = 200 mg/d; other = 150 mg/d.

During their use as feed additives, it is inevitable that Cu and Zn will be released to the environment. When used in livestock animals, both metals will be excreted by the animal in the faeces and will enter the soil environment when the faeces are applied, as a fertiliser to land, in the form of manure, slurry or litter. The Cu and Zn may then be transported from the soil to adjacent water bodies. When used in aquaculture, the metals may be released directly to the broader aquatic environment around an aquaculture facility or be taken up by fish and then excreted into the environment.

Under EU Regulation 1831/3003 (EC, 2003), in order to protect human health, animal health and the environment, feed additives should undergo a safety assessment through a Community procedure before being placed on the market, used or processed within the Community. EFSA have therefore developed a Technical Guidance for the assessment of the environmental impacts of feed additives (EFSA, 2008). This guideline proposes data requirements, models and approaches that can be used to assess the environmental risk of substances used in feed additives.

For Cu and Zn, risk assessments have also been done on the environmental risks arising from a wide range of uses (not just feed additives). These reports provide valuable information on the fate and effects of both Cu and Zn in natural environments.

Terms of reference

To prepare a report that:

Determines the contribution of Cu and Zn concentrations in the environment (based on updated information and models), due to the use of those metals at the current levels and forms used in animal feeds. The study should provide sufficient information on predicted exposure levels to enable assessment if current limits of Cu and Zn are safe to the environment.

Provides advice on the potential benefits to the environment if a reduction of the maximum permissible level of Cu and Zn in animal feed could be envisaged.

Acknowledgements

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Introduction and Objectives

INTRODUCTION

Copper and zinc are routinely used as additives in feed for livestock and aquaculture farming. Copper is an essential trace element that plays a vital role in the physiology of animals e.g foetal growth and early post-natal development, haemoglobin synthesis, connective tissue maturation, nerve function and bone development, and inflammatory processes. It is involved in different biochemical processes of animal metabolism such as enzyme-coenzyme catalytic reactions. Copper deficiency leads a range of symptoms including depression of growth, anaemia, bowing of the legs, spontaneous fractures, ataxia of newborns, cardiac and vascular disorders and depigmentation, decrease in some organs weight, depressed reproductive performance including egg production. Several investigations have shown that the addition of copper to the diets of pigs increases their growth performance and the positive effect on growth seems to be dependent on a simultaneous increase in feed intake. Zinc is an essential trace element in all living systems from bacteria, plants and animals to humans. Zinc deficiency causes lesions of the skin of pigs and results in poor growth, feathering and skeletal development of poultry. Both copper and zinc were initially authorised for all species under Directive 70/524/EEC concerning additives in feeding stuffs. In 2003, SCAN issued two opinions on the use of elements in feed additives and considered that there may be a risk associated with Cu and Zn. Consequently maximum limits of Cu and Zn in feed additives were reduced (Commission Regulation (EC) N0 1334/2003) these are:

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Under EU Regulation 1831/3003 (EC, 2003), in order to protect human health, animal health and the environment, feed additives should undergo a safety assessment through a Community procedure before being placed on the market, used or processed within the Community. EFSA have therefore developed a Technical Guidance for the assessment of the environmental impacts of feed additives (EFSA, 2008). This guideline proposes data requirements, models and approaches that can be used to assess the environmental risk of substances used in feed additives.

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OBJECTIVES

The overall aim of this project was to assess the environmental impact of Cu and Zn arising from use as additives in feed for livestock and aquaculture animals. The specific objectives were to:

1) Determine the contribution of feed additives to the concentrations of copper and zinc in the terrestrial and aquatic environments;

2) Provide sufficient information on predicted exposure levels to enable an assessment of whether current limits of Cu and Zn in feed additives are safe to the environment

3) Provide advice on the potential benefits to the environment if a reduction of the maximum permissible level of Cu and Zn in feed could be envisaged.

This report describes the pre-risk assessment for Cu and Zn used as feed additives in aquaculture and terrestrial livestock. The assessment has drawn upon a number of key reports:

- SCAN opinions on copper and zinc

- EU Risk Assessment Reports for zinc metal, zinc oxide, zinc chloride, zinc distearate, zinc sulphate and trizinc bis(orthophosphate)

- A voluntary risk assessment performed by the European Copper Institute (ECI) for copper and copper compounds on the EU working list: Cu, CuO, Cu_2O, $CuSO_4$, $Cu_2Cl(HO)_3$

- Studies into the long-term leaching and accumulation of Cu and Zn in Dutch agricultural soils

- SCHER Opinion on the RARs for Zn

A critical review of the Cu and Zn Risk Assessment Reports (RARs) is provided in the following Annexes:

Annex 1: Monteiro, S. et al (2010) Review of risk assessment reports for copper and copper compounds.

Annex 2: Monteiro, S. et al (2010) Review of risk assessment reports for zinc and its compounds

Risk assessment section

1. Assessment of ecological risks due to feed–derived copper and zinc in from aquaculture in the EU

1.1. Background

A range of practices is used to farm fish, depending on the species and the life stage of the fish. Approaches include cages, ponds, tanks and raceways in both freshwater and seawater. EFSA have proposed a series of simple models for estimating concentrations of feed additive in either water or sediment arising from aquaculture facilities (EFSA, 2008). The algorithms consider exposure arising from a) sea cage facilities; and b) raceways/ponds/tanks and recirculating systems. An outline of the models is provided below.

1.1.1. Sea cages

For estimation of initial PECs, it is assumed that all feed additives are excreted in the faeces and that the faecal material is deposited below the cages. It is therefore most appropriate to assess risks to sediment-dwelling organisms. The PEC is calculated using equations 1 and 2.

$$PEC_{faeces} = C_{additive}.CF \qquad \text{Equation 1}$$

Where: PEC_{faeces} = concentration in the faeces (mg/kg); $C_{additive}$ = concentration of the additive in the feed (mg/kg); ; and CF = conversion factor (kg feed to kg carbon in faeces)

$$PEC_{sediment} = \frac{PEC_{faeces}.k_{dep}.T_{production}}{RHO_{sediment}.Depth_{sediment}} \qquad \text{Equation 2}$$

Where: $PEC_{sediment}$ = concentration of the feed additive in the sediment; Kdep = maximum deposition rate of faeces (d^{-1}); $T_{production}$ = number of production days (d); RHO_{sed} = bulk density of the sediment (kg carbon/m^2/d); $Depth_{sediment}$ = mixing depth of sediment (m).

Default parameters for the model are provided in Table 1

Table 1. Default parameters used in the sea cage aquaculture exposure model

Parameter	Value
CF	15.1
K_{dep}	0.01
$T_{production}$	365
RHO_{sed}	1300
$Depth_{sediment}$	0.2

1.1.2. Raceway/ponds/tanks/recirculation systems

For these systems, the worst case assumption is that the complete dose will be excreted in the water phase. The concentration in surface water is estimated using Equation 2.3.

$$PEC_{sw} = C_{additive}.FR.(1 - F_{ret})/Flow.DF \quad \text{Equation 3}$$

Where PECsw = predicted environmental concentration in surface water; FR = Feed ration (kg feed/kg fish/d); Flow = flow of water through the system (l/kg fish/d); Fret = fraction of retention in the system. Default values for these parameters have been proposed by EFSA (EFSA, 2008) and these are summarised in Table 2.

Table 2. Default parameters for exposure assessment using the raceway/pond/tank/recirculation tank model

Species	FR	Flow	DF	Fret
Salmon	0.01	1400	10	0
Rainbow trout	0.02	1400	10	0
Seabass/seabream	0.01	400	10	0
Turbot	0.01	720	10	0

1.2. Risk assessment

1.2.1. Estimation of exposure concentrations

For copper, the values of copper concentration in feed authorised under Commission Regulation (EC) No 1334/2003 concerning additives in feeding stuffs was used i.e. for Cu 25 mg/kg feed and for Zn 200 mg/kg.

Using Equations 1 and 2, the concentrations of Cu and Zn in marine sediments, arising from the use of feed additives in sea cage aquaculture, are 5.2 mg/kg and 42.4 mg/kg respectively.

Using Equation 3, the surface concentrations, estimated for different fish types that are farmed in raceways/ponds/tanks and recirculation systems, range from 140 – 500 ng/l for Zn and 18 - 64 ng/l for Cu (Table 3)

Table 3 Estimate concentrations of Zn and Cu in surface waters arising from aquaculture treatments

Species	Concentration Zn (mg/l)	Concentration Cu (mg/l)
Salmon	0.00014	1.8×10^{-5}
Rainbow trout	0.00029	3.57×10^{-5}
Seabass/seabream	0.00050	6.4×10^{-5}
Turbot	0.00028	3.4×10^{-5}

It is important to recognise that these concentrations only consider inputs from the use of Cu and Zn in feed additives. Background Cu and Zn concentrations will however exist in natural systems so it is important that these are considered when assessing potential exposure. The EFSA Opinion Documents provide an indication of ambient concentrations of Cu and Zn in different systems so these were used to refine the exposure calculations.

For sediments, the previous RAR Reports have used background concentrations of 140 mg/kg and 16.1 mg/kg for Zn and Cu respectively. This gives total concentrations of 182 mg kg for Zn and 21,3 mg/kg for Cu.

Some experimental data are available for Cu and Zn in sediments from monitoring studies of aquaculture facilities. In a study in Canada (Chou et al., 2003), concentrations of Cu and Zn in sediment under the cages were 21-55 mg/kg and 72-353 mg/kg respectively. Samples taken 50 m away from the cages had lower Cu and Zn concentrations. Much of the input of Cu was attributed to the use of the metal in antifouling paints rather than as a feed additive. In a study of aquaculture facilities in the San Pedro River in Cadiz Bay in Spain, concentrations of Cu and Zn in sediment were found to be 22.6 and 60.7 mg/kg respectively (Mendiguchia et al., 2006). In this particular study, the only input of the metals was from use in feed. These concentrations are in close agreement with our predicted concentrations using the EFSA models, giving a degree of confidence in the predictions.

For surface waters, the background concentration of Zn is reported to range from 2.5 – 12 µg/l so a conservative value of 12 was used. Average background concentrations of Cu in marine and freshwater environments are 2.9 and 1.1 µg/l respectively. Using these values total concentrations were predicted to range from 12.1 – 12.5 µg/l for Zn and 1.13 – 2.96 µg/l for Cu (Table 4).

Table 4 Predicted total concentrations in surface waters around aquaculture facilities

Species	Ambient Zn concentration FW/Mar (µg/l)	Ambient Cu concentration FW/Mar (µg/l)	Total Zn concentratio n Fw/Mar (µg/l)	Total Cu concentratio n Fw/Mar (µg/l)
Salmon	12/12	2.9/1.1	12.1	2.92/1.13
Rainbow trout	12/12	2.9/1.1	12.3	2.94/1.14
Seabass/seabream	12/12	2.9/1.1	12.5	2.96/1.16
Turbot	12/12	2.9/1.1	12.3	2.93/1.13

1.2.2. Risk characterisation

In the RARs, predicted no effect concentrations (PNECs) have been proposed for Cu and Zn in sediment and surface waters for both the marine and freshwater environments. These have been derived in different ways: for Cu, the PNECs are based on a total Cu concentration whereas for Zn, the PNECs are based on an added Zn concentration (i.e. the background concentration is removed). Therefore to make the risk assessment comparable, the PNECs for Zn from the RAR reports were corrected by adding the background concentrations used above.

Risk Characterisation Ratios were then calculated from the exposure predictions and the PNECs for Cu and Zn (Tables 5-7). For all fish species in the cage/raceway/pond/tank and recirculating systems, predicted concentrations of Cu and

Zn were below PNECs indicating that the use of both metals in feed additives poses an acceptable risk to the environment. For cage systems, the exposure concentration for Cu was also below the PNEC indicating an acceptable risk. It is important to recognise that the predictions are likely to be 'worst case' as they predict concentrations immediately below the cages and do not consider potential dissipation processes e.g. due to sediment transport. It is also important to recognise that many Member States have control mechanisms for impacts of aquaculture that will further reduce the risks.

Table 5. Risk characterisation ratios for Cu and Zn in sediment arising from cage treatments

	PEC mg/kg	PNEC	RCR
Cu	21.3	338	0.06
Zn	182	189	0.96

Table 6 Predicted total concentrations in surface waters around aquaculture facilities

Species	Total Cu concentration Fw/Mar (µg/l)	PNEC Fw/Mar (µg/l)	RCR FW/Mar
Salmon	2.92/1.13	7.8/2.6	0.37/0.43
Rainbow trout	2.94/1.14	7.8/2.6	0.38/0.44
Seabass/seabream	2.96/1.16	7.8/2.6	0.38/0.45
Turbot	2.93/1.13	7.8/2.6	0.38/0.44

Table 7 Predicted total concentrations in surface waters around aquaculture facilities

Species	Total Zn concentration Fw/Mar (µg/l)	PNEC Fw/Mar (µg/l)	RCR FW/Mar
Salmon	12.1	19	0.64
Rainbow trout	12.3	19	0.65
Seabass/seabream	12.5	19	0.66
Turbot	12.3	19	0.65

2. Assessment of ecological risks due to feed–derived copper and zinc in manure applied to agricultural soils in the EU

2.1. Background

From the standpoint of terrestrial and aquatic, the application of animal manures containing feed–derived copper and zinc to agricultural soils presents two main potential risks:

i) Accumulation of metal within the topsoil to concentrations posing potential toxic risks to soil organisms;

ii) Leaching of metal from soil to surface waters in concentrations posing potential toxic risks to organisms resident in the water column and bottom sediments.

In common with other trace metals, copper and zinc have strong binding affinities for soil solids and thus tend to accumulate within soils. On the other hand, as the pool of accumulated metal increases in size it provides a source of metal for leaching to surface water and deeper soil/groundwater. Leaching can be promoted by ligands in the soil porewater, such as natural organic matter. Thus, long–term accumulation of metals within soils is often accompanied by increases in metal concentrations in drainage waters. Additionally, depending upon site hydrology and drainage, the potential exists for rapid movement of metal from topsoil to surface water in events. Thus the ecological risks of metal application to soils in animal manures are best assessed using a framework that integrates the physicochemical and hydrological processes that cause metals to accumulate in soils and pass to surface waters. The model used here, the Intermediate Dynamic Model for Metals (IDMM), is such a framework.

2.2. Approach

The aims of this work are threefold:

- to determine the contribution of feed additives to the concentrations of copper and zinc in the terrestrial and aquatic environments;
- to provide sufficient information on predicted exposure levels to enable an assessment of whether current limits of copper and zinc in feed additives are safe to the environment;
- provide advice on the potential benefits to the environment if a reduction of the maximum permissible level of Cu and Zn in feed could be envisaged.

These aims will be achieved by consideration of a set of soils representing a range of European agricultural settings. Past inputs of metals from different sources will be estimated. Future inputs of copper and zinc due to manure will be simulated using the IDMM and the results used to estimate Predicted Environmental Concentrations (PECs) for topsoils, surface waters and sediments. Risks will be assessed by comparison of PECs with Predicted No Effect Concentrations (PNECs) for topsoils, surface waters and sediments. The effects of a range of inputs of copper and zinc will be simulated, allowing the influence of reducing current levels of these metals in feed to be assessed.

For this work we have chosen to model the set of soil scenarios described by FOCUS (FOrum for Co-ordination of pesticide fate models and their USe) and a set of scenarios developed for application of the VetCalc simulation tool. The FOCUS scenarios were constructed for the simulation of pesticide behaviour in agricultural soils, while the VetCalc scenarios were designed for the simulation of the behaviour of veterinary medicines.

2.2.1. The Intermediate Dynamic Model for Metals

The IDMM is a dynamic model of intermediate complexity developed to allow calculation of long term metal accumulation in and leaching from the topsoil. The model comprises a single soil layer and runs on an annual timestep. On each timestep, deposited or applied metal, and metal derived from mineral weathering, is added to the pool already present and the metal pool is partitioned between the soil solids and porewater. Metal leaves the soil in drainage water and/or runoff, in either dissolved form (as calculated by soil-solution partitioning) or bound to soil particles eroded into the drainage water. The annual volume of water draining the soil is implicitly replenished from precipitation such that the porewater volume in each horizon remains constant. Partitioning of metal between the porewater and soil solids is dependent upon the porewater pH and the concentrations of dissolved organic matter and other ions present, as well as the soil organic matter concentration. The model computes initial porewater and soil metal concentrations by assuming a balance of all input and output fluxes (steady state). Key model variables, including metal input rates, porewater pH and porewater suspended solids concentration, are specified on an annual basis. A simple representation of the model structure, in terms of metal fluxes, is shown in Figure 1.

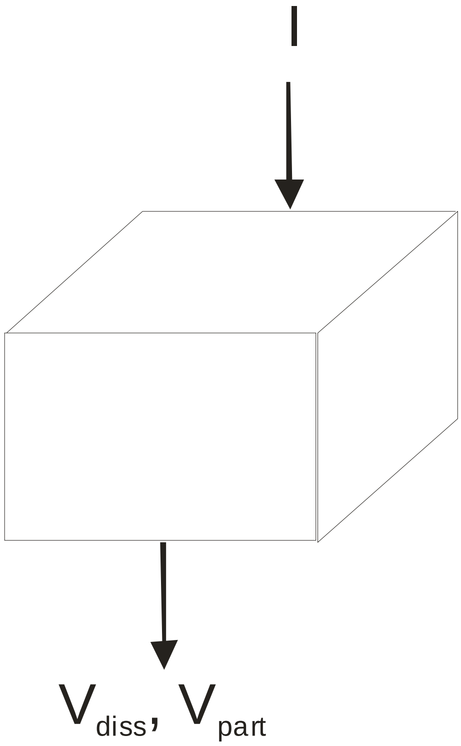

Figure 1. Box model representation of IDMM fluxes. I = metal input flux (e.g. from atmospheric deposition, V = metal output fluxes in drainage (dissolved and on eroded particles).

2.2.2. Application of the IDMM to agricultural soils

The IDMM was developed to simulate metal behaviour in mountainous regions of the UK, where soils typically comprise a thin layer (<50cm) over impermeable bedrock. Lowland agricultural soils present additional features that must be considered in the model:

- a deeper, more complex soil profile;
- potentially a more complex hydrology including loss to groundwater and modification by artificial drainage.

- effects of human intervention such as tilling and the addition of organic matter, e.g. animal manures.

The FOCUS scenarios comprise two types: drainage-dominated soils and runoff-dominated soils. To consider the special features of each of these types, a specific version of the IDMM has been constructed for each.

2.2.2.1. Model for drainage-dominated soil

The setup of the IDMM for a drainage scenario is shown in Figure 2.

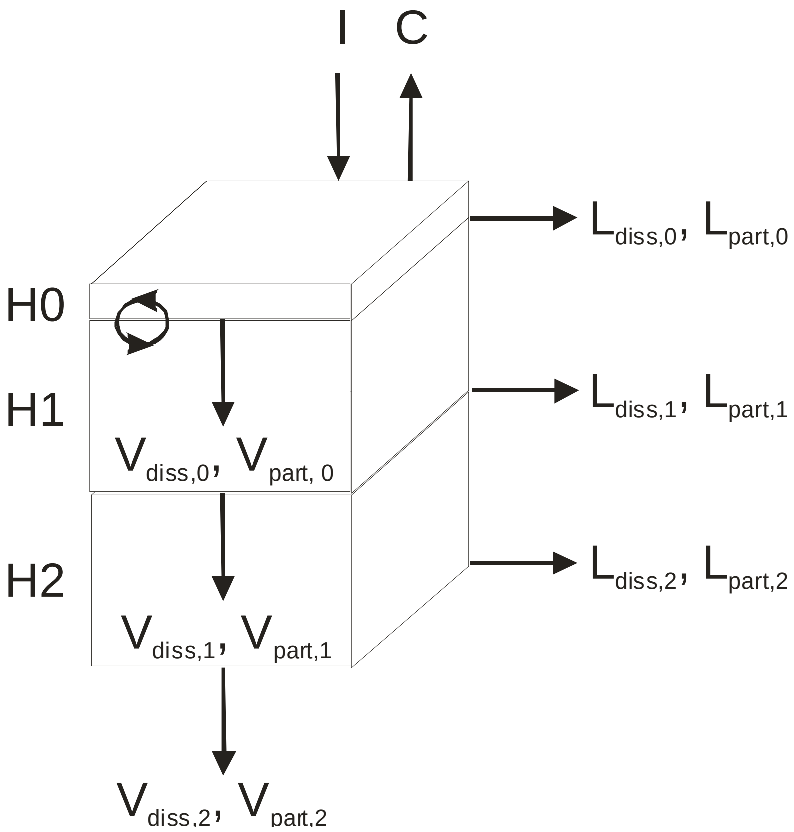

Figure 2. Box model of IDMM structure and metal fluxes when simulating a drainage soil. I = metal inputs, C = metal removal due to cropping, V = metal fluxes (dissolved and on eroded particles) in vertical drainage, L = metal fluxes (dissolved and on eroded particles) in lateral drainage, H0, H1 and H2 are respectively surface soil, topsoil and deep soil layers. The circle and arrows symbol represents mixing of the H0 and H1 layers.

Compared to the original IDMM, the drainage scenario model includes significant modifications:

The soil column is represented by three horizons, H0, H1 and H2, representing surface soil, topsoil and deep soil respectively. The surface soil layer has a depth of 5cm, the topsoil layer has a depth of 25cm and the deep soil layer extends from the bottom of the topsoil layer to the depth of artificial drainage.

Vertical transport of metals (in dissolved and particulate form) from each soil layer to the layer below, and from the deep soil to groundwater, is modelled. Additionally, lateral drainage (also in dissolved and particulate form) from each horizon to surface water is simulated. Thus, for example, it is possible to simulate the transport of suspended particulate matter (and associated metal) to surface waters in surface soil runoff.

The removal of metal from the system by uptake into crop plant and subsequent harvesting can be simulated.

Effects of manure addition on the composition of the surface soil layer are simulated, by considering the volume and composition (organic matter content) of added manure and adjusting the organic matter content of the surface soil layer accordingly. An increase in the organic matter content of the surface soil on addition of manure will increase the capacity of the soil layer to retain metals.

The surface soil and topsoil layers may be periodically mixed, to simulate tillage. In the absence of tillage, manure organic matter (and associated metals) applied to the surface soil may be predicted to accumulate strongly in this layer. Simulating tillage models the mixing of this organic matter and metal down into the topsoil layer.

In practice, the hydrology of the drainage soil scenarios considered here is dominated by vertical movement of water to drain depth, then lateral movement to surface waters via artificial drainage. Water fluxes in surface and topsoil runoff, and percolation fluxes from the base of the deep soil layer to groundwater, are very small in comparison.

2.2.2.2. Model for runoff-dominated soil

The setup of the IDMM for a runoff scenario is shown in Figure 3.

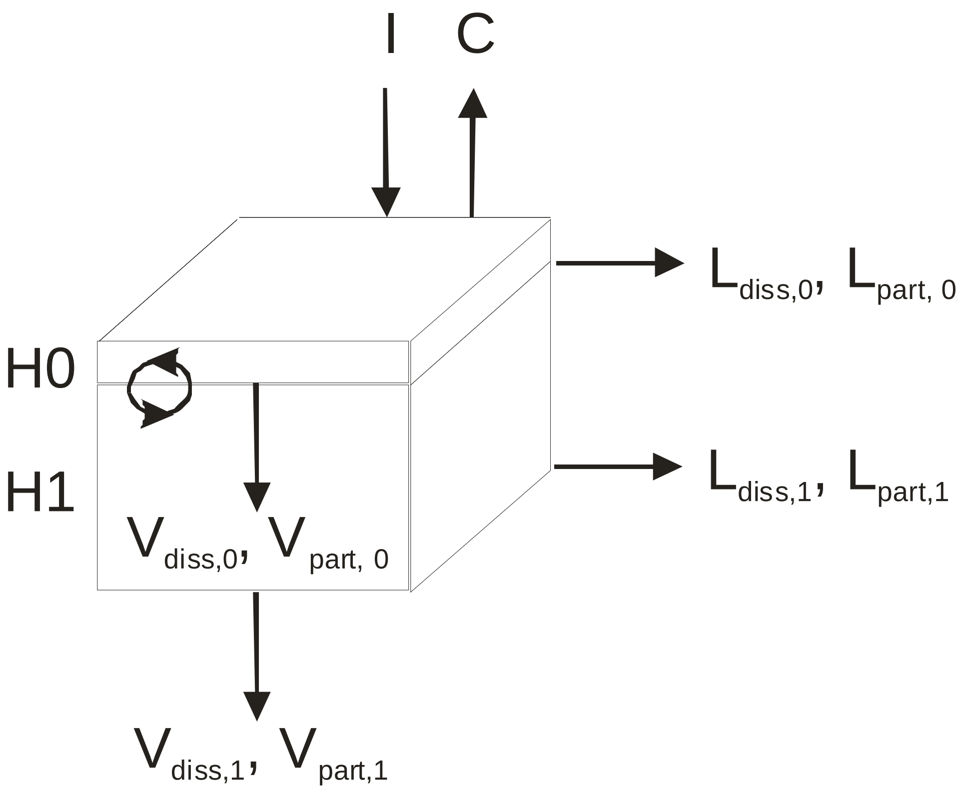

Figure 3. Box model of IDMM structure and metal fluxes when simulating a runoff soil. I = metal inputs, C = metal removal due to cropping, V = metal fluxes (dissolved and on eroded particles) in vertical drainage, L = metal fluxes (dissolved and on eroded particles) in lateral drainage, H0 and H1 are respectively surface soil and topsoil layers. The circle and arrows symbol represents mixing of the H0 and H1 layers.

The structure of the model is the same as that for a drainage soil, except for the absence of the deep soil layer. Water draining vertically from the topsoil layer is assumed to move directly to groundwater. As with the drainage soil model, it is possible to simulate the transport of suspended particulate matter (and associated metal) to surface waters in surface soil runoff.

2.2.2.3. Model for soil accumulation only

The VetCalc scenarios do not comprise sufficient data to allow modeling using either of the two previously described frameworks, thus only metal accumulation and leaching are considered in these scenarios. The version of the model used is shown in Figure 4.

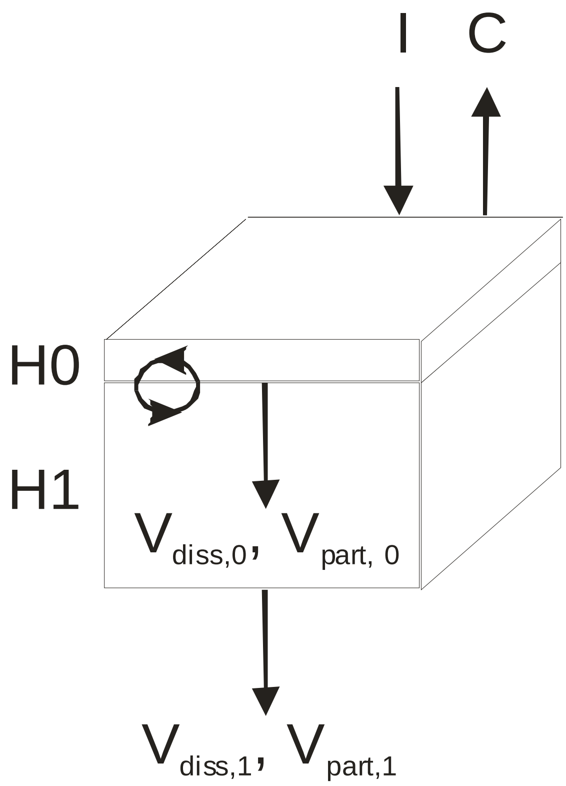

Figure 4. Box model of IDMM structure and metal fluxes when simulating a VetCalc scenario. I = metal inputs, C = metal removal due to cropping, V = metal fluxes (dissolved and on eroded particles) in drainage, H0 and H1 are respectively surface soil and topsoil layers. The circle and arrows symbol represents mixing of the H0 and H1 layers.

The model is similar to that used for the FOCUS runoff soils. All drainage is assumed to be vertical. Some lateral runoff may occur, depending upon the site hydrology, but since we seek to model only soil accumulation, only the total loss of metal in drainage and runoff is important.

2.2.3. Model features

2.2.3.1. Hydrology

The IDMM takes a simple approach to soil hydrology, consistent with the aim of simulating long term metal dynamics in soils. Each soil layer has a fixed water content. Annual vertical fluxes of water within the soil profile, and lateral fluxes to surface water, must be specified. On each annual timestep, the input water volume (precipitation and irrigation less evapotranspiration for the surface soil layer, drainage from the upper horizon for the upper and lower soil layers) is considered to mix completely with the soil prior to vertical drainage to a lower soil layer or to groundwater, or lateral runoff/drainage to surface water. The metal flux associated with vertical drainage to groundwater is considered lost from the system. Eroded soil particles may be transported in porewater, drainage and runoff. Metal pools and metal chemistry

We now describe the processes controlling metal retention and loss within each soil layer. Within each layer, the pool of metal present partitions between five phases:

1. dissolved in porewater;
2. bound to (eroded) solids eroded into runoff and porewater;
3. bound to the soil solids;
4. aged (occluded) within solids eroded into runoff and porewater;
5. aged within the soil solids.

The first three phases comprise the reactive pool of metal in the soil while the final two comprise the aged pool. Metal in the reactive pool is considered to be at equilibrium with respect to its speciation in the porewater and its partitioning between porewater and soil surfaces; thus the total metal in the reactive pool is an important control on the porewater concentrations and the leaching/drainage fluxes. The aged pool acts as a sink for a portion of the input metal, reducing the reactive pool size. Transfer of metal between the reactive and aged pools is modelled using reversible kinetics; thus aged metal may re-enter the reactive pool if conditions favour it.

Equilibrium partitioning of the reactive metal between the porewater and soil solids is dealt with by a two–step process. Firstly, bound metal is calculated from the free metal ion concentration in solution using an empirical expression:

$$\log K_f = \log(Q_M/[M_{free}]^n) = a + b.pH_{ss} + c.\log(OM)$$

where K_f is a Freundlich isotherm term, Q_M is the pool of metal bound to soil surfaces (mol/g dry soil), $[M_{free}]$ is the concentration of the free metal ion (M), pH_{ss} is the soil solution pH and OM is the organic matter content of the soil (% dry soil mass). The terms n, a, b, and c are fitted metal–specific parameters. The expression has been parameterised using datasets on free ion-reactive metal partitioning in soils of the UK. Parameters for copper and zinc are shown in Table 8.

The dissolved metal in soil solution is calculated from the free ion concentration using

Table 8. Parameters for calculation of the partitioning of copper and zinc between the free ion and reactive pool, as used in the IDMM. Values in brackets are standard error of parameters. See text for the meaning of the parameters.

	a	*b*	*c*	*n*
Cu	-4.59	1.14	0.53	1.00
Zn	-4.01	0.41	1.17	1.00

the WHAM6 chemical speciation model (Tipping 1994 and 1998). To calculate the dissolved metal WHAM requires porewater concentrations of binding ligands, major solution ions and concentrations of ions that compete with the metals for binding to ligands. The major binding ligands for metals in soil porewaters are dissolved organics, which are represented in WHAM6 by fulvic acid. Concentrations of fulvic acid are calculated from dissolved organic carbon (DOC) concentrations by assuming them to comprise 50% carbon and that DOC binds as if composed of 65% fulvic acid and 35% inert material (e.g. Bryan et al., 2002). This "binding activity" of DOC has been derived from experimental studies on the binding of copper to DOC under laboratory conditions. Concentrations of the major ions sodium, calcium, chloride, nitrate and sulphate are found by assuming default concentrations and then adjusting them to balance the electrical charge in the porewater. Free ion activities of Al and Fe(III), which are important competitors for metal binding in porewater, are estimated using an empirical equation for Al (Tipping 2005) and for Fe(III) by assuming equilibrium with solid amorphous $Fe(OH)_3$.

The IDMM does not explicitly consider the production and loss of DOC within the soil column; instead, concentrations of DOC in the porewater within each soil layer are explicitly specified. Research into the factors that influence the production and transport of DOC in soils has focused largely on non–agricultural systems and knowledge of DOC behaviour under agriculture is less well developed. Three alternative methods of specifying the DOC concentration were evaluated:

- a site-independent concentration of DOC in the porewater draining or leaching from each horizon.

- a site–independent flux of DOC from the surface and topsoil layers, coupled with site–independent proportional removal in the deep soil (for the drainage soils).
- calculating DOC as a function of soil layer properties, for example by using the empirical equation derived by Römkens and co–workers, expressing porewater DOC as a function of soil pH, % organic matter content and soil:solution (SS) ratio.

In practice, given the relative lack of knowledge regarding DOC concentrations and fluxes under agricultural soils, it was decided to use the simplest option and fix DOC concentrations in porewaters. This approach is taken in the calculation of critical loads of trace metals to soils where a value of 10 mg C/l is recommended for arable soils (0-30cm depth); this value was used for all surface and topsoils. In deep soil layers a value of 5 mgC/l was used.

2.2.3.2. Metal aging

Within each soil layer metal can enter and leave the aged pool. The term 'aging' refers to the processes that over time cause the amount of metal in the reactive pool to decline as a result of metal ion occlusion and fixation. Although the detailed processes by which aging occurs are not well known, the phenomenon is well known from laboratory studies where the decline in the soil reactive pool over time, following soil spiking with soluble metal, has been followed (e.g. Ma et al., 2006, Crout et al., 2006). For copper and zinc, literature data exist showing the declines in the reactive pool over reasonable time periods (1–3 years) following soil spiking. For copper, Ma et al. (2006) measured aging for 360 days in a set of 19 European soils of varying chemical composition (pH_{CaCl2} 2.98-7.52, clay 5–51%, organic carbon 0.41–23.32%, calcium carbonate 0–47.4%). For zinc, Crout et al. (2006) measured aging for 813 days in a set of 23 UK soils (pH_{H2O} 3.0–7.2, soil C 1-7.06%). The data were modelled using a single phase reversible kinetic scheme similar to that used by Crout et al. (2006). This model comprises the following equation:

$$d[M_{aged}]/dt = k_1.[M_{reactive}].[S_{aging}] - k_{-1}.[M_{aged}]$$

where $[M_{aged}]$ and $[M_{reactive}]$ are the pools of aged and reactive metal (mol/g dry soil), S_{aging} is the available aging capacity (mol/g dry soil) and k_1 and k_{-1} are the forward and backward kinetic constants, respectively. The total aging capacity ($[S_{aging}]_T = [S_{aging}] + \Sigma[M_{aged}]$) was fixed to 10^{-4} mol/g; in practice this was not important as the amounts of aged metal were a small fraction of this total. Values of k_1 and k_{-1} were fitted for each soil and their variability with soil parameters (e.g. porewater pH, % soil organic matter) was investigated. In the cases of both copper and zinc the most important soil parameter relating to the k values was porewater pH (pH_{ss}); thus the model was reformulated forcing k_{-1} to vary with pH_{ss}:

For copper: $\log k_1 = 2.0$ and $\log k_{-1} = -1.75-0.10(e^{pHss - 7.0})$;

For zinc: $\log k_1 = 1.5$ and $\log k_{-1} = -0.41-0.36.pH_{ss}$

2.2.3.3. Metal weathering

Knowledge of metal weathering rates in soils is sparse. For this work, weathering rates were calculated using a recommended method (de Vries et al., 2005); however, it should be borne in mind that the resulting estimates of weathering rates are rather uncertain. Weathering of mineral metal into the reactive pool was calculated using the method given by de Vries et al.(2005) where the relative weathering rates of metals and base cations are assumed proportional to their relative concentrations in the soil parent material. Weathering rates of base cations were calculated using the soil type–texture method given by De Vries and co–workers (2005). Concentrations of copper, zinc and base cations in parent materials were approximated by simple spatial interpolation of total topsoil and subsoil concentrations from the Forum of European Geochemical Societies (FOREGS) geochemical baseline database to give 'local mean' concentrations.

2.2.3.4. Soil erosion and metal transport

Erosion of soil during rain events is potentially a key pathway for metal transfer to surface waters. There is evidence in the literature of size-selective mobilisation of small soil particles enriched in organic matter during precipitation events (e.g. Wu et al., 2004); it has also been shown (Quinton and Catt, 2007) that such particles may be enriched in metals relative to the parent soil, as a result of their higher organic matter content. It is feasible that this flux of particulate metal from the soil is significant in comparison with dissolved fluxes, particularly if manure application results in a large pool of organic- and metal-enriched particles susceptible to mobilisation during rain events. In drained soil, rapid downward percolation of eroded particles is possible, resulting in transfer of particles to surface waters via drains. In runoff dominated soils, overland transport of eroded particles is a route to surface waters.

Transport of eroded soil particles was simulated in the IDMM as follows:

Annual mean sediment concentrations in drainage water were calculated, based on two studies of soil particle loss through drains (Petersen et al., 2002 and 2004) on sandy loam soils in Denmark. The annual mean sediment concentration is calculated by dividing the annual mass of particulate matter in drainage water (milligrams) by the annual drainage (litres). The sediment concentrations were 18.1 mg/l (range 2.5-32.6 mg/l) and 14.6 mg/l (range 0.9-33.0 mg/l) respectively. Modelled annual runoff and soil erosion at runoff-dominated FOCUS sites was used to calculate a mean sediment concentration at these sites of 24 mg/l (range 11-34 mg/l).

Based on the above calculations, porewater suspended particle concentrations of 15 mg/l for drainage dominated soils, and 25 mg/l for runoff dominated soils, were specified for the surface and topsoil layers.

Eroded particles generated in the surface and topsoil layers were assumed to transfer associated metal directly to surface water, via drainage and/or runoff, without any loss of particle-associated metal.

The concentration of particulate metal in drainage and runoff water (µg metal/g particulate matter) was assumed to be a factor of five greater than the concentration of soil–bound metal in the horizon from which the particulate matter originated. This assumption was adopted based on the work of Quinton and Catt (2007) who studied the metal content of particulate matter in surface runoff from plots in Woburn, UK, finding that metals were enriched by a factor of approximately four in particles in surface runoff, compared to the metal content of the bulk soil. This enrichment is likely due to the preferential mobilisation of fine, organic–rich particles in runoff and drainage. Copper and zinc bind strongly to organic matter compared to other soil components and are thus enriched in the particulate matter found in runoff and drainage.

2.2.3.5. Metal removal by crops

Metal removal by crops will reduce the topsoil pool and consequently reduce the extent of both soil accumulation and leaching. Metal removal in crops was handled by a simple model where the metal content of a crop at harvesting (mg per kg dry matter) was constant and independent of the topsoil metal pool or chemistry. Annual metal removal was thus function of the crop, the crop metal content and the crop yield (tonnes per ha dry mass). In principle, more complex models of metal uptake by crops, incorporating dependence of uptake on soil chemistry, could have been used. An example of such a model is that for Zn used by de Vries et al. (2004), where the Zn content of crops is modelled as a function of the soil total metal, the soil pH (KCl extraction), and the soil organic matter and clay contents. The IDMM does not predict the total metal content of the soil, but the sum of labile and aged content, thus the model of de Vries et al. cannot be directly used here. It is possible, however, to transform the relationship to one that describes crop metal contents as a function of the free metal ion concentration, which may then be incorporated into the IDMM. To do this, the following relationships must be quantified:

- the relationship between the total soil zinc and the reactive soil zinc concentrations;
- the relationship between the reactive soil zinc and the free zinc ion concentration;

- the relationship between the soil pH (KCl extraction) and the soil solution pH.

Romkens et al. (2004) provide a relationship between the total and reactive soil zinc concentrations, as a function of soil organic matter and clay contents. De Vries et al. (2005) provide a relationship between soil pH (KCl extraction) and the soil solution pH. These expressions were combined with the reactive soil metal-free ion relationship described in Section 2.3.2.1 to give an expression relating crop zinc content to free zinc ion, as a function of the soil pH and the soil organic matter and clay contents:

$$Zn_{crop}\ (mg/kg) = \tau_0 + \tau_1.pH_{ss} + \tau_2.\log(OM) + \tau_3.\log(clay) + \tau_4.\log[Zn^{2+}]$$

Copper uptake by crops was modelled using the method and data of Groenenberg et al. (2006), where crop copper concentration is assumed constant and independent of any soil copper pool or other soil property.

2.2.3.6. Organic matter inputs to the soil

Metals are retained strongly by soil, and the addition of organic matter such as manure has the potential to alter the chemical composition of the upper part of the soil and alter the binding properties with respect to metals. This was simulated in a simple way in the IDMM. On each annual timestep an applied mass of manure, with a defined organic and mineral content, was assumed to mix completely with the top 5cm of soil, and the properties of this layer, including bulk density and organic matter content were adjusted accordingly. To simulate the loss of added organic matter by mineralisation, on each timestep a fixed proportion of the organic matter added on the previous timestep was removed. Initially, this proportion was set to 70%.

2.2.4. Model application and outputs

The IDMM predicts past, present and future soil metal pools (labile and aged) and metal concentrations in drainage and runoff, by starting calculations from a point in time in the past which conditions are considered pristine, i.e. where metal inputs to the labile soil pools are derived only from soil weathering and from deposition of metal naturally present in the atmosphere. Under these conditions the system is assumed to be in steady state, i.e. the input and output fluxes to the labile and aged pools in each soil layer balance and there is no net accumulation or loss of metal from each soil layer. The model is then run from a defined point in the past to the present day (and into the future if forecasting if required) on an annual timestep with defined inputs of metal. In all applications here, the start date for modeling was 1500.

2.3. Scenarios for risk assessment

2.3.1. FOCUS and VetCalc scenarios

In order to facilitate the acquisition of relevant soil profile data suitable for simulating the effects of copper and zinc in manure input to agricultural land, it was decided to make use of existing soil scenarios constructed for the ecological risk assessment of pesticides and veterinary compounds in agriculture. Scenarios developed by the FOCUS (FOrum for Co-ordination of pesticide fate models and their USe) for pesticides, and scenarios developed for application of the VetCalc simulation tool for veterinary medicines (Mackay et al., 2005), were used. Both sets of scenarios are intended to cover a range of conditions of climate, soil type, hydrology and agricultural practice broadly representative of conditions within the EU. The two sets of scenarios have different emphases in terms of agriculture types: the FOCUS scenarios emphasise arable agriculture while the VetCalc scenarios are focused upon livestock production areas but also consider manure application to local arable land. Since there are many areas across the EU where both arable and livestock production are important, there is some overlap between the scenarios. In these cases a single scenario has been used in this work. The major characteristics of the scenarios are summarised in Tables 9–10.

The scenario descriptions differ in the amount of data provided that is useful for modelling metal dynamics in the IDMM. Both sets of scenarios contain detailed soil profile information including soil bulk density, pH and organic matter content. The FOCUS scenarios comprise six sites where the hydrology is dominated by percolation to field drains (the D sites) and four sites where hydrology is dominated by surface runoff (the R sites), and the necessary hydrological information is available to permit simulations of metals in drainage and runoff to be made. It was not possible to obtain sufficient hydrological data to allow simulation of drainage and runoff in the VetCalc scenarios. Thus they were used to model topsoil metal accumulation only.

1 **Table 9. Some basic characteristics of the FOCUS scenarios used in this work. All data from FOCUS (2001)**

Designation	Site name	Country	Latitude	Longitude	Mean temperature (°C)	Major arable crops
D1	Lanna	Sweden	58.33	13.05	6.1	grass, cereals, rape
D2	Brimstone	UK	51.65	-1.63	9.7	grass, cereals, rape, beans
D3	Vredepeel	Netherlands	51.53	5.87	9.9	grass, cereals ,rape, beet, potatoes, beans, maize, vegetables ,legumes, pome/stone fruit
D4	Skousbo	Denmark	55.62	12.08	8.2	grass, cereals ,rape, beet, potatoes, beans, maize, vegetables ,legumes, pome/stone fruit
D5	La Jailliere	France	47.45	0.97	11.8	grass, cereals, rape, legumes, maize, pome/stone fruit, sunflowers
D6	Thiva	Greece	38.38	23.10	16.7	cereals, potatoes, beans, vegetables, legumes, maize, vines, citrus, olives, cotton
R1	Weiherbach	Germany	49.00	8.67	10.0	cereals, rape, beet, potatoes, beans, vegetables, legumes, maize, vines, pome/stone fruit, sunflowers, hops
R2	Porto	Portugal	41.18	-8.07	14.8	grass, potatoes, beans, vegetables, legumes, maize, vines, pome/stone fruit
R3	Bologna	Italy	44.50	11.40	13.6	grass, cereals, rape, sugar beet, potatoes, beans, vegetables, legumes, maize, vines, pome/stone fruit, sunflower, soybean, tobacco.
R4	Roujan	France	43.50	3.32	14.0	cereals, beans, vegetables, legumes, maize, vines, pome/stone fruit, sunflower, soybean, citrus, olives

Table 10. Some basic characteristics of the VetCalc scenarios used in this work. All data from Mackay et al., 2005

Site name	Country	Latitude	Longitude	Mean temperature (°C)	Major livestock types	Major crop/vegetation types
Mowthorpe	UK	54.11	-0.64	9.8	Cattle, pigs, poultry	cereals, rape, beet, potatoes, beans, vegetables, legumes, maize
Clashmore	Ireland	52.03	-7.83	10.1	Cattle, sheep, pigs, poultry	grass, potatoes, beet, cereals, rape
Sevilla	Spain	37.37	5.98	17.9	Cattle, pigs, poultry	cereals, beans, vegetables, legumes, maize, vines, pome/stone fruit, sunflower, soybean, citrus, olives
Pwllpeiran	UK	52.39	-3.93	10.0	Cattle, sheep	grass
North Wyke	UK	50.93	-3.84	10.2	Sheep, cattle, poultry	grass, cereals, rape, beans
St. Breiuc	France	48.60	-2.90	10.9	Cattle, pigs, poultry	grass, cereals, rape, legumes, maize, pome/stone fruit, sunflowers
Jokioinen	Finland	62.00	24.00	4.1	Pigs, poultry	grass, cereals, rape, beans, potatoes, beet.
Ringkøbing	Denmark	56.11	8.24	7.5	Cattle, pigs, poultry	grass, cereals, rape, beet, potatoes, beans, maize, vegetables ,legumes, pome/stone fruit
Brandenburg	Germany	52.37	13.36	9.0	Cattle, pigs, poultry	grass, cereals, rape, beet, potatoes, beans, maize, vegetables ,legumes, pome/stone fruit

2.4. Model application

2.4.1. Temporal trends in metal inputs

For model testing and application to risk assessment, a temporal trend in metal inputs was constructed relating to each soil simulated. The inputs considered were atmospheric deposition, inputs in applied manure due to the use of feed additives, inputs in fertilizers, and inputs in sewage sludge. Not all inputs were considered at all sites; for model testing on upland soils in the UK only atmospheric deposition was considered as an input.

All the input trends covered the period 1500-2000. Trends for the risk assessment scenarios were extended to 2060 to predict metal behaviour in response to varying input trends. With the exception of the UK upland sites, it was not possible to feasibly construct local input trends. Therefore where possible trends were constructed based on national level data, with the exception of feed additive inputs for which a range of levels was used, based on the input rates calculated by the Scientific Commission on Animal Nutrition (SCAN) (EC 2003 a and b).

A historic trend in the atmospheric deposition of metals, based on the Lake District, UK (Tipping et al. 2006) was used as a basis to estimate country-specific trends for use with the scenarios. The trend for the Lake District is partly based (post-1970) on measurements of metal concentrations in precipitation, and partly upon assumptions made regarding the timing of the onset of industrial activity generating emissions of metals to the atmosphere. Under the UK-derived scenario anthropogenic metal deposition starts in 1850, peaks in the period 1960-1970 and then drops linearly to 2000 (Figure 5).

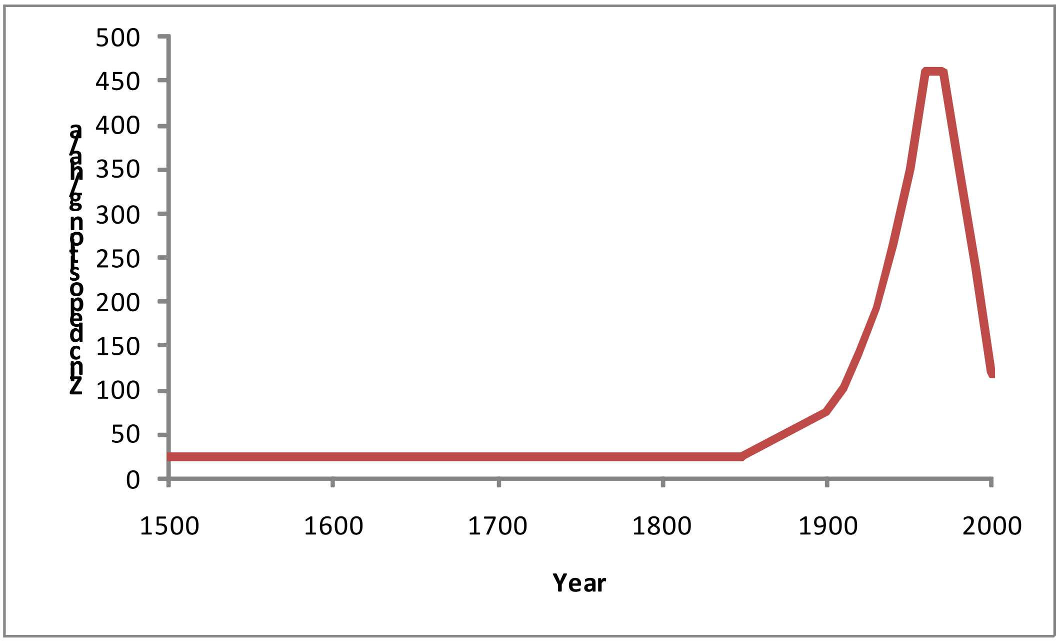

Figure 5. An example of the temporal trend in atmospheric metal deposition used by the IDMM to predict historic accumulation. This example is the zinc trend used for FOCUS site D1.

The choice of this trend as a basis was pragmatic, based on the need to estimate trends for a wide geographical area. It is appreciated, for example, that across parts of Europe the timing of the onset of industrialisation and thus of increased anthropogenic emissions may vary. On the other hand, metals emitted to the atmosphere may be transported considerable distances before being deposited, thus somewhat mitigating local trends in emissions. Magnitudes of deposition for 1850-2000 were obtained by scaling the Lake District trend using country-specific estimates of deposition for the late 1990s (Nicholson and Chambers 2007, Table 11) assuming a constant ratio of deposition equal to the ratio of country-specific estimate to Lake District estimate to be constant. Deposition from 2000 to 2060 was estimated by taking the annual mean deposition for the UK for 2005 (Fowler et al. 2006) and interpolating linearly, then scaling to other countries. Prior to 1850, global mean deposition rates (Nriagu, 1996) were assumed. If deposition rates calculated for dates after 2000 were below the global mean values, they were set to the global mean. Post 2010, deposition was assumed constant to 2060.

Table 11. Metal inputs from atmospheric deposition, assumed to refer to 2000 for calculation purposes, for the risk assessment scenarios

Site	Cu g/ha/a	Zn g/ha/a
D1	15	118
D2	57	221
D3	20	100
D4	8	80
D5	1.7	29
D6[1]	3	24
R1	12	137
R2[1]	3	24
R3	60	289
R4	1.7	29
Mowthorpe	57	221
Clashmore	13	235
Sevilla	3	24
Pwllpeiran	57	221
North Wyke	57	221
St Breiuc	1.7	29
Jokioinen	6.5	30
Ringkøbing	8	80
Brandenburg	53	540

[1] No data available for the country, values from Spain assumed.

Inputs due to fertiliser use (International Fertiliser Association, 2010) were assumed to start in 1930, to rise linearly to 1990, and then to fall linearly at the same rate to 2010 as a result of legislative restrictions on their application rates, after which they were assumed constant. Input rates in 1990 were calculated from the sum of N, P, K and lime inputs to UK soils (Nicholson and Chambers 2007) and were used for all scenarios.

Inputs due to sewage sludge were not considered, since it was deemed unlikely that both sludge and manure would be applied to the same land.

Input rates of metals due to use of feed additives and land spreading of animal manure were based on the maximum allowable metal contents of feed additives for different livestock types (EC, 2003a). The animal types considered were those listed in the EFSA Opinion on environmental risk assessment of feed additives (EFSA, 2007) and input rates were calculated using the method used previously by the SCAN (EC 2003 b and c), based on maximum allowable rates of nitrogen input (170 and 350 kg N/ha/a) from manure spreading on nitrogen-vulnerable and non-vulnerable soils respectively. We additionally simulated the application of piglet manure, since the SCAN report on copper indicated a particularly high input rate of this metal due to the application of this manure type.

For the simulation of the Kleine Aa catchment, metal inputs via manure were assumed to start in 1930 and increase linearly to 2000.

For the risk assessment scenarios, metal inputs via manure were assumed to start in 1950, to increase linearly to 120% of the projected future input rate in 1970, to remain constant to 2000 and then to decrease to the project future input rate in 2010, then remaining constant to 2060. The livestock-type specific metal doses used in the modelling are listed in Table 12.

The estimation of past rates of organic matter addition to soils is difficult, since manure has been used for centuries to add fertility to the soil. Exploratory calculations on the effect of manure addition on topsoil organic matter content were done when testing the model on the Kleine Aa catchment. In the simulations manure additions were started in 1930 and rose linearly to 2kg dw/ha/a in 2000.

Table 12. The soil input levels of copper and zinc simulated in this work. The terms vul and nonvul refer to maximum permissible loading rates to nitrogen-vulnerable and –nonvulnerable soils

Livestock type	Cu input g/ha/a		Zn input g/ha/ a	
	vul	nonvul	vul	nonvul
Fattening pigs	446	919	2678	5513
Sows with piglets	279	575	1675	3448
Piglets	2365	4868	2086	4295
Dairy cows	467	961	2000	4117
Fattening cattle	459	946	1968	4052
Veal calves	239	492	3815	6556
Sheep-goats	246	507	2462	5069
Fattening lambs	530	1092	3182	6551
Broilers	519	1068	3112	6408
Laying hens	494	1018	2967	5785
Turkeys	468	964	2810	4295

2.4.2. Calculation of metal accumulation and total soil metal pools

For comparison with soil PNECs for copper and zinc, soil PECs must be expressed as the total metal content (µg g^{-1} dry soil) in the soil layer(s) of concern for toxic effects. As noted previously, the IDMM predicts not the total soil metal but the sum of the labile and aged pools, not including other forms of inert metal (e.g. in unweathered form in primary and secondary minerals). This is not a problem for prediction of total concentrations as long as an estimate of this inert metal can be made. Assuming the inert metal concentration not to vary over time, the change in total soil metal equals the modelled change in the sum of the labile and aged metal pools.

The FOCUS scenarios do not include data on soil metal contents; therefore, the total soil metal at the sites must be estimated. Where possible, metal contents were estimated from the report by Utermann et al. (2006), which summarises surveyed total metal contents in topsoils according to soil texture, for some European countries. Specific total metal concentrations for each scenario were taken as the median concentration in topsoils having the same texture as the topsoil at the scenario site, for that country. Data for Finnish soils were not separated according to soil texture in this report. For the Jokioinen scenario, a texture-related topsoil metal concentration was estimated from the data provided by Tarvainen and Kuusisto (1999), which summarises the Finnish portion of the Baltic Soil Survey. Data for UK scenarios (D2, Mowthorpe, Pwllpeiran, North Wyke) were not provided by Utemann et al., therefore the median topsoil metal concentrations provided by Zhao et al. (2007) were used instead. Utermann et al. provided no suitable data for the Netherlands, Denmark, Spain, Portugal, Greece or Sweden. For the Netherlands (scenario D3), median texture-specific concentrations given by de Vries et al. (2004) and Groenenberg et al. (2006) were used. For Denmark a pragmatic decision was made to use the available data for Germany. For the remaining scenarios (D1, D6, R2 and Seville) it was necessary to estimate topsoil metal using the FOREGS geochemical database, which comprises several hundred measurements of total topsoil metal covering Western and Central Europe. While FOREGS is a reasonably comprehensive database, it cannot be considered to be of good quality for estimating topsoil metal concentrations, since the organic top layer of the soil profile is removed prior to analysis. However, in the absence of available data for the four scenarios listed, it was necessary to use it. Total topsoil metal, M_{total} (µg/g dry soil), at the FOCUS sites was estimated by distance weighted interpolation of the five nearest FOREGS measurements to each site. This estimated total soil metal was then used to calculate inert metal pools at the FOCUS sites using IDMM-predicted labile and inert pools for the year 1990, simulated under atmospheric deposition only to provide baseline accumulation with no additional metal inputs. The inert metal was calculated as the difference between the measured total topsoil metal and the simulated metal concentration in the surface and topsoil layers together. This was consistently positive for zinc, i.e. the presence of a substantial inert pool was suggested. For copper, predicted metal concentrations were close to the observed values and in some cases exceeded them. Where predicted concentrations exceeded the observed total, the inert metal pool was fixed to zero.

Table 13. Some basic physiochemical characteristics of the scenario topsoils.

Site	Bulk density g cm^{-3}	pH_{ss}	%OM	%clay	Texture
D1 (Lanna)	1.35	7.7	4.0	47	Silty clay
D2 (Brimstone)	1.25	7.7	4.8	55	Clay
D3 (Vredepeel)	1.35	6.0	4.6	3	Sand
D4 (Skousbo)	1.51	7.4	2.6	12	Loam
D5 (La Jailliere)	1.56	7.1	3.8	20	Loam
D6 (Thiva)	1.35	7.9	2.4	30	Clay loam
R1 (Weiherbach)	1.43	7.8	2.4	13	Silt loam
R2 (Porto)	1.20	5.4	6.8	13	Sandy loam
R3 (Bologna)	1.46	8.3	2.0	34	Clay loam
R4 (Roujan)	1.52	8.7	1.2	25	Sandy clay loam
Mowthorpe	1.40	6.6	2.0	22	Sandy loam
Clashmore	1.44	5.1	3.6	18	Sandy clay loam
Sevilla	1.22	7.4	1.9	13	Sandy silt loam
Pwllpeiran	0.97	5.1	10.3	26	Clay loam
North Wyke	1.20	5.1	5.3	42	Clay
St. Breiuc	1.40	6.5	1.5	22	Sandy loam
Jokioinen	1.29	6.2	8.1	4	Sandy loam
Ringkøbing	1.52	4.3	3.2	4	Loamy sand
Brandenburg	1.58	5.1	1.4	10	Sandy silt loam

Table 14. Metal inputs from atmospheric deposition, assumed to refer to 2000 for calculation purposes.

Site	Cu g/ha/a	Zn g/ha/a
D1	15	118
D2	57	221
D3	20	100
D4	8	80
D5	1.7	29
D6[1]	3	24
R1	12	137
R2[1]	3	24
R3	60	289
R4	1.7	29
Mowthorpe	57	221
Clashmore	13	235
Sevilla	3	24
Pwllpeiran	57	221
North Wyke	57	221
St Breiuc	1.7	29
Jokioinen	6.5	30
Ringkøbing	8	80
Brandenburg	53	540

[1] No data available for the country, values from Spain assumed.

In this work we have calculated PECs as the combined metal content of the surface (H0) and topsoil (H1) layers. The IDMM outputs the predicted reactive and aged metal contents of these layers on an annual basis. To calculate the PEC, account must also be taken of inert soil metal, thus the expression for the PEC is:

$$PEC\ (\mu g\ g^{-1}) = \frac{\left[\left(M_{lab,su} + M_{aged,su} + M_{inert,su}\right)\cdot \rho_{su}\right] + \left[\left(M_{lab,top} + M_{aged,top} + M_{inert,top}\right)\cdot \rho_{top}\right]}{\rho_{su} + \rho_{top}}$$

where M is the metal content in a given pool (µg g^{-1} dry soil) and ρ is the bulk density of the soil layer (g cm^{-3}). The subscripts *lab*, *aged* and *inert* refer to the labile, aged and inert metal pools respectively, and su and top refer to the surface and topsoil layers respectively. In this work the inert metal pools for the surface and topsoils are always equal, being derived from the topsoil metal concentrations described earlier in this Section. For the FOCUS and VetCalc scenarios used here, inert metal pools in each soil layer were estimated as the difference between the estimated total metal concentration and the IDMM-modelled sum of the labile and aged metal concentrations for 2010.

2.4.3. Calculation of surface water PECs in the FOCUS scenarios

Calculation of surface water and sediment PECs was done based upon the FOCUS scenario methodology. For each scenario, one or more water body types is defined as a receiving water. The water body types are a pond, a drainage ditch and a stream. Each type has a baseflow component in addition to receiving drainage from the upstream land area. In applying the FOCUS models, which operate on a daily timestep, the waterbodies are considered to have defined characteristics that are used to compute their hydrological behaviour and allow variable flow and water residence time. Given the simpler hydrological picture used in the IDMM and the annual timestep employed, the waterbody characteristics were simplified. Minimum baseflows for each scenario/waterbody combination were used to compute an annual baseflow in mm/a that was considered to mix with the drainage and leaching from the catchment. The baseflow was assumed to have concentrations of copper and zinc equal to those estimated by weighted interpolation from the five closest measured surface water concentrations in the FOREGS database. Each waterbody was considered to receive drainage from the upstream catchment, as per FOCUS:

- The pond receives drainage from an area of 3.45ha.
- The drainage ditch receives drainage from an area of 3ha.
- The stream receives drainage from an upstream catchment of area 100ha.

In the FOCUS scenarios, a single pesticide application is considered to be made to only a proportion of the catchment at any one time. Since manure application is associated with returning organic matter and nutrients to agricultural soils on a wide scale, it seems reasonable to assume that it will be done catchment wide, and the assumption has thus been made that the entire upstream catchment receives manure.

Pond baseflow was essentially negligible. Ditch and stream baseflow as a proportion of total discharge varied among scenarios, with D2 having notably low baseflow in both waterbodies. The greatest degree of baseflow dilution was seen in the stream for scenario R1.

The surface water PEC must be calculated as a time–averaged concentration, as this reflects the mean exposure of aquatic organisms. Thus the temporal variation in drainage and/or runoff must be considered. To do this, a hydrographic profile for each FOCUS site, comprising daily drainflow or runoff, was obtained from the FOCUS Surface Waters report. These profiles were used to calculate daily mixing of baseflow with drainflow and/or runoff. The resulting daily surface water metal concentrations were averaged for each year.

Input concentrations from the IDMM to the calculation procedure were the volume-weighted mean annual concentrations of metal in the lateral runoff/drainage from all the soil layers. This includes metal (labile and aged) bound to eroded soil particles. For the calculation of surface water PECs (as dissolved metal) and sediment PECs (as total sediment metal), the following scheme was applied. Time averaged surface water concentrations of dissolved + labile soil particle metal were re-partitioned between the water and sediment phases using the WHAM6 model, to calculate dissolved metal PECs. For the calculation of sediment PECs, the composition and concentration of suspended particulate matter (SPM) in the receiving water was set equal to the standard values used by FOCUS, namely an SPM concentration of 15 mg/l and an organic carbon content of 5%. Following the methodology recommended by the by the EU Technical Guidance Document on Risk Assessment[1], whereby the substance of interest binds to suspended particles which then deposit to the stream bed, the concentration of metal (labile and aged) partitioned into SPM was taken to be the sediment PEC. Volume weighted annual mean concentrations of dissolved + labile soil particle metal and drainage/runoff water were considered to be diluted by the baseflow and then to repartition between solution and SPM (calculation of repartitioning was done using WHAM). The volume weighted mean labile SPM-bound metal was then combined with the aged particle-associated metal in drainage/runoff, assuming a total SPM concentration of 15 mg/l, to calculate the final SPM-bound metal concentration which was used as the sediment PEC.

The calculation of metal partitioning between dissolved and labile SPM-bound forms was done using the WHAM model, utilising a water composition estimated by taking the distance–weighted mean of the compositions of the five waters closest to the scenario site in the FOREGS database. Compositional parameters taken from FOREGS comprised the water pH and dissolved concentrations of organic carbon, sodium, magnesium, potassium, calcium, chloride, nitrate, sulphate and alkalinity. Dissolved organic matter was simulated by assuming it to be 50% of the organic matter, and to comprise 65% fulvic acid. Iron(III) and aluminium were simulated by assuming their solution activities to be controlled by solid hydroxide phases. The active binding phase of the SPM was assumed to be organic matter, which was simulated by assuming it to comprise 50% humic acid and 50% fulvic acid, i.e. to be 100% "active" with respect to metal binding. This represents a worst case estimate of sediment PEC, resulting from a maximum metal binding activity of the suspended sediment.

2.5. Model testing

A literature search was undertaken to find datasets on which to test and evaluate the IDMM prior to its application to the risk assessment scenarios. A number of studies were found on the application of metals to agricultural land in manure, however combined studies of soil accumulation and leaching were very rare, with only one example found in the literature. For practical reasons, it was decided to focus upon this study, located in the Kleine Aa catchment in Switzerland. Additionally, we examined CEH datasets looking at the accumulation of metals in upland soils of the Lake District and Lochnagar (both UK).

2.5.1. Metal accumulation and leaching in UK upland soils

We have previously (2000) surveyed soil and surface water metal (nickel, copper, zinc, cadmium, lead) concentrations in upland soils of the Lake District, UK, and Lochnagar, Scotland. The soils are largely shallow (approximately 25-30cm depth) over impermeable bedrock. Vegetation is largely open grassland although bare rock comprises a significant proportion (between 20 and 50%) of the catchments studied. The soils are highly organic (43-76% organic matter by mass) and acidic, with pristine pH values in the range 5.0-5.8. Acidification of the soils was simulated by specifying temporal pH trends calculated using the fully mechanistic CHUM-AM catchment

model (e.g. Tipping et al., 2006). Predicted pH values for 2000 were in the range 4.1-5.2. The single-horizon version of the IDMM (Figure 1) was used. Dissolved organic carbon in drainage water was set to 1mg/l, based on surface water measurements. Predicted labile metal pools were compared with estimated pools based on surveys of 0.1M acid-extractable metals in catchment soils. Predicted drainage water concentrations were compared with annual mean estimates of concentrations in catchment streamwaters and in Lochnagar (Tipping et al., 2007).

Predicted soil metal pools (grams per square metre of catchment) and surface water concentrations are shown in Figure . Agreement between observation and prediction is impressive with all copper and zinc pools and concentrations predicted to within a factor of three.

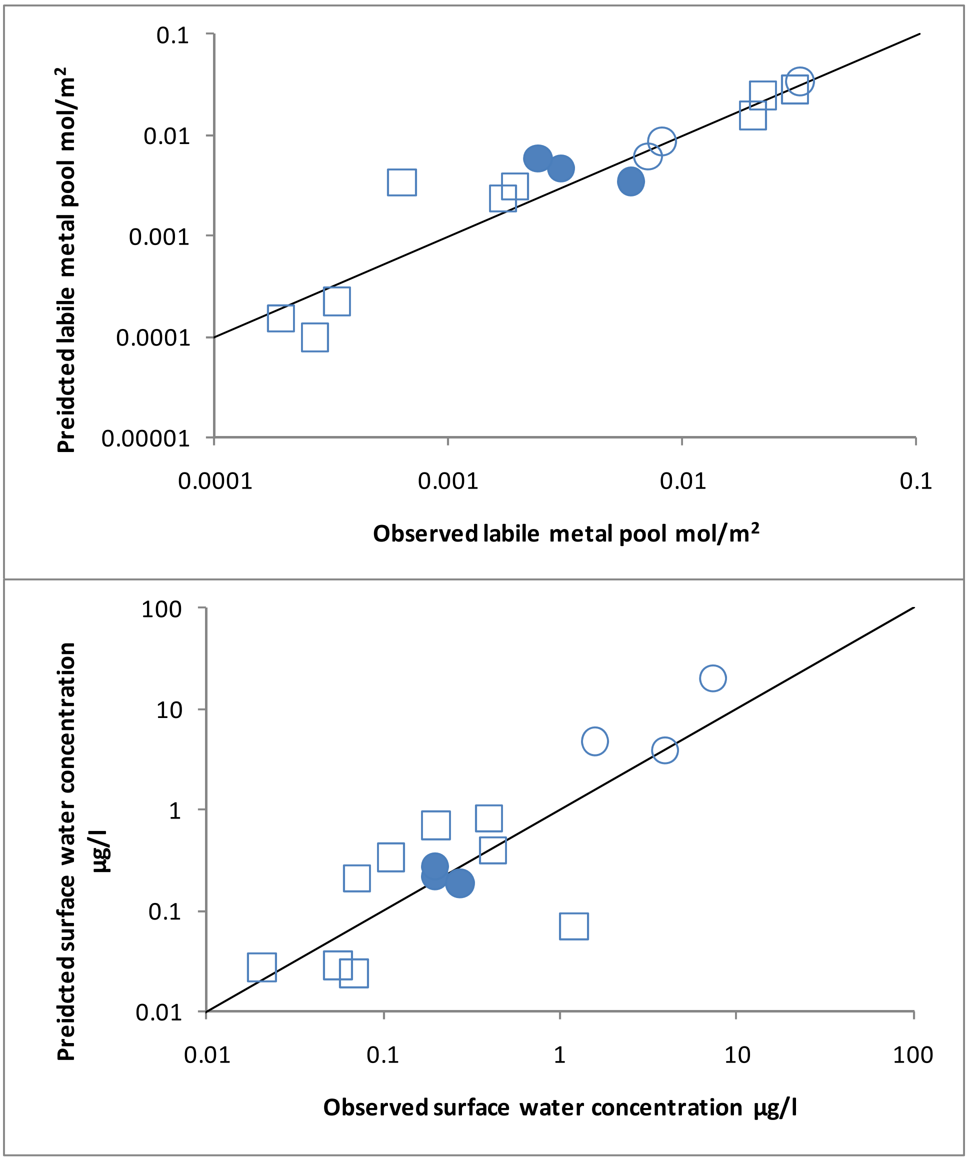

Figure 6. Observed and IDMM-predicted soil pools and surface water concentrations of metals in Gaitscale and Hardknott Gill catchments (Lake District, UK) and Lochnagar, Scotland. Filled circles are copper predictions, open circles are zinc predictions, open squares are predictions for nickel, cadmium and lead.

2.5.2. Metal dynamics in the Kleine Aa catchment, Switzerland (Xue et al., 2000 and 2003; Gachter et al., 1998)

The Kleine Aa is a small (6.9 km^2) catchment located at the southern end of Lake Sempach, Switzerland. Land use is primarily (75%) intensive agriculture, mainly maintained grassland used for dairy farming. A high livestock density dictates high annual inputs of cattle manure (in slurry form) of up to 180 m^3 ha^{-1} a^{-1}. Estimated annual inputs of Cu and Zn due to feed additive use and slurry application are 180-3240 and 1000-8000 g/ha. About 40% of the catchment is artificially drained. Soils are mostly (90%) shallow, loamy till-derived materials, however, 10% of the catchment is drained wetlands comprising soils of high (>20%) organic carbon.

Xue and co-workers measured bulk densities, total organic carbon, copper and zinc contents in samples of the mineral and organic soils. They also sampled drainage waters draining the mineral and organic portions of the catchment in the winter of 1999-2000 and measured dissolved copper, zinc and organic carbon. Thus, monitoring data were available against which to compare the predictions of the IDMM. Time series of copper and zinc inputs in atmospheric deposition (for the years 1500-2000) were constructed, utilizing measurements of atmospheric deposition for 2000 (Herausgegebaun et al., 2008). Copper and zinc inputs in manure were assumed to commence in 1930 and to increase linearly to 2000. Three sets of manure input rates were simulated: low (180 and 1000 g/ha/a for Cu and Zn respectively), medium (1710 and 4500 g/ha/a) and high (3240 and 8000 g/ha/a). These rates respectively represent the lower limits, median and higher limits of the ranges quoted by Xue and co-workers. The model was run to simulate both the mineral and organic soils initially using the default DOC concentrations (Section 0). The default for the deep soil of 5 mg C/l is reasonable for the mineral soil (mean measured DOC = 3.1±1.1 mg/l, n = 4) but is considerably less than the DOC in water draining the organic soil (mean measured DOC = 34.3±10.4 mg/l). Thus, the model was also run for the organic soil with default DOC concentrations (in all soil layers) of 35 mg/l. This allows a simple test of sensitivity to DOC concentration.

Predictions of soil metal pools against available measurements are shown in Figure 7. It should be noted that the measurements and predictions are not strictly comparable, since the measured total metal pools will contain an unknown proportion of metal that is neither labile nor aged (e.g. unweathered metal in primary and secondary minerals). This should introduce a negative bias in the predictions compared to the observations. However, uncertainties in other factors, such as the cumulative metal inputs over time, are likely to be of equal if not greater significance.

The following points may be made regarding the results:

- The IDMM correctly predicts that the organic soil has higher metal concentrations (on a soil mass basis) than the mineral soil, resulting from its lower bulk density.

- The observed metal concentrations agree well with the predictions in the mineral soil and for zinc in the organic soil, notwithstanding the high dependence of the predicted metal pool on the input rate of zinc.
- The observed copper in the organic soil is outside the range of predicted copper, but is not greatly higher than the upper end of the predicted range. Given the uncertainties in the cumulative inputs of copper, and the likelihood that inputs are heterogeneous across the catchment anyway, this remains a reasonable

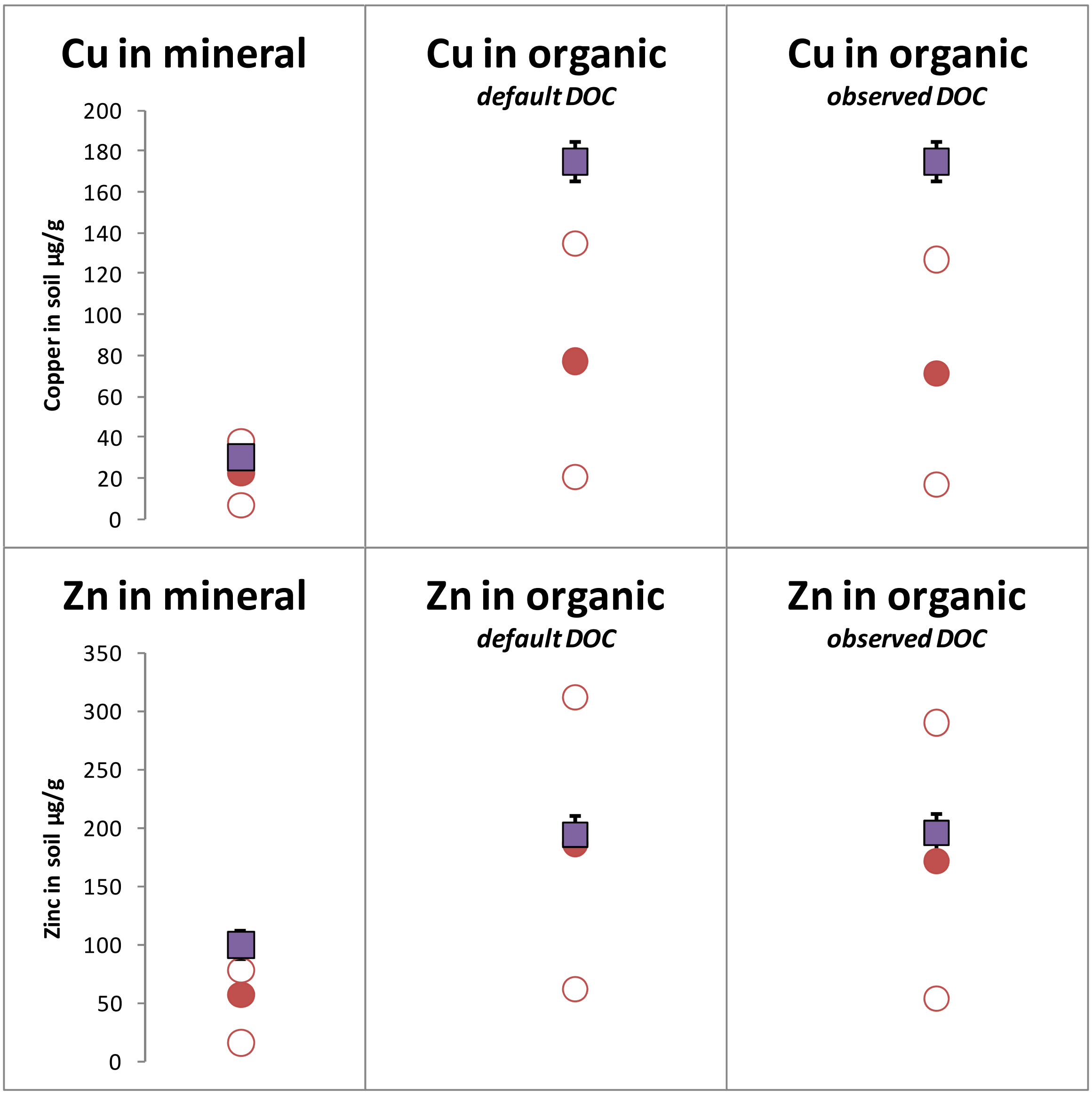

Figure 7.Comparison of total copper and zinc concentrations (0-30cm depth) in the mineral and organic soils of the Kleine Aa catchment, with IDMM predictions of labile+aged metal in 2000 (0-30cm depth). Squares: mean of measured metal (error bars = ±1 standard deviation); closed circles: IDMM prediction for median metal input rate; open circles: IDMM predictions for high and low metal input rates.

prediction.

- The predicted metal accumulation in the organic soil is rather insensitive to changing the porewater DOC concentrations from their defaults to the values based on the observations. This is not surprising, since metal accumulation is strongly favoured and annual losses in drainage are small compared to the total labile+aged pool present.

Predictions of dissolved metal concentrations in drainage water are shown in Figure 8. The findings can be summarized as follows:

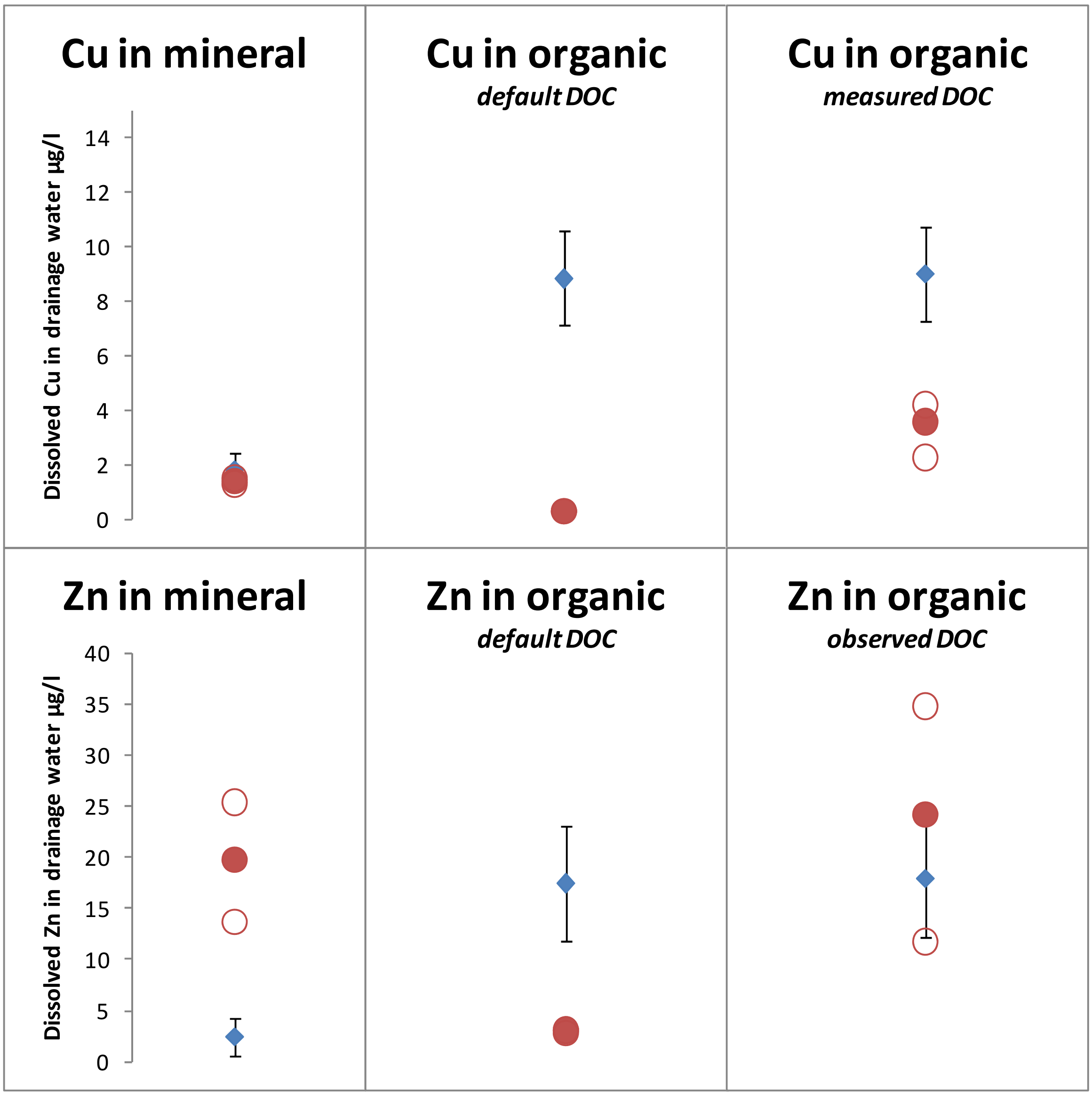

Figure 8. Comparison of dissolved copper and zinc concentrations in water draining the mineral and organic soils of the Kleine Aa catchment, (1999-200, *n* = 4), with IDMM predictions of dissolved metal in 2000. Diamonds: mean of measured metal (error bars = ±1 standard deviation); closed circles: IDMM prediction using median metal input rate; open circles: IDMM predictions using high and low metal input rates.

Observed and predicted copper in water draining the mineral soil agree well. Inspection of the time series of predicted copper (data not shown) indicates that the prediction concentrations are close to steady state; i.e. the predicted chemistry of the deep soil has not been influenced by copper inputs due to its very strong retention in the surface soil.

Predicted copper in waters draining the organic soil is somewhat sensitive to the chosen DOC concentration, which is not surprising given the strong affinity of copper for binding to organic matter. Use of the measured DOC provides a superior prediction compared to use of the default value. Although the range of predicted concentrations obtained using the measured DOC does not overlap the range of ±1 standard deviation of the observations, the prediction is nonetheless reasonable, particularly given the limited time period and small number of measurements made ($n = 4$).

The model overestimates the observed zinc draining the mineral soil. Inspection of the predicted time series trend shows that the measured zinc concentration is also exceeded by the predicted steady state pristine zinc concentration (10.1 µg/l, compared to a mean observed Zn of 2.4 µg/l) and that the model predicts that zinc in drainage water. This is not a serious overestimation within the context of model uncertainties, but it does suggest that one or more parameters, such as the metal weathering rate, are poorly estimated for this soil. A steady state calculation using a weathering rate of zero gave a predicted pristine concentration of 2.7 µg/l, which is in excellent agreement with the observed mean of 2.4 µg/l.

The predicted Zn in water draining the organic soil is sensitive to the choice of DOC concentration. Use of the default DOC underestimates the observed Zn, while use of the measured DOC produces a range of prediction that overlap the observations. It should be noted that the organic soil simulated here has a rather high organic matter content for an agricultural soil and so it not surprising that the default DOC is lower than that measured. The FOCUS soils all have organic matter contents similar to the mineral rather than the organic soil, so use the default DOC concentrations does not appear inappropriate.

Simulating the addition of manure to the mineral surface soil, combined with annual mixing of the surface soil and topsoil layers, caused a rapid and unrealistic increase in the organic matter content of the two layers. Increasing the mineralisation rate of added manure to 90% of its weight restricted the addition of organic carbon to the topsoil to a reasonable degree. However, this increase in soil organic matter content (a doubling from ~1% to ~2% over 70 years) did not significantly affect the metal retention of the soil, since retention was strong in the absence of additional organic matter. Given this fact, and the considerable uncertainties involved in estimating the net input of organic matter from manure to soils over time, it was decided not to simulate the addition of organic matter in the risk assessment scenarios.

2.6. Risk assessment using FOCUS and VetCalc scenarios

2.6.1. PNECs for soil, surface water and sediment

2.6.1.1. Soil PNECs

Soil PNECs were calculated using a Microsoft Excel spreadsheet tool produced by Arche Consulting, Ghent, Belgium. The tool calculates soil PNECs for a number of metals including copper and zinc, largely following the methodologies in the relevant EU Risk Assessment (RAR) documents. There are some deviations from the RAR methodologies, which for copper and zinc can be summarised as:

- The approach for bioavailability correction for Zn was updated according to the methodology used in the RARs for Cu and Ni. In the latter RARs, one of three specific models for plants, invertebrates and microbial processes is applied to each No Observed Effect Concentration (NOEC) to correct for site specific effects in metal bioavailability, prior to calculation of a PNEC. In the Zn RAR, a more pragmatic 'bioavailability factor' approach is used to correct a generic PNEC for site-specific conditions.
- Both the added and total risk approach are implemented for Zn and other metals, whereas in the Zn RAR only the added risk approach was used. To implement the total risk approach for Zn, a background concentration of 51 µg/g was used for NOECs lacking a specific background concentration; this value is the median of all the quoted background Zn concentrations in the toxicity database.
- The PNEC values are calculated using a species sensitivity distribution with a lognormal distribution, as opposed to the RARs where the best fitting distribution was used.
- The tool requires values of soil pH, organic matter and clay content in order to make the best prediction of the site–specific PNEC. These parameters were all available in the descriptions of the scenarios.

It was decided to use the total PNEC approach for copper and the added PNEC approach for zinc. Although it would be possible to use any combination of added and total soil PNECs, since both may be calculated, this combination is consistent with the water and sediment PNECs, since for these only the added risk approach can be applied for zinc, and only the total risk approach for copper. Ambient background concentrations for zinc were set to the 'local mean' concentrations calculated from the FOREGS data.

Table 15. Soil and surface water PNECs for the scenario sites. The zinc PNECs include ambient background concentrations from the FOREGS database.

	Copper		Zinc	
	Soil	Water	Soil	Water
Site	µg/g	µg/l	µg/g	µg/l
D1	139	30.1	123	11.4[1]
D2	157	1.9	331	13.7
D3	55	17.4	131	30.3
D4	67	47.0	121	57.9
D5	97	4.1	152	14.3
D6	94	1.3	296	8.5
R1	64	3.0	201	8.4
R2	98	4.0	208	12.9
R3	90	2.4	325	11.0
R4	62	4.1	336	11.9
Mowthorpe	86		176	
Clashmore	85		207	
Sevilla	61		170	
Pwllpeiran	141		251	
North Wyke	145		255	
St Brieuc	78		235	
Jokioinen	83		158	
Ringkøping	36		31	
Brandenburg	46		88	

[1] comprises a generic PNEC for soft waters of 3.1 µg/l and an ambient background concentration of 8.3 µg/l

2.6.1.2. Surface water PNECs

Surface water PNECs were calculated using a Microsoft Excel spreadsheet tool produced by Watts & Crane Associates, UK. The tool calculates PNECs using empirical equations fitted to outputs of the tools used to calculate site–specific PNECs in the Cu and Zn RARs, with the intention of reducing the input data requirements to a practical level., The water quality parameters required for PNEC calculation are the pH, calcium and DOC concentrations. For each site values of these parameters were calculated from the FOREGS database for surface waters. Additionally, the Zn PNEC is expressed as an added concentration and so requires an estimate of ambient background Zn; this was also calculated from the FOREGS data.

2.6.1.3. Sediment PNECs

Sediment PNEC values were obtained from the RARs. In neither case are site–specific PNECs available; the generic values are 87 µg total Cu/dry weight sediment and 49 µg added Zn/g dry weight sediment. In order to estimate ambient background sediment Zn at each site, the IDMM was run for 2010 assuming no manure input and the expected sediment Zn content was calculated and assumed to be the ambient background.

2.6.1.4. Other considerations

Metal uptake by crops was considered using the models described previously. It was not considered possible within the scope of this study to individually model the effects of each crop listed for each site. Thus a simplified approach was taken, whereby a single crop was simulated under each scenario. Inspection of the relevant crops for each scenario (Table 9) indicated that cereals were important at all the sites except R2 and Pwllpeiran. For the sites where cereals were important, simulations were done using wheat as the crop. For R2, simulations were done using maize, and for Pwllpeiran no crop was simulated, since there is no arable agriculture at this location. Yields of crops were required in order to calculate the offtake. Current yield data were obtained from information provided by the IPSC Agriculture Unit of the Joint Research Centre (MARS, 2009) and comprised mean yields (tons per ha) for the period 2004–2008. Estimates of yields from 1400 were constructed by assuming them to be 1 ton fresh weight per ha to 1700, to increase linearly to 2 tons fresh weight per ha in 1930, to increase linearly to the current yields in 2000 and then to remain constant.

For three scenarios (Clashmore, Pwllpeiran and North Wyke), additional simulations were done without simulation of annual tillage (mixing) of the surface and topsoil. Thus, added metal will accumulate strongly in the surface soil layer. This lack of mixing with the topsoil layer, would be expected to produce relatively high metal concentrations in the surface soil layer compared to the topsoil. In scenarios where tillage is simulated these additions are ‘diluted’ by mixing into the topsoil, so their accumulation near the surface is accordingly lowered.

2.7. Results

Topsoil, surface water and sediment PECs related directly to manure are provided in the Appendix. In presenting the results in the main text we show graphically the results of simulating three loading rates per metal. These loading rates correspond approximately to the bottom, middle and top of the range of loading rates for each metal, and are intended to provide a visual representation of possible trends. The loading rates are 200, 700 and 5000 g/ha/a for copper and 1500, 4000 and 7000 g/ha/a for zinc.

2.7.1. Initial model runs

Initial runs were performed to the role of metal weathering in controlling predicted surface water metal concentrations (following the experience gained in modelling the Kleine Aa catchment). Weathering of metal into the deep soil labile pool and thence to surface water gave ranges of copper between 1.3-12.0 µg/l in the drainage from the deep soil horizons of the D sites. For zinc, the range was 9.7-60.9 µg/l, with the concentration exceeding 30 µg/l at four of the sites. These are rather high concentrations for a pristine situation, reflecting the uncertainty associated with rates of weathering. Simulations without metal weathering gave ranges of 0.8-1.7 µg/l for copper and 8.2-16.5 µg/l for zinc. Therefore, it was decided to remove consideration of weathering from the model. At most sites this had only a small effect on the predicted pristine surface water metal concentrations.

2.7.2. Metals in topsoils

Trends in soil metal are shown in Figures 9-15 for three loading rates. Accumulation from 2010 to 2060 varied by a factor of 1.8 for and 2.9 for Zn at the highest loading rates. Accumulation was closely correlated with the density of the surface and topsoil (r = -0.76 for copper and -0.63 for zinc at manure input rates of 800 g/ha/a and 5000 g/ha/a respectively). Accumulation tended to be higher in soils of higher organic matter content, due to the greater metal binding capacity this affords the soil, but there was little effect of soil pH (Figure 16).

PECs for 2020, 2030 and 2060 are tabulated in the Appendix. For copper, only piglet manure application is predicted to result in PNEC exceedence within the period 2010-2060, however exceedence of the PNEC was predicted in all the scenarios. In eight scenarios a potential risk due to application of piglet manure to N-vulnerable soils is indicated. Of the scenarios, local production of pigs is important for D3 and Ringkøbing, with some pig production at R3 and Brandenburg.

Livestock-type specific PECs for zinc varied by a smaller degree than those for copper. Consequently, in situations where zinc accumulation exceeded the PNEC this usually happened for multiple manure types. Exceedence of the zinc PNEC was found in eight scenarios in 2060 (D1, D3, D4, D5, Seville, Jokioinen and Ringkobing), in five scenarios in 2030 and in four scenarios in 2020. Exceedences were predominantly observed at the higher loading rates associated with N-nonvulnerable soils, although exceedences due to the lower loading rates associate with N-vulnerable soils were observed for D4 and Ringkobing. Exceedences in 2060 due to application of sheep or poultry manures were predicted at all seven sites, and for cattle at all sites except Seville. In the cases of scenarios D1, D3 and D4 poultry production is likely to be a far more likely source of manure for land spreading than sheep production since the regions containing the scenarios are not important areas for sheep. The Ringkøbing scenario, which is notably the most sensitive of the scenarios modelled, is located in an area of important bovine, swine and poultry production, and thus potential risk may result from the spreading of a number of locally produced manure types. At this site PEC exceedences due to all manure types are predicted by 2020 for N-nonvulnerable soils, and four manure types are predicted to cause exceedence by 2020 if applied to N-vulnerable areas. The vulnerability of this scenario is strongly linked to the low PNEC, which is less than half the next lowest value. This low PNEC is related to the low topsoil pH of 4.3 relative to the other soils, and probably also to the low topsoil clay content. Scenario D4 is also predicted to be rather vulnerable, with exceedences predicted due to seven of the eleven manure types in 2020 for N-nonvulnerable soils and in 2060 for N-vulnerable soils.

Figure 15 shows the effect of not invoking soil tilling in a simulation and allowing metal to build up in the surface soil, for the medium loadings of copper and zinc. In all cases the surface soil becomes enriched in metal at the expense of the topsoil. This is particularly true for copper, where losses in drainage appear to be essentially negligible. Zinc exhibits greater mobility, as would be expected from its chemistry, and accumulates in the topsoil at concentrations close to those predicted when tillage is allowed. In all cases metal is predicted to accumulate in the surface soil at or close to the PNEC within at most 50-100 years of the onset of feed additive use. There is thus a risk of exceeding the PNEC within a few decades of the onset of applying any of bovine and poultry manures, particularly so in the case of N-not vulnerable soils. The three locations for which no-tillage was simulated are all important for dairy farming and thus the soils show some vulnerability to locally produced manure types.

In practice, potential effects of metal accumulation in the surface soil layer are likely to be highly localised and relate to organisms dwelling at the soil surface and specifically within 0-5cm depth; organisms that inhabit deeper soil (5-30cm) are less likely to be impacted unless they exhibit traits that periodically exposes them to the surface layer. This is likely to be the case for invertebrates such as burrowing earthworms but less so for plants, unless they have active roots within the surface layer. Loss processes not considered here, such as erosion (wind and water) and burial due to animal activity, will also affect removal of metal from the surface layer.

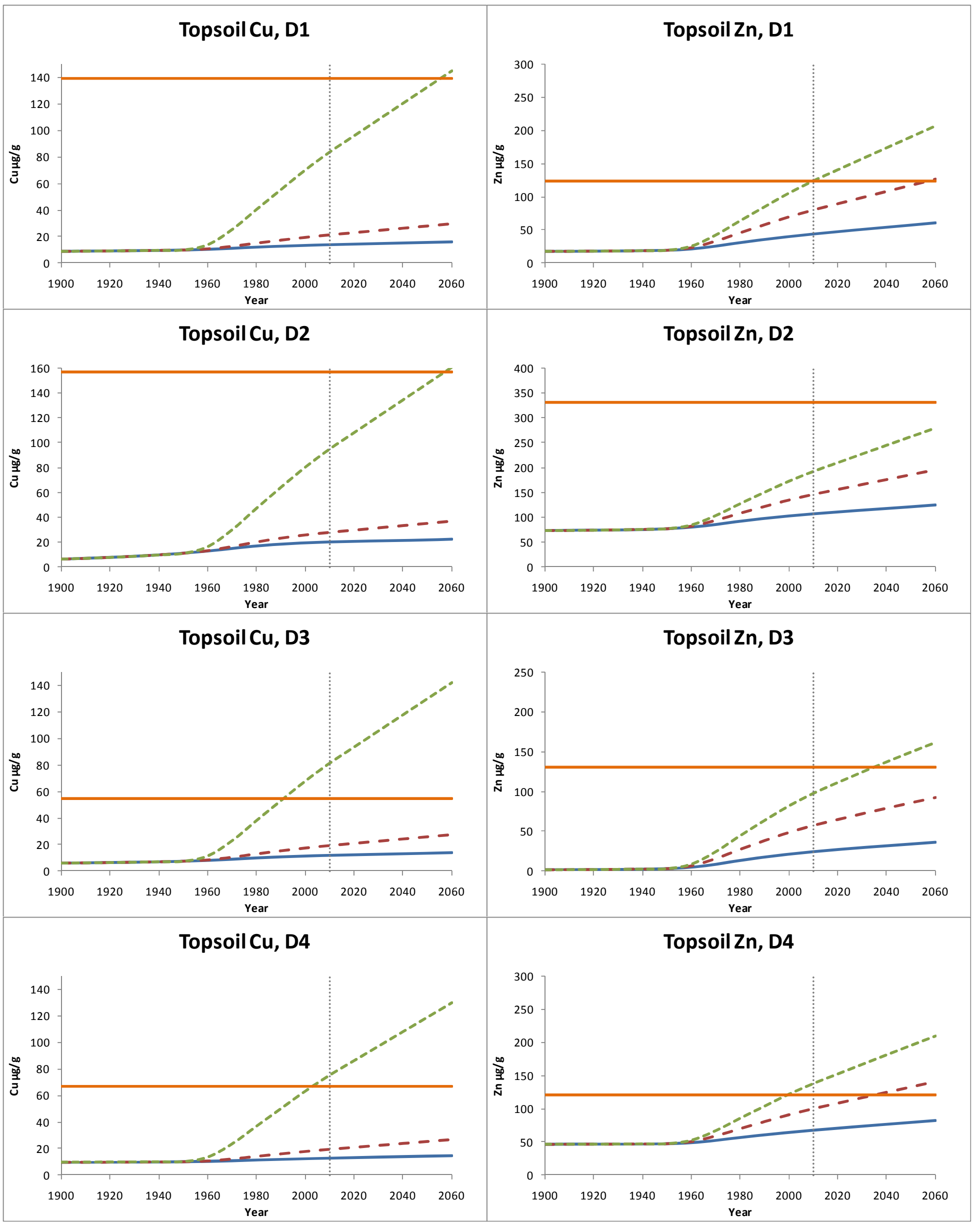

Figure 9. Time trends of predicted topsoil copper and zinc in scenarios D1-D4, for three input rates (blue line: 200 g Cu/ha/a and 1500 g Zn/ha/a; red dash: 700 g Cu/ha/a and 4000 g Zn/ha/a; green dash: 5000 g Cu/ha/a and 7000 g Zn/ha/a). The horizontal orange lines are the site-specific soil PNECs.

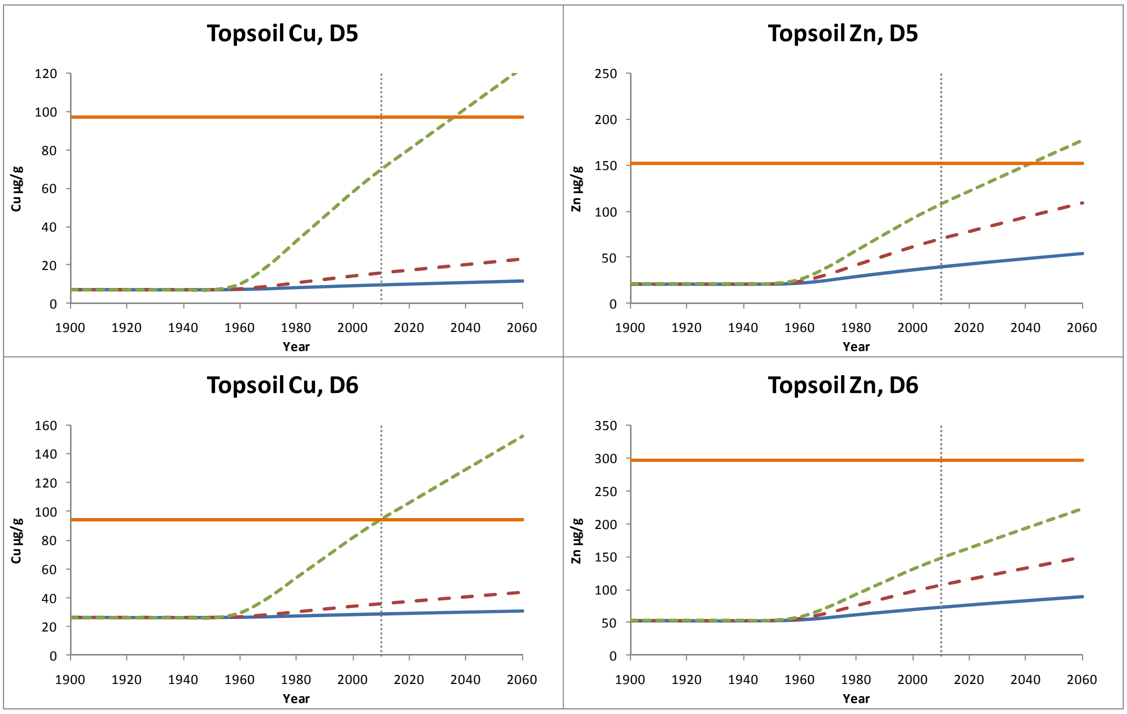

Figure 10. Time trends of predicted topsoil copper and zinc in scenarios D5-D6, for three input rates (blue line: 200 g Cu/ha/a and 1500 g Zn/ha/a; red dash: 700 g Cu/ha/a and 4000 g Zn/ha/a; green dash: 5000 g Cu/ha/a and 7000 g Zn/ha/a). The horizontal orange lines are the site-specific soil PNECs.

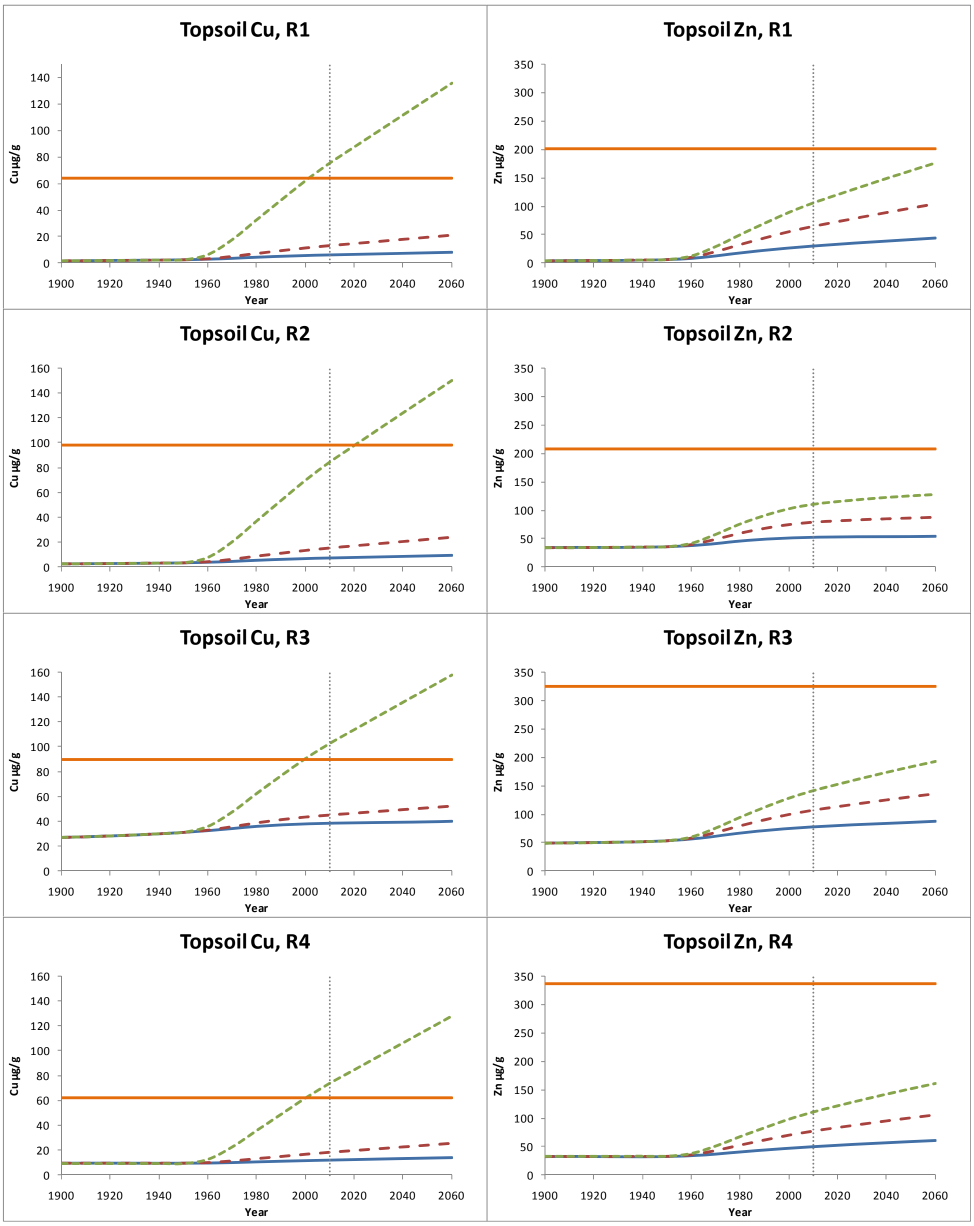

Figure 11. Time trends of predicted topsoil copper and zinc in scenarios R1-R4, for three input rates (blue line: 200 g Cu/ha/a and 1500 g Zn/ha/a; red dash: 700 g Cu/ha/a and 4000 g Zn/ha/a; green dash: 5000 g Cu/ha/a and 7000 g Zn/ha/a). The horizontal orange lines are the site-specific soil PNECs.

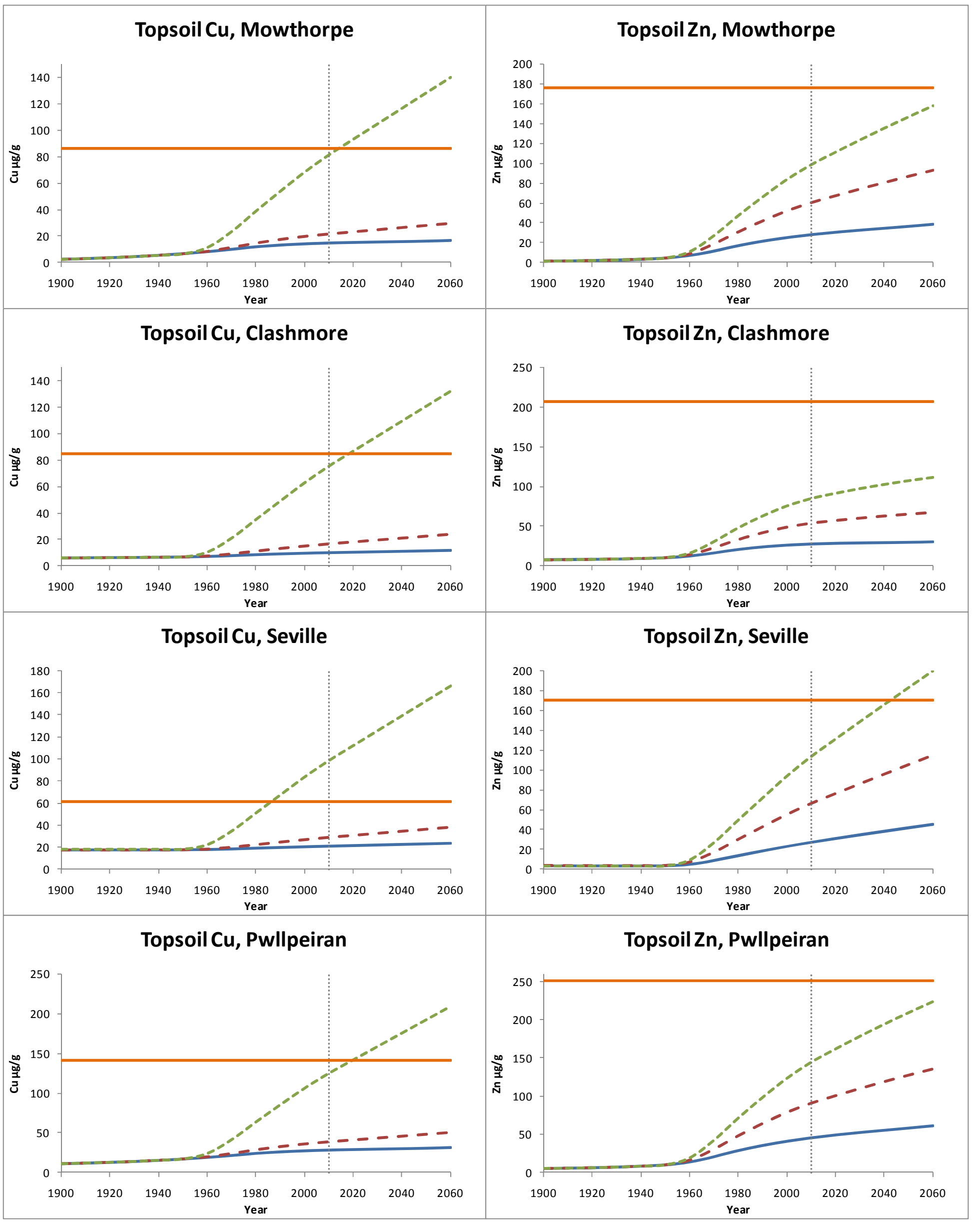

Figure 12. Time trends of predicted topsoil copper and zinc in scenarios Mowthorpe, Clashmore, Sevilla and Pwllpeiran, for three input rates (blue line: 200 g Cu/ha/a and 1500 g Zn/ha/a; red dash: 700 g Cu/ha/a and 4000 g Zn/ha/a; green dash: 5000 g Cu/ha/a and 7000 g Zn/ha/a). The horizontal orange lines are the site-specific soil PNECs.

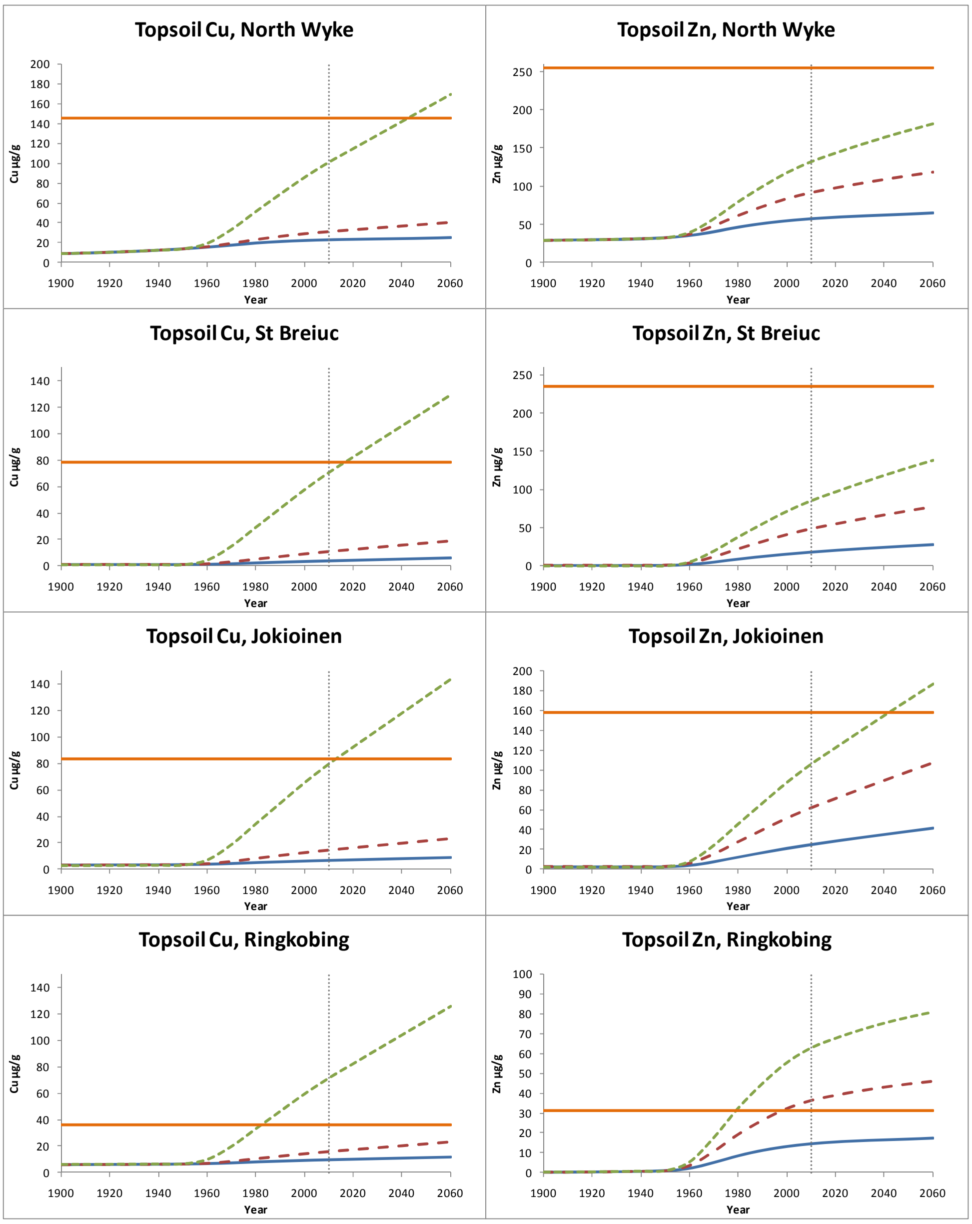

Figure 13. Time trends of predicted topsoil copper and zinc in scenarios North Wyke, St Breiuc, Jokioinen and Ringkobing, for three input rates (blue line: 200 g Cu/ha/a and 1500 g Zn/ha/a; red dash: 700 g Cu/ha/a and 4000 g Zn/ha/a; green dash: 5000 g Cu/ha/a and 7000 g Zn/ha/a). The horizontal orange lines are the site-specific soil PNECs.

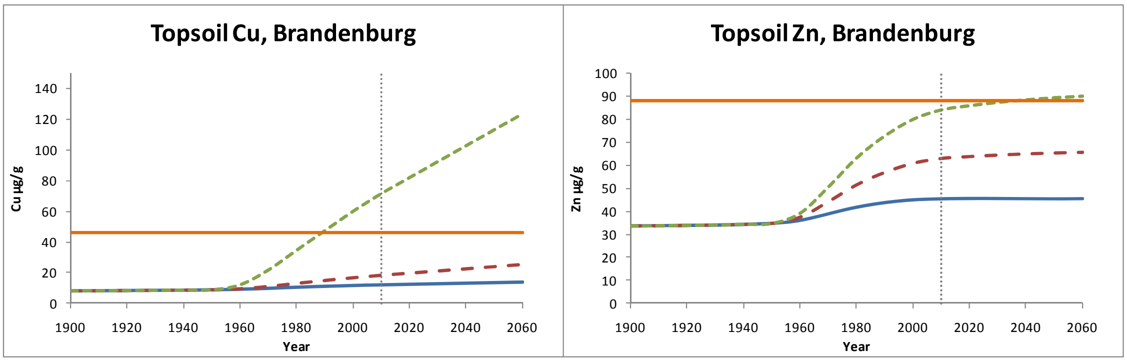

Figure 14. Time trends of predicted topsoil copper and zinc in scenario Brandenburg, for three input rates (blue line: 200 g Cu/ha/a and 1500 g Zn/ha/a; red dash: 700 g Cu/ha/a and 4000 g Zn/ha/a; green dash: 5000 g Cu/ha/a and 7000 g Zn/ha/a). The horizontal orange lines are the site-specific soil PNECs.

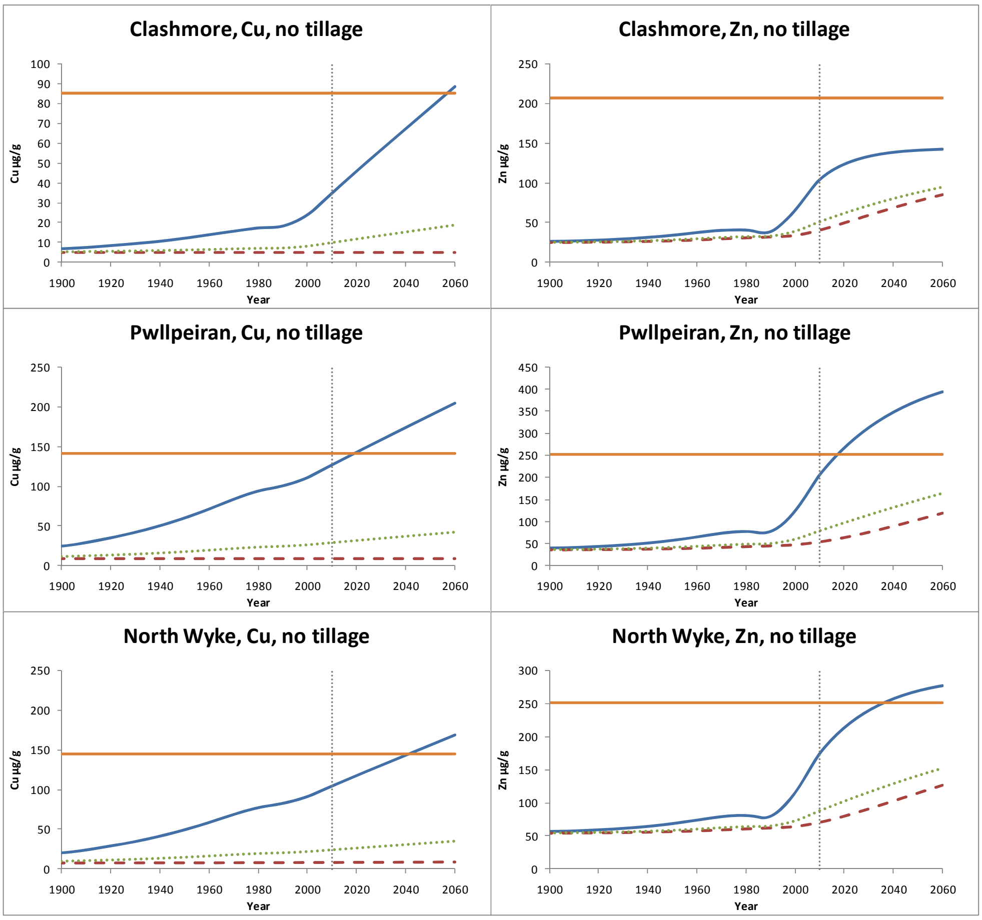

Figure 15. Time trends of predicted topsoil copper and zinc in the no-tillage scenarios Clashmore, Pwllpeiran and North Wyke. Solid line: metal in the surface soil; dashed line: metal in the topsoil; dotted line: metal predicted for both horizons when tillage is applied. Input rates are 700 g Cu/ha/a and 4000 g Zn/ha/a. The horizontal orange lines are the site-specific soil PNECs.

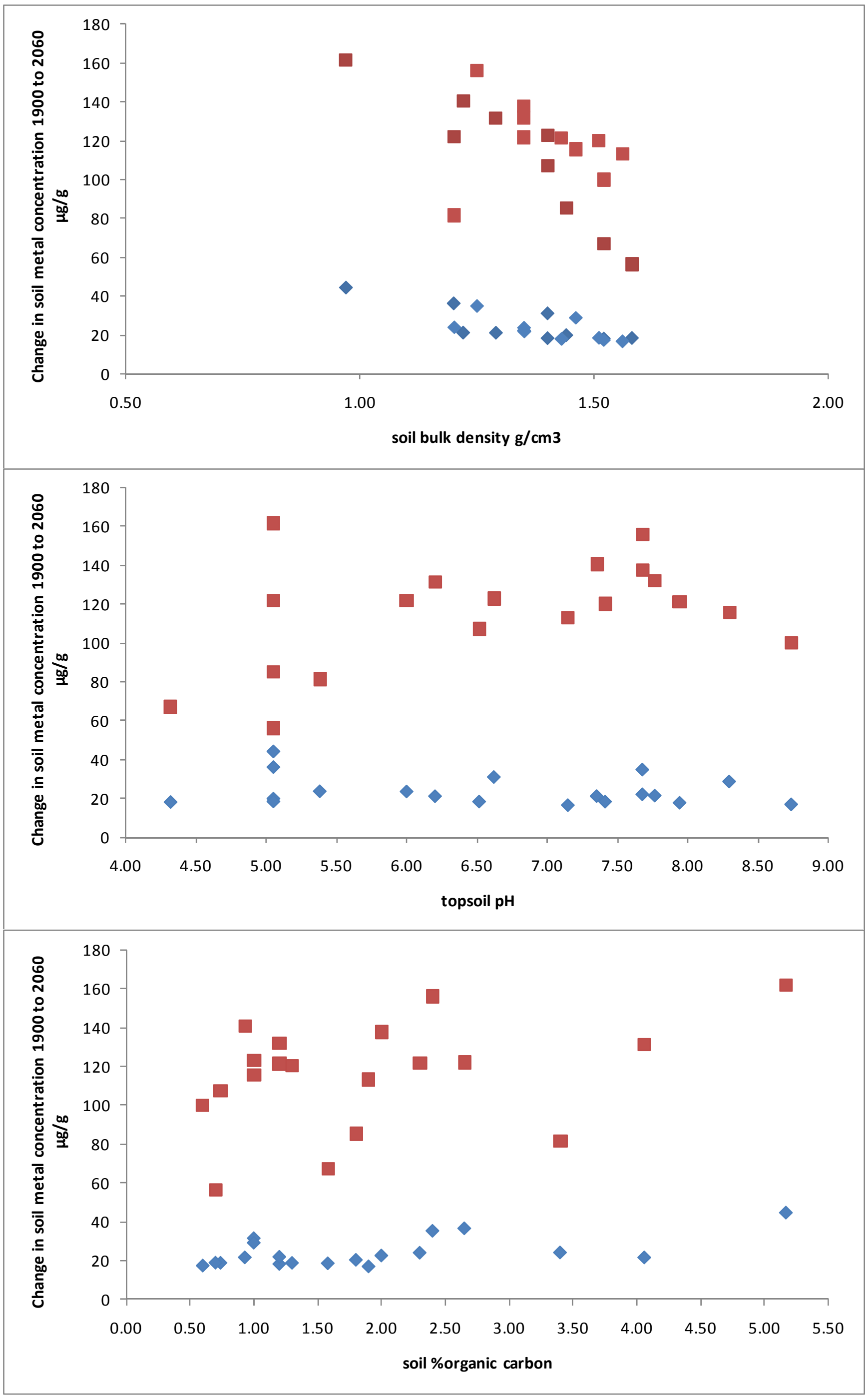

Figure 16. Relationships between the change in copper (diamonds) and zinc (squares) concentration from 1900 to 2060, and some basic soil properties. Input rates due to feed additives are 700g Cu/ha/a and 5000 g Zn/ha/a

2.7.3. Metals in surface waters

Predicted trends in surface water concentrations of dissolved copper and zinc are shown in Figures 17-21.

The model predicted no potential risk to surface waters in scenarios D1, D4, D5 or D6, within the 50 year timescale. Neither was a potential risk predicted for zinc in D2 or copper in D5, R3 or R4.

The copper PEC was predicted to exceed the site-specific PNEC in the D2 stream and ditch scenarios, only in response to the application of piglet manure, at either the N-vulnerable or N-nonvulnerable rates. Aside from this the only exceedence found for copper was in R2, in 2060, for application of piglet manure at the N-nonvulnerable rate. The site–specific PNEC for the D2 scenario is rather low (1.9 µg/l). Exploratory calculations indicated that this low value was the result of the high pH (8.3) and calcium concentration (106 mg/l) estimated for this surface water from the FOREGS dataset. It is therefore reasonable to assume that the exceedence is driven by the low site-specific PNEC as well as inputs of copper to the soil.

Exceedence of the zinc PNEC was predicted for

- D3 (by 2020, in response to all manure types);
- D5 (by 2060, in response to 7 of 11 manure types applied at the N-nonvulnerable loading rate only);
- R1 stream (exceedence by 9, 10 and 11 manure types by 2020, 2030 and 2060 respectively, at the N-nonvulnerable loading rate, and exceedence by six manure types by 2060 if applied at the N-vulnerable loading rate);
- R1 pond (exceedence by 2020 due to all manure types applied at the N-nonvulnerable loading rate, exceedence by 2030 by four manure types if applied at the N-vulnerable loading rate and exceedence by 2060 by seven manure types if applied at the N-vulnerable loading rate);
- R2 stream (by 2020, irrespective of manure type or loading rate);
- R3 stream (by 2060, in response to 7 manure types applied at the N-nonvulnerable loading rate);
- R4 stream (by 2020 in response to 7 manure types, by 2030 in response to 8 manure types and by 2060 in response to all manure types – all applied at the N-nonvulnerable loading rate).

The R1 stream scenario is vulnerable to almost all manure types applied to N-non vulnerable soils, and would be potentially vulnerable over 50 years to most manure types applied at the N-vulnerable loading rate as well. The R1 pond scenario is less vulnerable to manure applied at the N-vulnerable loading rate but is vulnerable to almost all manures at the N-nonvulnerable loading rate. The R2 scenario is predicted to be vulnerable to all manure types and loadings. The sensitivity of this scenario to metal inputs is clearly linked to the high annual runoff, which transports accumulated metals from the surface and topsoil layers to surface waters. The R3 stream is sensitive relatively few manure types (broilers and lambs) applied at the N-nonvulnerable loading rate. The R4 stream is sensitive to all manure types, except sow, applied at the N-nonvulnerable loading rate.

Exceedences in scenario D3 are extensive. All zinc input rates estimated by SCAN results in PNEC exceedence at this site in 2020 and beyond. This sensitivity to zinc input results from the low pH (5.5) and low organic matter content (0.2%) of the deep soil, coupled with the low pH (6.0) of the topsoil, which favours both leaching of zinc from the topsoil and relatively poor retention in the deep soil. The hydrology of drainflow at this site, which exhibits slow, relatively uniform drainage rather than the 'flashy' response to rainfall events that is seen at the other drainage sites, also contributes to the high predicted PECs. These factors in combination indicate a soil type highly vulnerable to leaching zinc to surface waters at potentially harmful concentrations.

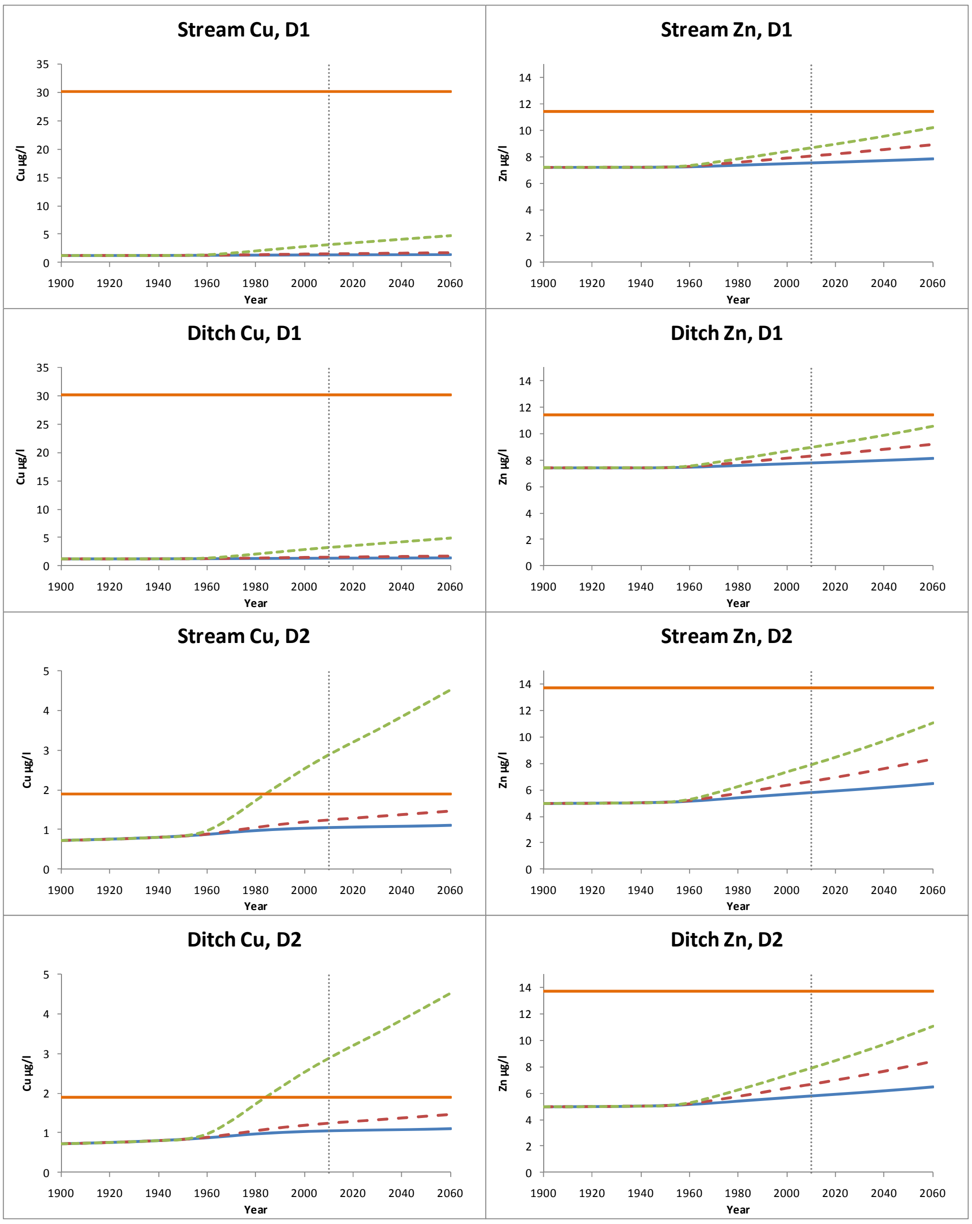

Figure 17. Time trends of predicted surface water dissolved copper and zinc in scenarios D1 (stream), D1 (ditch), D2 (stream) and D2 (ditch), for three input rates (blue line: 200 g Cu/ha/a and 1500 g Zn/ha/a; red dash: 700 g Cu/ha/a and 4000 g Zn/ha/a; green dash: 5000 g Cu/ha/a and 7000 g Zn/ha/a). The solid horizontal lines are the site-specific surface water PNECs, the dashed horizontal lines are the 'reasonable worst case' PNECs.

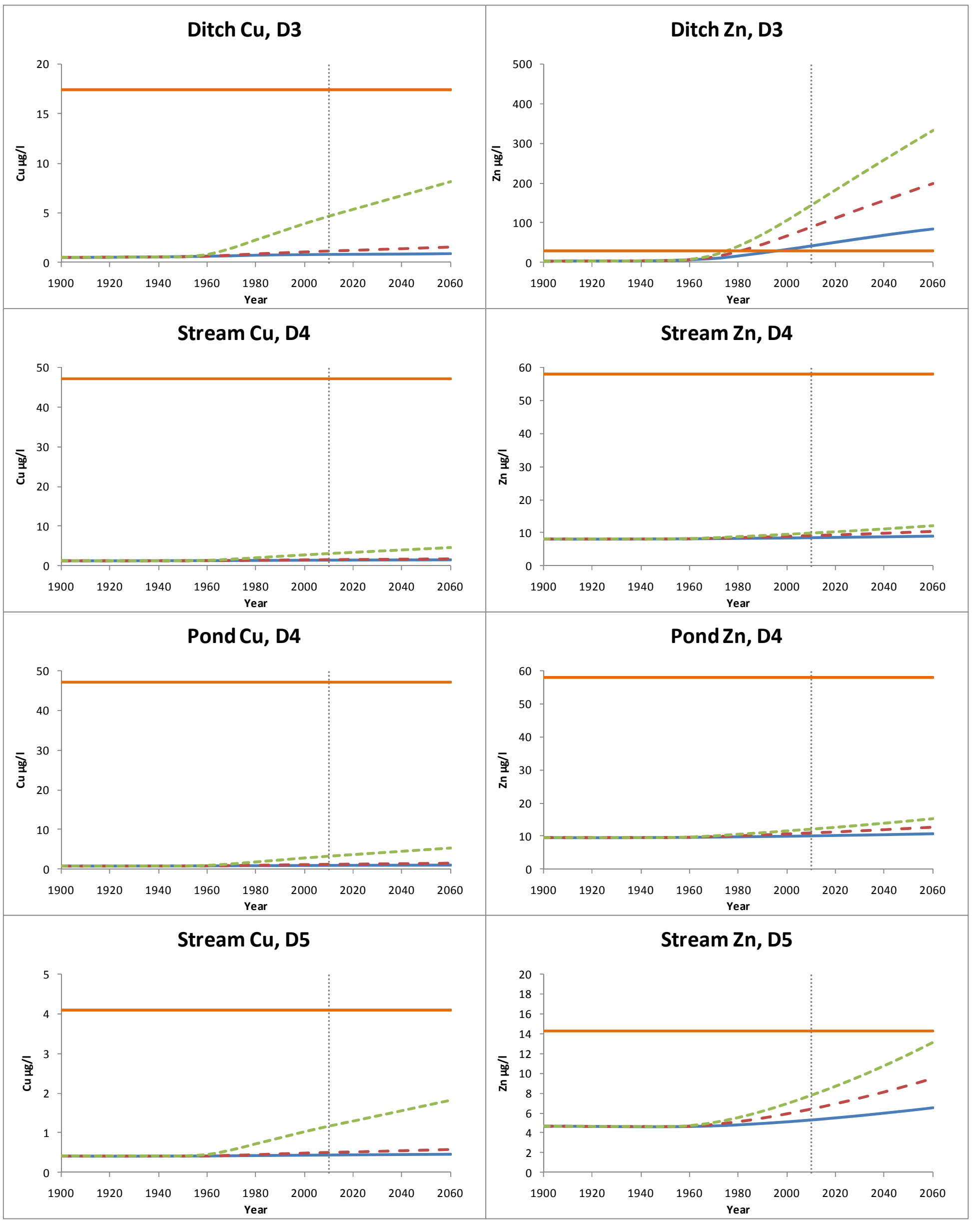

Figure 18. Time trends of predicted surface water dissolved copper and zinc in scenarios D3 (ditch), D4 (stream), D4 (pond) and D5 (stream), for three input rates (blue line: 200 g Cu/ha/a and 1500 g Zn/ha/a; red dash: 700 g Cu/ha/a and 4000 g Zn/ha/a; green dash: 5000 g Cu/ha/a and 7000 g Zn/ha/a). The solid horizontal lines are the site-specific surface water PNECs, the dashed horizontal lines are the 'reasonable worst case' PNECs.

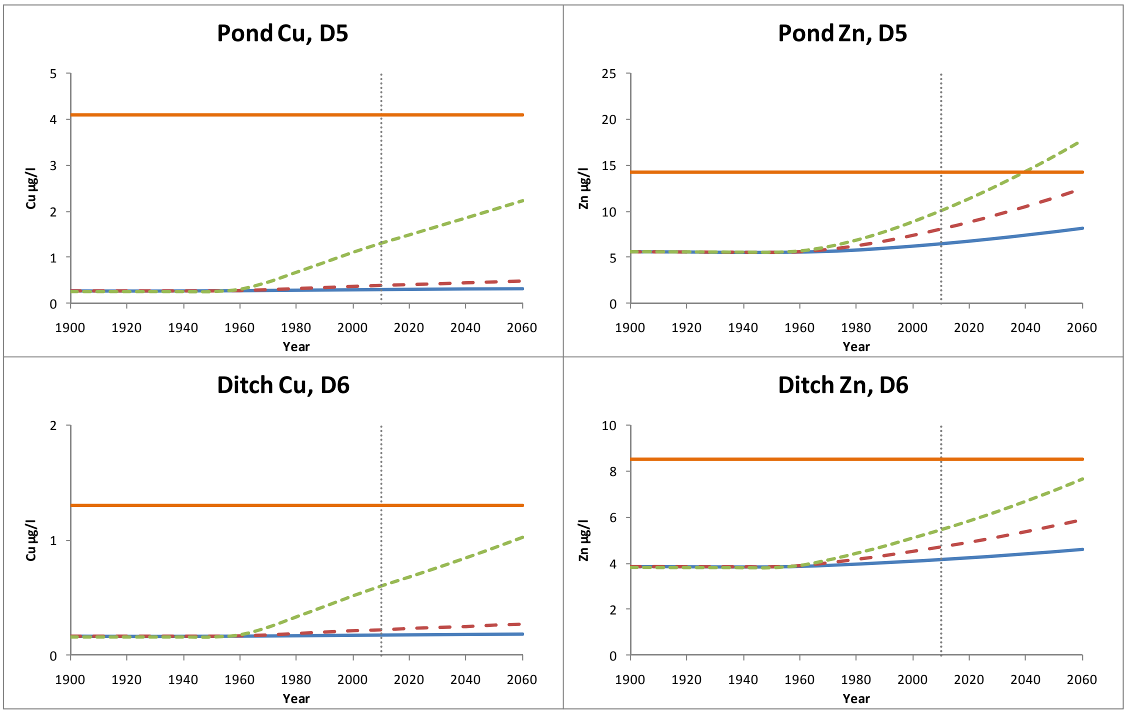

Figure 19. Time trends of predicted surface water dissolved copper and zinc in scenarios D5 (pond) and D6 (ditch), for three input rates (blue line: 200 g Cu/ha/a and 1500 g Zn/ha/a; red dash: 700 g Cu/ha/a and 4000 g Zn/ha/a; green dash: 5000 g Cu/ha/a and 7000 g Zn/ha/a). The solid horizontal lines are the site-specific surface water PNECs, the dashed horizontal lines are the 'reasonable worst case' PNECs.

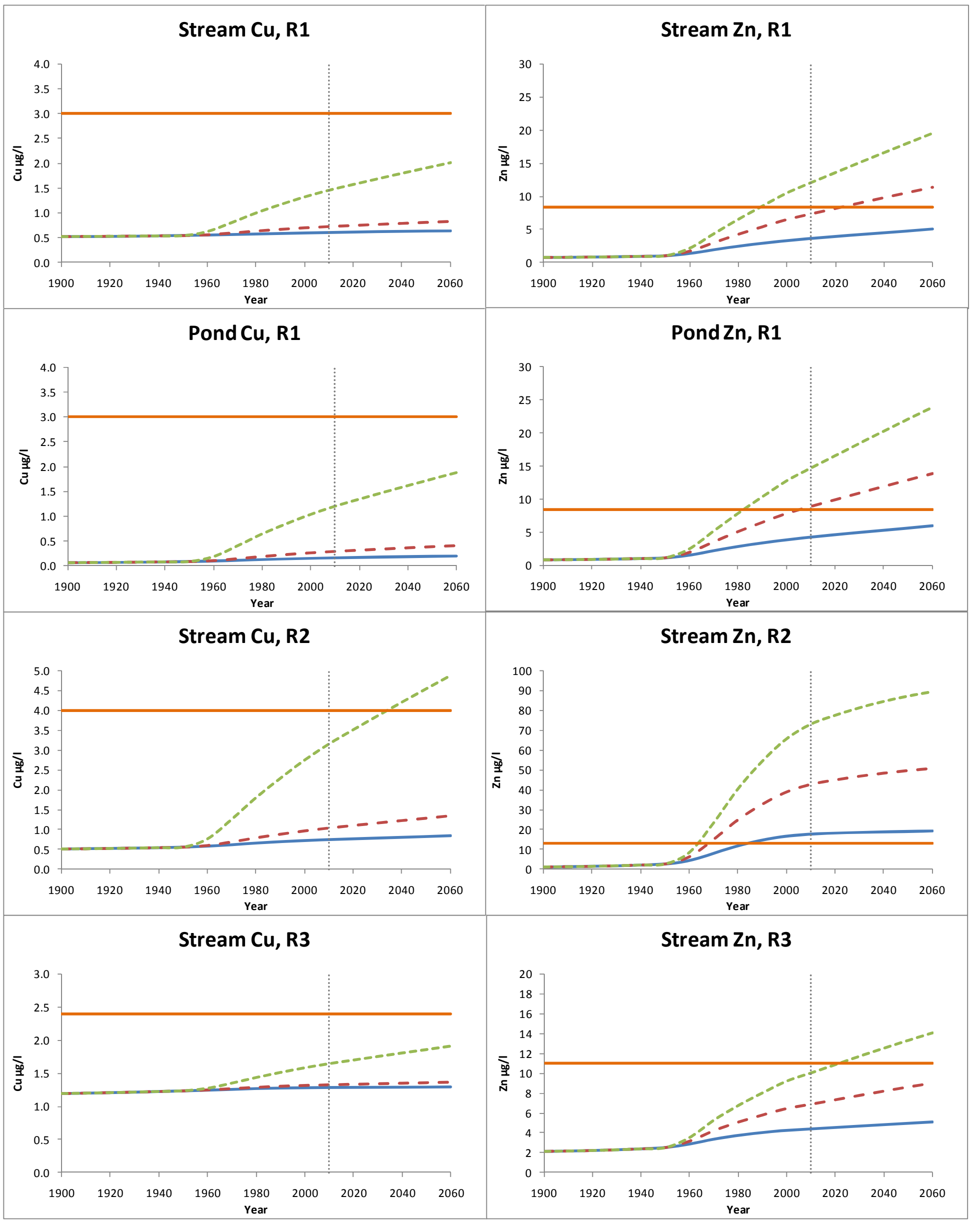

Figure 20. Time trends of predicted surface water dissolved copper and zinc in scenarios R1 (stream), R1 (pond), R2 (stream) and R3 (stream), for three input rates (blue line: 200 g Cu/ha/a and 1500 g Zn/ha/a; red dash: 700 g Cu/ha/a and 4000 g Zn/ha/a; green dash: 5000 g Cu/ha/a and 7000 g Zn/ha/a). The solid horizontal lines are the site-specific surface water PNECs, the dashed horizontal lines are the 'reasonable worst case' PNECs.

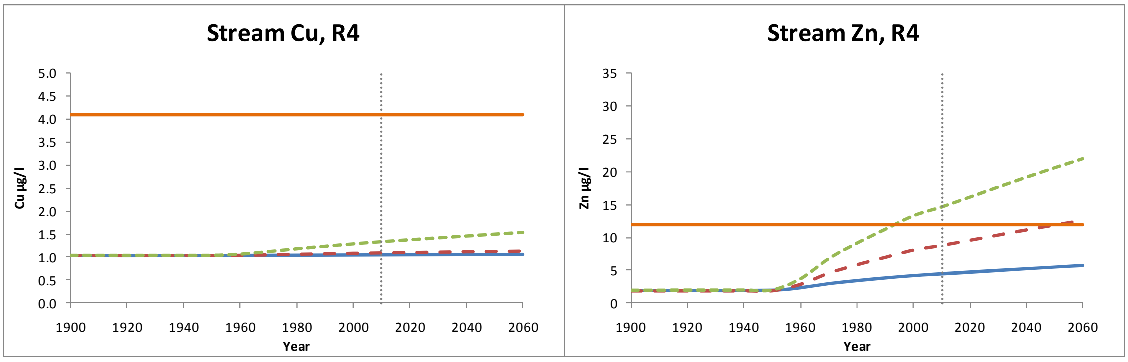

Figure 21. Time trends of predicted surface water dissolved copper and zinc in scenario R4 (stream), for three input rates (blue line: 200 g Cu/ha/a and 1500 g Zn/ha/a; red dash: 700 g Cu/ha/a and 4000 g Zn/ha/a; green dash: 5000 g Cu/ha/a and 7000 g Zn/ha/a). The solid horizontal lines are the site-specific surface water PNECs, the dashed horizontal lines are the 'reasonable worst case' PNECs.

2.7.4. Metals in sediments

Predicted exceedances of sediment PNECs were widespread, particularly for zinc. All manure types and both application rates resulted in predicted exceedences by 2020 in all the scenarios (Figures 22-26). Exceedences of copper PNECs, while not as frequent, were still numerous. In two scenarios (D2 and R3) exceedences were predicted due to all manure types and loading rates (Figures 23-26). The predictions of the D2 scenario are of particular note since this is a cracking clay soil of the type vulnerable to bypass flow during events and thus potentially to extensive transport of particles to drainage as is simulated here. Exceedences due to multiple manure types were seen in all the other scenarios with the exception of D3 ditch where only piglet manure was predicted to cause exceedence. It may be noted that with the exception of piglet manure, the other manure types result in rather similar PECs for a given time period and loading rate, thus where exceedence due to some manure types is predicted, the other manure types are often close (>95% of the PNEC) to exceedence.

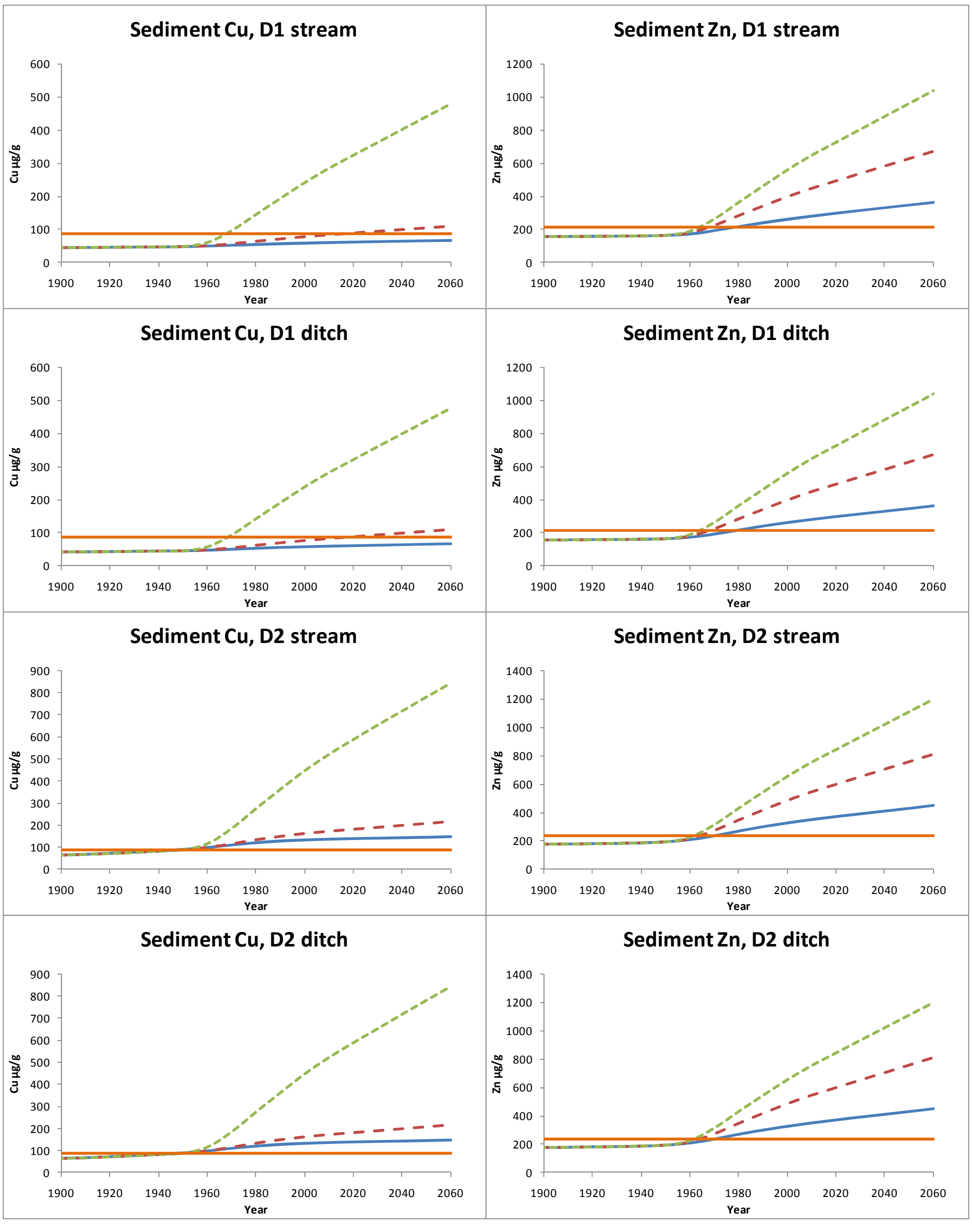

Figure 22. Time trends of predicted sediment copper and zinc in scenarios D1 (stream), D1 (ditch), D2 (stream) and D2 (ditch), for three input rates (blue line: 200 g Cu/ha/a and 1500 g Zn/ha/a; red dash: 700 g Cu/ha/a and 4000 g Zn/ha/a; green dash: 5000 g Cu/ha/a and 7000 g Zn/ha/a). The horizontal orange lines are the sediment PNECs.

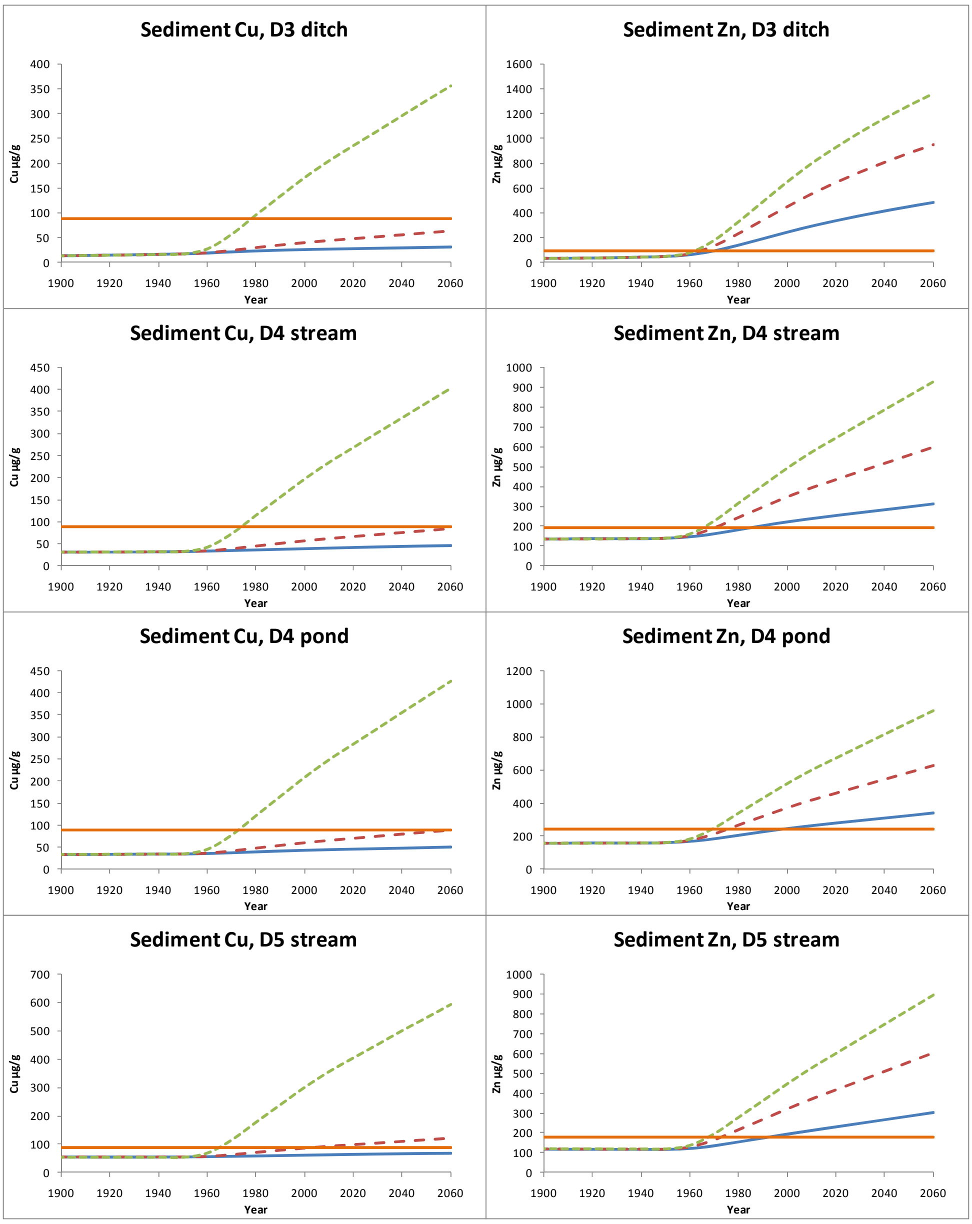

Figure 23. Time trends of predicted sediment dissolved copper and zinc in scenarios D3 (ditch), D4 (stream), D4 (pond) and D5 (stream), for three input rates (blue line: 200 g Cu/ha/a and 1500 g Zn/ha/a; red dash: 700 g Cu/ha/a and 4000 g Zn/ha/a; green dash: 5000 g Cu/ha/a and 7000 g Zn/ha/a). The horizontal orange lines are the sediment PNECs.

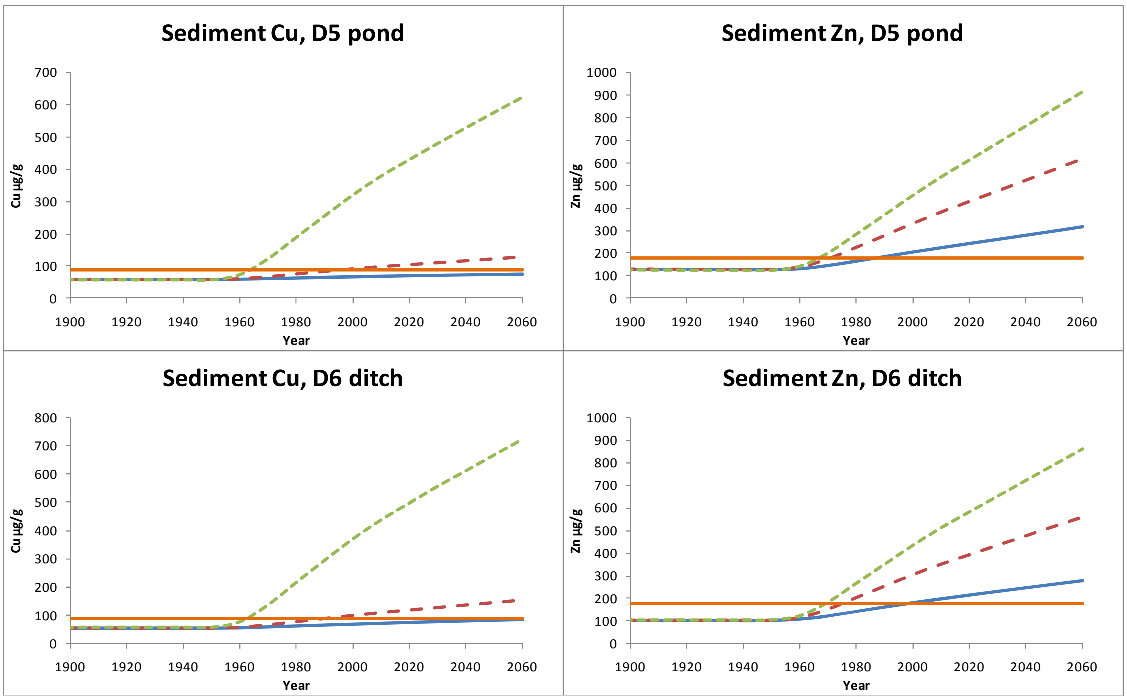

Figure 24. Time trends of predicted sediment dissolved copper and zinc in scenarios D5 (pond) and D6 (ditch), R1 (stream) and R1 (pond), for three input rates (blue line: 200 g Cu/ha/a and 1500 g Zn/ha/a; red dash: 700 g Cu/ha/a and 4000 g Zn/ha/a; green dash: 5000 g Cu/ha/a and 7000 g Zn/ha/a). The horizontal orange lines are the sediment PNECs.

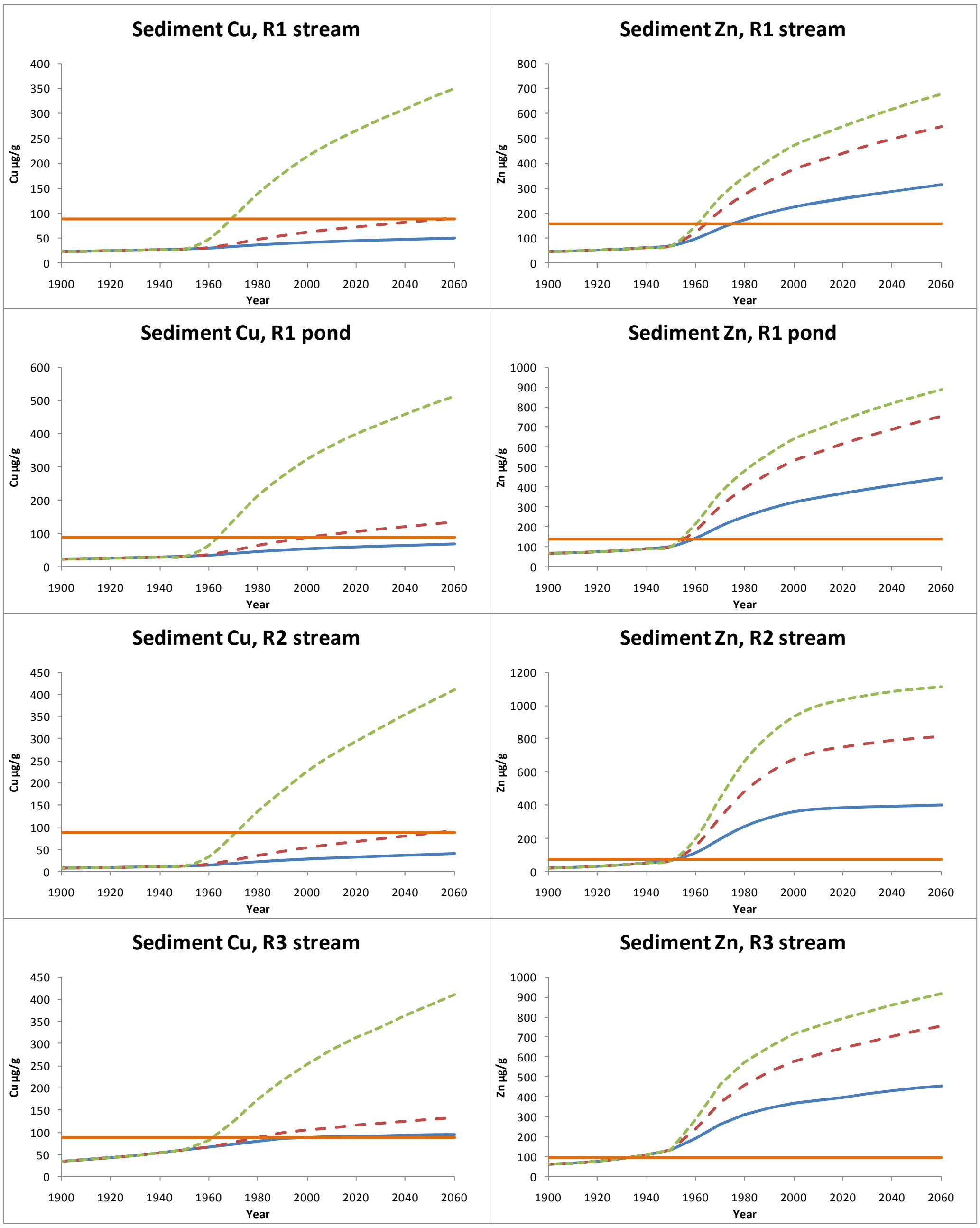

Figure 25. Time trends of predicted sediment dissolved copper and zinc in scenarios R1 (stream), R1 (pond), R2 (stream), and R3 (stream), for three input rates (blue line: 200 g Cu/ha/a and 1500 g Zn/ha/a; red dash: 700 g Cu/ha/a and 4000 g Zn/ha/a; green dash: 5000 g Cu/ha/a and 7000 g Zn/ha/a). The horizontal orange lines are the sediment PNECs.

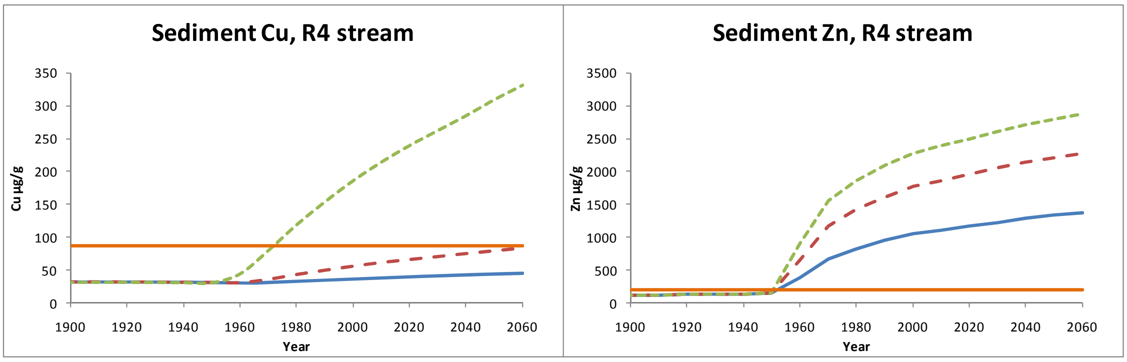

Figure 26. Time trends of predicted sediment dissolved copper and zinc in scenario R4 (stream), for three input rates (blue line: 200 g Cu/ha/a and 1500 g Zn/ha/a; red dash: 700 g Cu/ha/a and 4000 g Zn/ha/a; green dash: 5000 g Cu/ha/a and 7000 g Zn/ha/a). The horizontal orange lines are the sediment PNECs.

2.7.5. Drainage and runoff waters

Predicted concentrations of metals in runoff from the topsoil (Figures 27-29) provide a 'absolute worst case' estimate of transient surface water exposure at extreme drainage or runoff discharge. All the scenarios showed sensitivity to metal loading. Increases in predicted runoff copper were less severe than for zinc; in the extreme case of scenario D3 runoff zinc was predicted to approach 1000 µg/l in 2060 at higher loadings, while copper in runoff was always predicted to be below 20 µg/l. There was considerable variability in the concentrations of zinc in drainage and runoff across the locations, as the leaching behavior of this metal is more sensitive to soil chemistry than copper. In the absence of PNECs for assessing transient exposure of freshwater organisms to copper and zinc, the risks associated with these extreme event concentrations cannot be quantitatively assessed, thus they presented here largely for information. Nonetheless, the high sensitivity of runoff metal to increasing soil loading indicates potential risks that may need to be investigated further.

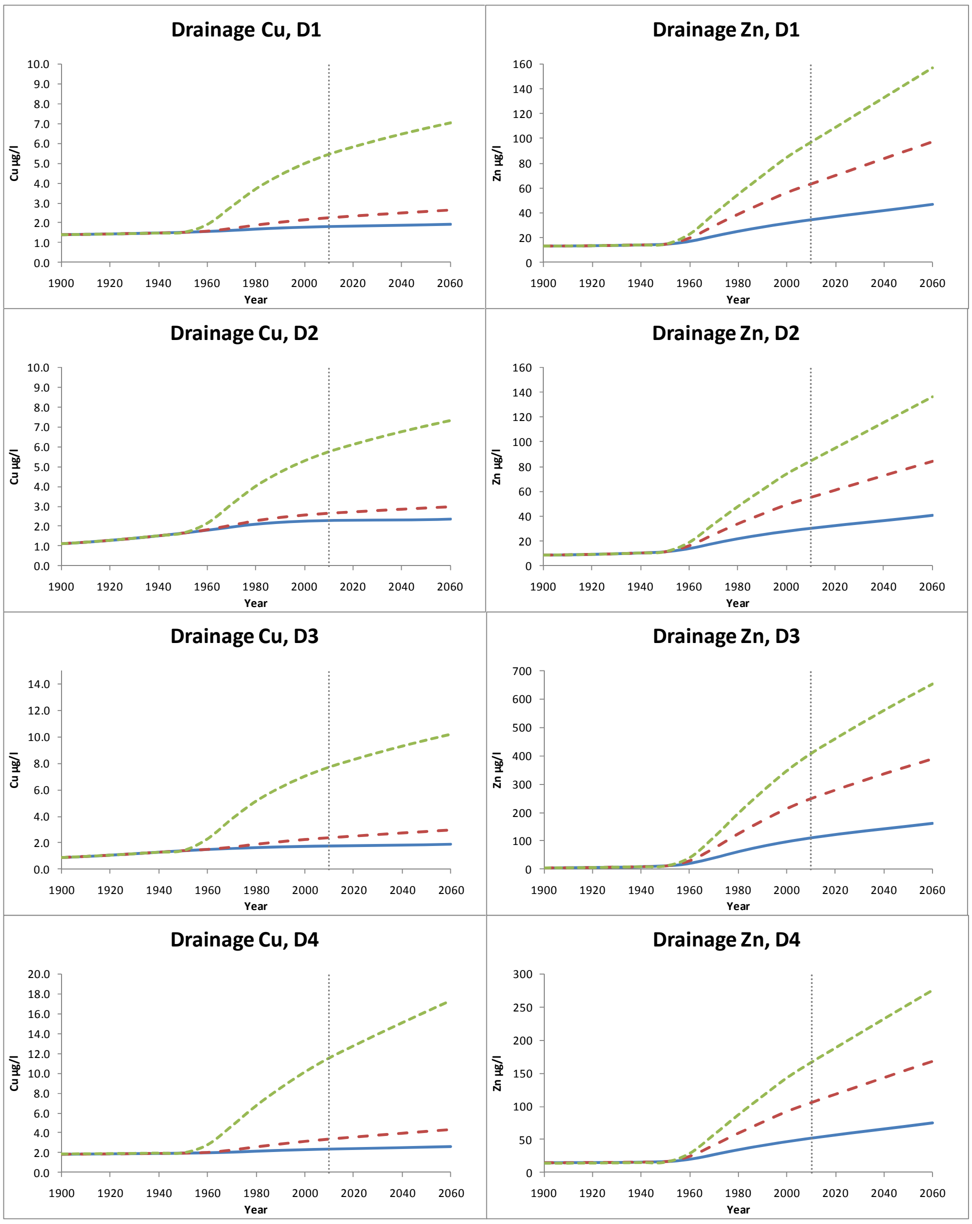

Figure 27. Time trends of dissolved copper and zinc in topsoil drainage for scenarios D1-D4, for three input rates (blue line: 200 g Cu/ha/a and 1500 g Zn/ha/a; red dash: 700 g Cu/ha/a and 4000 g Zn/ha/a; green dash: 5000 g Cu/ha/a and 7000 g Zn/ha/a).

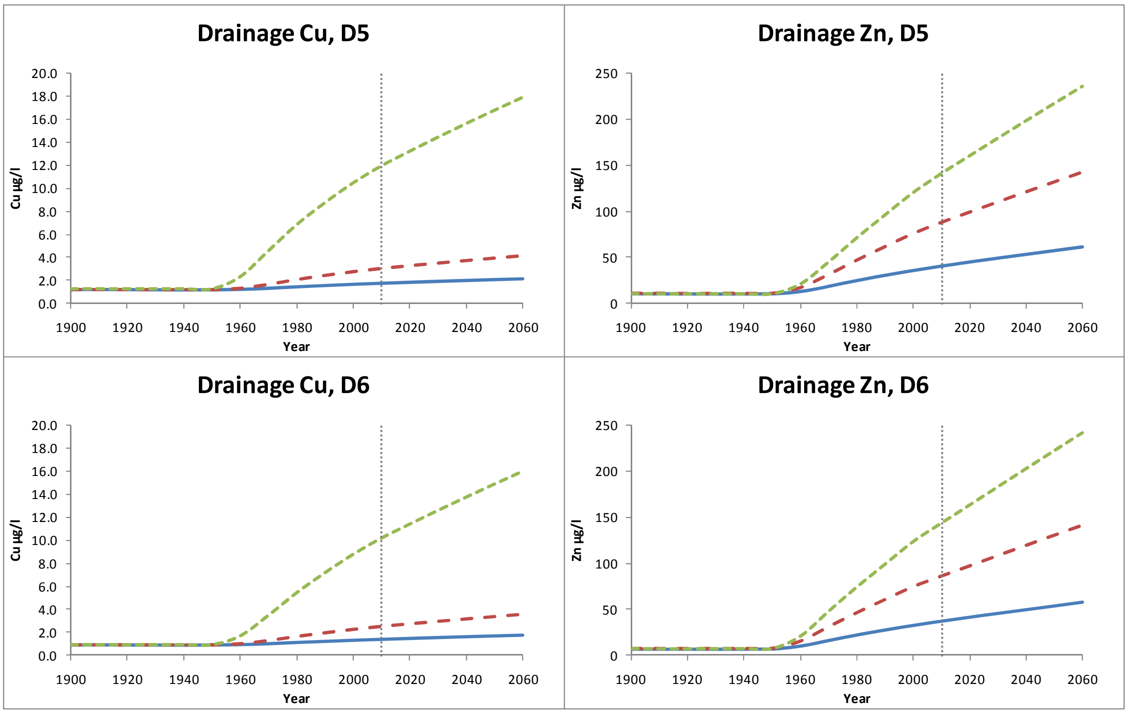

Figure 28. Time trends of dissolved copper and zinc in topsoil drainage for scenarios D5-D6, for three input rates (blue line: 200 g Cu/ha/a and 1500 g Zn/ha/a; red dash: 700 g Cu/ha/a and 4000 g Zn/ha/a; green dash: 5000 g Cu/ha/a and 7000 g Zn/ha/a).

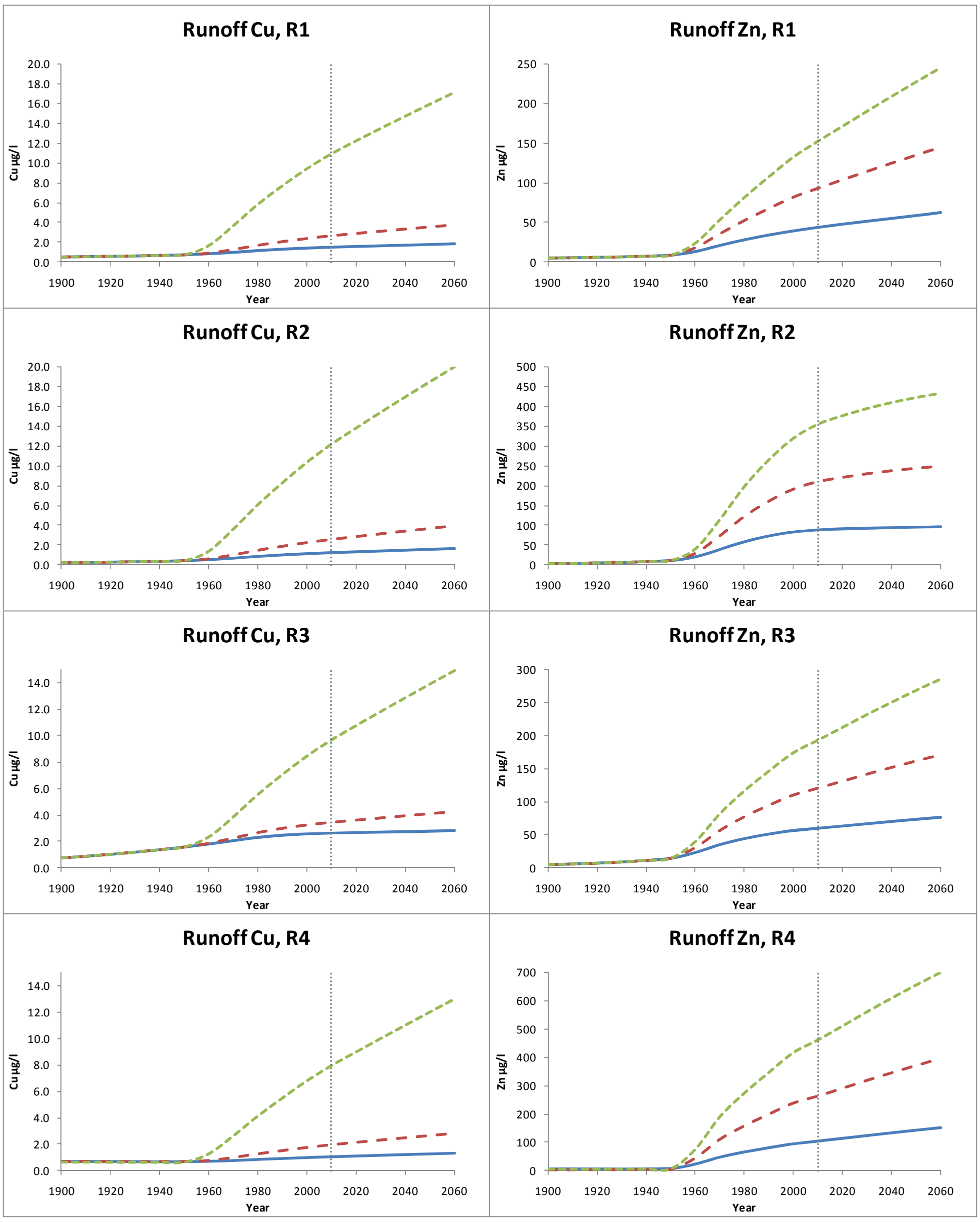

Figure 29. Time trends of predicted runoff dissolved copper and zinc in the R scenarios, for three input rates (blue line: 200 g Cu/ha/a and 1500 g Zn/ha/a; red dash: 700 g Cu/ha/a and 4000 g Zn/ha/a; green dash: 5000 g Cu/ha/a and 7000 g Zn/ha/a).

2.8. Discussion

2.8.1. Model performance and uncertainties

The IDMM is intermediate in complexity between simple dynamic 'box models' of soil and more models where complex soil hydrology is simulated on short timesteps of minutes to days. The use of a more complex model, while feasible, would not be compatible with the need to simulate metal accumulation and the consequent effects on metal concentrations in drainage and runoff over a period of several decades. So in conception the IDMM has a level of complexity and parameter requirement suited to the type of risk assessment applied here.

Despite the relative simplicity of the IDMM, the model requires an appreciable level of parameterization, and there will be uncertainties associated with each. Key sets of parameters are:

- Soil properties, e.g. bulk density, pH and organic matter content, concentrations of DOC in porewater;
- Hydrological parameters, i.e. relative volumes of water draining and leaching from each soil layer;
- Metal weathering rates;
- Historic metal inputs.
- Additionally, there will be uncertainty associated with the parameterization of processes within the model:
- Parameters of the transfer function for soil-solution partitioning and for metal binding to DOC in porewater;
- Parameters of the aging model;
- Uptake of metals by crops;
- Metal enrichment of eroded soil particles.

For some of the above processes, particularly the solid-solution partitioning and metal binding to DOC, there are sufficient amounts of data available for calibration and validation (e.g. Tipping et al. 2003). The modelling of metal aging is less advanced. The aging model developed for this work is relatively simple, and it is known that soil parameters besides pH can also influence aging rates (Buekers et al. 2007), although data are currently rather sparse. The further development and refinement of aging models is an active area of research. It is worth noting that other models that simulate metal movement through soil (e.g. de Vries et al. 2004) may well do so by considering the partitioning of the total metal pool between soil and water as a function of soil properties, rather than by considering aging. This has the advantage of allowing the total metal pool to be simulated, rather than the sum of the labile and aged pools, and avoids the need to invoke an inert pool of metal to explain the total pool, as we have done here. However, the approach taken in the IDMM does allow for a better understanding and appreciation of the changes in soil metal pools in time in response to changing inputs. It also demonstrates that the partitioning of metal between labile, aged and inert pools is likely to be a function of inputs over time, as well as soil properties, suggesting that it may be superior to an approach where total metal is partitioned on the basis of soil properties alone. This is currently a somewhat tentative conclusion, though, and more research is needed to further understand how metals partition among different forms in soils.

For the other factors noted the amount of available data for model parameterization is small, and consequently it is necessary to take a pragmatic approach to parameter selection. In this category are the concentrations of DOC in porewater, and the enrichment of eroded soil particles in metal. It has long been appreciated that the strong binding of most metals to DOC implies that DOC losses from soil are likely to be important for metal leaching, more so for copper than for zinc since the former is a stronger binder to DOC. Understanding of what drives DOC concentrations from soils is however still not at a stage where robust prediction is possible, particularly so for agricultural soils. The approach taken was there considered to be the most pragmatic option possible. Estimation on the basis of soil properties, such as the approach of Römkens et al. (2004), is conceptually attractive, but must be considered with caution if based on laboratory extraction of DOC since the concentrations found are typically higher than those seen in field samples (e.g. from lysimeters). Given the increasing interest in potential impacts of metals entering agricultural soils, more research on DOC losses is needed to improve confidence in model predictions.

There is a general lack of good quality validation data against which to test a dynamic soil model such as the IDMM, so, for example, there was no opportunity to directly validate the predictions made for risk assessment purposes against observations at any of the sites simulated. There is a thus pressing need for high quality, site specific data on metal fluxes through agricultural soils to surface waters. Particularly useful would be flux and concentration data for a range of timescales, since this would enable further testing of the model concepts and allow the investigation of the influence of events on long term leaching and surface water concentrations. Nonetheless, the available datasets proved useful in improving confidence in the ability of the model to predict future metal pools with a degree of success. The UK uplands dataset is valuable because it provides information on metal accumulation in a relatively simple soil system where some of the more complex hydrological and pedological features of the FOCUS soils are absent. The ability of the model to reproduce observed pools of labile metals, and surface water dissolved metal concentrations (Section 2.7) suggests that the description of the metal chemistry is sound, and that the simple picture of hydrology used is appropriate for long-term simulation. As a dataset on an agricultural catchment having received inputs of manure for a number of decades, the Kleine Aa dataset was highly useful for testing. Comparisons of predicted metal pools in the mineral soil and dissolved metal concentrations in drainage water were highly encouraging. In the latter case the choice of zinc weathering rate was shown to be critical. The literature on rates of metal weathering from rocks and soils is virtually non-existent, which presents problem to the modeller. The weathering rates calculated for the scenario soils were seen to give variable performance, with considerable overestimation of the likely pristine porewater concentrations in some cases. This uncertainty drove the decision to set all weathering rates to zero for the main simulations, which taking the scenarios as a whole produced satisfactory ranges of 'pristine' metal concentrations in drainage and runoff. Nonetheless, it must be recognised that the relative lack of validation makes assessment of the plausibility of the results somewhat challenging and the possibility that risks may be either underestimated or overestimated cannot be discounted. In this context, a precautionary approach to managing metal inputs to the arable environment is advisable.

2.8.2. Comparison of the IDMM with Dutch models

A potentially useful comparison that can be done is to compare the outputs of the IDMM against those of the models used by de Vries et al. (2004) and Groenenberg et al. (2006) to consider the long term accumulation and leaching of zinc and copper, respectively, in Dutch arable soils. In Tables 16 and 17 predicted topsoil fluxes of copper and zinc at the FOCUS D sites for the year 2010 are compared against mean values computed for four Netherlands soil types under agricultural use. The comparison is confined to the FOCUS D sites as they are considered the most topographically and hydrological similar to the Netherlands situation. Both sets of fluxes refer to 0-30cm depth so are comparable in that respect. The copper input rates of Groenenberg et al. (2004) are somewhat higher than those presented for the IDMM, but not greatly, while the zinc input rates presented by de Vries et al. (2004) are approximately half those used in the IDMM simulations. In the IDMM dataset, accumulation, leaching and crop offtake of copper made up 79-92%, 2-5% and 5-18% of the input copper, respectively. The corresponding figures for the Groenenberg et al. (2004) data are 66-76%, 6-17% and 14-24% respectively. Some caution is required in comparing the two sets of results since the Netherlands data are means of a large number of simulations over a relatively small geographical area while the IDMM outputs refer to single sites with a wide geographical spread. The IDMM predicts smaller leaching fluxes and somewhat higher accumulation than the Groenenberg model, but overall the two sets of results are rather comparable. Greater discrepancies may be noted when comparing the IDMM zinc predictions with those of de Vries et al. (2004). The IDMM predicts a greater degree of accumulation than the de Vries model (mean of 85% of inputs, compared with 52% for the de Vries model) and a smaller proportion (7% compared to 35%) of crop uptake. It must be noted that the de Vries et al. data for crop uptake reflect the simulation of a wider range of crops than was done in the IDMM simulations, and it is possible that the observed discrepancy is due to this;

nonetheless, this discrepancy warrants further investigation. Leaching fluxes of zinc vary considerably within both datasets and in both cases are higher in sandy soils.

Overall, there is a certain, encouraging degree of agreement between the IDMM and the copper model. Agreement with the zinc model is less certain, and the reasons why crop uptake rates differ between the two models need to be investigated further.

Table 16. Comparison of IDMM-predicted topsoil copper fluxes for the FOCUS D sites with the fluxes predicted by Groenenberg et al. (2006).

	Site	Soil type	Input	Adsorption	Aging	Total accumulation	Leaching	Crop uptake
						all g/ha/a		
IDMM (this study)	D1	Silty clay	207	91	84	175	5	27
	D2	Clay	218	88	84	172	12	35
	D3	Sand	209	100	64	164	8	37
	D4	Loam	206	93	77	170	4	32
	D5	Loam	206	98	73	171	4	30
	D6	Clay loam	206	94	96	190	5	11
Alterra model (Groeneberg et al. 2006)	-	Sand	345	-	-	237	59	48
	-	Sand calcareous	256	-	-	185	29	42
	-	Clay	239	-	-	158	24	57
	-	Clay calcareous	295	-	-	224	17	54

Table 17. Comparison of IDMM-predicted topsoil zinc fluxes for the FOCUS D sites with the fluxes predicted by de Vries et al. (2004).

	Site	Soil type	Input	Adsorption	Aging	Total accumulation	Leaching	Crop uptake
						all g/ha/a		
IDMM (this study)	D1	Silty clay	1564	221	1174	1396	61	108
	D2	Clay	1605	210	1162	1372	88	146
	D3	Sand	1557	484	574	1058	327	172
	D4	Loam	1549	272	1083	1355	77	118
	D5	Loam	1541	337	1005	1341	78	122
	D6	Clay loam	1541	193	1205	1397	110	34
Alterra model (de Vries et al. 2004)	-	Sand	1039	-	-	271	377	392
	-	Sand calcareous	868	-	-	463	86	319
	-	Clay	911	-	-	521	43	347
	-	Clay calcareous	899	-	-	642	19	238

2.8.3. Contribution of animal feeds to metal levels in the environment

The presence of metals in animal feeds and consequent loading to agricultural land via manure application will increase metal levels in soils and their receiving waters, if applied in sufficient quantities.

Metals added to soils can persist for decades to centuries, depending upon the input rate, the soil type and the tendency for metal to be removed in drainage and runoff.

The annual loss of soil metal to receiving waters in dissolved or particle-bound form is usually a very small proportion of the total soil pool, thus metals entering the soil system as a result of animal feed supplementation may act as a source of metals to receiving waters and sediments for decades to centuries.

2.8.4. Risks associated with current levels of feed additives

The risks of potentially toxic metal additions to agricultural soil are not immediate, but are associated with the slow accumulation of a pool of soil-bound metal, on a timescale of decades or longer, to a point where its concentration is sufficient to either affect soil organisms directly, and/or to give rise to metal concentrations in runoff and drainage that raise concentrations in receiving waters to levels toxic to aquatic and sediment organisms.

Based on the range of soil types simulated in this work and the timescale considered, potential risks to soil organisms due to copper have been identified as a result of application of piglet manure. However, of the nine scenarios where a potential risk was identified, only two have locally significant pig production. Levels of copper in other types of manure are too low to create a potential risk within the timescale considered.

Potential risks to soil organisms from zinc were identified in a smaller number of scenarios than copper. However, the range of metal loading rates giving rise to potential risk overlapped with zinc loading rates associated with a wide range of manure types. Thus the potential risks to soil due to zinc inputs in manures are more widespread and associated with a wider range of livestock.

Potential risks associated with the exposure of aquatic organisms to toxic levels of dissolved metals, following loss from the soil in drainage and runoff, were predicted at fewer locations than direct soil effects. Effects of copper were predicted at fewer locations than zinc, largely because copper is retained more strongly than zinc by the soil solids. Predicted zinc concentrations in receiving waters varied widely due to the sensitivity of metal leaching behaviour to the soil chemistry. In the extreme case of an acidic, low organic matter soil D3, the surface water PNEC was predicted to be exceeded after 10 years by the continuous application of any type of manure. The potential risks to surface waters due to zinc are highly dependent upon the chemistry of the soil receiving inputs.

Predicted concentrations of metals in the sediments of receiving waters, derived from erosion of metal-enriched particles and transport in drainage and runoff, responded dramatically to increases in metal inputs due to manure application. Potential risks were predicted within 50 years in all scenarios, and frequently within much shorter timescales. In most of the scenarios potential risk was predicted for all manure types. Copper and zinc responded similarly to increased loadings, since the process is physical rather than chemical. Caution must be exercised not to overinterpret these findings, since they are based on a conceptual submodel of particle flux and metal enrichment supported by a minimal amount of data. Nevertheless, the possibility of significant enrichment of receiving water sediments with metals, as a result of manuring, needs proper consideration. More research is required to establish the degree to which erosion of metal-enriched particles could be a significant vector of metals from agricultural soils is a widespread and significant process.

2.8.5. Benefits of reducing metal contents of feed additives

The potential risks due to excessive metal levels in the environment, particularly in soils and their receiving waters, develop over timescales of decades in response to continuous inputs. Conversely, reducing inputs of metals to the environment following excessive inputs tends to produce only slow reductions in levels, due to the strong binding of metals to soils and their consequent persistence. Thus, a proactive, preventative approach to the management of metal inputs to agricultural soils is highly appropriate. Given the current uncertainties involved in assessing and validating long term models of metal behaviour, and the possibility that risks may be currently underestimated, a precautionary approach to managing metal inputs to soils is highly attractive, since it provides researchers with a window of opportunity to refine, test and validate predictive models to give more realistic risk assessments.

Whether done proactively, or retrospectively following excessive metal accumulation, reducing metal contents in feed additives will reduce or reverse metal accumulation in soils receiving animal manure inputs. For soils not yet at risk, reducing metal accumulation will increase the amount of time before the soil becomes at risk, allowing alternative manure management options to be considered. For soils already at risk, reducing or reversing metal accumulation will limit the extent of potential ecological damage, albeit most likely on at least a decadal timescale.

If current rates of metal accumulation are considered acceptable, reductions in the metal content of feed additives could allow higher rates of manure application if this is desirable and consistent with associated legislation on the permitted inputs of other elements to the soil environment.

Conclusions and Recommendations

CONCLUSIONS

AQUACULTURE

- Simple models recommended by EFSA for the assessment of environmental risks of aquaculture treatments were used to estimate exposure for Cu and Zn in surface waters and sediments. The predictions are likely to be 'worst case' as they predict concentrations immediately below the cages and do not consider potential dissipation processes e.g. due to sediment transport.
- Water concentrations, estimated for different fish types farmed in raceways/ponds/tanks and recirculation systems, ranged from 12.2 – 12.6 µg/l for Zn and 1.13 – 2.99 µg/l for Cu. Concentrations in marine sediments, arising from the use of feed additives in sea cage aquaculture, were 21.3 mg/kg and 182mg/kg respectively
- For all fish species in the cage/raceway/pond/tank and recirculating systems, predicted concentrations of Cu and Zn were below PNECs indicating that the use of both metals in feed additives for fish poses an acceptable risk to the environment. For cage systems, the exposure concentration for Cu was also below the PNEC indicating an acceptable risk.

Livestock

The predicted risks to soils due to application of copper and zinc to agricultural land in animal manures are largely influenced by input loading rate (i.e. by manure type), by soil sensitivity and by tillage frequency.

Risks of exceeding the soil copper PNEC are predicted only for long term (50 years) application of manure derived from piglet rearing, in all the scenarios. In only two of these scenarios (D3 and Ringkøbing) is swine rearing locally significant.

Risks of exceeding the soil zinc PNEC are predicted at fewer sites than for copper, but the number of manure types whose continuous application presents a risk of exceedence is larger. This is particularly so in the most sensitive scenario (Ringkøbing) where the application of most manure types for 50 years is predicted to result in PNEC exceedence. This is largely due to the ecological sensitivity of this acidic sandy soil to zinc accumulation, as indicated by the low PNEC of 31 mg Zn/kg soil.

Application of manures to nontilled soils results in accumulation of metal close in the surface. In the scenarios in question, no exceedence of metal PNECs in soil is seen if the average metal concentration in the 0-30cm layer is considered; however some exceedence is found in two-thirds of the scenarios for the 0-5cm layer, depending upon the predicted accumulation rate.

Risks of exceeding the freshwater PNECs are fewer than those for soil, particularly for copper where only two potential exceedences are identified. This is due to the relatively strong retention of copper by soils, resulting in only small predicted increases in average surface water concentrations in response to manure application. In contrast, leaching of zinc in drainage and runoff is more pronounced in response to increasing manure application. In the extreme case of an acidic sandy soil (D3), the surface water PNEC is predicted to be exceeded after 10 years by the continuous application of any manure type. Apart from this scenario, zinc concentrations in surface waters tend to be more sensitive to application rate in the runoff scenarios rather than the drainage scenarios, although this does not necessarily lead to potential risks regardless of manure type within the considered timeframe.

Concentrations of zinc and copper in topsoil runoff are sensitive to increasing manure application in all scenarios. In particular, zinc application leads to predicted runoff concentrations above 100 µg/l in 2060 at all sites under the highest application rates, and in the most sensitive soil (D3) to concentrations over 600 µg/l. While these concentrations represent ‘absolute worst case’ conditions for surface water organism exposure under transient conditions of high discharge and should be taken only as indicative of potential exposure, there is a clear need to establish these metal concentrations are indeed realistic prediction of the situation that may arise under long term manure application.

Predicted risk due to sediment PNEC exceedence is identified in all the scenarios, and is associated with transport of metal-enriched particles to surface waters in drainage and runoff. More research is required to investigate whether this process is indeed a significant influence on metal transfer to sediments at the concentrations predicted.

The systems most vulnerable to metal input in manure are clearly acid sandy soils, represented in the scenarios by the D3 and Ringkøbing sites. The distribution of these scenarios within Europe is largely in Flanders, the Netherlands, northwestern Germany and Denmark. There is a clear need to better establish whether such soils are as sensitive to metal inputs as is predicted here, for example by field surveys of copper and zinc concentrations in drainflow from fields with known histories of metal input rates. Since problems of high metal concentrations in drainflow and runoff, once established, would be difficult to remediate, it is important to proactively assess soil sensitivity before setting policy on manure application.

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Appendices

APPENDIX A - PREDICTED ENVIRONMENTAL CONCENTRATIONS (PECS) OF COPPER AND ZINC IN TOPSOILS, FRESHWATERS AND FRESHWATER SEDIMENTS

TOPSOIL COPPER CONCENTRATIONS, D1 (mg/kg)

	2020 vul	2030 vul	2060 vul	2020 nonvul	2030 nonvul	2060 nonvul
Fattening pigs	18	19	22	26	29	35
Sows with piglets	16	16	18	21	22	26
Dairy cows	19	20	23	27	29	36
Fattening cattle	19	20	23	27	29	36
Veal calves	15	15	17	19	20	24
Sheep-goats	15	15	17	19	21	24
Fattening lambs	20	21	25	29	32	40
Broilers	20	21	24	29	31	39
Laying hens	19	20	24	28	31	38
Turkeys	19	20	23	27	29	36
Piglets	51	57	74	93	105	**141**

TOPSOIL COPPER CONCENTRATIONS, D2 (mg/kg)

	2020 vul	2030 vul	2060 vul	2020 nonvul	2030 nonvul	2060 nonvul
Fattening pigs	25	26	29	34	36	43
Sows with piglets	22	23	25	27	29	33
Dairy cows	25	26	30	34	37	44
Fattening cattle	25	26	30	34	36	44
Veal calves	21	22	23	26	27	31
Sheep-goats	21	22	24	26	27	31
Fattening lambs	26	28	32	37	40	48
Broilers	26	28	31	36	39	47
Laying hens	26	27	31	35	38	46
Turkeys	25	26	30	34	37	44
Piglets	60	66	85	106	119	**157**

TOPSOIL COPPER CONCENTRATIONS, D3 (mg/kg)

	2020 vul	2030 vul	2060 vul	2020 nonvul	2030 nonvul	2060 nonvul
Fattening pigs	17	18	21	25	27	33
Sows with piglets	14	14	16	19	20	24
Dairy cows	17	18	21	25	28	34
Fattening cattle	17	18	21	25	27	34
Veal calves	13	14	15	17	19	22
Sheep-goats	13	14	15	18	19	22
Fattening lambs	18	19	23	28	30	38
Broilers	18	19	23	27	30	37
Laying hens	17	19	22	26	29	36
Turkeys	17	18	21	25	28	34
Piglets	49	**55**	**72**	**91**	**103**	**139**

TOPSOIL COPPER CONCENTRATIONS, D4 (mg/kg)

	2020 vul	2030 vul	2060 vul	2020 nonvul	2030 nonvul	2060 nonvul
Fattening pigs	17	18	21	24	26	32
Sows with piglets	14	15	17	19	20	24
Dairy cows	17	18	21	25	27	33
Fattening cattle	17	18	21	25	27	33
Veal calves	14	14	16	18	19	22
Sheep-goats	14	14	16	18	19	22
Fattening lambs	18	19	23	27	29	36
Broilers	18	19	22	26	29	36
Laying hens	18	19	22	26	28	34
Turkeys	17	18	21	25	27	33
Piglets	46	51	**67**	**84**	**95**	**127**

TOPSOIL COPPER CONCENTRATIONS, D5 (mg/kg)

	2020 vul	2030 vul	2060 vul	2020 nonvul	2030 nonvul	2060 nonvul
Fattening pigs	14	14	17	21	22	28
Sows with piglets	11	12	13	15	17	20
Dairy cows	14	15	18	21	23	29
Fattening cattle	14	15	17	21	23	29
Veal calves	11	11	12	14	15	18
Sheep-goats	11	11	13	14	15	19
Fattening lambs	15	16	19	23	25	32
Broilers	15	16	19	23	25	32
Laying hens	14	15	18	22	24	30
Turkeys	14	15	18	21	23	29
Piglets	42	47	62	79	89	**120**

TOPSOIL COPPER CONCENTRATIONS, D6 (mg/kg)

	2020 vul	2030 vul	2060 vul	2020 nonvul	2030 nonvul	2060 nonvul
Fattening pigs	33	34	37	41	43	49
Sows with piglets	31	31	33	35	37	41
Dairy cows	34	35	38	42	44	50
Fattening cattle	34	35	38	41	44	50
Veal calves	30	31	32	34	35	39
Sheep-goats	30	31	32	34	36	39
Fattening lambs	35	36	40	44	46	54
Broilers	35	36	39	43	46	53
Laying hens	34	35	39	43	45	52
Turkeys	34	35	38	42	44	50
Piglets	64	70	86	**104**	**115**	**149**

TOPSOIL COPPER CONCENTRATIONS, R1 (mg/kg)

	2020 vul	2030 vul	2060 vul	2020 nonvul	2030 nonvul	2060 nonvul
Fattening pigs	11	12	14	19	21	27
Sows with piglets	8	8	10	13	14	18
Dairy cows	11	12	15	19	21	28
Fattening cattle	11	12	15	19	21	28
Veal calves	7	7	9	11	12	16
Sheep-goats	7	8	9	12	13	16
Fattening lambs	12	13	17	21	24	32
Broilers	12	13	16	21	24	31
Laying hens	11	12	16	20	23	30
Turkeys	11	12	15	19	22	28
Piglets	43	49	**66**	**85**	**97**	**132**

TOPSOIL COPPER CONCENTRATIONS, R2 (mg/kg)

	2020 vul	2030 vul	2060 vul	2020 nonvul	2030 nonvul	2060 nonvul
Fattening pigs	12	13	17	21	24	31
Sows with piglets	9	10	12	15	16	20
Dairy cows	13	14	17	22	24	32
Fattening cattle	13	14	17	22	24	31
Veal calves	8	9	11	13	14	18
Sheep-goats	9	9	11	13	15	18
Fattening lambs	14	15	19	24	27	36
Broilers	14	15	19	24	27	35
Laying hens	13	14	18	23	26	33
Turkeys	13	14	17	22	25	32
Piglets	48	55	73	95	**108**	**146**

TOPSOIL COPPER CONCENTRATIONS, R3 (mg/kg)

	2020 vul	2030 vul	2060 vul	2020 nonvul	2030 nonvul	2060 nonvul
Fattening pigs	43	44	46	50	52	58
Sows with piglets	40	41	42	45	46	49
Dairy cows	43	44	47	51	53	59
Fattening cattle	43	44	47	50	52	58
Veal calves	39	40	41	43	44	47
Sheep-goats	40	40	41	44	45	48
Fattening lambs	44	45	48	53	55	62
Broilers	44	45	48	52	55	61
Laying hens	43	44	47	52	54	60
Turkeys	43	44	47	51	53	59
Piglets	73	78	**93**	**112**	**122**	**155**

TOPSOIL COPPER CONCENTRATIONS, R4 (mg/kg)

	2020 vul	2030 vul	2060 vul	2020 nonvul	2030 nonvul	2060 nonvul
Fattening pigs	16	17	20	23	25	31
Sows with piglets	14	14	16	18	19	23
Dairy cows	16	17	20	24	26	32
Fattening cattle	16	17	20	24	26	32
Veal calves	13	13	15	17	18	21
Sheep-goats	13	14	15	17	18	21
Fattening lambs	17	18	22	26	28	35
Broilers	17	18	21	26	28	35
Laying hens	17	18	21	25	27	33
Turkeys	16	17	20	24	26	32
Piglets	45	50	**65**	**83**	**93**	**125**

TOPSOIL COPPER CONCENTRATIONS, MOWTHORPE (mg/kg)

	2020 vul	2030 vul	2060 vul	2020 nonvul	2030 nonvul	2060 nonvul
Fattening pigs	19	20	23	27	29	35
Sows with piglets	16	17	18	21	22	26
Dairy cows	19	20	23	27	29	36
Fattening cattle	19	20	23	27	29	36
Veal calves	15	16	17	20	21	24
Sheep-goats	16	16	18	20	21	24
Fattening lambs	20	21	25	29	32	39
Broilers	20	21	25	29	31	39
Laying hens	20	21	24	28	30	37
Turkeys	19	20	23	27	29	36
Piglets	50	56	72	**91**	**102**	**137**

TOPSOIL COPPER CONCENTRATIONS, CLASHMORE (mg/kg)

	2020 vul	2030 vul	2060 vul	2020 nonvul	2030 nonvul	2060 nonvul
Fattening pigs	14	15	18	22	24	30
Sows with piglets	12	12	14	16	17	21
Dairy cows	15	15	18	22	24	31
Fattening cattle	14	15	18	22	24	30
Veal calves	11	11	13	15	16	19
Sheep-goats	11	11	13	15	16	19
Fattening lambs	16	17	20	24	27	34
Broilers	15	16	20	24	26	33
Laying hens	15	16	19	23	25	32
Turkeys	15	16	18	22	25	31
Piglets	45	50	66	84	**95**	**128**

TOPSOIL COPPER CONCENTRATIONS, SEVILLE (mg/kg)						
	2020 vul	2030 vul	2060 vul	2020 nonvul	2030 nonvul	2060 nonvul
Fattening pigs	26	28	31	35	38	45
Sows with piglets	23	24	26	29	30	35
Dairy cows	27	28	32	36	39	46
Fattening cattle	27	28	31	36	38	46
Veal calves	22	23	25	27	28	32
Sheep-goats	23	23	25	27	29	33
Fattening lambs	28	29	34	38	41	50
Broilers	28	29	33	38	41	49
Laying hens	27	29	32	37	40	48
Turkeys	27	28	32	36	39	46
Piglets	**62**	**69**	**88**	**109**	**123**	**162**

TOPSOIL COPPER CONCENTRATIONS, PWLLPEIRAN (mg/kg)						
	2020 vul	2030 vul	2060 vul	2020 nonvul	2030 nonvul	2060 nonvul
Fattening pigs	35	36	41	46	49	58
Sows with piglets	31	32	35	38	40	46
Dairy cows	35	37	42	47	50	60
Fattening cattle	35	37	41	47	50	59
Veal calves	30	31	33	36	38	43
Sheep-goats	30	31	34	36	38	43
Fattening lambs	37	39	44	50	54	65
Broilers	37	38	44	50	53	64
Laying hens	36	38	43	48	52	62
Turkeys	35	37	42	47	50	60
Piglets	80	88	112	139	**155**	**205**

TOPSOIL COPPER CONCENTRATIONS, NORTH WYKE (mg/kg)

	2020 vul	2030 vul	2060 vul	2020 nonvul	2030 nonvul	2060 nonvul
Fattening pigs	28	29	33	37	40	47
Sows with piglets	25	26	28	31	32	37
Dairy cows	29	30	33	38	41	48
Fattening cattle	28	30	33	38	40	48
Veal calves	24	25	27	29	30	34
Sheep-goats	24	25	27	29	31	35
Fattening lambs	30	31	35	40	43	52
Broilers	30	31	35	40	43	51
Laying hens	29	30	34	39	42	50
Turkeys	29	30	33	38	41	48
Piglets	65	71	90	112	126	**165**

TOPSOIL COPPER CONCENTRATIONS, ST BREIUC (mg/kg)

	2020 vul	2030 vul	2060 vul	2020 nonvul	2030 nonvul	2060 nonvul
Fattening pigs	8	9	12	16	18	24
Sows with piglets	10	11	14	19	21	29
Dairy cows	9	10	13	17	19	25
Fattening cattle	8	9	13	16	19	25
Veal calves	5	5	7	9	10	13
Sheep-goats	5	5	7	9	10	14
Fattening lambs	10	11	14	19	21	29
Broilers	9	11	14	18	21	28
Laying hens	9	10	13	18	20	27
Turkeys	9	10	13	17	19	25
Piglets	40	45	62	**80**	**92**	**126**

TOPSOIL COPPER CONCENTRATIONS, JOKIOINEN (mg/kg)						
	2020	2030	2060	2020	2030	2060
	vul	vul	vul	nonvul	nonvul	nonvul
Fattening pigs	12	13	16	20	22	29
Sows with piglets	13	14	18	23	26	34
Dairy cows	12	13	17	21	23	30
Fattening cattle	12	13	16	20	23	30
Veal calves	8	9	10	12	14	17
Sheep-goats	8	9	10	13	14	18
Fattening lambs	13	14	18	23	26	34
Broilers	13	14	18	23	25	33
Laying hens	12	14	17	22	24	32
Turkeys	12	13	17	21	23	31
Piglets	46	52	70	**90**	**102**	**140**

TOPSOIL COPPER CONCENTRATIONS, RINGKOBING (mg/kg)						
	2020	2030	2060	2020	2030	2060
	vul	vul	vul	nonvul	nonvul	nonvul
Fattening pigs	14	15	17	21	23	28
Sows with piglets	15	16	19	23	26	33
Dairy cows	14	15	18	21	23	29
Fattening cattle	14	15	18	21	23	29
Veal calves	10	11	12	14	15	18
Sheep-goats	11	11	12	15	16	19
Fattening lambs	15	16	19	23	26	33
Broilers	15	16	19	23	25	32
Laying hens	14	15	18	22	24	31
Turkeys	14	15	18	21	23	30
Piglets	**42**	**48**	**63**	**80**	**91**	**122**

TOPSOIL COPPER CONCENTRATIONS, BRANDENBURG (mg/kg)						
	2020	2030	2060	2020	2030	2060
	vul	vul	vul	nonvul	nonvul	nonvul
Fattening pigs	16	17	19	23	25	30
Sows with piglets	17	18	21	25	28	34
Dairy cows	16	17	20	23	25	31
Fattening cattle	16	17	20	23	25	31
Veal calves	13	13	15	17	18	20
Sheep-goats	13	14	15	17	18	21
Fattening lambs	17	18	21	25	28	34
Broilers	17	18	21	25	27	34
Laying hens	17	18	21	24	26	32
Turkeys	16	17	20	23	25	31
Piglets	44	**49**	**63**	**80**	**90**	**120**

SURFACE WATER COPPER CONCENTRATIONS, D1 STREAM (µg/l)						
	2020	2030	2060	2020	2030	2060
	vul	vul	vul	nonvul	nonvul	nonvul
Fattening pigs	1.5	1.5	1.6	1.7	1.7	1.9
Sows with piglets	1.4	1.4	1.4	1.5	1.5	1.7
Dairy cows	1.5	1.5	1.6	1.7	1.7	1.9
Fattening cattle	1.5	1.5	1.6	1.7	1.7	1.9
Veal calves	1.4	1.4	1.4	1.5	1.5	1.6
Sheep-goats	1.4	1.4	1.4	1.5	1.5	1.6
Fattening lambs	1.5	1.5	1.6	1.7	1.8	2.0
Broilers	1.5	1.5	1.6	1.7	1.8	2.0
Laying hens	1.5	1.5	1.6	1.7	1.8	2.0
Turkeys	1.5	1.5	1.6	1.7	1.7	1.9
Piglets	2.3	2.5	2.9	3.4	3.7	4.7

	SURFACE WATER COPPER CONCENTRATIONS, D1 DITCH (µg/l)					
	2020	2030	2060	2020	2030	2060
	vul	vul	vul	nonvul	nonvul	nonvul
Fattening pigs	1.5	1.5	1.6	1.7	1.8	2.0
Sows with piglets	1.4	1.4	1.5	1.6	1.6	1.7
Dairy cows	1.5	1.5	1.6	1.7	1.8	2.0
Fattening cattle	1.5	1.5	1.6	1.7	1.8	2.0
Veal calves	1.4	1.4	1.5	1.5	1.6	1.6
Sheep-goats	1.4	1.4	1.5	1.5	1.6	1.7
Fattening lambs	1.5	1.6	1.7	1.8	1.9	2.1
Broilers	1.5	1.6	1.7	1.8	1.9	2.1
Laying hens	1.5	1.6	1.6	1.8	1.8	2.0
Turkeys	1.5	1.5	1.6	1.7	1.8	2.0
Piglets	2.4	2.6	3.0	3.6	3.9	4.9

	SURFACE WATER COPPER CONCENTRATIONS, D2 STREAM (µg/l)					
	2020	2030	2060	2020	2030	2060
	vul	vul	vul	nonvul	nonvul	nonvul
Fattening pigs	1.2	1.2	1.3	1.4	1.4	1.6
Sows with piglets	1.1	1.1	1.2	1.2	1.3	1.4
Dairy cows	1.2	1.2	1.3	1.4	1.5	1.6
Fattening cattle	1.2	1.2	1.3	1.4	1.4	1.6
Veal calves	1.1	1.1	1.1	1.2	1.2	1.3
Sheep-goats	1.1	1.1	1.1	1.2	1.2	1.3
Fattening lambs	1.2	1.2	1.3	1.5	1.5	1.7
Broilers	1.2	1.2	1.3	1.4	1.5	1.7
Laying hens	1.2	1.2	1.3	1.4	1.5	1.7
Turkeys	1.2	1.2	1.3	1.4	1.5	1.6
Piglets	**2.0**	**2.2**	**2.6**	**3.1**	**3.4**	**4.4**

	SURFACE WATER COPPER CONCENTRATIONS, D2 DITCH (µg/l)					
	2020	2030	2060	2020	2030	2060
	vul	vul	vul	nonvul	nonvul	nonvul
Fattening pigs	1.2	1.2	1.3	1.4	1.4	1.6
Sows with piglets	1.1	1.1	1.2	1.2	1.3	1.4
Dairy cows	1.2	1.2	1.3	1.4	1.5	1.7
Fattening cattle	1.2	1.2	1.3	1.4	1.5	1.6
Veal calves	1.1	1.1	1.1	1.2	1.2	1.3
Sheep-goats	1.1	1.1	1.1	1.2	1.2	1.3
Fattening lambs	1.2	1.2	1.3	1.5	1.5	1.7
Broilers	1.2	1.2	1.3	1.5	1.5	1.7
Laying hens	1.2	1.2	1.3	1.4	1.5	1.7
Turkeys	1.2	1.2	1.3	1.4	1.5	1.7
Piglets	**2.0**	**2.2**	**2.6**	**3.1**	**3.4**	**4.4**

	SURFACE WATER COPPER CONCENTRATIONS, D3 DITCH (µg/l)					
	2020	2030	2060	2020	2030	2060
	vul	vul	vul	nonvul	nonvul	nonvul
Fattening pigs	1.0	1.1	1.2	1.5	1.6	2.0
Sows with piglets	0.9	0.9	1.0	1.2	1.2	1.4
Dairy cows	1.1	1.1	1.3	1.5	1.6	2.0
Fattening cattle	1.1	1.1	1.3	1.5	1.6	2.0
Veal calves	0.8	0.9	0.9	1.1	1.1	1.3
Sheep-goats	0.8	0.9	0.9	1.1	1.2	1.3
Fattening lambs	1.1	1.2	1.4	1.7	1.8	2.2
Broilers	1.1	1.2	1.3	1.6	1.8	2.2
Laying hens	1.1	1.1	1.3	1.6	1.7	2.1
Turkeys	1.1	1.1	1.3	1.5	1.7	2.0
Piglets	2.9	3.2	4.2	5.3	5.9	8.0

	SURFACE WATER COPPER CONCENTRATIONS, D4 STREAM (µg/l)					
	2020 vul	2030 vul	2060 vul	2020 nonvul	2030 nonvul	2060 nonvul
Fattening pigs	1.5	1.6	1.6	1.7	1.8	1.9
Sows with piglets	1.5	1.5	1.5	1.6	1.6	1.7
Dairy cows	1.5	1.6	1.6	1.8	1.8	2.0
Fattening cattle	1.5	1.6	1.6	1.7	1.8	2.0
Veal calves	1.4	1.5	1.5	1.6	1.6	1.7
Sheep-goats	1.4	1.5	1.5	1.6	1.6	1.7
Fattening lambs	1.6	1.6	1.7	1.8	1.9	2.1
Broilers	1.6	1.6	1.7	1.8	1.9	2.0
Laying hens	1.6	1.6	1.7	1.8	1.8	2.0
Turkeys	1.5	1.6	1.6	1.8	1.8	2.0
Piglets	2.4	2.5	2.9	3.4	3.7	4.6

	SURFACE WATER COPPER CONCENTRATIONS, D4 POND (µg/l)					
	2020 vul	2030 vul	2060 vul	2020 nonvul	2030 nonvul	2060 nonvul
Fattening pigs	1.2	1.2	1.3	1.4	1.5	1.7
Sows with piglets	1.1	1.1	1.1	1.2	1.3	1.4
Dairy cows	1.2	1.2	1.3	1.4	1.5	1.7
Fattening cattle	1.2	1.2	1.3	1.4	1.5	1.7
Veal calves	1.0	1.0	1.1	1.2	1.2	1.3
Sheep-goats	1.0	1.1	1.1	1.2	1.2	1.3
Fattening lambs	1.2	1.2	1.4	1.5	1.6	1.9
Broilers	1.2	1.2	1.3	1.5	1.6	1.8
Laying hens	1.2	1.2	1.3	1.5	1.6	1.8
Turkeys	1.2	1.2	1.3	1.5	1.5	1.7
Piglets	2.3	2.4	3.0	3.7	4.1	5.3

	SURFACE WATER COPPER CONCENTRATIONS, D5 STREAM (µg/l)					
	2020	2030	2060	2020	2030	2060
	vul	vul	vul	nonvul	nonvul	nonvul
Fattening pigs	0.5	0.5	0.5	0.6	0.6	0.7
Sows with piglets	0.5	0.5	0.5	0.5	0.5	0.6
Dairy cows	0.5	0.5	0.5	0.6	0.6	0.7
Fattening cattle	0.5	0.5	0.5	0.6	0.6	0.7
Veal calves	0.5	0.5	0.5	0.5	0.5	0.5
Sheep-goats	0.5	0.5	0.5	0.5	0.5	0.5
Fattening lambs	0.5	0.5	0.5	0.6	0.6	0.7
Broilers	0.5	0.5	0.5	0.6	0.6	0.7
Laying hens	0.5	0.5	0.5	0.6	0.6	0.7
Turkeys	0.5	0.5	0.5	0.6	0.6	0.7
Piglets	0.8	0.9	1.1	1.3	1.4	1.8

	SURFACE WATER COPPER CONCENTRATIONS, D5 POND (µg/l)					
	2020	2030	2060	2020	2030	2060
	vul	vul	vul	nonvul	nonvul	nonvul
Fattening pigs	0.4	0.4	0.4	0.5	0.5	0.6
Sows with piglets	0.3	0.3	0.3	0.4	0.4	0.5
Dairy cows	0.4	0.4	0.4	0.5	0.5	0.6
Fattening cattle	0.4	0.4	0.4	0.5	0.5	0.6
Veal calves	0.3	0.3	0.3	0.4	0.4	0.4
Sheep-goats	0.3	0.3	0.3	0.4	0.4	0.4
Fattening lambs	0.4	0.4	0.4	0.5	0.6	0.7
Broilers	0.4	0.4	0.4	0.5	0.5	0.7
Laying hens	0.4	0.4	0.4	0.5	0.5	0.6
Turkeys	0.4	0.4	0.4	0.5	0.5	0.6
Piglets	0.8	0.9	1.2	1.5	1.6	2.2

	SURFACE WATER COPPER CONCENTRATIONS, D6 DITCH (µg/l)					
	2020 vul	2030 vul	2060 vul	2020 nonvul	2030 nonvul	2060 nonvul
Fattening pigs	0.2	0.2	0.2	0.3	0.3	0.3
Sows with piglets	0.2	0.2	0.2	0.2	0.2	0.2
Dairy cows	0.2	0.2	0.2	0.3	0.3	0.3
Fattening cattle	0.2	0.2	0.2	0.3	0.3	0.3
Veal calves	0.2	0.2	0.2	0.2	0.2	0.2
Sheep-goats	0.2	0.2	0.2	0.2	0.2	0.2
Fattening lambs	0.2	0.2	0.2	0.3	0.3	0.3
Broilers	0.2	0.2	0.2	0.3	0.3	0.3
Laying hens	0.2	0.2	0.2	0.3	0.3	0.3
Turkeys	0.2	0.2	0.2	0.3	0.3	0.3
Piglets	0.4	0.4	0.6	0.7	0.7	1.0

	SURFACE WATER COPPER CONCENTRATIONS, R1 STREAM (µg/l)					
	2020 vul	2030 vul	2060 vul	2020 nonvul	2030 nonvul	2060 nonvul
Fattening pigs	0.7	0.7	0.7	0.8	0.8	0.9
Sows with piglets	0.6	0.7	0.7	0.7	0.7	0.8
Dairy cows	0.7	0.7	0.7	0.8	0.8	0.9
Fattening cattle	0.7	0.7	0.7	0.8	0.8	0.9
Veal calves	0.6	0.6	0.7	0.7	0.7	0.7
Sheep-goats	0.6	0.6	0.7	0.7	0.7	0.7
Fattening lambs	0.7	0.7	0.8	0.8	0.8	0.9
Broilers	0.7	0.7	0.8	0.8	0.8	0.9
Laying hens	0.7	0.7	0.7	0.8	0.8	0.9
Turkeys	0.7	0.7	0.7	0.8	0.8	0.9
Piglets	1.1	1.1	1.3	1.6	1.7	2.0

	SURFACE WATER COPPER CONCENTRATIONS, R1 POND (µg/l)					
	2020	2030	2060	2020	2030	2060
	vul	vul	vul	nonvul	nonvul	nonvul
Fattening pigs	0.2	0.3	0.3	0.4	0.4	0.5
Sows with piglets	0.2	0.2	0.2	0.3	0.3	0.4
Dairy cows	0.2	0.3	0.3	0.4	0.4	0.5
Fattening cattle	0.2	0.3	0.3	0.4	0.4	0.5
Veal calves	0.2	0.2	0.2	0.3	0.3	0.3
Sheep-goats	0.2	0.2	0.2	0.3	0.3	0.3
Fattening lambs	0.3	0.3	0.3	0.4	0.4	0.5
Broilers	0.3	0.3	0.3	0.4	0.4	0.5
Laying hens	0.3	0.3	0.3	0.4	0.4	0.5
Turkeys	0.3	0.3	0.3	0.4	0.4	0.5
Piglets	0.7	0.8	1.0	1.3	1.5	1.8

	SURFACE WATER COPPER CONCENTRATIONS, R2 STREAM (µg/l)					
	2020	2030	2060	2020	2030	2060
	vul	vul	vul	nonvul	nonvul	nonvul
Fattening pigs	0.9	1.0	1.1	1.2	1.3	1.5
Sows with piglets	0.8	0.9	1.0	1.0	1.1	1.2
Dairy cows	0.9	1.0	1.1	1.2	1.3	1.5
Fattening cattle	0.9	1.0	1.1	1.2	1.3	1.5
Veal calves	0.8	0.8	0.9	1.0	1.0	1.1
Sheep-goats	0.8	0.9	0.9	1.0	1.0	1.1
Fattening lambs	1.0	1.0	1.2	1.3	1.4	1.6
Broilers	1.0	1.0	1.2	1.3	1.4	1.6
Laying hens	1.0	1.0	1.1	1.3	1.3	1.6
Turkeys	0.9	1.0	1.1	1.2	1.3	1.5
Piglets	2.0	2.2	2.7	3.4	3.8	**4.8**

	SURFACE WATER COPPER CONCENTRATIONS, R3 STREAM (µg/l)					
	2020 vul	2030 vul	2060 vul	2020 nonvul	2030 nonvul	2060 nonvul
Fattening pigs	1.3	1.3	1.3	1.4	1.4	1.4
Sows with piglets	1.3	1.3	1.3	1.3	1.3	1.4
Dairy cows	1.3	1.3	1.3	1.4	1.4	1.4
Fattening cattle	1.3	1.3	1.3	1.4	1.4	1.4
Veal calves	1.3	1.3	1.3	1.3	1.3	1.3
Sheep-goats	1.3	1.3	1.3	1.3	1.3	1.3
Fattening lambs	1.3	1.3	1.3	1.4	1.4	1.4
Broilers	1.3	1.3	1.3	1.4	1.4	1.4
Laying hens	1.3	1.3	1.3	1.4	1.4	1.4
Turkeys	1.3	1.3	1.3	1.4	1.4	1.4
Piglets	1.5	1.5	1.6	1.7	1.7	1.9

	SURFACE WATER COPPER CONCENTRATIONS, R4 STREAM (µg/l)					
	2020 vul	2030 vul	2060 vul	2020 nonvul	2030 nonvul	2060 nonvul
Fattening pigs	1.1	1.1	1.1	1.1	1.1	1.1
Sows with piglets	1.1	1.1	1.1	1.1	1.1	1.1
Dairy cows	1.1	1.1	1.1	1.1	1.1	1.1
Fattening cattle	1.1	1.1	1.1	1.1	1.1	1.1
Veal calves	1.1	1.1	1.1	1.1	1.1	1.1
Sheep-goats	1.1	1.1	1.1	1.1	1.1	1.1
Fattening lambs	1.1	1.1	1.1	1.1	1.1	1.2
Broilers	1.1	1.1	1.1	1.1	1.1	1.2
Laying hens	1.1	1.1	1.1	1.1	1.1	1.1
Turkeys	1.1	1.1	1.1	1.1	1.1	1.1
Piglets	1.2	1.2	1.3	1.4	1.4	1.5

SEDIMENT COPPER CONCENTRATIONS, D1 STREAM (mg/kg)	2020 vul	2030 vul	2060 vul	2020 nonvul	2030 nonvul	2060 nonvul
Fattening pigs	75	78	**88**	**101**	**107**	**128**
Sows with piglets	66	68	74	82	86	**99**
Dairy cows	76	79	**90**	**103**	**110**	**132**
Fattening cattle	75	79	**89**	**102**	**109**	**131**
Veal calves	63	65	70	77	81	**92**
Sheep-goats	64	66	71	78	82	**93**
Fattening lambs	79	83	**95**	**110**	**118**	**143**
Broilers	79	83	**94**	**109**	**117**	**141**
Laying hens	77	81	**92**	**106**	**114**	**137**
Turkeys	76	79	**90**	**103**	**110**	**132**
Piglets	**179**	**197**	**252**	**316**	**353**	**467**

SEDIMENT COPPER CONCENTRATIONS, D1 DITCH (mg/kg)	2020 vul	2030 vul	2060 vul	2020 nonvul	2030 nonvul	2060 nonvul
Fattening pigs	75	79	**88**	**101**	**108**	129
Sows with piglets	66	68	74	82	87	**100**
Dairy cows	76	80	**90**	**103**	**111**	133
Fattening cattle	76	79	**90**	**102**	**110**	**131**
Veal calves	64	66	71	78	81	**92**
Sheep-goats	64	66	71	79	82	94
Fattening lambs	80	84	**96**	**110**	**119**	144
Broilers	79	83	**95**	**109**	**117**	**142**
Laying hens	78	82	**93**	**106**	**114**	**138**
Turkeys	76	80	**90**	**103**	**111**	**133**
Piglets	**180**	**198**	**254**	**317**	**355**	**469**

SEDIMENT COPPER CONCENTRATIONS, D2 STREAM (mg/kg)	2020 vul	2030 vul	2060 vul	2020 nonvul	2030 nonvul	2060 nonvul
Fattening pigs	**160**	**165**	**182**	**203**	**215**	**250**
Sows with piglets	**144**	**147**	**157**	**171**	**179**	**200**
Dairy cows	**162**	**167**	**184**	**207**	**219**	**256**
Fattening cattle	**161**	**166**	**183**	**206**	**218**	**254**
Veal calves	**141**	**143**	**151**	**164**	**170**	**188**
Sheep-goats	**141**	**144**	**153**	**165**	**171**	**190**
Fattening lambs	**167**	**174**	**194**	**219**	**233**	**275**
Broilers	**166**	**173**	**192**	**217**	**230**	**272**
Laying hens	**164**	**170**	**189**	**212**	**225**	**264**
Turkeys	**162**	**167**	**185**	**207**	**220**	**257**
Piglets	**336**	**367**	**460**	**567**	**631**	**823**

SEDIMENT COPPER CONCENTRATIONS, D2 DITCH (mg/kg)	2020 vul	2030 vul	2060 vul	2020 nonvul	2030 nonvul	2060 nonvul
Fattening pigs	**159**	**165**	**181**	**203**	**215**	**250**
Sows with piglets	**144**	**147**	**157**	**171**	**178**	**200**
Dairy cows	**161**	**167**	**184**	**207**	**219**	**256**
Fattening cattle	**161**	**166**	**183**	**205**	**217**	**254**
Veal calves	**140**	**143**	**151**	**164**	**170**	**188**
Sheep-goats	**141**	**144**	**152**	**165**	**171**	**190**
Fattening lambs	**167**	**174**	**193**	**219**	**233**	**275**
Broilers	**166**	**172**	**192**	**216**	**230**	**271**
Laying hens	**164**	**170**	**188**	**212**	**225**	**264**
Turkeys	**161**	**167**	**184**	**207**	**219**	**256**
Piglets	**335**	**367**	**459**	**565**	**630**	**821**

	SEDIMENT COPPER CONCENTRATIONS, D3 DITCH (mg/kg)					
	2020	2030	2060	2020	2030	2060
	vul	vul	vul	nonvul	nonvul	nonvul
Fattening pigs	38	40	47	57	62	78
Sows with piglets	31	32	36	43	46	55
Dairy cows	39	41	48	59	64	80
Fattening cattle	38	41	48	58	63	79
Veal calves	30	31	34	40	42	50
Sheep-goats	30	31	34	40	43	51
Fattening lambs	41	44	52	64	70	89
Broilers	41	44	52	63	69	87
Laying hens	40	42	50	61	67	84
Turkeys	39	41	49	59	64	80
Piglets	**115**	**129**	**171**	**216**	**245**	**332**

	SEDIMENT COPPER CONCENTRATIONS, D4 STREAM (mg/kg)					
	2020	2030	2060	2020	2030	2060
	vul	vul	vul	nonvul	nonvul	nonvul
Fattening pigs	54	57	65	76	82	**100**
Sows with piglets	46	48	53	60	63	74
Dairy cows	55	58	66	78	84	**103**
Fattening cattle	54	57	66	77	83	**102**
Veal calves	44	46	50	56	59	68
Sheep-goats	44	46	50	57	60	69
Fattening lambs	58	61	71	84	**91**	**112**
Broilers	57	61	70	83	**90**	**111**
Laying hens	56	59	68	81	87	**107**
Turkeys	55	58	67	78	84	**103**
Piglets	**144**	**159**	**206**	**261**	**293**	**389**

SEDIMENT COPPER CONCENTRATIONS, D4 POND (mg/kg)

	2020 vul	2030 vul	2060 vul	2020 nonvul	2030 nonvul	2060 nonvul
Fattening pigs	57	60	69	81	87	**105**
Sows with piglets	49	51	56	64	67	79
Dairy cows	58	61	70	83	**89**	**108**
Fattening cattle	58	61	70	82	**88**	**107**
Veal calves	47	49	53	60	63	72
Sheep-goats	48	49	54	60	64	74
Fattening lambs	61	65	75	**89**	**96**	**119**
Broilers	61	64	74	**88**	**95**	**117**
Laying hens	60	63	73	85	**92**	**113**
Turkeys	58	61	71	83	**89**	**109**
Piglets	**151**	**168**	**216**	**274**	**308**	**409**

SEDIMENT COPPER CONCENTRATIONS, D5 STREAM (mg/kg)

	2020 vul	2030 vul	2060 vul	2020 nonvul	2030 nonvul	2060 nonvul
Fattening pigs	81	84	**94**	**111**	**119**	**142**
Sows with piglets	70	72	77	**89**	**94**	**107**
Dairy cows	82	86	**96**	**114**	**122**	**147**
Fattening cattle	82	85	**96**	**113**	**121**	**145**
Veal calves	67	69	73	84	87	**99**
Sheep-goats	68	69	74	85	**89**	**101**
Fattening lambs	86	**90**	**103**	**122**	**132**	**160**
Broilers	85	**89**	**102**	**121**	**130**	**158**
Laying hens	84	**88**	**99**	**118**	**126**	**153**
Turkeys	82	86	**97**	**114**	**122**	**147**
Piglets	**205**	**226**	**290**	**367**	**411**	**544**

SEDIMENT COPPER CONCENTRATIONS, D5 POND (mg/kg)

	2020 vul	2030 vul	2060 vul	2020 nonvul	2030 nonvul	2060 nonvul
Fattening pigs	86	**90**	**101**	**119**	**127**	**152**
Sows with piglets	75	77	83	**95**	**100**	**114**
Dairy cows	**88**	**91**	**103**	**122**	**130**	**156**
Fattening cattle	87	**91**	**102**	**121**	**129**	**155**
Veal calves	72	73	78	**89**	**93**	**105**
Sheep-goats	72	74	79	**90**	**95**	**107**
Fattening lambs	**92**	**96**	**110**	**131**	**140**	**170**
Broilers	**91**	**95**	**108**	**129**	**139**	**168**
Laying hens	**89**	**94**	**106**	**126**	**135**	**162**
Turkeys	**88**	**91**	**103**	**122**	**130**	**157**
Piglets	**219**	**240**	**308**	**392**	**437**	**578**

SEDIMENT COPPER CONCENTRATIONS, D6 DITCH (mg/kg)

	2020 vul	2030 vul	2060 vul	2020 nonvul	2030 nonvul	2060 nonvul
Fattening pigs	**97**	**102**	**119**	**139**	**151**	**186**
Sows with piglets	82	85	**95**	**108**	**116**	**137**
Dairy cows	**99**	**104**	**122**	**143**	**155**	**191**
Fattening cattle	**98**	**104**	**120**	**141**	**154**	**189**
Veal calves	78	81	**89**	**101**	**107**	**125**
Sheep-goats	79	82	**90**	**102**	**109**	**127**
Fattening lambs	**104**	**111**	**131**	**154**	**169**	**210**
Broilers	**103**	**110**	**129**	**152**	**166**	**207**
Laying hens	**101**	**107**	**125**	**148**	**161**	**200**
Turkeys	**99**	**105**	**122**	**143**	**156**	**192**
Piglets	**268**	**299**	**390**	**492**	**557**	**744**

SEDIMENT COPPER CONCENTRATIONS, R1 STREAM (mg/kg)	2020 vul	2030 vul	2060 vul	2020 nonvul	2030 nonvul	2060 nonvul
Fattening pigs	59	62	71	87	**94**	**112**
Sows with piglets	49	51	57	67	71	82
Dairy cows	60	64	73	**89**	**96**	**115**
Fattening cattle	60	63	72	**89**	**95**	**114**
Veal calves	47	48	53	62	65	75
Sheep-goats	47	49	54	63	66	76
Fattening lambs	64	68	78	**97**	**105**	**127**
Broilers	63	67	77	**96**	**103**	**125**
Laying hens	62	65	75	**93**	**100**	**120**
Turkeys	60	64	73	**90**	**97**	**116**
Piglets	**173**	**190**	**236**	**321**	**356**	**452**

SEDIMENT COPPER CONCENTRATIONS,R1 POND (mg/kg)	2020 vul	2030 vul	2060 vul	2020 nonvul	2030 nonvul	2060 nonvul
Fattening pigs	85	**90**	**104**	**132**	**142**	**172**
Sows with piglets	68	71	81	**97**	**104**	**123**
Dairy cows	87	**92**	**107**	**136**	**147**	**178**
Fattening cattle	86	**91**	**106**	**135**	**145**	**176**
Veal calves	64	67	75	**89**	**95**	**111**
Sheep-goats	65	68	76	**91**	**97**	**113**
Fattening lambs	**93**	**99**	**116**	**149**	**162**	**196**
Broilers	**92**	**98**	**115**	**147**	**159**	**193**
Laying hens	**89**	**95**	**111**	**142**	**153**	**186**
Turkeys	87	**92**	**108**	**136**	**148**	**178**
Piglets	**276**	**303**	**378**	**527**	**582**	**735**

SEDIMENT COPPER CONCENTRATIONS, R2 STREAM (mg/kg)						
	2020	2030	2060	2020	2030	2060
	vul	vul	vul	nonvul	nonvul	nonvul
Fattening pigs	51	56	68	85	**93**	**117**
Sows with piglets	39	42	50	60	66	81
Dairy cows	53	57	70	**88**	**97**	**122**
Fattening cattle	52	57	69	87	**95**	**120**
Veal calves	37	39	46	54	59	73
Sheep-goats	37	40	47	56	60	74
Fattening lambs	57	62	77	**97**	**107**	**136**
Broilers	56	61	75	**95**	**105**	**133**
Laying hens	55	59	73	**92**	**101**	**128**
Turkeys	53	57	70	**88**	**97**	**122**
Piglets	**187**	**208**	**269**	**364**	**408**	**532**

SEDIMENT COPPER CONCENTRATIONS, R3 STREAM (mg/kg)						
	2020	2030	2060	2020	2030	2060
	vul	vul	vul	nonvul	nonvul	nonvul
Fattening pigs	**103**	**106**	**115**	**127**	**133**	**152**
Sows with piglets	**95**	**96**	**101**	**110**	**114**	**125**
Dairy cows	**104**	**107**	**116**	**129**	**136**	**155**
Fattening cattle	**104**	**107**	**116**	**128**	**135**	**154**
Veal calves	**93**	**94**	**98**	**105**	**109**	**118**
Sheep-goats	**93**	**95**	**99**	**106**	**110**	**119**
Fattening lambs	**107**	**111**	**121**	**136**	**143**	**165**
Broilers	**107**	**110**	**120**	**134**	**142**	**164**
Laying hens	**106**	**109**	**118**	**132**	**139**	**160**
Turkeys	**104**	**107**	**116**	**129**	**136**	**155**
Piglets	**199**	**217**	**266**	**325**	**362**	**463**

SEDIMENT COPPER CONCENTRATIONS, R4 STREAM (mg/kg)

	2020 vul	2030 vul	2060 vul	2020 nonvul	2030 nonvul	2060 nonvul
Fattening pigs	54	57	65	79	86	**103**
Sows with piglets	44	46	52	61	64	76
Dairy cows	55	58	67	82	**88**	**107**
Fattening cattle	54	57	66	81	87	**105**
Veal calves	42	44	49	56	59	69
Sheep-goats	43	44	49	57	60	70
Fattening lambs	58	62	72	**89**	**96**	**117**
Broilers	57	61	71	**88**	**95**	**115**
Laying hens	56	60	69	85	**92**	**111**
Turkeys	55	58	67	82	**88**	**107**
Piglets	159	**174**	**219**	**296**	**327**	**419**

Table A2. Predicted Environmental Concentrations of zinc. The terms vul and nonvul refer to PECs predicted for the application of the maximum permissible manure loading to nitrogen-vulnerable and nonvulnerable soils respectively. Predictions in bold exceed the PNEC for that compartment.

TOPSOIL ZINC CONCENTRATIONS, D1 (mg/kg)

	2020 vul	2030 vul	2060 vul	2020 nonvul	2030 nonvul	2060 nonvul
Fattening pigs	67	74	92	115	**128**	**167**
Sows with piglets	51	54	66	80	88	112
Dairy cows	56	61	74	92	101	**130**
Fattening cattle	55	60	73	91	100	**128**
Veal calves	76	83	105	**133**	**148**	**194**
Sheep-goats	64	70	86	108	120	**155**
Fattening lambs	76	83	105	**133**	**148**	**194**
Broilers	75	82	104	130	**145**	**190**
Laying hens	72	79	100	**125**	**140**	**182**
Turkeys	70	76	96	120	**133**	**174**
Piglets	57	62	77	95	105	**135**

TOPSOIL ZINC CONCENTRATIONS, D2 (mg/kg)

	2020 vul	2030 vul	2060 vul	2020 nonvul	2030 nonvul	2060 nonvul
Fattening pigs	132	138	158	183	197	238
Sows with piglets	114	118	130	146	154	180
Dairy cows	119	124	139	158	168	198
Fattening cattle	119	124	138	157	167	197
Veal calves	141	149	172	202	218	267
Sheep-goats	128	134	152	175	188	225
Fattening lambs	141	149	172	202	218	267
Broilers	140	147	170	199	215	263
Laying hens	137	144	166	194	209	254
Turkeys	134	141	162	188	202	245
Piglets	121	126	141	161	172	203

TOPSOIL ZINC CONCENTRATIONS, D3 (mg/kg)

	2020 vul	2030 vul	2060 vul	2020 nonvul	2030 nonvul	2060 nonvul
Fattening pigs	45	49	63	88	98	127
Sows with piglets	29	32	40	56	63	80
Dairy cows	34	38	47	67	74	96
Fattening cattle	34	37	47	66	73	94
Veal calves	52	58	74	104	116	**151**
Sheep-goats	41	46	58	81	91	117
Fattening lambs	52	58	74	104	116	**151**
Broilers	51	57	73	102	114	**148**
Laying hens	49	54	69	97	109	**141**
Turkeys	47	52	66	92	103	**134**
Piglets	36	39	49	69	77	100

TOPSOIL ZINC CONCENTRATIONS, D4 (mg/kg)

	2020 vul	2030 vul	2060 vul	2020 nonvul	2030 nonvul	2060 nonvul
Fattening pigs	88	93	109	**130**	**142**	**175**
Sows with piglets	73	76	86	100	107	**127**
Dairy cows	78	82	94	110	118	**143**
Fattening cattle	77	81	93	109	117	**141**
Veal calves	96	102	**121**	**146**	**160**	**200**
Sheep-goats	85	90	104	**124**	**134**	**165**
Fattening lambs	96	102	**121**	**146**	**159**	**200**
Broilers	95	101	120	**144**	**157**	**196**
Laying hens	92	98	116	**139**	**152**	**189**
Turkeys	90	96	113	**134**	**146**	**182**
Piglets	79	83	96	112	**121**	**147**

TOPSOIL ZINC CONCENTRATIONS, D5 (mg/kg)

	2020 vul	2030 vul	2060 vul	2020 nonvul	2030 nonvul	2060 nonvul
Fattening pigs	59	65	80	100	111	143
Sows with piglets	45	48	57	70	77	97
Dairy cows	50	53	65	80	88	112
Fattening cattle	49	53	64	79	87	111
Veal calves	67	73	91	115	128	**167**
Sheep-goats	56	61	75	94	104	134
Fattening lambs	67	73	91	115	128	**167**
Broilers	66	72	90	113	126	**164**
Laying hens	64	69	86	109	121	**157**
Turkeys	61	67	83	104	116	150
Piglets	51	55	67	83	91	116

TOPSOIL ZINC CONCENTRATIONS, D6 (mg/kg)

	2020 vul	2030 vul	2060 vul	2020 nonvul	2030 nonvul	2060 nonvul
Fattening pigs	96	101	118	140	152	187
Sows with piglets	80	84	94	108	115	137
Dairy cows	85	89	102	118	127	153
Fattening cattle	85	89	101	117	126	151
Veal calves	103	110	130	156	170	212
Sheep-goats	92	97	113	133	144	176
Fattening lambs	103	110	130	156	170	212
Broilers	102	109	129	154	168	208
Laying hens	100	106	125	149	162	201
Turkeys	98	104	121	144	156	193
Piglets	86	91	104	121	130	157

TOPSOIL ZINC CONCENTRATIONS, R1 (mg/kg)

	2020 vul	2030 vul	2060 vul	2020 nonvul	2030 nonvul	2060 nonvul
Fattening pigs	52	57	72	97	108	140
Sows with piglets	36	39	48	64	71	91
Dairy cows	41	45	56	74	83	107
Fattening cattle	40	44	55	73	82	105
Veal calves	60	66	84	113	126	165
Sheep-goats	48	53	67	90	100	129
Fattening lambs	60	66	84	113	126	165
Broilers	59	65	83	111	124	161
Laying hens	56	62	79	106	118	154
Turkeys	54	59	75	101	113	146
Piglets	42	46	58	77	86	111

TOPSOIL ZINC CONCENTRATIONS, R2 (mg/kg)

	2020 vul	2030 vul	2060 vul	2020 nonvul	2030 nonvul	2060 nonvul
Fattening pigs	66	67	70	98	101	108
Sows with piglets	54	55	56	75	76	80
Dairy cows	58	59	60	82	84	89
Fattening cattle	58	59	60	82	84	88
Veal calves	72	73	76	110	114	122
Sheep-goats	63	64	67	93	96	102
Fattening lambs	72	73	76	110	114	122
Broilers	71	72	75	108	112	120
Laying hens	69	71	73	105	108	116
Turkeys	67	69	71	101	105	111
Piglets	59	60	62	84	87	91

TOPSOIL ZINC CONCENTRATIONS, R3 (mg/kg)

	2020 vul	2030 vul	2060 vul	2020 nonvul	2030 nonvul	2060 nonvul
Fattening pigs	95	99	110	133	142	165
Sows with piglets	82	84	91	106	111	125
Dairy cows	86	89	97	115	121	138
Fattening cattle	86	89	96	114	120	137
Veal calves	102	107	120	147	157	185
Sheep-goats	92	96	106	127	135	156
Fattening lambs	102	107	120	147	157	185
Broilers	101	106	118	145	155	182
Laying hens	99	104	116	141	151	176
Turkeys	97	101	113	137	146	170
Piglets	87	90	99	117	123	141

TOPSOIL ZINC CONCENTRATIONS, R4 (mg/kg)

	2020 vul	2030 vul	2060 vul	2020 nonvul	2030 nonvul	2060 nonvul
Fattening pigs	67	71	82	103	111	133
Sows with piglets	54	57	63	76	82	96
Dairy cows	58	61	69	85	91	108
Fattening cattle	58	61	69	84	90	107
Veal calves	73	78	91	116	125	152
Sheep-goats	64	68	78	97	104	125
Fattening lambs	73	78	91	116	125	152
Broilers	72	77	90	114	123	150
Laying hens	70	75	87	110	119	144
Turkeys	68	73	84	106	115	138
Piglets	59	62	71	87	94	111

TOPSOIL ZINC CONCENTRATIONS, MOWTHORPE (mg/kg)

	2020 vul	2030 vul	2060 vul	2020 nonvul	2030 nonvul	2060 nonvul
Fattening pigs	48	52	64	89	99	125
Sows with piglets	33	36	43	59	65	81
Dairy cows	38	41	50	69	76	95
Fattening cattle	37	40	49	68	75	94
Veal calves	55	61	75	105	116	148
Sheep-goats	45	49	60	83	92	116
Fattening lambs	55	60	75	105	116	148
Broilers	54	59	74	102	114	145
Laying hens	52	57	70	98	109	138
Turkeys	50	54	67	93	103	131
Piglets	39	42	51	72	79	99

TOPSOIL ZINC CONCENTRATIONS, CLASHMORE (mg/kg)

	2020 vul	2030 vul	2060 vul	2020 nonvul	2030 nonvul	2060 nonvul
Fattening pigs	42	44	48	74	79	89
Sows with piglets	31	31	33	51	53	59
Dairy cows	34	35	38	58	61	69
Fattening cattle	34	35	38	58	61	68
Veal calves	48	50	55	86	91	104
Sheep-goats	40	41	45	69	73	83
Fattening lambs	48	50	55	86	91	104
Broilers	47	49	54	84	89	102
Laying hens	45	47	52	81	86	98
Turkeys	44	45	50	77	82	93
Piglets	35	37	39	60	64	71

TOPSOIL ZINC CONCENTRATIONS, SEVILLE (mg/kg)						
	2020 vul	2030 vul	2060 vul	2020 nonvul	2030 nonvul	2060 nonvul
Fattening pigs	53	59	78	104	118	158
Sows with piglets	34	38	50	67	75	100
Dairy cows	40	45	60	79	89	119
Fattening cattle	40	45	59	78	88	117
Veal calves	62	70	93	123	139	187
Sheep-goats	49	55	72	96	109	145
Fattening lambs	62	70	93	123	139	**187**
Broilers	60	68	91	120	136	**183**
Laying hens	58	65	87	115	130	**174**
Turkeys	55	62	82	109	123	165
Piglets	42	47	62	82	93	124

TOPSOIL ZINC CONCENTRATIONS, PWLLPEIRAN (mg/kg)						
	2020 vul	2030 vul	2060 vul	2020 nonvul	2030 nonvul	2060 nonvul
Fattening pigs	74	80	97	132	145	180
Sows with piglets	53	57	67	90	98	119
Dairy cows	60	64	77	103	113	139
Fattening cattle	59	64	76	102	111	137
Veal calves	84	92	112	153	169	211
Sheep-goats	69	75	90	123	135	167
Fattening lambs	84	91	112	153	169	211
Broilers	83	90	110	150	165	207
Laying hens	80	87	105	144	159	198
Turkeys	76	83	101	137	151	188
Piglets	62	66	79	107	117	144

TOPSOIL ZINC CONCENTRATIONS, NORTH WYKE (mg/kg)

	2020 vul	2030 vul	2060 vul	2020 nonvul	2030 nonvul	2060 nonvul
Fattening pigs	77	81	90	121	129	150
Sows with piglets	62	63	68	89	94	106
Dairy cows	67	69	75	99	105	120
Fattening cattle	66	68	75	98	104	119
Veal calves	85	89	101	137	147	172
Sheep-goats	74	77	85	114	121	141
Fattening lambs	85	89	100	137	147	172
Broilers	84	88	99	135	144	169
Laying hens	82	86	96	130	139	163
Turkeys	79	83	93	125	134	156
Piglets	68	71	77	102	108	124

TOPSOIL ZINC CONCENTRATIONS, ST BREIUC (mg/kg)

	2020 vul	2030 vul	2060 vul	2020 nonvul	2030 nonvul	2060 nonvul
Fattening pigs	37	41	52	76	85	108
Sows with piglets	44	49	62	91	101	129
Dairy cows	28	30	38	57	63	81
Fattening cattle	27	30	38	56	62	79
Veal calves	44	49	62	91	101	129
Sheep-goats	34	38	47	70	78	100
Fattening lambs	44	49	62	91	101	129
Broilers	43	48	60	89	99	126
Laying hens	41	45	57	85	94	120
Turkeys	39	43	54	80	89	114
Piglets	29	32	40	59	66	84

TOPSOIL ZINC CONCENTRATIONS, JOKIOINEN (mg/kg)

	2020 vul	2030 vul	2060 vul	2020 nonvul	2030 nonvul	2060 nonvul
Fattening pigs	49	55	72	97	110	147
Sows with piglets	57	64	86	115	130	**174**
Dairy cows	37	41	55	73	83	110
Fattening cattle	36	41	54	72	81	109
Veal calves	57	64	86	115	130	**174**
Sheep-goats	45	50	67	89	101	135
Fattening lambs	57	64	86	115	130	**174**
Broilers	56	63	84	112	127	170
Laying hens	53	60	80	107	121	**163**
Turkeys	51	57	76	102	115	154
Piglets	38	43	57	76	86	115

TOPSOIL ZINC CONCENTRATIONS, RINGKOBING (mg/kg)

	2020 vul	2030 vul	2060 vul	2020 nonvul	2030 nonvul	2060 nonvul
Fattening pigs	26	28	**31**	**53**	**57**	**64**
Sows with piglets	**31**	**33**	**37**	**63**	**67**	**76**
Dairy cows	20	21	23	**40**	**42**	**47**
Fattening cattle	20	21	23	**40**	**42**	**47**
Veal calves	**31**	**33**	**37**	**63**	**67**	**76**
Sheep-goats	24	26	28	**49**	**52**	**59**
Fattening lambs	**31**	**33**	**37**	**63**	**67**	**76**
Broilers	**31**	32	**36**	**62**	**66**	**74**
Laying hens	29	**31**	**34**	**59**	**63**	**71**
Turkeys	28	29	**32**	**56**	**59**	**67**
Piglets	21	22	24	**42**	**44**	**50**

TOPSOIL ZINC CONCENTRATIONS, BRANDENBURG (mg/kg)

	2020 vul	2030 vul	2060 vul	2020 nonvul	2030 nonvul	2060 nonvul
Fattening pigs	54	54	55	75	76	78
Sows with piglets	58	58	59	82	84	86
Dairy cows	49	49	49	64	65	66
Fattening cattle	49	49	49	64	65	66
Veal calves	58	58	59	82	84	86
Sheep-goats	52	53	53	71	72	74
Fattening lambs	58	58	59	82	84	86
Broilers	57	57	58	81	83	85
Laying hens	56	56	57	79	80	82
Turkeys	55	55	56	77	78	80
Piglets	49	50	50	66	66	68

SURFACE WATER ZINC CONCENTRATIONS, D1 STREAM (µg/l)

	2020 vul	2030 vul	2060 vul	2020 nonvul	2030 nonvul	2060 nonvul
Fattening pigs	7.9	8.0	8.4	8.6	8.8	9.5
Sows with piglets	7.6	7.7	7.9	8.1	8.2	8.7
Dairy cows	7.7	7.8	8.1	8.2	8.4	9.0
Fattening cattle	7.7	7.8	8.1	8.2	8.4	8.9
Veal calves	8.0	8.1	8.6	8.8	9.1	10.0
Sheep-goats	7.8	7.9	8.3	8.5	8.7	9.4
Fattening lambs	8.0	8.1	8.6	8.8	9.1	10.0
Broilers	8.0	8.1	8.5	8.8	9.1	9.9
Laying hens	8.0	8.1	8.5	8.7	9.0	9.8
Turkeys	7.9	8.0	8.4	8.6	8.9	9.7
Piglets	7.7	7.8	8.1	8.3	8.5	9.0

SURFACE WATER ZINC CONCENTRATIONS, D1 DITCH (µg/l)

	2020 vul	2030 vul	2060 vul	2020 nonvul	2030 nonvul	2060 nonvul
Fattening pigs	8.1	8.2	8.6	8.8	9.1	9.9
Sows with piglets	7.9	7.9	8.2	8.3	8.5	9.0
Dairy cows	7.9	8.0	8.3	8.5	8.7	9.3
Fattening cattle	7.9	8.0	8.3	8.5	8.7	9.2
Veal calves	8.3	8.4	8.8	9.1	9.4	10.3
Sheep-goats	8.1	8.2	8.5	8.7	9.0	9.7
Fattening lambs	8.3	8.4	8.8	9.1	9.4	10.3
Broilers	8.2	8.4	8.8	9.1	9.4	10.3
Laying hens	8.2	8.3	8.7	9.0	9.3	10.1
Turkeys	8.2	8.3	8.7	8.9	9.2	10.0
Piglets	8.0	8.1	8.4	8.5	8.7	9.3

SURFACE WATER ZINC CONCENTRATIONS, D2 STREAM (µg/l)

	2020 vul	2030 vul	2060 vul	2020 nonvul	2030 nonvul	2060 nonvul
Fattening pigs	6.4	6.6	7.4	7.7	8.2	9.8
Sows with piglets	5.9	6.1	6.5	6.8	7.0	8.0
Dairy cows	6.1	6.2	6.8	7.1	7.4	8.6
Fattening cattle	6.1	6.2	6.8	7.0	7.4	8.5
Veal calves	6.6	6.9	7.8	8.2	8.8	10.6
Sheep-goats	6.3	6.5	7.2	7.5	7.9	9.4
Fattening lambs	6.6	6.9	7.8	8.2	8.8	10.6
Broilers	6.6	6.9	7.7	8.1	8.7	10.5
Laying hens	6.5	6.8	7.6	8.0	8.5	10.3
Turkeys	6.5	6.7	7.5	7.9	8.3	10.0
Piglets	6.1	6.3	6.9	7.2	7.5	8.7

	SURFACE WATER ZINC CONCENTRATIONS, D2 DITCH (µg/l)					
	2020	2030	2060	2020	2030	2060
	vul	vul	vul	nonvul	nonvul	nonvul
Fattening pigs	6.4	6.6	7.4	7.7	8.2	9.8
Sows with piglets	5.9	6.1	6.5	6.8	7.0	8.0
Dairy cows	6.1	6.2	6.8	7.1	7.4	8.6
Fattening cattle	6.1	6.2	6.8	7.0	7.4	8.5
Veal calves	6.6	6.9	7.8	8.2	8.8	10.6
Sheep-goats	6.3	6.5	7.2	7.5	7.9	9.4
Fattening lambs	6.6	6.9	7.8	8.2	8.8	10.6
Broilers	6.6	6.9	7.7	8.1	8.7	10.5
Laying hens	6.5	6.8	7.6	8.0	8.5	10.3
Turkeys	6.5	6.7	7.5	7.9	8.3	10.0
Piglets	6.1	6.3	6.9	7.2	7.5	8.7

	SURFACE WATER ZINC CONCENTRATIONS, D3 DITCH (µg/l)					
	2020	2030	2060	2020	2030	2060
	vul	vul	vul	nonvul	nonvul	nonvul
Fattening pigs	**79.9**	**94.9**	**137.8**	**147.5**	**177.6**	**265.3**
Sows with piglets	**56.0**	**65.6**	**92.7**	**98.3**	**117.4**	**172.5**
Dairy cows	**63.7**	**75.1**	**107.3**	**114.2**	**136.9**	**202.6**
Fattening cattle	**63.0**	**74.2**	**105.9**	**112.7**	**135.0**	**199.7**
Veal calves	**92.0**	**109.7**	**160.6**	**172.3**	**208.1**	**312.3**
Sheep-goats	**74.8**	**88.6**	**128.1**	**136.9**	**164.7**	**245.4**
Fattening lambs	**91.9**	**109.6**	**160.5**	**172.2**	**207.9**	**312.0**
Broilers	**90.3**	**107.6**	**157.4**	**168.8**	**203.7**	**305.6**
Laying hens	**86.8**	**103.3**	**150.8**	**161.7**	**195.0**	**292.1**
Turkeys	**83.0**	**98.8**	**143.8**	**154.0**	**185.6**	**277.6**
Piglets	**65.8**	**77.7**	**111.2**	**118.5**	**142.1**	**210.6**

SURFACE WATER ZINC CONCENTRATIONS, D4 STREAM (µg/l)						
	2020 vul	2030 vul	2060 vul	2020 nonvul	2030 nonvul	2060 nonvul
Fattening pigs	8.9	9.1	9.6	9.8	10.2	11.3
Sows with piglets	8.6	8.7	9.1	9.2	9.4	10.1
Dairy cows	8.7	8.8	9.2	9.4	9.6	10.5
Fattening cattle	8.7	8.8	9.2	9.4	9.6	10.5
Veal calves	9.1	9.3	9.9	10.2	10.6	12.0
Sheep-goats	8.8	9.0	9.5	9.7	10.0	11.1
Fattening lambs	9.1	9.3	9.9	10.2	10.6	12.0
Broilers	9.1	9.2	9.9	10.1	10.5	11.9
Laying hens	9.0	9.2	9.8	10.0	10.4	11.7
Turkeys	9.0	9.1	9.7	9.9	10.3	11.5
Piglets	8.7	8.9	9.3	9.4	9.7	10.6

SURFACE WATER ZINC CONCENTRATIONS, D4 POND (µg/l)						
	2020 vul	2030 vul	2060 vul	2020 nonvul	2030 nonvul	2060 nonvul
Fattening pigs	10.7	11.0	11.7	12.0	12.4	14.0
Sows with piglets	10.3	10.4	10.9	11.1	11.4	12.3
Dairy cows	10.4	10.6	11.2	11.4	11.7	12.9
Fattening cattle	10.4	10.6	11.2	11.3	11.7	12.8
Veal calves	11.0	11.2	12.1	12.4	13.0	14.8
Sheep-goats	10.6	10.9	11.6	11.8	12.2	13.6
Fattening lambs	11.0	11.2	12.1	12.4	13.0	14.8
Broilers	10.9	11.2	12.1	12.4	12.9	14.7
Laying hens	10.9	11.1	12.0	12.2	12.7	14.5
Turkeys	10.8	11.0	11.8	12.1	12.6	14.2
Piglets	10.5	10.7	11.3	11.4	11.8	13.0

SURFACE WATER ZINC CONCENTRATIONS, D5 STREAM (µg/l)						
	2020 vul	2030 vul	2060 vul	2020 nonvul	2030 nonvul	2060 nonvul
Fattening pigs	6.2	6.6	7.9	7.8	8.6	11.3
Sows with piglets	5.6	5.8	6.7	6.6	7.1	8.8
Dairy cows	5.8	6.1	7.1	7.0	7.6	9.6
Fattening cattle	5.8	6.0	7.1	7.0	7.6	9.6
Veal calves	6.5	6.9	8.5	8.4	9.4	12.6
Sheep-goats	6.0	6.4	7.7	7.6	8.3	10.8
Fattening lambs	6.5	6.9	8.5	8.4	9.4	12.6
Broilers	6.4	6.9	8.4	8.3	9.3	12.4
Laying hens	6.3	6.8	8.3	8.2	9.0	12.1
Turkeys	6.2	6.7	8.1	8.0	8.8	11.7
Piglets	5.8	6.1	7.2	7.1	7.7	9.9

SURFACE WATER ZINC CONCENTRATIONS, D5 POND (µg/l)						
	2020 vul	2030 vul	2060 vul	2020 nonvul	2030 nonvul	2060 nonvul
Fattening pigs	7.8	8.3	10.2	10.1	11.2	**15.1**
Sows with piglets	6.9	7.3	8.5	8.4	9.1	11.6
Dairy cows	7.2	7.6	9.1	9.0	9.8	12.7
Fattening cattle	7.2	7.6	9.0	8.9	9.7	12.6
Veal calves	8.2	8.8	11.1	11.0	12.3	**16.9**
Sheep-goats	7.6	8.1	9.9	9.8	10.8	**14.3**
Fattening lambs	8.2	8.8	11.1	11.0	12.3	**16.9**
Broilers	8.1	8.8	11.0	10.9	12.2	**16.7**
Laying hens	8.0	8.6	10.7	10.6	11.9	**16.1**
Turkeys	7.9	8.5	10.5	10.3	11.5	**15.6**
Piglets	7.3	7.7	9.2	9.1	10.0	13.0

	SURFACE WATER ZINC CONCENTRATIONS, D6 DITCH (µg/l)					
	2020 vul	2030 vul	2060 vul	2020 nonvul	2030 nonvul	2060 nonvul
Fattening pigs	4.5	4.7	5.2	5.4	5.7	6.8
Sows with piglets	4.2	4.3	4.6	4.8	5.0	5.6
Dairy cows	4.3	4.5	4.8	5.0	5.2	6.0
Fattening cattle	4.3	4.4	4.8	5.0	5.2	6.0
Veal calves	4.7	4.9	5.5	5.7	6.1	7.4
Sheep-goats	4.5	4.6	5.1	5.3	5.5	6.5
Fattening lambs	4.7	4.9	5.5	5.7	6.1	7.4
Broilers	4.7	4.8	5.4	5.7	6.0	7.3
Laying hens	4.6	4.8	5.4	5.6	5.9	7.1
Turkeys	4.6	4.7	5.3	5.5	5.8	6.9
Piglets	4.4	4.5	4.9	5.0	5.3	6.1

	SURFACE WATER ZINC CONCENTRATIONS, R1 STREAM (µg/l)					
	2020 vul	2030 vul	2060 vul	2020 nonvul	2030 nonvul	2060 nonvul
Fattening pigs	6.0	6.5	8.1	**10.9**	**12.1**	**15.5**
Sows with piglets	4.2	4.5	5.4	7.3	8.0	**10.1**
Dairy cows	4.8	5.2	6.3	**8.5**	**9.4**	**11.9**
Fattening cattle	4.7	5.1	6.2	**8.4**	**9.2**	**11.7**
Veal calves	6.8	7.5	**9.4**	**12.8**	**14.2**	**18.3**
Sheep-goats	5.6	6.1	7.5	**10.2**	**11.2**	**14.4**
Fattening lambs	6.8	7.5	**9.4**	**12.8**	**14.2**	**18.3**
Broilers	6.7	7.4	**9.2**	**12.5**	**13.9**	**17.9**
Laying hens	6.5	7.1	**8.8**	**12.0**	**13.3**	**17.1**
Turkeys	6.2	6.8	**8.4**	**11.4**	**12.7**	**16.3**
Piglets	4.9	5.3	6.5	**8.8**	**9.7**	**12.3**

SURFACE WATER ZINC CONCENTRATIONS, R1 POND (µg/l)						
	2020 vul	2030 vul	2060 vul	2020 nonvul	2030 nonvul	2060 nonvul
Fattening pigs	7.1	7.8	**9.7**	**13.3**	**14.7**	**18.9**
Sows with piglets	5.0	5.4	6.5	**8.8**	**9.7**	**12.2**
Dairy cows	5.7	6.2	7.5	**10.3**	**11.3**	**14.4**
Fattening cattle	5.6	6.1	7.4	**10.1**	**11.2**	**14.2**
Veal calves	8.2	**9.0**	**11.4**	**15.5**	**17.3**	**22.3**
Sheep-goats	6.7	7.3	**9.0**	**12.3**	**13.6**	**17.5**
Fattening lambs	8.2	**9.0**	**11.4**	**15.5**	**17.3**	**22.3**
Broilers	8.1	**8.9**	**11.2**	**15.2**	**16.9**	**21.8**
Laying hens	7.8	**8.5**	**10.7**	**14.6**	**16.2**	**20.9**
Turkeys	7.4	8.1	**10.2**	**13.9**	**15.4**	**19.8**
Piglets	5.9	6.4	7.8	**10.6**	**11.8**	**15.0**

SURFACE WATER ZINC CONCENTRATIONS, R2 STREAM (µg/l)						
	2020 vul	2030 vul	2060 vul	2020 nonvul	2030 nonvul	2060 nonvul
Fattening pigs	**30.8**	**31.9**	**34.2**	**61.2**	**64.1**	**70.1**
Sows with piglets	**20.1**	**20.5**	**21.5**	**39.1**	**40.6**	**44.0**
Dairy cows	**23.6**	**24.2**	**25.6**	**46.2**	**48.2**	**52.4**
Fattening cattle	**23.2**	**23.9**	**25.2**	**45.6**	**47.5**	**51.6**
Veal calves	**36.3**	**37.7**	**40.6**	**72.4**	**75.9**	**83.4**
Sheep-goats	**28.5**	**29.5**	**31.5**	**56.5**	**59.0**	**64.5**
Fattening lambs	**36.2**	**37.6**	**40.6**	**72.3**	**75.8**	**83.3**
Broilers	**35.5**	**36.8**	**39.7**	**70.8**	**74.2**	**81.5**
Laying hens	**33.9**	**35.2**	**37.9**	**67.6**	**70.8**	**77.7**
Turkeys	**32.2**	**33.4**	**35.9**	**64.1**	**67.1**	**73.6**
Piglets	**24.5**	**25.2**	**26.7**	**48.2**	**50.3**	**54.7**

	SURFACE WATER ZINC CONCENTRATIONS, R3 STREAM (µg/l)					
	2020 vul	2030 vul	2060 vul	2020 nonvul	2030 nonvul	2060 nonvul
Fattening pigs	5.9	6.2	7.0	9.2	9.8	**11.6**
Sows with piglets	4.7	4.9	5.3	6.8	7.2	8.2
Dairy cows	5.1	5.3	5.9	7.5	8.0	9.3
Fattening cattle	5.0	5.2	5.8	7.5	7.9	9.2
Veal calves	6.5	6.8	7.8	10.4	**11.2**	**13.3**
Sheep-goats	5.6	5.9	6.6	8.6	9.2	10.9
Fattening lambs	6.5	6.8	7.8	10.4	**11.1**	**13.3**
Broilers	6.4	6.7	7.7	10.2	**11.0**	**13.1**
Laying hens	6.2	6.5	7.4	9.8	10.6	**12.6**
Turkeys	6.0	6.3	7.2	9.5	10.2	**12.1**
Piglets	5.2	5.4	6.0	7.7	8.2	9.6

	SURFACE WATER ZINC CONCENTRATIONS, R4 STREAM (µg/l)					
	2020 vul	2030 vul	2060 vul	2020 nonvul	2030 nonvul	2060 nonvul
Fattening pigs	7.0	7.6	9.0	**13.0**	**14.1**	**17.5**
Sows with piglets	4.9	5.2	6.0	8.6	9.3	11.3
Dairy cows	5.6	6.0	7.0	10.0	10.9	**13.3**
Fattening cattle	5.6	5.9	6.9	9.9	10.7	**13.1**
Veal calves	8.1	8.7	10.5	**15.1**	**16.6**	**20.6**
Sheep-goats	6.6	7.1	8.4	**12.0**	**13.1**	**16.1**
Fattening lambs	8.1	8.7	10.5	**15.1**	**16.5**	**20.5**
Broilers	7.9	8.6	10.3	**14.8**	**16.2**	**20.1**
Laying hens	7.6	8.2	9.9	**14.2**	**15.5**	**19.2**
Turkeys	7.3	7.9	9.4	**13.5**	**14.8**	**18.3**
Piglets	5.8	6.2	7.3	10.4	11.3	**13.8**

SEDIMENT ZINC CONCENTRATIONS, D1 STREAM (mg/kg)

	2020 vul	2030 vul	2060 vul	2020 nonvul	2030 nonvul	2060 nonvul
Fattening pigs	**392**	**422**	**513**	**620**	**684**	**872**
Sows with piglets	**311**	**330**	**385**	**454**	**493**	**610**
Dairy cows	**337**	**360**	**427**	**507**	**555**	**695**
Fattening cattle	**335**	**357**	**423**	**502**	**549**	**687**
Veal calves	**433**	**469**	**577**	**703**	**780**	**1005**
Sheep-goats	**375**	**402**	**485**	**584**	**643**	**816**
Fattening lambs	**432**	**469**	**577**	**703**	**779**	**1004**
Broilers	**427**	**462**	**568**	**691**	**766**	**986**
Laying hens	**415**	**449**	**549**	**667**	**738**	**948**
Turkeys	**402**	**434**	**529**	**641**	**709**	**907**
Piglets	**344**	**368**	**438**	**522**	**571**	**718**

SEDIMENT ZINC CONCENTRATIONS, D1 DITCH (mg/kg)

	2020 vul	2030 vul	2060 vul	2020 nonvul	2030 nonvul	2060 nonvul
Fattening pigs	**393**	**424**	**515**	**622**	**685**	**875**
Sows with piglets	**313**	**331**	**387**	**455**	**495**	**613**
Dairy cows	**339**	**361**	**428**	**509**	**556**	**698**
Fattening cattle	**336**	**358**	**424**	**504**	**550**	**689**
Veal calves	**434**	**470**	**579**	**706**	**781**	**1008**
Sheep-goats	**376**	**404**	**487**	**586**	**644**	**819**
Fattening lambs	**434**	**470**	**579**	**705**	**780**	**1007**
Broilers	**428**	**464**	**570**	**694**	**767**	**989**
Laying hens	**417**	**450**	**551**	**670**	**740**	**951**
Turkeys	**404**	**436**	**531**	**644**	**710**	**910**
Piglets	**346**	**369**	**439**	**524**	**573**	**720**

SEDIMENT ZINC CONCENTRATIONS, D2 STREAM (mg/kg)

	2020 vul	2030 vul	2060 vul	2020 nonvul	2030 nonvul	2060 nonvul
Fattening pigs	**494**	**532**	**644**	**782**	**861**	**1097**
Sows with piglets	**392**	**415**	**483**	**572**	**621**	**767**
Dairy cows	**425**	**453**	**535**	**640**	**699**	**874**
Fattening cattle	**422**	**450**	**530**	**634**	**692**	**863**
Veal calves	**546**	**591**	**725**	**888**	**983**	**1264**
Sheep-goats	**472**	**507**	**609**	**737**	**810**	**1026**
Fattening lambs	**545**	**591**	**724**	**888**	**982**	**1263**
Broilers	**538**	**582**	**713**	**873**	**965**	**1240**
Laying hens	**523**	**566**	**690**	**843**	**931**	**1192**
Turkeys	**507**	**547**	**665**	**810**	**893**	**1140**
Piglets	**434**	**463**	**549**	**658**	**720**	**902**

SEDIMENT ZINC CONCENTRATIONS, D2 DITCH (mg/kg)

	2020 vul	2030 vul	2060 vul	2020 nonvul	2030 nonvul	2060 nonvul
Fattening pigs	**493**	**531**	**643**	**780**	**861**	**1095**
Sows with piglets	**392**	**415**	**483**	**571**	**621**	**766**
Dairy cows	**425**	**453**	**535**	**639**	**699**	**873**
Fattening cattle	**422**	**449**	**530**	**632**	**691**	**862**
Veal calves	**545**	**590**	**724**	**886**	**982**	**1262**
Sheep-goats	**472**	**506**	**609**	**735**	**809**	**1024**
Fattening lambs	**544**	**590**	**724**	**885**	**982**	**1261**
Broilers	**537**	**582**	**712**	**871**	**965**	**1238**
Laying hens	**523**	**565**	**689**	**840**	**930**	**1190**
Turkeys	**507**	**547**	**664**	**808**	**893**	**1139**
Piglets	**434**	**463**	**549**	**657**	**719**	**901**

SEDIMENT ZINC CONCENTRATIONS, D3 DITCH (mg/kg)	2020 vul	2030 vul	2060 vul	2020 nonvul	2030 nonvul	2060 nonvul
Fattening pigs	**529**	**600**	**784**	**959**	**1096**	**1453**
Sows with piglets	**377**	**424**	**548**	**646**	**734**	**966**
Dairy cows	**426**	**481**	**624**	**748**	**851**	**1124**
Fattening cattle	**422**	**475**	**617**	**738**	**840**	**1108**
Veal calves	**606**	**688**	**904**	**1117**	**1278**	**1699**
Sheep-goats	**497**	**562**	**733**	**892**	**1018**	**1348**
Fattening lambs	**606**	**688**	**903**	**1117**	**1277**	**1698**
Broilers	**595**	**676**	**887**	**1095**	**1252**	**1664**
Laying hens	**573**	**650**	**852**	**1049**	**1200**	**1593**
Turkeys	**549**	**623**	**815**	**1000**	**1143**	**1517**
Piglets	**440**	**496**	**645**	**775**	**883**	**1166**

SEDIMENT ZINC CONCENTRATIONS, D4 STREAM (mg/kg)	2020 vul	2030 vul	2060 vul	2020 nonvul	2030 nonvul	2060 nonvul
Fattening pigs	**341**	**369**	**452**	**549**	**609**	**783**
Sows with piglets	**267**	**284**	**335**	**397**	**434**	**542**
Dairy cows	**291**	**312**	**373**	**446**	**491**	**620**
Fattening cattle	**289**	**309**	**369**	**442**	**485**	**613**
Veal calves	**378**	**412**	**511**	**625**	**697**	**905**
Sheep-goats	**325**	**351**	**427**	**516**	**571**	**731**
Fattening lambs	**378**	**412**	**511**	**625**	**696**	**904**
Broilers	**373**	**406**	**503**	**614**	**684**	**888**
Laying hens	**362**	**394**	**486**	**592**	**659**	**853**
Turkeys	**351**	**380**	**468**	**569**	**632**	**815**
Piglets	**298**	**319**	**383**	**459**	**506**	**641**

SEDIMENT ZINC CONCENTRATIONS, D4 POND (mg/kg)

	2020 vul	2030 vul	2060 vul	2020 nonvul	2030 nonvul	2060 nonvul
Fattening pigs	**367**	**396**	**482**	**581**	**641**	**823**
Sows with piglets	**291**	**309**	**361**	**425**	**462**	**574**
Dairy cows	**316**	**337**	**400**	**476**	**520**	**655**
Fattening cattle	**314**	**334**	**396**	**471**	**515**	**647**
Veal calves	**405**	**440**	**543**	**660**	**731**	**948**
Sheep-goats	**351**	**377**	**456**	**547**	**603**	**769**
Fattening lambs	**405**	**439**	**542**	**659**	**731**	**947**
Broilers	**400**	**433**	**534**	**648**	**719**	**930**
Laying hens	**389**	**421**	**516**	**626**	**693**	**894**
Turkeys	**377**	**407**	**498**	**601**	**665**	**855**
Piglets	**322**	**344**	**411**	**489**	**536**	**676**

SEDIMENT ZINC CONCENTRATIONS, D5 STREAM (mg/kg)

	2020 vul	2030 vul	2060 vul	2020 nonvul	2030 nonvul	2060 nonvul
Fattening pigs	**338**	**372**	**478**	**582**	**654**	**876**
Sows with piglets	**251**	**273**	**337**	**404**	**449**	**586**
Dairy cows	**279**	**305**	**382**	**461**	**515**	**680**
Fattening cattle	**277**	**302**	**378**	**456**	**509**	**671**
Veal calves	**381**	**422**	**549**	**671**	**757**	**1022**
Sheep-goats	**319**	**351**	**447**	**543**	**610**	**813**
Fattening lambs	**381**	**422**	**548**	**671**	**757**	**1021**
Broilers	**375**	**415**	**539**	**658**	**742**	**1001**
Laying hens	**363**	**401**	**518**	**633**	**713**	**959**
Turkeys	**349**	**385**	**496**	**605**	**681**	**914**
Piglets	**287**	**313**	**395**	**477**	**533**	**705**

SEDIMENT ZINC CONCENTRATIONS, D5 POND (mg/kg)

	2020 vul	2030 vul	2060 vul	2020 nonvul	2030 nonvul	2060 nonvul
Fattening pigs	**351**	**387**	**496**	**603**	**678**	**905**
Sows with piglets	**262**	**284**	**351**	**419**	**466**	**607**
Dairy cows	**291**	**317**	**398**	**479**	**535**	**704**
Fattening cattle	**288**	**314**	**393**	**473**	**528**	**694**
Veal calves	**396**	**439**	**569**	**695**	**785**	**1056**
Sheep-goats	**332**	**365**	**465**	**563**	**632**	**841**
Fattening lambs	**396**	**439**	**568**	**695**	**784**	**1055**
Broilers	**390**	**432**	**558**	**682**	**770**	**1035**
Laying hens	**377**	**417**	**537**	**655**	**739**	**991**
Turkeys	**363**	**401**	**515**	**627**	**706**	**945**
Piglets	**299**	**326**	**410**	**495**	**553**	**729**

SEDIMENT ZINC CONCENTRATIONS, D6 DITCH (mg/kg)

	2020 vul	2030 vul	2060 vul	2020 nonvul	2030 nonvul	2060 nonvul
Fattening pigs	**314**	**344**	**434**	**542**	**607**	**793**
Sows with piglets	**233**	**252**	**307**	**376**	**416**	**531**
Dairy cows	**259**	**282**	**348**	**430**	**478**	**616**
Fattening cattle	**257**	**279**	**344**	**425**	**472**	**608**
Veal calves	**355**	**391**	**498**	**627**	**703**	**925**
Sheep-goats	**296**	**324**	**406**	**507**	**566**	**737**
Fattening lambs	**354**	**391**	**498**	**626**	**703**	**924**
Broilers	**349**	**385**	**489**	**615**	**690**	**906**
Laying hens	**337**	**371**	**470**	**590**	**662**	**868**
Turkeys	**324**	**357**	**450**	**564**	**632**	**827**
Piglets	**266**	**290**	**359**	**444**	**494**	**639**

SEDIMENT ZINC CONCENTRATIONS, R1 STREAM (mg/kg)						
	2020	2030	2060	2020	2030	2060
	vul	vul	vul	nonvul	nonvul	nonvul
Fattening pigs	**405**	**434**	**506**	**723**	**784**	**920**
Sows with piglets	**292**	**311**	**359**	**491**	**529**	**618**
Dairy cows	**329**	**351**	**407**	**566**	**612**	**716**
Fattening cattle	**325**	**347**	**402**	**559**	**604**	**706**
Veal calves	**462**	**497**	**580**	**840**	**913**	**1072**
Sheep-goats	**381**	**408**	**474**	**673**	**729**	**855**
Fattening lambs	**461**	**497**	**579**	**839**	**912**	**1071**
Broilers	**454**	**488**	**569**	**823**	**894**	**1050**
Laying hens	**437**	**470**	**548**	**790**	**857**	**1007**
Turkeys	**420**	**451**	**525**	**754**	**818**	**959**
Piglets	**338**	**362**	**419**	**586**	**634**	**742**

SEDIMENT ZINC CONCENTRATIONS, R1 POND (mg/kg)						
	2020	2030	2060	2020	2030	2060
	vul	vul	vul	nonvul	nonvul	nonvul
Fattening pigs	**578**	**614**	**713**	**1022**	**1092**	**1281**
Sows with piglets	**421**	**445**	**512**	**698**	**744**	**867**
Dairy cows	**472**	**500**	**577**	**803**	**857**	**1002**
Fattening cattle	**467**	**495**	**571**	**793**	**846**	**989**
Veal calves	**657**	**700**	**815**	**1185**	**1268**	**1491**
Sheep-goats	**544**	**578**	**670**	**952**	**1017**	**1192**
Fattening lambs	**657**	**699**	**814**	**1185**	**1267**	**1489**
Broilers	**646**	**687**	**800**	**1162**	**1243**	**1461**
Laying hens	**623**	**663**	**771**	**1115**	**1192**	**1401**
Turkeys	**598**	**636**	**740**	**1065**	**1138**	**1336**
Piglets	**485**	**515**	**595**	**831**	**887**	**1037**

SEDIMENT ZINC CONCENTRATIONS, R2 STREAM (mg/kg)

	2020 vul	2030 vul	2060 vul	2020 nonvul	2030 nonvul	2060 nonvul
Fattening pigs	**636**	**655**	**697**	**1190**	**1238**	**1343**
Sows with piglets	**440**	**448**	**468**	**786**	**813**	**872**
Dairy cows	**503**	**515**	**542**	**917**	**951**	**1025**
Fattening cattle	**497**	**509**	**535**	**904**	**938**	**1010**
Veal calves	**735**	**759**	**812**	**1393**	**1453**	**1581**
Sheep-goats	**594**	**610**	**648**	**1103**	**1147**	**1242**
Fattening lambs	**734**	**758**	**812**	**1392**	**1452**	**1580**
Broilers	**721**	**744**	**796**	**1364**	**1422**	**1547**
Laying hens	**692**	**714**	**763**	**1306**	**1361**	**1479**
Turkeys	**662**	**682**	**727**	**1243**	**1294**	**1405**
Piglets	**520**	**533**	**562**	**952**	**988**	**1065**

SEDIMENT ZINC CONCENTRATIONS, R3 STREAM (mg/kg)

	2020 vul	2030 vul	2060 vul	2020 nonvul	2030 nonvul	2060 nonvul
Fattening pigs	**590**	**622**	**700**	**1002**	**1068**	**1226**
Sows with piglets	**444**	**464**	**515**	**701**	**743**	**843**
Dairy cows	**491**	**515**	**575**	**799**	**848**	**967**
Fattening cattle	**487**	**510**	**569**	**789**	**838**	**955**
Veal calves	**663**	**701**	**794**	**1153**	**1232**	**1419**
Sheep-goats	**558**	**588**	**660**	**937**	**998**	**1144**
Fattening lambs	**663**	**701**	**794**	**1152**	**1231**	**1418**
Broilers	**653**	**690**	**781**	**1131**	**1209**	**1392**
Laying hens	**632**	**667**	**754**	**1088**	**1162**	**1336**
Turkeys	**609**	**643**	**725**	**1041**	**1111**	**1276**
Piglets	**504**	**529**	**591**	**825**	**876**	**1000**

	SEDIMENT ZINC CONCENTRATIONS, R4 STREAM (mg/kg)					
	2020	2030	2060	2020	2030	2060
	vul	vul	vul	nonvul	nonvul	nonvul
Fattening pigs	**1753**	**1843**	**2065**	**3027**	**3181**	**3559**
Sows with piglets	**1302**	**1369**	**1536**	**2099**	**2206**	**2471**
Dairy cows	**1448**	**1522**	**1708**	**2399**	**2522**	**2823**
Fattening cattle	**1434**	**1508**	**1691**	**2370**	**2491**	**2789**
Veal calves	**1981**	**2082**	**2332**	**3496**	**3673**	**4109**
Sheep-goats	**1656**	**1741**	**1951**	**2827**	**2971**	**3325**
Fattening lambs	**1979**	**2081**	**2330**	**3493**	**3671**	**4106**
Broilers	**1948**	**2048**	**2294**	**3429**	**3603**	**4030**
Laying hens	**1883**	**1979**	**2217**	**3294**	**3462**	**3872**
Turkeys	**1812**	**1905**	**2134**	**3149**	**3309**	**3702**
Piglets	**1487**	**1563**	**1753**	**2480**	**2606**	**2917**

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1. INTRODUCTION

A voluntary risk assessment was performed by the European Copper Institute (ECI) for copper and copper compounds on the EU working list: Cu, CuO, Cu_2O, $CuSO_4$, $Cu_2Cl(HO)_3$. The final report was finalized in June 2008 (ECI, 2008).

The present report provides a review on the regional risk assessment performed. In this risk assessment (RA) the **total approach** was used for both the exposure and effects assessment.

Opinions on the performance and risk characterization of this risk assessment from the Scientific Committee on Health and Environmental Risks (SCHER) and from the Technical Committee on New and Existing Substances (TC NES) are summarized within the present report.

More recent copper toxicity studies found in the literature and that are in agreement with the selection criteria of the data used for this risk assessment are also included but were not used for the derivation of predicted non effect concentrations.

2. OVERALL RESULTS FOR THE REGIONAL ENVIRONMENTAL RISK ASSESSMENT FOR COPPER AND COPPER COMPOUNDS

The risk assessment was performed for the compounds presented in Table 1.

Table 1. Compounds that were included in the voluntary risk assessment

Coumpound	**IUPAC name**	**CAS number**	**EINEC NUMBER**
Cu	Copper	7440-50-8	231-159-6
$CuSO_4.5H_2O$	Copper (II) sulphate pentahydrate	7758-98-7	231-847-6
Cu_2O	Copper (I) oxide	1317-39-1	215-270-7
CuO	Copper (II) oxide	1317-38-0	215-269-1
$Cu_2Cl(HO)_3$	Dicopper chloride trihydroxide	1332-65-6	215-572-9

Possible conclusions for the risk assessment were:

Conclusion (i) There is a need for further information and/or testing.
Conclusion (ii) There is at present no need for further information and/or testing and no need for risk reduction measures beyond those which are being applied already.
Conclusion (iii) There is a need for limiting the risk; risk reduction measures which are already being applied shall be taken into account.

The regional environmental risk characterization concluded that there were no regional concerns - **conclusion (ii)-** for any of the compartments considered (aquatic compartment, including sediments and terrestrial compartment).

3. ENVIRONMENTAL FATE

3.1. Introduction

Copper is a transition metal and has more than one oxidation state. The principal forms are cuprous (Cu (I), Cu^{+}) and cupric (Cu (II), Cu^{2+}). When Cu (II) is introduced in the environment, it binds to inorganic and organic ligands contained within water, soil, and sediments. In all environmental compartments, the binding affinities of Cu(II) with inorganic and organic matter is dependent on pH, the oxidation-reduction potential in the local environment, and the presence of competing metal ions and inorganic anions.

3.2. Degradation

Metals do not degrade in the environment according to the Organization for Economic Cooperation and Development (OECD, 1998). However, metals can be transformed by environmental processes to either increase or decrease the availability of toxic species.

3.3. Adsorption

The behaviour of copper in the environment is affected by adsorption to soil, sediments, colloids and suspended particles. The principal adsorbents for copper in the different environment compartments are inorganic particles such as clay minerals and iron, manganese and aluminium oxides as well as organic materials. The most important factors influencing the adsorption of copper are pH, and organic matter. Adsorption of copper has been shown to increase with pH and organic matter restricts heavy metal movement and bioavailability (Tyler and McBride, 1982).

3.3.1. Aquatic environment

An extensive literature review was performed on the partitioning of copper in the aquatic environment and the following partition coefficients have been derived for Cu metal and Cu compounds:

- Partition coefficient in suspended matter (Heijerick *et al,* 2005a):
  Kp_{susp} = 30,246 l/kg (log Kp (pm/w) = 4.48) (50th percentile)

- Partition coefficient in sediment (Heijerick *et al,* 2005a):
  Kp_{sed} = 24,409 l/kg (log Kp(sed/w) = 4.39) (50th percentile)

The 50th percentile value of the distribution function represents a typical suspended matter/sediment partition coefficient for EU waters and will be used for the derivation of regional PECs.

3.3.2. Terrestrial environment

Partition coefficients for copper in soil were derived from the data of Sauvé et al. (2000) since the data covers a wide range of soils conditions that are relevant for the risk assessment. Therefore, the median Kd value used for the regional risk assessment was 2120 L/kg.

4. EXPOSURE ASSESSMENT

4.1. Aquatic environment

In order to derive predicted environmental concentrations (PECs) of copper in the aquatic environment, monitoring data for the European freshwaters, sediments and marine waters was collected.
Monitoring data includes both the natural background and the concentration added by anthropogenic activities. For risk assessment purposes of metals, it is recommended to take into account background concentrations, ambient concentrations and bioavailability of exposure concentrations. Therefore, dissolved copper concentrations have been preferably used since they are a better indicator of metal toxicity in the aquatic environment. In the same way, the total amount of copper in sediments is not available for biological uptake since adsorption to Acid Volatile Sulphide (AVS), clay minerals and organic matter can occur.
Considering the amount of measured data available and the uncertainties related to the modelled data, it has been considered that the measured data was more reliable to derive a regional PEC.

4.1.1. PECs freshwater

Three databases were used for the exposure assessment of copper in European surface waters: the Surface Water Database (SWAD), the GEMS (Global Environmental Monitoring System)/Water-database and the COMMPS-database (Combined Monitoring-based and Modelling-based Priority Setting).

The Regional Worst-Case (RWC)-ambient PECs for the different surface waters has been computed as 90^{th} percentiles of the measured copper concentration in the sampled surface waters, which is in agreement with the procedures as described in the TGD (TGD, 2003). Based on the data sets available in SWAD, COMMPS and GEMS-Water, 11 regional/country specific RWC-ambient PEC values for total copper in surface water have been derived and are summarized in Table 2.

Table 2. Derived RWC-ambient PECs for different European countries. Bold values were used to derive a RWC- ambient PEC for Europe

Country - region	**RWC-ambient PEC (min;max) µg /L Cu dissoved**
Belgium - average Belgium - Flanders Belgium - Walloon	**3.05** 4.4 (1.3; 20.1) 1.7 (1.1; 5.2)
Denmark	**0.5** (0.49; 0.50)
Finland – Barentz arca	**1.9***
Germany - average	**4.3**
Northern Ireland	**4.7** (3.0; 7.7)
Portugal	**1.8** (1.5; 4.9)
The Netherlands	**3.4** (2.6; 4.8)
Great Britain **England** **Wales** **Scotland**	 **3.5** (0.9; 14.1) **1.9** (0.5; 6.9) **2.8** (1.0; 5.4)
Sweden	1.8 (0.6; 7.2)
France	5.2 (2.5; 10.6)
Austria	2 (1; 4.2)
RWC-ambient PECs	
Average	**2.8** (0.5; 4.7)
Median	**2.9****

* no site-specific 90th percentile values available
** Log-Beta distribution; critical value=0.209, confidence>0.15 (estimated value)

The regions/countries for which monitoring data were available include regions/countries with high population densities, traffic densities and industrial activities. Therefore, it was concluded that the monitoring data are representative for the surface waters in the EU.
The reliable, county-specific $Cu_{diss.}$ RWC-ambient PEC values are situated between 0.5 (Denmark) and 4.7 (Northern Ireland). The median, which represents a general **RWC-ambient PEC for Europe**, is **2.9 µg/L Cu_{diss}**.

4.1.2. PECs freshwater sediment

Two databases were used for the exposure assessment of copper in European freshwater sediments: the Sediment Database (SEDD) and the COMMPS-database.
The RWC-ambient PECs for freshwater sediments in different countries are presented in Table 3.

Table 3. Derived RWC-ambient PEC for different European countries. Bold values were used to derive a RWC- ambient PEC for Europe

Country - region	**RWC-ambient PEC mg Cu/kg**
Belgium	**75.4**
France - average	**46.8**
France – Artois-Picardie	47.6
France – Rhone-Mediterranean area	45.8
Sweden	**52.2**
The Netherlands - waterbase	**88.3**
The Netherlands - COMMPS	(94.4)
Spain- COMMPS	79.0
RWC-ambient PECs	
Average	**68.3** (45.8; 88.3)
Median	**67.5***

* Log-Logistic distribution; critical value:0.22575; confidence:>0.15

RWC-ambient Cu-sediment PECs were situated between 45.8 mg Cu/kg and 88.3 mg Cu/kg. The median, which represents a general **RWC-ambient PEC for Europe**, was **67.5 mg Cu/kg dry weight.**

4.1.3. PECs marine water

The data used for the derivation of PEC values for the marine environment were provided by ICES (International Council for the Exploration of the Sea), 2006. Since the data was old, the ICES information was supplemented with other information from the Protection of the Marine Environment of the North-East Atlantic (OSPAR), the Helsinki Commission (HELCOM) and literature.
The PEC values for marine waters representing the 90^{th} percentile per region are summarized in Table 4.

Table 4. Derived RWC-ambient PEC marine water for different European countries.

Country	**RWC-ambient PEC µg /L Cu $_{\text{dissoved}}$**
Belgium	0.8
Denmark	1.1
The Netherlands	1.1
Norway	1.1
Sweden	1.4
UK	2.7
Median	**1.1**

An overall median of the 90^{th} percentiles of **1.1 µg Cu/L** was derived from the data and represents the **RWC-ambient PEC marine waters** for Europe.

4.1.4. PECs marine sediments

As for the derivation of PEC marine waters, the data used for the derivation of PEC values for marine sediments were provided by ICES, 2006. The ICES information was supplemented with other information from OSPAR, HELCOM and literature.
RWC-ambient PECs marine sediments for different European countries are summarized in Table 5.

Table 5. Derived RWC-ambient PEC for marine sediments for different European countries.

Country	**RWC-ambient PEC mg Cu /kg dry weight**
Belgium	4.2
Denmark	33.6
Germany	18.5
Ireland	11.9
The Netherlands	6.2
Norway	55.3
Sweden	27.1
United Kingdom	12.8
Europe - median	**16.1**

The median **RWC- ambient PEC for marine sediments** in Europe was **16.1 mg Cu/kg dry weight.**

4.2. Terrestrial environment

For the terrestrial exposure assessment both monitoring and modelled environmental data might be used to assess the risk. Monitoring data are preferred when enough reliable data is available (TGD, 2003). Therefore, for European soils the PEC was derived from collected monitoring data.

Data was collected from the ICP-data set which is one of the outcomes of the "International Co-operative Programme on Assessment and Monitoring of Air Pollution Effects on Forests" for forest soils, from an agricultural soil data set from Reinman et al. (2003), from the JRC-report (Gawlik et al. (2003), from the LABO Bund / Länder-Arbeitsgemeinschaft Bodenschutz) data set, the INRA-data set, and from specific countries data sets.

The individual Cu-soil data were then classified into three different categories - agricultural, forest, grassland.

4.2.1. PECs agricultural soils

The derived RWC-ambient PECs in European agricultural soils are summarised in Table 6.

Table 6. RWC-ambient PECs derived for agricultural soils. Values in bold were used to derive a RWC-ambient PEC for Europe

Country-region	RWC-ambient PEC mg Cu/kg	Data source
Austria	**31.8**	JRC-dataset
Belgium	**16.5**	De Temmerman et al. 2003
Finland –average	**46.5**	
	41.0	JRC-dataset
	52.0	Reinman et al., 2003
France	**30.6**	JRC-dataset
Germany - average	**21.3**	
	28.6	JRC-dataset
	13.4	Reinman et al., 2003
	21.8	LABO-data set
Italy (northern)	**57.4**	ANPA data set
The Netherlands - average	**30.3**	
	34.2	Data set D. Brus
	26.4	JRC-dataset
Norway	**36.1**	Reinman et al., 2003
Spain	**32.1**	Lopez Arias and Grau Gorbi, 2004
Sweden - average	**23.5**	
	25.4	Reinman et al., 2003
	21.6	Eriksson et al., 1997
Europe		
Average	**32.6** (16.1; 57.5)	
Median	**31.2**	

The median **RWC-ambient PEC for agricultural soils** was **31.2 mg Cu/kg dry weight** and was considered as a typical Cu-value for European agricultural soils.

4.2.2. PECs forest soils

The derived RWC-ambient PECs in European forest soils are summarised in Table 7.

Table 7. RWC-ambient PECs derived for agricultural soils. Values in bold were used to derive a RWC-ambient PEC for Europe

Country-region	RWC-ambient PEC mg Cu/kg	Data source
Austria- average	**32.1**	
	36.7	ICP-forest data set
	27.5	JRC-dataset
Germany - average	**23.4**	
	16.9	ICP-forest data set
	21.1	LABO data set
	32.2	JRC-dataset
The Netherlands - average	**7.3**	
	11	Data set D. Brus
	7.3	JRC-dataset
	3.7	ICP-forest data set
Portugal	**40.2**	ICP-forest data set
Europe		
Average	**25.8** (7.3; 40.2)	
Median	**24.4**	

The median **RWC-ambient PEC for forest soils** was **24.4 mg Cu/kg dry weight** and was considered as a typical Cu-value for European forest soils.

4.2.3. PECs grassland soil

The derived RWC-ambient PECs in European grassland soils are summarised in Table 8.

Table 8. RWC-ambient PECs derived for grassland soils. Values in bold were used to derive a RWC-ambient PEC for Europe

Country-region	RWC-ambient PEC mg Cu/kg	Data source
Austria- average	**36.8**	JRC-dataset
Germany - average	**33.7**	
	26.3	LABO data set
	41.0	JRC-dataset
Ireland	**28.9**	JRC-dataset
The Netherlands	**44.0**	JRC-dataset
Spain	**28.0**	Lopez Arias and Grau Gorbi, 2004
Europe		
Average	**35.9** (28.9; 44.0)	
Median	**32.8**	

The median **RWC-ambient PEC for grassland soils** was **32.8 mg Cu/kg dry weight** and was considered as a typical Cu-value for European grassland soils.

5. EFFECTS ASSESSMENT

5.1. General approach

The total risk approach has been used in this risk assessment on copper and copper compounds. The total approach includes the background concentration of copper as well as the added concentration from anthropogenic activities.

To assess the environmental effects of copper to organisms from different environmental compartments a large amount of literature data are available that includes acute and chronic exposure scenarios. Since a wide amount of reliable data is available, chronic effects have been used to derive Predicted No Effect Concentrations (PNECs) for all compartments.
To assess the effects of copper to the different organisms:

- Only chronic effects were used to derive PNECs for all compartments;
- All papers were evaluated for relevance and reliability in accordance with Technical Guidance Document (TGD) principles;
- No Observed Effect Concentrations (NOECs) or 10% Effect Concentration (EC10) were used to derive PNECs;
- Copper specific characteristics such as bioavailability, essentiality and homeostasis were integrated in the assessment.

5.2. Specific characteristics for copper

5.2.1. Essentiality

Copper is an essential nutrient, which implies that organisms will have a minimum requirement for copper and a maximum concentration at which copper will be toxic. Copper is known to be a component of more than 20 enzymes. For each species and for all essential elements an “optimal concentration range for essential elements” (OCEE) is required for normal function. This OCEE is determined by the natural bioavailable concentration range of that essential element in the species natural habitat. However, if the concentration range is too high, the element becomes toxic.

5.2.2. Bioavailability

For metals it is important to define the actual or bioavailable concentration. Due to a number of processes, copper will be present in different forms, some of which are more bioavailable than others, therefore affecting its toxicity to organisms. Several abiotic factors may change copper bioavailability including pH, hardness and dissolved organic carbon (DOC) for the water compartment and cation exchange capacity (CEC) for the terrestrial compartment. These factors have been integrated in this risk assessment.

5.3. Selection of ecotoxicological data

According to the Guidelines from the Technical Guidance Document (TGD, 2003) a study is accepted or rejected based on both reliability and relevance of the data for environmental risk assessment.
For the aquatic environment, toxicity data on algae, invertebrates and fish for fresh and marine waters and sediments are from single-species that study endpoints including growth, reproduction and mortality.
For the terrestrial environment, toxicity data on invertebrates and plants are from single-species tests that study endpoints such as survival, growth and/or reproduction. Data on microorganisms are from tests in which microbe-mediated soil processes were studied (e.g. C- and N- mineralization). These tests are multiple species tests because these processes reflect the action of many species in soil microbial communities.

5.3.1. Reliability

Standardised tests by organizations such as the OECD and US EPA were considered highly reliable when test methodology, performance and data reporting were included. Non-standardised tests were accepted but require a thorough check on their compliance with reliability criteria.

Type of test

In this risk assessment (RA) only chronic tests with reliable endpoints were considered. Chronic exposure is defined as >4 days for all invertebrates and fish. For organisms including unicellular algae, other microorganisms (bacteria, protozoa) and even invertebrates an exposure of 4 days already covers one or more generations, thus chronic NOEC values for exposure times of less than 4 days may be derived for these organisms. Tests on the embryo-larval stages of organisms or germination of plants characterize effects on the very sensitive life stages of organisms. In some cases abnormal development can be seen within a 24-48 h period and therefore NOEC values for sensitive life stages tests have also been included.
Typical chronic exposure duration for sediment dwelling organisms is derived from standard test durations. Effects associated with sub-lethal endpoints can be observed after a 28 to 42 days exposure duration (ASTM, 2003). Long-term sediment toxicity tests to measure effects on survival, growth, emergence and reproduction are determined after 20 up to 65 days of exposure (ASTM, 2003). In the Cu RA chronic exposure to sediment dwelling organisms was defined as > 20 days.
For higher plants chronic exposure tests range between 4 and 21 days.
For soil invertebrates, chronic test exposure range between 3 to 6 weeks and for soil microorganisms test duration was variable and lasts 28 days for the carbon transformation test and for the nitrogen transformation test.
For terrestrial soil tests, adequate time should elapse between mixing metal compounds in the test medium and the introduction of biota.

Description of test materials and methods

Tests should be performed according to standardised guidelines with a detailed description of methodology used.

Chemical analysis

Copper is a natural element and has background levels in the different environmental compartments that may contribute to the total available copper and thus significantly contribute to Cu toxicity. Therefore, for the aquatic environment (excluding sediments), only effect levels based on actual (measured) concentrations, which include Cu background concentration, have been considered as highly reliable. If it is not mentioned whether the NOEC/EC_{10} values are based on measured or nominal concentrations, reported values have been considered as nominal (added) concentrations. However, for the terrestrial environment and sediments, this approach greatly reduces the amount of data used since the background concentration of copper is usually not reported. Therefore, the background concentration of copper has been estimated using a measured values approach.

Test acceptability

Minimal requirements for endpoints such as growth, reproduction and mortality are often given in standard procedures (e.g. control mortality for chronic exposure < 20%). For algae, control division rate are suggested to be 1.33 for the OECD guideline (2002) and 1.0 for the ASTM (2003) guideline. In addition, there must be evidence that the concentration of the test substance has been maintained and preferably 80% of the nominal concentration throughout the test (OECD, 2002)

Concentration effect relationships

In all chronic test studies, clear dose-response should be observed. Since effect concentrations are statistically derived, information on statistics should be used as data criterion. However, if data include sufficient details to perform appropriate statistics that permit to derive reliable NOEC/EC_{10} values, the data has been retained. EC_{10} values have been considered equivalent to NOEC. If values are visually derived the data was considered unreliable.
Only studies that include a control and at least two Cu concentrations were accepted for this risk assessment.

5.3.2. Relevance

According to the TGD not all data considered reliable can be used for risk assessment. Because of the difficulties to compare different NOECs from different data with different endpoints, only chronic toxicity data from studies in which survival, filtration rate, reproduction, growth and per capita rate of increase were retained for the invertebrates and fish. For algae the only relevant endpoint used for PNEC derivation was growth.

Aquatic environment

Abiotic factors can influence speciation, bioavailability and toxicity of copper. Therefore, for the aquatic environment, water characteristics have been taken into account for both freshwater and marine selection of data. Both natural and artificial water were accepted if chemical characteristics are similar to the ranges that would be found in natural fresh/marine waters. Water characteristics that have been taken into

account for freshwater data selection were pH and hardness (without boundaries). The dissolved organic carbon (DOC) level in the toxicity tests was not used as a criterion but should be estimated in every test media. If not reported, DOC concentrations were estimated from available water surface databases or from scientific literature. The copper background concentrations were not used as a selection criterion.
For sediments, studies that had atypical concentrations of physico-chemical variables that are unlikely to occur in European sediments (e.g. silicate artificial substrate with extremely low organic carbon content) were rejected. Sediments that had an AVS content higher than 0.77 mmol/kg dry weight have also been rejected.

Terrestrial environment

Toxicity data on terrestrial organisms were from tests that study relevant endpoints such as growth, survival, reproduction, litter breakdown and abundance. Relevant points for microorganisms focused on functional parameters such as respiration, nitrification and mineralization and microbial growth. Enzymatic processes were considered less relevant.

For the terrestrial environment, only data from studies in natural or artificial (OECD) soils have been used in the Cu risk assessment (RA). Ideally, data should represent results from European soils but that would reduce the amount of data to be used, thus data from outside Europe have also been used excluding data from tropical and subtropical regions. The main soil parameters used for data selection and that influence copper bioavailability were organic matter (OM), CEC, pH and clay. When CEC is not reported it was estimated from the % of clay, pH, %OM using a regression model (Helling et al., 1964):

$$CEC=(30+4.4pH) \times clay/100+ (-34.66+29.72\ pH) \times OM/100$$

5.4. “Total” versus “added approach” for the PNEC derivation

The TGD (2003) does not provide information on how to deal with substances that have a natural background concentration in the environment. In the EU RA of metals both these approaches have been used.

The use of the “added risk approach” avoids the problem of deriving PNECs values below the natural background concentration, as it could be the case when the total risk approach is used. In this approach, both the PEC and PNEC are expressed as Cu from anthropogenic sources, resulting in a PEC_{add} and $PNEC_{add}$. This approach implies that only the anthropogenic amount of the substance is relevant for the effect assessment of the test substance. Therefore, a contribution of the natural background concentration is ignored.
For the use of this approach an accurate background concentration of the test substance is needed and according to CSTEE (2004) the current knowledge on the geographic distribution of metal background is insufficient for this approach to be correctly used.
Furthermore, the CSTEE (2004) opinion was the added risk approach may increase the overall uncertainty of PNEC values since not only accurate information on background concentrations is not available but also because there is also lack of

information on a number of biological/ecological processes including acclimatation/adaptation and field community responses.

Thus, considering the above reasons, the total approach was used on copper and copper compounds risk assessment since the most accurate risk characterization should be made by establishing both exposure and effects data sets on the same level of bioavailability on a site specific area (e.g. basin, watershed or regional basis).
In this RA, information of background variability, and its influence on a number of biological/ecological processes was considered for the derivation of PNEC values.

5.5. PNEC derivation

In an environmental risk assessment, the PEC is compared to the PNEC which is the environmental level at which no adverse effect is expected.
The PNEC is derived from ecotoxicity data from different organisms from different trophic levels under laboratory conditions. Current methods to determine PNEC include the "safety factor" approach and the statistical extrapolation model approach.
Generally, preference is given to the safety approach and the statistical approach is recommended as a supplementary approach (TGD, 1996; TGD revisions, 2003).

5.5.1. Safety factor approach versus statistical approach

As a general approach in risk assessment, a safety factor is applied to the lowest ecotoxicity values observed for the test substance. This safety factor is variable with the size of the database and includes uncertainty of the ecotoxicity value. Preference is given to the statistical approach since this models uses all available NOECs as inputs thus deriving a PNEC less dependent on one toxicological value and with a large number of chronic NOECs allows the calculation of a reliable estimate of the distribution of species and thus on more reliable PNEC values. Additionally, when the total risk approach uses the safety factor method and is applied to substances that already have a natural background, it often leads to the derivation of PNEC values below the natural background concentration range. PNECs values derived using the safety factor would also be situated at concentrations that would be deficient for many organisms. Therefore, the safety approach is considered not biologically realistic and not retained for PNEC derivation on essential elements.
Considering the reasons described above, the statistical approach was used in this risk assessment. This model assumes a parametric distribution for the different ecotoxicity data (NOECs) observed for a number of species. In order to estimate the uncertainty associated with the use of a dataset, 95% and 50% confidence limits can be calculated for this median 5th percentile (HC_5) value. In this Cu RA the PNECs is set at the level of 50% lower confidence value of HC_5.

5.5.2. Approach toxicity assessment for organisms

For the PNEC derivation only the most reliable ecotoxicity data from standard and non-standardised tests were incorporated in the risk assessment. In the effect assessment chronic NOEC/EC_{10} values are used rather than 50% Effect Concentration (EC_{50}) values to derive PNEC values. Acute effect values were not considered in this report. Ecotoxicity data was selected according to reliability and relevance as stated above.

5.5.3. Method used for the derivation of NOEC values

The methods used for the derivation of NOEC values are the same as outlined in the TGD (1996; revisions, 2003). They were real NOEC values or were derived from effect concentrations.
When possible, real NOEC values were derived from the data reported:

Statistical analysis – the NOEC is the highest concentration showing no statistical effect compared to the control. Significance level is p=0.05 (optional, the p=0.01 level is reported instead of the p=0.05). There also need to be a clear concentration effect-response relationship.

If the real NOEC value could not be derived the following procedure was used:

- If the EC_{10} values were available, the NOEC was set at this value, on condition that the value fell within the concentration range.
- In more recent data there was the preference for the ECx (where x is a low effect between 5 and 20%) instead of the NOEC. In those studies the EC_{10} was used if no NOEC was reported.
- Furthermore, if the individual data were reported, a number of EC_{10} values were calculated.

As enough data was found in the literature on real NOECs, it was decided not to derive NOEC values from Lowest Observed Effect Concentrations (LOEC) or Maximum Acceptable Toxicant Concentration (MATC).

5.5.4. Method used for the aggregation of NOEC data

- If for one species several chronic NOEC values based on the same endpoint were available, they were averaged by calculating the geometric mean, resulting in a "species mean" NOEC. NOEC values should be from equivalent tests and same exposure time. Nevertheless, NOEC derived from tests with a short exposure time may be used together with NOEC values derived from longer exposure time if the data indicated that a sensitive life stage was tested.
- If for one species there were several NOECs derived for different endpoints, then the lowest value was selected (the most sensitive endpoint). The lowest value was determined on the basis of the geometric mean if more than one NOEC value was reported. The most sensitive endpoint per species is further used as input in the species sensitivity distribution (SSD).
- In some cases NOEC values for different life stages for a specific organism were reported. If it is evident that a life stage is more sensitive, then the result for the most sensitive life stage was selected.
- For the different environment compartments, the influence of the test media characteristics on the NOEC values was evaluated and accounted for prior to the derivation of species-specific geomean NOEC values.

5.5.5. Approach for PNEC/$PNEC_{add}$ derivation

The PNECs for the different compartments were calculated from the chronic NOEC data extracted from the different databases. For the derivation of PNECadd the results of the toxicity tests were corrected if possible for background copper concentration.

PNEC values were derived using the two ecotoxicological extrapolation methods, both described in the TGD:

- The PNEC was calculated from the lowest acute LC_{50} or EC_{50} or preferably from the lowest NOEC/EC_{10} using assessment factors that depended on the available toxicity data (TGD-Chapter 3)
- In case the chronic database is sufficiently large, the PNEC was calculated by means of statistical extrapolation, using all available NOECs values as input (TGD chapter 3, appendix V).

In the TGD, the first extrapolation method is preferred and it is recommended to use statistical extrapolation as a supplementary approach. However, when large amounts of ecotoxicity data are available, the statistical approach is being preferred for the derivation of PNEC.

In a London workshop on the use of statistical extrapolation for the derivation of PNEC values, some recommendations were made to calculate PNEC values provided that chronic database meet certain requirements (EC, 2001).

- General requirements: at least 10 NOEC values and preferably 15 values are available for different species.
- Taxonomic requirements: at least 8 taxonomic groups, using the EPA list of 8 groups required for the derivation of the final chronic value (PNEC equivalent) as a starting point.
- Distribution function: the log-normal distribution (the methods of Wagner & Løkke (1991) and Aldenberg & Jaworska (2000)) and the log-logistic distribution (Aldenberg & Slob, 1993) are pragmatic choices because of its mathematical properties. Several other approaches could be used to derive variability distributions and percentiles from parametric (e.g. log-normal, Weibull distributions) and non-parametric methods. To select the most appropriate distribution function for the available data, both statistical (e.g. Kolmogorov-Smirnov, Andersen-Darling tests) and visual (e.g. Q-Q plots) goodness-of-fit techniques were used. To select the most appropriate distribution for a given data set, goodness of fit statistics (software BestFit, Palisade Inc.) were used. Goodness of fit tests are formal statistic tests of the hypothesis that the data represents an independent sample from an assumed distribution. These tests compare the actual data and the theoretic distribution considered. The Andersen-Darling test is preferred since it emphasizes tail values. This test is a quadratic statistic that measures the vertical discrepancy in a cumulative distribution function-type probability plot and is sensitive to departures of the distributions in the tails (Stephens, 1982). The calculated goodness-of-fit statistic measures how good the fit is and is used by comparing the values to the goodness-of-fit of other distributions. Additionally, critical values are calculated and used to determine if a fitted distribution should be accepted or rejected at a specific level of confidence. Usually, a significant level of 0.05 is used, and implies that a value of the test-statistic below the 95th percentile of distribution for the statistic is acceptable and leads to the inability to reject the hypothesis.
- Level of protection: the 5th percentile value with 50% ($HC_{5\text{-}50}$) confidence should be used

- Uncertainty considerations: Depending on the database and the confidence limits for that database, and assessment factor (AF) should be applied on the 5th percentile value and therefore PNEC= 5th percentile value/AF. This AF should be between 1 and 5. To determine the size of AF the following points are mentioned:
    - The overall quality of the database and endpoints covered (e.g. if all the data are generated from real chronic studies covering sensitive life stages);
    - The diversity and representativeness of the taxonomic groups covered by the database;
    - The mode of action of the chemical;
    - Statistical uncertainties around 5th percentile estimate (as reflected in the goodness-of-fit or the size of confidence interval);
    - Comparisons between field and mesocosms studies and the 5th percentile and mesocosm/field studies to evaluate the laboratory to field extrapolation.

6. EFFECTS ASSESSMENT- AQUATIC ENVIRONMENT

6.1. Results freshwater toxicity

The copper aquatic effects database contains a large number of high quality chronic NOEC values (139 chronic NOECs for 27 species). For the freshwater compartment, the effect assessment of copper is based on NOECs/EC_{10}s collected for freshwater organisms.
Data on chronic toxicity tests resulting in NOEC values for freshwater algae, invertebrates and fish are summarized in Tables 9, 10 and 11, respectively. Some recent studies (grey) were found in the literature and were added to the tables. However, these chronic NOEC/EC_{10} values were not included in the PNEC derivation in the copper RA.

6.1.1. Toxicity data for freshwater algae

In the Cu RA, 34 chronic studies reporting the NOEC for freshwater algae/higher plants were found and used for PNEC derivation. The species mean NOEC for freshwater algae range from 54 µg/l Cu for *Pseudokircherniella subcapitata* (endpoint growth; geometric mean of 12 test values) to 183 µg/l Cu for *Chlorella vulgaris* (endpoint growth; geometric mean of 17 test values). *Lemna minor* NOEC (growth) was 30 µg/l Cu (1 result).

6.1.2. Toxicity data for freshwater invertebrates

In the Cu RA, 54 chronic studies reporting NOEC for freshwater invertebrates were found and used for PNEC derivation. The species NOEC for freshwater invertebrates range from 6.0 µg/l Cu for the snail Juga plicifera (endpoint mortality; 1 test value) to 54.3 µg/l Cu amphipod Hyalella azteca (endpoint mortality; geometric mean value of 6 test results).
More recent chronic toxicity test studies were found in the literature and the database has now 89 NOEC values reported. However, these NOEC/EC10 values were not included in the PNEC derivation in this RA.

6.1.3. Toxicity data for freshwater fish

In the Cu RA, 51 chronic studies reporting NOEC for freshwater fish were found and used for PNEC derivation. The “species mean” NOEC values for freshwater fish range from 11.6 µg/l Cu for rainbow trout Oncorhynchus mykiss (endpoint growth; geometric mean of 4 test values) to 120 µg/l Cu for the loach Noemacheilus barbatulus (endpoint mortality; one test result). Recent studies were not found in the literature.

Table 9. NOEC values and physico-chemical parameters for freshwater algae/higher plants (accepted studies)

ORGANISM (CODE)	TEST TYPE	TEST COMPOUND	TEST WATER	PH	HARDNESS	EXPOSURE TIME	CRITERION	RESULT µg Cu /L	REFERENCE
Chlamydomonas reinhardtii	F	$CuSO_4$	art (DOC:0.5 mg/L)	6.2	25	10-d	NOECg	22	Schäfer et al., 1994
Chlamydomonas reinhardtii	S	$CuCl_2$	art (DOC:9.84 mg/L)	6	250	3-d	NOECg	178	De Schamphelaere and Janssen, 2006
Chlamydomonas reinhardtii	S	$CuCl_2$	art (DOC:9.84 mg/L)	7	250	3-d	NOECg	108	De Schamphelaere and Janssen, 2006
Chlamydomonas reinhardtii	S	$CuCl_2$	art (DOC:9.84 mg/L)	8.1	250	3-d	NOECg	96	De Schamphelaere and Janssen, 2006
Chlorella vulgaris (Code: Ankevven 1)	S	$CuCl_2$	art (DOC:5.2 mg/L)	6	100	3-d	NOECg	108.3	De Schamphelaere and Janssen, 2006
Chlorella vulgaris (Code: Ankevven 2)	S	$CuCl_2$	art (DOC:15.5 mg/L)	6	100	3-d	NOECg	407.4	De Schamphelaere and Janssen, 2006
Chlorella vulgaris (Code: Ankevven 3)	S	$CuCl_2$	art (DOC:5.0 mg/L)	7.9	400	3-d	NOECg	55.6	De Schamphelaere and Janssen, 2006
Chlorella vulgaris (Code: Ankevven 4)	S	$CuCl_2$	art (DOC:1.5 mg/L)	7	250	3-d	NOECg	36.4	De Schamphelaere and Janssen, 2006
Chlorella vulgaris (Code: Ankevven 5)	S	$CuCl_2$	art (DOC:15.8 mg/L)	8	400	3-d	NOECg	172.9	De Schamphelaere and Janssen, 2006
Chlorella vulgaris (Code: Ankevven 6)	S	$CuCl_2$	art (DOC:10.8 mg/L)	7	250	3-d	NOECg	98.9	De Schamphelaere and Janssen, 2006
Chlorella vulgaris (Code: Ankevven 7)	S	$CuCl_2$	art (DOC:10.0 mg/L)	7	500	3-d	NOECg	85.4	De Schamphelaere and Janssen, 2006
Chlorella vulgaris (Code: Ankevven 8)	S	$CuCl_2$	art(DOC:9.9 mg/L)	8.8	250	3-d	NOECg	161.9	De Schamphelaere and Janssen, 2006
Chlorella vulgaris (Code: Ankevven 9)	S	$CuCl_2$	art (DOC: 19.1mg/L)	7	250	3-d	NOECg	282.9	De Schamphelaere and Janssen, 2006
Chlorella vulgaris (Code: Ankevven 10)	S	$CuCl_2$	art (DOC:5.0 mg/L)	6	400	3-d	NOECg	187.8	De Schamphelaere and Janssen, 2006
Chlorella vulgaris (Code: Ankevven 11)	S	$CuCl_2$	art (DOC:15.2 mg/L)	6	400	3-d	NOECg	510.2	De Schamphelaere and Janssen, 2006
Chlorella vulgaris (Code: Ankevven 12)	S	$CuCl_2$	art (DOC:5.3 mg/L)	7.9	100	3-d	NOECg	31.0	De Schamphelaere and Janssen, 2006
Chlorella vulgaris (Code: Ankevven 13)	S	$CuCl_2$	art (DOC:15.7 mg/L)	7.9	100	3-d	NOECg	188.0	De Schamphelaere and Janssen, 2006
Chlorella vulgaris (Code: Ankevven 14)	S	$CuCl_2$	art (DOC:10.3 mg/L)	5.5	250	3-d	NOECg	404.1	De Schamphelaere and Janssen, 2006

Table 9. (cont.) NOEC values and physico-chemical parameters for freshwater algae/higher plants (accepted studies)

ORGANISM (CODE)	TEST TYPE	TEST COMPOUND	TEST WATER	PH	HARDNESS	EXPOSURE TIME	CRITERION	RESULT µg Cu /L	REFERENCE
Chlorella vulgaris (Code: Ankevven 15)	S	$CuCl_2$	art (DOC:10.3 mg/L)	7.1	25	3-d	NOECg	158.7	De Schamphelaere and Janssen, 2006
Chlorella vulgaris (Code: Ankevven 16)	S	$CuCl_2$	art (DOC:10.8 mg/L)	7	250	3-d	NOECg	83.9	De Schamphelaere and Janssen, 2006
Chlorella vulgaris (Code: Ankevven 17)	S	$CuCl_2$	art (DOC:10.2 mg/L)	7	250	3-d	NOECg	132.3	De Schamphelaere and Janssen, 2006
Pseudokirchneriella subcapitata (Code:Bihain-1)	S	$CuCl_2$	art (DOC: 5.23mg/L)	6.19	18	3-d	NOECg	63.9	De Schamphelaere et al., 2003
Pseudokirchneriella subcapitata (Code:Bihain-2)	S	$CuCl_2$	river (DOC: 15.8mg/L)	6.22	18	3-d	NOECg	110.6	De Schamphelaere et al., 2003
Pseudokirchneriella subcapitata (Code:Bihain-6)	S	$CuCl_2$	river (DOC: 9.99mg/L)	7.09	18	3-d	NOECg	57.5	De Schamphelaere et al., 2003
Pseudokirchneriella subcapitata (Code:Bihain-7)	S	$CuCl_2$	river (DOC: 9.89mg/L)	7.04	18	3-d	NOECg	59.1	De Schamphelaere et al., 2003
Pseudokirchneriella subcapitata (Code:Ossenkolk-1)	S	$CuCl_2$	river (DOC: 5.31mg/L)	6.2	2.5	3-d	NOECg	111.2	De Schamphelaere et al., 2003
Pseudokirchneriella subcapitata (Code:Ossenkolk-2)	S	$CuCl_2$	river (DOC: 15.6mg/L)	6.2	2.5	3-d	NOECg	112.8	De Schamphelaere et al., 2003
Pseudokirchneriella subcapitata (Code:Ossenkolk-3)	S	$CuCl_2$	river (DOC: 5.75mg/L)	8.07	2.5	3-d	NOECg	49.4	De Schamphelaere et al., 2003
Pseudokirchneriella subcapitata (Code:Ossenkolk-4)	S	$CuCl_2$	river (DOC: 2.06mg/L)	7.08	2.5	3-d	NOECg	19.4	De Schamphelaere et al., 2003
Pseudokirchneriella subcapitata (Code:Ossenkolk-5)	S	$CuCl_2$	river (DOC: 16.1mg/L)	8.05	2.5	3-d	NOECg	174	De Schamphelaere et al., 2003
Pseudokirchneriella subcapitata (Code:Ossenkolk-6)	S	$CuCl_2$	river (DOC: 11.1mg/L)	7.09	2.5	3-d	NOECg	53.7	De Schamphelaere et al., 2003
Pseudokirchneriella subcapitata (Code:Ossenkolk-7)	S	$CuCl_2$	river (DOC: 10.5mg/L)	7.12	2.5	3-d	NOECg	67.7	De Schamphelaere et al., 2003
Pseudokirchneriella subcapitata (Code:Ossenkolk-9)	S	$CuCl_2$	river (DOC: 19.9mg/L)	7.11	2.5	3-d	NOECg	170.8	De Schamphelaere et al., 2003
Pseudokirchneriella subcapitata (Code:Ankeveen-1)	S	$CuCl_2$	river (DOC: 5.07mg/L)	6.18	130	3-d	NOECg	40.8	De Schamphelaere et al., 2003

Table 9. (cont.) NOEC values and physico-chemical parameters for freshwater algae/higher plants (accepted studies)

ORGANISM (CODE)	TEST TYPE	TEST COMPOUND	TEST WATER	PH	HARDNESS	EXPOSURE TIME	CRITERION	RESULT µg Cu /L	REFERENCE
Pseudokirchneriella subcapitata (Code:Ankeveen-2)	S	$CuCl_2$	river (DOC: 14.9mg/L)	6.17	130	3-d	NOECg	89.2	De Schamphelaere et al., 2003
Pseudokirchneriella subcapitata (Code:Ankeveen-5)	S	$CuCl_2$	river (DOC: 15.2mg/L)	7.78	130	3-d	NOECg	97.2	De Schamphelaere et al., 2003
Pseudokirchneriella subcapitata (Code:Ankeveen-7)	S	$CuCl_2$	river (DOC: 10.4mg/L)	7.02	130	3-d	NOECg	60.2	De Schamphelaere et al., 2003
Pseudokirchneriella subcapitata (Code:Ankeveen-8)	S	$CuCl_2$	river (DOC: 10.5mg/L)	8.58	130	3-d	NOECg	37.6	De Schamphelaere et al., 2003
Pseudokirchneriella subcapitata (Code:Ankeveen-9)	S	$CuCl_2$	river (DOC: 18.2mg/L)	6.98	130	3-d	NOECg	91.3	De Schamphelaere et al., 2003
Pseudokirchneriella subcapitata (Code:Ankeveen-13)	S	$CuCl_2$	river (DOC: 15.3mg/L)	8.05	130	3-d	NOECg	53.3	De Schamphelaere et al., 2003
Pseudokirchneriella subcapitata (Code:Ankeveen-14)	S	$CuCl_2$	river (DOC: 9.84mg/L)	5.68	130	3-d	NOECg	54.6	De Schamphelaere et al., 2003
Pseudokirchneriella subcapitata (Code:Ankeveen-15)	S	$CuCl_2$	river (DOC: 10.4mg/L)	7.19	130	3-d	NOECg	49.2	De Schamphelaere et al., 2003
Pseudokirchneriella subcapitata (Code:Ankeveen-1)	S	$CuSO_4$	SW (DOC: 17.8 mg/L)	7.3	7-238	3-d	NOECg	164	Heijerick et al., 2005b
Pseudokirchneriella subcapitata (Code:Ankeveen-2)	S	$CuSO_4$	SW (DOC: 20.4mg/L)	7.5	7-238	3-d	NOECg	65.5	Heijerick et al., 2005b
Pseudokirchneriella subcapitata (Code:Bihain)	S	$CuSO_4$	SW (DOC: 8.91 mg/L)	5.94	7-238	3-d	NOECg	46.5	Heijerick et al., 2005b
Pseudokirchneriella subcapitata (Code:Clywydog-4)	S	$CuSO_4$	SW (DOC: 2.72 mg/L)	6.31	7-238	3-d	NOECg	52.9	Heijerick et al., 2005b
Pseudokirchneriella subcapitata (Code:Clywydog-5)	S	$CuSO_4$	SW (DOC: 2.34 mg/L)	6.1	7-238	3-d	NOECg	61.8	Heijerick et al., 2005b
Pseudokirchneriella subcapitata (Code:Markemeer-1)	S	$CuSO_4$	SW (DOC: 6.42 mg/L)	8.26	7-238	3-d	NOECg	49	Heijerick et al., 2005b
Pseudokirchneriella subcapitata (Code:Markemeer-2)	S	$CuSO_4$	SW (DOC: 8.24 mg/L)	8.3	7-238	3-d	NOECg	35.4	Heijerick et al., 2005b
Pseudokirchneriella subcapitata (Code:Mole)	S	$CuSO_4$	SW (DOC: 6.13 mg/L)	7.55	7-238	3-d	NOECg	56.4	Heijerick et al., 2005b

Table 9. (cont.) NOEC values and physico-chemical parameters for freshwater algae/higher plants (accepted studies)

ORGANISM (CODE)	TEST TYPE	TEST COMPOUND	TEST WATER	PH	HARDNESS	EXPOSURE TIME	CRITERION	RESULT µg Cu /L	REFERENCE
Pseudokirchneriella subcapitata (Code:Monate)	S	$CuSO_4$	SW (DOC: 2.52 mg/L)	8.23	7-238	3-d	NOECg	17.9	Heijerick et al., 2005b
Pseudokirchneriella subcapitata (Code:Rhine)	S	$CuSO_4$	SW (DOC: 1.98 mg/L)	8.06	7-238	3-d	NOECg	19.3	Heijerick et al., 2005b
Pseudokirchneriella subcapitata (Code:Segrino)	S	$CuSO_4$	SW (DOC: 1.70 mg/L)	8.2	7-238	3-d	NOECg	15.7	Heijerick et al., 2005b
Pseudokirchneriella subcapitata (Code:Skarsjon)	S	$CuSO_4$	SW (DOC: 10.3 mg/L)	5.52	7-238	3-d	NOECg	94.7	Heijerick et al., 2005b
Pseudokirchneriella subcapitata (Code:Somerain)	S	$CuSO_4$	SW (DOC: 1.55 mg/L)	6.39	7-238	3-d	NOECg	4.2	Heijerick et al., 2005b
Pseudokirchneriella subcapitata	S	$CuSO_4$	art (DOC: <1 mg/L)	7.8	7-238	3-d	NOECg	13.5	Heijerick et al., 2005b
Lemna minor	S	$CuSO_4$	art (DOC:0.5 mg/L	6.5	26.8	7-d	NOECg	30	Teisseire et al., 1998

NOEC- no observed effect concentration; NR- not reported; S- static test; F – flow-trough test; R- renewal test; DOC – dissolved organic carbon; g – growth; art. – artificial; $CuSO_4$ – copper sulphate; $CuCl_2$ – copper chloride; d-days.

Table 10. NOEC values and physico-chemical parameters for freshwater invertebrates (accepted studies)

ORGANISM (LIFESTAGE / SIZE)	TEST TYPE	TEST COMPOUND	TEST WATER	PH	HARDNESS	EXPOSURE TIME	CRITERION	RESULT µg Cu /L	REFERENCE
Brachionus calyciflorus	S	$CuCl_2$	art (DOC:4.91mg/L)	6	100	2-d	NOECg	8.2	De Schamphelaere et al.,2006
Brachionus calyciflorus	S	$CuCl_2$	art (DOC:14.5mg/L)	6	100	2-d	NOECg	31.2	De Schamphelaere et al.,2006
Brachionus calyciflorus	S	$CuCl_2$	art (DOC:4.83mg/L)	7.8	100	2-d	NOECg	47.8	De Schamphelaere et al.,2006
Brachionus calyciflorus	S	$CuCl_2$	art (DOC:14.7mg/L)	7.8	100	2-d	NOECg	103	De Schamphelaere et al.,2006
Daphnia magna (Code: Bihain 1)	S	$CuCl_2$	art (DOC:5.59 mg/L)	6.09	100	3-w	NOECr	30.3	De Schamphelaere and Janssen, 2004
Daphnia magna (Code: Bihain 2)	S	$CuCl_2$	art (DOC:16.9 mg/L)	6.08	100	3-w	NOECr	79.7	De Schamphelaere and Janssen, 2004
Daphnia magna (Code: Bihain 3)	S	$CuCl_2$	art (DOC:6.27 mg/L)	7.88	400	3-w	NOECr	81.2	De Schamphelaere and Janssen, 2004
Daphnia magna (Code: Bihain 4)	S	$CuCl_2$	art (DOC:2.13 mg/L)	6.99	250	3-w	NOECr	40.8	De Schamphelaere and Janssen, 2004
Daphnia magna (Code: Bihain 5)	S	$CuCl_2$	art (DOC:18.1 mg/L)	7.94	400	3-w	NOECr	121	De Schamphelaere and Janssen, 2004
Daphnia magna (Code: Bihain 6)	S	$CuCl_2$	art (DOC:9.84 mg/L)	7.05	250	3-w	NOECr	112	De Schamphelaere and Janssen, 2004
Daphnia magna (Code: Bihain 7)	S	$CuCl_2$	art (DOC:9.98 mg/L)	7.06	500	3-w	NOECr	111	De Schamphelaere and Janssen, 2004
Daphnia magna (Code: Bihain 8)	S	$CuCl_2$	art (DOC:10.2 mg/L)	8.42	250	3-w	NOECr	121	De Schamphelaere and Janssen, 2004
Daphnia magna (Code: Bihain 9)	S	$CuCl_2$	art (DOC:21.6 mg/L)	7.05	250	3-w	NOECr	228	De Schamphelaere and Janssen, 2004
Daphnia magna (Code: Ossenkolk-1)	S	$CuCl_2$	art (DOC:6.19 mg/L)	6.09	100	3-w	NOECr	31.8	De Schamphelaere and Janssen, 2004
Daphnia magna (Code: Ossenkolk-2)	S	$CuCl_2$	art (DOC:16.9 mg/L)	6.06	100	3-w	NOECr	84.7	De Schamphelaere and Janssen, 2004
Daphnia magna (Code: Ossenkolk-3)	S	$CuCl_2$	art (DOC:5.69 mg/L)	7.88	400	3-w	NOECr	78.6	De Schamphelaere and Janssen, 2004
Daphnia magna (Code: Ossenkolk-4)	S	$CuCl_2$	art (DOC:2.32 mg/L)	7.02	250	3-w	NOECr	31.8	De Schamphelaere and Janssen, 2004
Daphnia magna (Code: Ossenkolk-5)	S	$CuCl_2$	art (DOC:17.8 mg/L)	7.91	400	3-w	NOECr	145	De Schamphelaere and Janssen, 2004

Table 10. (cont.) NOEC values and physico-chemical parameters for freshwater invertebrates (accepted studies)

ORGANISM (LIFESTAGE / SIZE)	TEST TYPE	TEST COMPOUND	TEST WATER	PH	HARDNESS	EXPOSURE TIME	CRITERION	RESULT µg Cu /L	REFERENCE
Daphnia magna (Code: Ossenkolk-6)	S	$CuCl_2$	art (DOC:12.8 mg/L)	6.96	250	3-w	NOECr	162.5	De Schamphelaere and Janssen, 2004
Daphnia magna (Code: Ossenkolk-7)	S	$CuCl_2$	art (DOC:11.9 mg/L)	7	500	3-w	NOECr	114	De Schamphelaere and Janssen, 2004
Daphnia magna (Code: Ossenkolk-8)	S	$CuCl_2$	art (DOC:11.2 mg/L)	8.35	250	3-w	NOECr	135	De Schamphelaere and Janssen, 2004
Daphnia magna (Code: Ossenkolk-9)	S	$CuCl_2$	art (DOC:20.1 mg/L)	7.01	250	3-w	NOECr	190	De Schamphelaere and Janssen, 2004
Daphnia magna (Code: Ankeveen-1)	S	$CuCl_2$	art (DOC:5.04 mg/L)	6.15	100	3-w	NOECr	29.4	De Schamphelaere and Janssen, 2004
Daphnia magna (Code: Ankeveen-2)	S	$CuCl_2$	art (DOC:14.5 mg/L)	6.16	100	3-w	NOECr	89.2	De Schamphelaere and Janssen, 2004
Daphnia magna (Code: Ankeveen-3)	S	$CuCl_2$	art (DOC:5.15 mg/L)	7.83	400	3-w	NOECr	68.8	De Schamphelaere and Janssen, 2004
Daphnia magna (Code: Ankeveen-4)	S	$CuCl_2$	art (DOC:1.74 mg/L)	7.16	250	3-w	NOECr	41.9	De Schamphelaere and Janssen, 2004
Daphnia magna (Code: Ankeveen-5)	S	$CuCl_2$	art (DOC:15.6 mg/L)	7.85	400	3-w	NOECr	153.1	De Schamphelaere and Janssen, 2004
Daphnia magna (Code: Ankeveen-6)	S	$CuCl_2$	art (DOC:10.2 mg/L)	7.15	250	3-w	NOECr	90.2	De Schamphelaere and Janssen, 2004
Daphnia magna (Code: Ankeveen-7)	S	$CuCl_2$	art (DOC:10.1 mg/L)	7.15	500	3-w	NOECr	85.9	De Schamphelaere and Janssen, 2004
Daphnia magna (Code: Ankeveen-8)	S	$CuCl_2$	art (DOC:12.3 mg/L)	8.32	250	3-w	NOECr	120.3	De Schamphelaere and Janssen, 2004
Daphnia magna (Code: Ankeveen-9)	S	$CuCl_2$	art (DOC:16.1 mg/L)	7.08	250	3-w	NOECr	213	De Schamphelaere and Janssen, 2004
Daphnia magna (Code: Ankeveen-10)	S	$CuCl_2$	art (DOC:4.81 mg/L)	6.05	400	3-w	NOECr	46.7	De Schamphelaere and Janssen, 2004
Daphnia magna (Code: Ankeveen-11)	S	$CuCl_2$	art (DOC:13.2 mg/L)	6.06	400	3-w	NOECr	93.1	De Schamphelaere and Janssen, 2004
Daphnia magna (Code: Ankeveen-12)	S	$CuCl_2$	art (DOC:4.81 mg/L)	7.88	100	3-w	NOECr	76.7	De Schamphelaere and Janssen, 2004

Table 10. (cont.) NOEC values and physico-chemical parameters for freshwater invertebrates (accepted studies)

ORGANISM (LIFESTAGE / SIZE)	TEST TYPE	TEST COMPOUND	TEST WATER	PH	HARDNESS	EXPOSURE TIME	CRITERION	RESULT µg Cu /L	REFERENCE
Daphnia magna (Code: Ankeveen-13)	S	$CuCl_2$	art (DOC:13.5 mg/L)	7.89	100	3-w	NOECr	196	De Schamphelaere and Janssen, 2004
Daphnia magna (Code: Ankeveen-14)	S	$CuCl_2$	art (DOC:9.02 mg/L)	5.62	250	3-w	NOECr	56.8	De Schamphelaere and Janssen, 2004
Daphnia magna (Code: Ankeveen-15)	S	$CuCl_2$	art (DOC:9.11 mg/L)	7.05	25	3-w	NOECr	101	De Schamphelaere and Janssen, 2004
Daphnia magna (Code: Ankeveen-16)	S	$CuCl_2$	art (DOC:10.0 mg/L)	7.07	250	3-w	NOECr	93.5	De Schamphelaere and Janssen, 2004
Daphnia magna (Code: Ankeveen-17)	S	$CuCl_2$	art (DOC:10.3 mg/L)	7.06	250	3-w	NOECr	87.4	De Schamphelaere and Janssen, 2004
Daphnia magna (neonates)	R	$CuCl_2$	lake (DOC: 2 mg/L)	8.1	225	7-d	NOECg	12.6	Van Leeuwen et al., 1988
Daphnia magna (neonates)	R	$CuSO_4$	lake (DOC: 2.72mg/L)	6.31	10	3-w	NOECr	28	Heijerick et al., 2002
Daphnia magna (neonates)	R	$CuSO_4$	lake (DOC: 2.34mg/L)	6.1	12.4	3-w	NOECr	21.5	Heijerick et al., 2002
Daphnia magna (neonates)	R	$CuSO_4$	lake (DOC: 8.24mg/L)	8.3	238	3-w	NOECr	71.4	Heijerick et al., 2002
Daphnia magna (neonates)	R	$CuSO_4$	river (DOC: 1.99mg/L)	8.06	191	3-w	NOECr	68.8	Heijerick et al., 2002
Daphnia magna (neonates)	R	$CuSO_4$	river (DOC: 6.13mg/L)	7.55	132	3-w	NOECr	106	Heijerick et al., 2002
Daphnia magna (neonates)	R	$CuSO_4$	lake (DOC: 20.4mg/L)	7.5	134	3-w	NOECr	181	Winner, 1985
Daphnia magna (neonates)	R	CuCl2	lake (DOC: 2mg/L)	8.1	225	3-w	NOECm	36.8	Van Leeuwen et al., 1988
Daphnia magna (neonates)	F	CuCl2	lake (DOC: 2mg/L)	8.1	225	3-w	NOECg	36.8	Van Leeuwen et al., 1988
Daphnia pulex (neonates <24h)	R	$CuSO_4$	art (DOC: 0.1mg/L)	8.6	57.5	42-d	NOECm	4	Winner, 1985
Daphnia pulex (neonates <24h)	R	$CuSO_4$	art (DOC: 0.475mg/L)	8.5	57.5	42-d	NOECm	20	Winner, 1985
Daphnia pulex (neonates <24h)	R	$CuSO_4$	art (DOC: 0.85mg/L)	8.7	57.5	42-d	NOECm	30	Winner, 1985
Daphnia pulex (neonates <24h)	R	$CuSO_4$	art (DOC: 0.1mg/L)	8.7	115	42-d	NOECm	5	Winner, 1985
Daphnia pulex (neonates <24h)	R	$CuSO_4$	art (DOC: 0.475mg/L)	8.55	115	42-d	NOECm	20	Winner, 1985
Daphnia pulex (neonates <24h)	R	$CuSO_4$	art (DOC: 0.85mg/L)	8.55	115	42-d	NOECm	40	Winner, 1985
Daphnia pulex (neonates <24h)	R	$CuSO_4$	art (DOC: 0.175mg/L)	8.55	230	42-d	NOECm	10	Winner, 1985

Table 10. (cont.) NOEC values and physico-chemical parameters for freshwater invertebrates (accepted studies)

ORGANISM (LIFESTAGE / SIZE)	TEST TYPE	TEST COMPOUND	TEST WATER	PH	HARDNESS	EXPOSURE TIME	CRITERION	RESULT µg Cu /L	REFERENCE
Daphnia pulex (neonates <24h)	R	$CuSO_4$	art (DOC: 0.475mg/L)	8.6	230	42-d	NOECm	15	Winner, 1985
Daphnia pulex (neonates <24h)	R	$CuSO_4$	art (DOC: 0.85mg/L)	8.6	230	42-d	NOECm	20	Winner, 1985
Gammarus pulex (mixed sizes 1.5 to 14 mm)	F	NR	tap (DOC: 1 mg/L)	8	103	100-d	NOEC pop	11	Maund et al., 1992
Ceriodaphnia dubia (<24h)	S	$CuSO_4$	river (DOC: 2 mg/L)	7	22	7-d	NOECm	19	Jop et al., 1995
Ceriodaphnia dubia (<24h)	S	$CuSO_4$	art (DOC: 0.5 mg/L)	6.95	20	7-d	NOECm	4	Jop et al., 1995
Ceriodaphnia dubia (<24h)	S	$CuSO_4$	river (DOC: 5.7 mg/L)	8.25	100	7-d	NOECm	122	Spehar and Fianolt, 1985
Ceriodaphnia dubia (<24h)	S	$CuSO_4$	river (DOC: 5.7 mg/L)	8.25	100	7-d	NOECm	20	Cerda and Olive, 1993
Ceriodaphnia dubia (<24h)	R	$CuSO_4$	art (DOC: 0.5 mg/L)	7.6	85	7-d	NOECr	10	Cerda and Olive, 1993
Ceriodaphnia dubia (<24h)	S	$CuSO_4$	river (DOC: 2.9 mg/L)	9	98	7-d	NOECr	10	Belanger and Cherry, 1990
Ceriodaphnia dubia (<24h)	S	$CuSO_4$	river (DOC: 2 mg/L)	8	114	7-d	NOECr	20	Belanger and Cherry, 1990
Ceriodaphnia dubia (<24h)	S	$CuSO_4$	river (DOC: 2 mg/L)	9	114	7-d	NOECr	20	Belanger and Cherry, 1990
Ceriodaphnia dubia (<24h)	S	$CuSO_4$	river (DOC: 3 mg/L)	6	182	7-d	NOECr	20	Belanger and Cherry, 1990
Ceriodaphnia dubia (<24h)	S	$CuSO_4$	river (DOC: 2.9 mg/L)	8.15	94	7-d	NOECr	6.3	Belanger et al., 1989
Ceriodaphnia dubia (<24h)	S	$CuSO_4$	river (DOC: 3 mg/L)	8.31	179	7-d	NOECr	24.1	Belanger et al., 1989
Ceriodaphnia dubia (<24h)	S	$CuSO_4$	art (DOC: 0.5 mg/L)	6.3-7.6	20	7-d	NOECr	4	Jop et al., 1995
Ceriodaphnia dubia (<24h)	S	$CuSO_4$	river (DOC: 2 mg/L)	6.6-7.4	22	7-d	NOECr	10	Jop et al., 1995
Ceriodaphnia dubia (<24h)	S	$CuSO_4$	river (DOC: 5.7 mg/L)	8.25	100	7-d	NOECr	31.6	Spehar and Fianolt, 1985
Hyalella azteca (2-3 weeks old)	R	$CuSO_4$	spring (DOC:1mg/L)	7.65	36	10-d	NOECm	50	Deaver and Rogers, 1996
Hyalella azteca (2-3 weeks old)	R	$CuSO_4$	spring (DOC:1mg/L)	7.8	50	10-d	NOECm	50	Deaver and Rogers, 1996
Hyalella azteca (2-3 weeks old)	R	$CuSO_4$	spring (DOC:1mg/L)	8.05	64	10-d	NOECm	82	Deaver and Rogers, 1996
Hyalella azteca (2-3 weeks old)	R	$CuSO_4$	spring (DOC:1mg/L)	7.5	22	10-d	NOECm	82	Deaver and Rogers, 1996
Hyalella azteca (2-3 weeks old)	R	$CuSO_4$	spring (DOC:1mg/L)	6.95	<10	10-d	NOECm	30	Deaver and Rogers, 1996
Hyalella azteca (<7 days old)	R	NR	tap (DOC: 1mg/L)	7.6	128	35-d	NOECm	32	Othman and Pascoe, 2002

Table 10. (cont.) NOEC values and physico-chemical parameters for freshwater invertebrates (accepted studies)

ORGANISM (LIFESTAGE / SIZE)	TEST TYPE	TEST COMPOUND	TEST WATER	PH	HARDNESS	EXPOSURE TIME	CRITERION	RESULT µg Cu /L	REFERENCE
Chironomus riparius (eggs <12 h)	R	$CuSO_4$	art (DOC:0.5 mg/L)	6.8	151	10-d	NOECg	16.9	Taylor et al., 1991
Clistoronia magnifica (larvae 1st gen)	F	$CuCl_2$	well (DOC:1.3 mg/L)	7.3	26	240-d	NOEClc	8.3	Nebeker et al., 1984
Clistoronia magnifica (larvae 2nd gen)	F	$CuCl_2$	well (DOC:1.3 mg/L)	7.3	26	240-d	NOEClc	13	Nebeker et al., 1984
Paratanytarsus parthenogeneticus (larvae-7 days old)	NR	$CuSO_4$	art (DOC:0.5 mg/L)	6.9	25	16-d	NOECg	40	Hatakeyama and Yasuno, 1981
Paratanytarsus parthenogeneticus (larvae-7 days old)	NR	$CuSO_4$	art (DOC:0.5 mg/L)	6.9	25	16-d	NOECr	40	Hatakeyama and Yasuno, 1981
Dreissenia polymorpha (18-22 mm)	S	$CuCl_2$	lake (DOC:<7.34 mg/L)	7.9	150	63-77 d	NOECfr	13	Kraak et al., 1994
Dreissenia polymorpha (18-22 mm)	R	$CuSO_4$	tap (DOC:1.0 mg/L)	7.8	296	27-d	NOECfr	21	Mersch et al., 1993
Villosa iris (glochidia)	F	$CuSO_4$	river (DOC:3.0 mg/L)	8.4	152	30-d	NOECm	19.1	Jacobson et al., 1997
Campeloma decisum (11-27 mm snail)	F	$CuSO_4$	tap (DOC:1.0 mg/L)	8.15	44.9	42-d	NOECm	8	Arthur and Leonard, 1970
Campeloma decisum (11-27 mm snail)	F	$CuSO_4$	tap (DOC:1.0 mg/L)	8.15	44.9	42-d	NOECm	8	Arthur and Leonard, 1970
Juga plicifera (mature)	F	$CuCl_2$	well (DOC:1.3 mg/L)	7.1	21	30-d	NOECm	6	Nebeker et al., 1986

NOEC- no observed effect concentration; NR- not reported; S- static test; F – flow-trough test; R- renewal test; DOC – dissolved organic carbon; g – growth; r – reproduction; m – mortality; lc – life cycle; fr- filtration rate; art. – artificial; $CuSO_4$ – copper sulphate; $CuCl_2$ – copper chloride; d-days; w - weeks

Table 11. NOEC values and physico-chemical parameters for freshwater fish (accepted studies)

ORGANISM (LIFESTAGE / SIZE)	TEST TYPE	TEST COMPOUND	TEST WATER	PH	HARDNESS	EXPOSURE TIME	CRITERION	RESULT µg Cu /L	REFERENCE
Catostomus commersoni (embryo)	F	$CuSO_4$	lake (DOC: 1.0 mg/L)	7.6	45	40-d	NOECg	12.9	McKim et al., 1978
Catostomus commersoni (embryo)	F	$CuSO_4$	lake (DOC: 1.0 mg/L)	7.6	45	40-d	NOECm	12.9	McKim et al., 1978
Esox lucius (embryo)	F	$CuSO_4$	lake (DOC: 1.0 mg/L)	7.6	45	35-d	NOECg	34.9	McKim et al., 1978
Esox lucius (embryo)	F	$CuSO_4$	lake (DOC: 1.0 mg/L)	7.6	45	35-d	NOECm	34.9	McKim et al., 1978
Ictalarus punctatus (recently hatched)	F	$CuSO_4$	well (DOC: 1.3mg/L)	7.65	186.3	60-d	NOECg	13	Sauter et al., 1976
Ictalarus punctatus (recently hatched)	F	$CuSO_4$	well (DOC: 1.3mg/L)	7.65	186.3	60-d	NOECm	13	Sauter et al., 1976
Noemacheilus barbatulus (adult 8.7-12.1 cm)	F	$CuSO_4$	well (DOC: 1.3mg/L)	8.26	249	64-d	NOECm	120	Solbe and Cooper, 1976
Oncorhyncus kisutch (recently hatched)	F	NR	river (DOC: 2.9 mg/L)	7.4	31.8	60-d	NOECg	21	Mudge et al., 1993
Oncorhyncus kisutch (recently hatched)	F	NR	river (DOC: 2.9 mg/L)	7.4	31.8	60-d	NOECm	18	Mudge et al., 1993
Oncorhyncus kisutch (young)	F	NR	river (DOC: 2.9 mg/L)	7.15	24.4	61-d	NOECg	22	Mudge et al., 1993
Oncorhyncus kisutch (young)	F	NR	river (DOC: 2.9 mg/L)	7	28.7	61-d	NOECg	28	Mudge et al., 1993
Oncorhyncus kisutch (young)	F	NR	river (DOC: 2.9 mg/L)	7.15	24.4	61-d	NOECm	24	Mudge et al., 1993
Oncorhyncus mykiss (eggs)	F	$CuCl_2$	well (DOC: 1.3 mg/L)	7.65	120	63-d	NOECg	16	Seim et al., 1984
Oncorhyncus mykiss (embryo)	F	$CuSO_4$	lake (DOC: 1.0 mg/L)	7.6	45	45-d	NOECg	11.4	McKim et al., 1978
Oncorhyncus mykiss (embryo)	F	$CuSO_4$	lake (DOC: 1.0 mg/L)	7.6	45	45-d	NOECm	11.4	McKim et al., 1978
Oncorhyncus mykiss (fry - 0.12g; 2.6 cm)	F	$CuCl_2$	well (DOC: 0.2 mg/L)	7.5	24.6	60-d	NOECg	2.2	Marr et al., 1996
Oncorhyncus mykiss (recently hatched)	F	NR	river (DOC: 2.9 mg/L)	7.2	24.4	61-d	NOECg	45	Mudge et al., 1993
Oncorhyncus mykiss (recently hatched)	F	NR	river (DOC: 2.9 mg/L)	7.15	24.4	61-d	NOECm	24	Mudge et al., 1993
Oncorhyncus mykiss (recently hatched)	F	NR	river (DOC: 2.9mg/L)	7	28.7	61-d	NOECm	28	Mudge et al., 1993

Table 11 (cont.). NOEC values and physico-chemical parameters for freshwater fish (accepted studies)

ORGANISM (LIFESTAGE / SIZE)	TEST TYPE	TEST COMPOUND	TEST WATER	PH	HARDNESS	EXPOSURE TIME	CRITERION	RESULT µg Cu /L	REFERENCE
Perca fluviatilis (juvenile (3.8-4.3 g)	F	$CuSO_4$	tap (DOC: 1 mg/L)	7.8	194	30-d	NOECg	39	Collvin, 1985
Perca fluviatilis (juvenile (3.8g)	F	$CuSO_4$	tap (DOC: 1 mg/L)	7.8	178	30-d	NOECm	188	Collvin, 1984
Pimephales notatus (young - 15-16 mm- 2nd gen)	F	$CuSO_4$	spring (DOC: 0.55 mg/L)	8.1	201	30-d	NOECg	44	Horning and Neiheisel, 1979
Pimephales notatus (young - 15-16 mm)	F	$CuSO_4$	spring (DOC: 0.55 mg/L)	8.1	201	60-d	NOECg	71.8	Horning and Neiheisel, 1979
Pimephales notatus (young - 15-16 mm)	F	$CuSO_4$	spring (DOC: 0.55 mg/L)	8.1	201	60-d	NOECm	71.8	Horning and Neiheisel, 1979
Pimephales promelas (embryo-larval)	F	$CuSO_4$	lake (DOC: 1.0 mg/L)	7.05	44	32-d	NOECg	4.8	Spehar and Fianolt, 1985
Pimephales promelas (embryo-larval)	F	$CuSO_4$	lake (DOC: 1.0 mg/L)	7.05	44	32-d	NOECm	4.8	Spehar and Fianolt, 1985
Pimephales promelas (larvae 4 weeks old)	F	$CuSO_4$	spring (DOC: 0.55 mg/L)	7.9	202	187-d	NOECr	25.5	Pickering et al., 1977
Pimephales promelas (larvae 4 weeks old)	F	$CuSO_4$	spring (DOC: 0.55 mg/L)	7.9	202	97-d	NOECr	23	Pickering et al., 1977
Pimephales promelas (larvae 4 weeks old)	F	$CuSO_4$	spring (DOC: 0.55 mg/L)	7.9	202	7-d	NOECr	22.5	Pickering et al., 1977
Pimephales promelas (larvae 4 weeks old))	F	$CuSO_4$	spring (DOC: 0.55 mg/L)	7.85	202	187-d	NOECg	59.5	Pickering et al., 1977
Pimephales promelas (larvae)	F	$CuSO_4$	GW (DOC: 1.3 mg/L)	8.17	202	28-d	NOECm	61	Scudder et al., 1988
Pimephales promelas (ljuvenile:32-38 mm; 5 months old)	F	$CuSO_4$	river(DOC: 2 mg/L)	8.1	274	270-d	NOECr	66	Brungs et al., 1976
Pimephales promelas (young 10-15 mm)	F	$CuSO_4$	spring (DOC: 0.55 mg/L)	8	198	330-d	NOECm	33	Mount, 1968
Pimephales promelas (young 10-15 mm)	F	$CuSO_4$	spring (DOC: 0.55 mg/L)	8	198	330-d	NOECr	14.5	Mount, 1968
Pimephales promelas (young - 10-15 mm)	F	$CuSO_4$	spring (DOC: 0.55 mg/L)	8	198	330-d	NOECg	33	Mount, 1968

Table 11 (cont.). NOEC values and physico-chemical parameters for freshwater fish (accepted studies)

ORGANISM (LIFESTAGE / SIZE)	TEST TYPE	TEST COMPOUND	TEST WATER	PH	HARDNESS	EXPOSURE TIME	CRITERION	RESULT µg Cu /L	REFERENCE
Pimephales promelas (young 10-20 mm)	F	$CuSO_4$	spring (DOC: 0.55 mg/L)	6.9	31.4	327-d	NOECg	10.6	Mount and Stephan, 1969
Pimephales promelas (young 10-20 mm)	F	$CuSO_4$	spring (DOC: 0.55 mg/L)	6.9	31.4	327-d	NOECm	10.6	Mount and Stephan, 1969
Pimephales promelas (young 10-20 mm)	F	$CuSO_4$	spring (DOC: 0.55 mg/L)	6.9	31.4	327-d	NOECr	10.6	Mount and Stephan, 1969
Salvelinus fontinalis (alevins/juveniles)	F	$CuSO_4$	tap (DOC: 1 mg/L)	7.5	45	189-d	NOECg	9.5	McKim and Benoit, 1971
Salvelinus fontinalis (alevins/juveniles)	F	$CuSO_4$	tap (DOC: 1 mg/L)	7.5	45	189-d	NOECm	9.5	McKim and Benoit, 1971
Salvelinus fontinalis (embryo)	F	$CuSO_4$	lake (DOC: 1.0 mg/L)	7.6	45	60-d	NOECg	22.3	McKim et al., 1978
Salvelinus fontinalis (embryo)	F	$CuSO_4$	lake (DOC: 1.0 mg/L)	7.6	45	60-d	NOECm	22.3	McKim et al., 1978
Salvelinus fontinalis (yearling)	F	$CuSO_4$	tap (DOC: 1 mg/L)	7.5	45	244-d	NOECg	17.4	McKim and Benoit, 1971
Salvelinus fontinalis (yearling)	S	$CuSO_4$	tap (DOC: 1 mg/L)	7.45	45	244-d	NOECm	17.4	McKim and Benoit, 1971
Salvelinus fontinalis (yearling)	F	$CuSO_4$	tap (DOC: 1 mg/L)	7.45	45	244-d	NOECr	17.4	McKim and Benoit, 1971
Salvelinus fontinalis (young(fry))	F	$CuSO_4$	well (DOC: 1.3mg/L)	6.85	37.5	30-d	NOECg	7	Sauter et al., 1976
Salvelinus fontinalis (young(fry))	F	$CuSO_4$	well (DOC: 1.3mg/L)	6.9	187	30-d	NOECg	21	Sauter et al., 1976
Salvelinus fontinalis (young(fry))	F	$CuSO_4$	well (DOC: 1.3mg/L)	6.85	37.5	60-d	NOECm	13	Sauter et al., 1976
Salvelinus fontinalis (young(fry))	F	$CuSO_4$	well (DOC: 1.3mg/L)	6.9	187	30-d	NOECm	21	Sauter et al., 1976
Salvelinus fontinalis (young(fry))	F	$CuSO_4$	well (DOC: 1.3mg/L)	6.85	37.5	60-d	NOECr	7	Sauter et al., 1976
Salvelinus fontinalis (young(fry))	F	$CuSO_4$	well (DOC: 1.3mg/L)	6.9	187	30-d	NOECr	49	Sauter et al., 1976

NOEC- no observed effect concentration; NR- not reported; S- static test; F – flow-trough test; DOC – dissolved organic carbon; g – growth; r – reproduction; m – mortality; art. – artificial; $CuSO_4$ – copper sulphate; $CuCl_2$ – copper chloride; d-days.

6.1.4. Abiotic factors influencing the aquatic toxicity of copper in freshwater

Physico-chemical water characteristic such as hardness, pH, DOC, ionic strength and redox potential influences the chemical speciation of copper in water and thus may influence bioavailability and toxicity.
The main factor that influences copper toxicity in freshwater is likely to be hardness. Toxicity of metals is assumed to be inversely related to hardness.

Background concentration

Copper background levels in freshwaters in Europe typically vary between 0.2 and 5 µg Cu/L (Zuurdeeg, 1992). However, the actual relation between copper backgrounds and toxicity cannot be quantified yet. Therefore, a total risk approach is used for copper RA.
According to the metallo-region concept, adaptation to natural background levels and also to test conditions may influence the sensitivity to metals. Acclimation/adaptation of daphnia magna and rainbow trout was observed for copper (Bossuyt and janssen, 2003a; Taylor et al., 2000).

6.1.5. Derivation of the Predicted No Effect Concentration surface waters ($PNEC_{freshwater}$)

$HC_{5\text{-}50}$ derived from statistical extrapolation

The Biotic Ligand Models (BLM) have been validated and applied to the toxicity database. Therefore, NOEC values obtained for the different species were normalized for hardness, pH and DOC for seven typical EU scenario's. Normalised NOEC values using the BLM are summarized in table 12.
$HC_{5\text{-}50}$ were then derived and calculated using the statistical extrapolation method.
Normalised $HC_{5\text{-}50}$ values for copper range between 7.8 to 22.1 µg Cu/L when using the best fitting distribution and between 7.8 to 27.2 µg Cu/L when using the log-normal distribution. The differences in freshwater $HC_{5\text{-}50}$ values are related to differences in physico-chemical characteristics of the surface waters.

Table 12. Comparison of the intra-species variability before and after normalization of NOEC values for pH, hardness and DOC.

	Non-normalised	**Normalised**
Algae		
Chlamydomonas reinhardtii (n=4)	8.1	1.4
Chlorella vulgaris (n=17)	16.5	2.5
Pseudokircherniella subcapitata (n=12)	10.4	6.2
Invertebrates		
Ceriodaphnia dubia (n=14)	30.5	9.4

Daphnia magna (n=9)	14.4	4.6
Daphnia pulex (n=9)	10.0	2.4
Hyalella azteca (n=5)	2.7	2.4
Brachionus calyciflorus (n=4)	12.6	2.5
Clistoronia magnifica (n=2)	1.5	1.6
Fish		
Oncorhynchus kisutch (n=5)	1.6	3.0
Oncorhynchus mykiss (n=7)	20.5	2.5
Perca fluviatilis (n=2)	4.8	2.4
Pimephales notatus (n=3)	1.6	1.3
Pimephales promelas (n=14)	13.8	8.0
Salvelinus fontanilis (n=14)	7.0	5.5

PNEC derived from the assessment factor method

A PNEC derived from the assessment method:

- Using an assessment factor of 10 on the lowest specific chronic NOEC values leads to a PNEC between 0.8 and 2.2 µg Cu/L for the most sensitive eco-region. This value is within the background concentration of copper and below the optimal copper levels. Therefore it is not useful for the Cu RA.
- Using an assessment factor of 1 on the mesocosms/field NOEAEC values allows the derivation of a PNEC value between 3.6 and 20 µg Cu/L. These values fall within the range of optimal concentrations for normal copper background levels in Europe.

6.1.6. Summary and final derivation of the $\mathbf{PNEC_{freshwater}}$

The use of statistical extrapolation using all NOECs in the ecotoxicity database was preferred for the PNEC derivation.

The final proposed PNEC is related to uncertainties considerations covering:

- The mechanism of action
- The overall quality of the database
- The statistical uncertainties and endpoints
- The robustness of the HC5-50 values
- The conservative factor
- Validations from multi-species mesocosm studies
- Comparison with natural backgrounds and optimal concentration ranges.

Considering the regional variability and local risk characterization, the $\mathbf{PNEC_{freshwater}}$ for the EU region is **7.8 µg Cu/L**.

6.2. Results for marine toxicity

A derivation of a separate PNEC for freshwater and marine environments has been calculated due to differences in physiology and related differences in ecotoxicological behaviour between freshwater and marine organisms.

For the marine compartment, the effect assessment of copper is based on NOECs/EC_{10} collected for marine organisms. High quality chronic single-species toxicity tests that were retained for PNEC derivation contains 56 individual NOEC (EC10) values resulting in 24 different species NOEC values (fish, invertebrates and algae).

6.2.1. Chronic toxicity data for marine organisms

Data on chronic toxicity tests resulting in NOEC values for marine algae, invertebrates and fish are summarized in Tables 13, 14 and 15, respectively. Some recent studies (grey) were found in the literature and were added to the studies but these were not included for PNEC derivation in the copper RA. Other studies that were based on nominal concentrations that either included sufficient information of copper background levels or that copper background levels could be estimated were also retained but considered as lower quality studies.

6.2.2. Toxicity data for marine algae

Toxicity data on chronic single-species resulting in NOEC/EC10 values for marine algae are summarized in Table 13. Eleven high quality chronic studies reporting non-normalized NOEC/EC10 values for marine algae for 4 individual species are presented in the table in bold and these were used for PNEC derivation. The high quality single-species NOEC values for marine algae range from 2.5 µg Cu /L for Phaeodactylum tricornutum (Simpson, 2003) to 50.1 µg Cu /L for Macrocystis pyrifera (Anderson et al., 1990).

6.2.3. Toxicity data for marine invertebrates

Toxicity data on chronic single-sppecies resulting in NOEC/EC10 values for marine invertebrates are summarized in Table 14. High quality chronic studies reporting non-normalized NOEC/EC10 values for marine invertebrates are presented in the table in bold. From the high quality database, 32 individual NOECs for 18 different species were selected. The NOEC values range from 5.9 µg Cu/L for Mytilus galloprovincialis (Rosen, 2005) to 145 µg Cu/L for the crustacea Penaeus monodon (Ahsanullah et al, 1995).

6.2.4. Toxicity data for marine fish

Toxicity data on chronic single-species resulting in 13 NOEC/EC10 values for marine fish are summarized in Table 15. Chronic NOECs values for only 2 fish species were used but indicate that fish are less sensitive to copper than invertebrates or algae. For the same fish species, the most sensitive endpoint was used for PNEC derivation and was abnormality in young fish for *Atherinops affinis* and growth parameters of the hatchlings (length and weight) for *Cyprinodon variegates*. NOEC values range from 55 µg Cu/L for *Atherinops affinis* (Anderson et al., 1991) and 57.8 µg Cu/L for *Cyprinodon variegates* (Hurd, 2006a).

Table 13. Chronic NOEC/EC10 values for marine algae. High quality chronic NOEC values are in bold.

Organisms & lifestage	Test compound	Test water	Test	Temp (ºC)	Cu backg. (µg/L)	DOC (mg/L)	pH	Salinity (g/L)	Test duration	Criterion	Chemical analysis	NOEC (µg/L)	Reference
Chaetoceros sp.	$CuSO_4$	Art. medium	S	25	0.5 (est)	0.3 (est)	Nr	Nr	7.5 d	NOECg	nom	2.5	Zhang et al. 1992
Chlamydomonas bullosa	$CuCl_2$	Art. seawater	S	15	0.5 (est)	0.3 (est)	Nr	Nr	96 h	EC10g	nom	4.6	Visviki and Rachlin 1994
Dunaliella minuta	$CuCl_2$	Art. seawater	S	15	0.5 (est)	0.3 (est)	7.4	Nr	96 h	EC10g	nom	136	Visviki and Rachlin 1991
Dunaliella salina	Nr	Art. seawater	S	Nr	0.5 (est)	0.3 (est)	Nr	Nr	96 h	NOECg	nom	336	Visviki and Rachlin 1994
Dunaliella tertiolecta	Nr	Nutrient deficient filtered natural seawater	S	19	0.5 (est)	2.0 (est)	8.2	Nr	96 h	NOECg	nom	3160	Miao et al. 2005
Fucus vesiculosis (zoospore)	$CuCl_2$	Nat filtered seawater	F	21	4.2 (meas)	1.67 (meas)	8.1	30.9	14 d	NOECg	meas	**11**	Brooks, 2006a
Fucus vesiculosis (zoospore)	$CuCl_2$	Nat filtered seawater+ 0.09 mg DOC/L added as HA	F	21	2.5 (meas)	1.05 (meas)	8.1	31.1	14 d	NOECg	meas	**14**	Brooks, 2006a
Fucus vesiculosis (zoospore)	$CuCl_2$	Nat filtered seawater+ 0.56 mg DOC/L added as HA	F	21	2.3 (meas)	2.11 (meas)	8.1	31	14 d	NOECg	meas	**18.5**	Brooks, 2006a
Fucus vesiculosis (zoospore)	$CuCl_2$	Nat filtered seawater+ 1.65 mg DOC/L added as HA	F	21	2.9 (meas)	2.56 (meas)	8.1	31.4	14 d	NOECg	meas	**32**	Brooks, 2006a
Fucus vesiculosis (zoospore)	CuCl2	Nat filtered seawater+ 2.03 mg DOC/L added as HA	F	21	2.8 (meas)	2.88 (meas)	8.1	30.9	14 d	NOECg	meas	**46**	Brooks, 2006a
Gymnodinium splendens	$CuSO_4$	Filtered natural seawater	S	nr	1.1 (est)	2.0 (est)	Nr	32	72 h	NOECb	nom	10	Saifullah, 1978
Laminaria saccharina, gametophytes (young sporophyte (1-3 cm))	$CuSO_4$	Filtered seawater	R(4 d)	10	1.1 (est)	2.0 (est)	Nr	Nr	9 d	NOECg	nom	50	Chung and Brinkhuis, 1986

Table 13. (cont.) Chronic NOEC/EC10 values for marine algae. High quality chronic NOEC values are in bold.

Organisms & lifestage	Test compound	Test water	Test	Temp (ºC)	Cu backg. (µg/L)	DOC (mg/L)	pH	Salinity (g/L)	Test duration	Criterion	Chemical analysis	NOEC (µg/L)	Reference
Laminaria saccharina, gametophytes (young sporophyte (1-3 cm))	$CuSO_4$	Filtered seawater	R(4 d)	10	1.1 (est)	2.0 (est)	Nr	Nr	9 d	NOECg	nom	4.4	Chung and Brinkhuis, 1986
Macrocystis pyrifera (zoospore)	copper	Art filtered seawater	S,R	13-15	<0.6 (meas)	2.0 (est)	7.8 - 8.3	35-37	19 d	NOECsg	meas	**10.2**	Anderson et al., 1990
Macrocystis pyrifera (zoospore)	copper	Art filtered seawater	S,R	13-15	<0.6 (meas)	2.0 (est)	7.8 - 8.3	35-37	19 d	NOECger	meas	(50.1)	Anderson et al., 1990
Macrocystis pyrifera (zoospore)	copper	Art filtered seawater	S,R	13-15	<0.6 (meas)	2.0 (est)	7.8 - 8.3	35-37	19 d	NOECger t g	meas	**10.2**	Anderson et al., 1990
Nitzschia thermalis	$CuSO_4$	Art. seawater (Aquil) excl EDTA	S	16	0.5 (est)	0.3 (est)	nr	nr	nr	NOECg	nom	32	Metaxas and Lewis, 1991
Phaeodactylum tricomutum (10^3 cell/mL)	$CuSO_4$	Nat filtered seawater	S	20	Nr	1.0 (meas)	8.2 - 8.3	31	72 h	EC10gr	meas	**2.9**	Simpson et al., 2003
Phaeodactylum tricomutum (10^4 cell/mL)	$CuSO_4$	Nat filtered seawater	S	20	<0.4 (meas)	2.19 (meas)	8.2 - 8.3	31	72 h	NOECgr	meas	**7.5**	Smyth and Kent, 2006a
Phaeodactylum tricornutum	$CuCl_2$	Filtered natural seawater DOC removed C18 filter	S	18	1.1 (est)	0.5 (est)	7.6	35	Nr	NOECg	nom	50	Cid et al. 1995
Prorocentrans micans	$CuSO_4$	Filtered natural seawater	S	nr	1.1 (est)	2.0 (est)	Nr	32	72 h	NOECb	nom	5	Saifullah, 1978
Prorocentrum minimum	Nr	Nutrient deficient filtered natural seawater	S	19	0.5 (est)	2.0 (est)	8.2	Nr	96 h	NOECg	nom	632	Miao et al. 2005
Scrippsiella faeroense	$CuSO_4$	Filtered natural seawater	S	Nr	1.1 (est)	2.0 (est)	Nr	32	72 h	NOECb	nom	5	Saifullah, 1978

Table 13. (cont.) Chronic NOEC/EC10 values for marine algae. High quality chronic NOEC values are in bold.

Organisms & lifestage	Test compound	Test water	Test	Temp (ºC)	Cu backg. (µg/L)	DOC (mg/L)	pH	Salinity (g/L)	Test duration	Criterion	Chemical analysis	NOEC (µg/L)	Reference
Skeletonema costantum (10^3 cell/mL)	$CuSO_4$	Nat filtered seawater	S	20	<0.4 (meas)	2.19 (meas)	8.2 - 8.3	31	72 h	NOECgr	meas	**5.7**	Smyth and Kent, 2006b
Scrippsiella faeroense	$CuSO_4$	Filtered natural seawater	S	Nr	1.1 (est)	2.0 (est)	Nr	32	72 h	NOECb	nom	5	Saifullah, 1978
Skeletonema costantum (10^3 cell/mL)	$CuSO_4$	Nat filtered seawater	S	20	<0.4 (meas)	2.19 (meas)	8.2 - 8.3	31	72 h	NOECgr	meas	**5.7**	Smyth and Kent, 2006b
Skeletonema costatum	$CuSO_4$	Art. seawater (Aquil) excl EDTA	S	16	0.5 (est)	0.3 (est)	Nr	Nr	Nr	NOECg	nom	25	Metaxas and Lewis 1991
Skeletonema costatum (10^4 cells/mL)	$CuSO_4$	Art. sea water	S	24	0.5 (est)	0.3 (est)	Nr	30	12 d	NOECg	nom	500	Rao and Latheef, 1989
Synechococcus sp.	Nr	Nutrient deficient filtered natural seawater	S	19	0.5 (est)	2.0 (est)	8.2	Nr	96 h	NOECg	nom	8.7	Miao et al. 2005
Thallasiosira weisflogii	Nr	Nutrient deficient filtered natural seawater	S	19	0.5 (est)	2.0 (est)	8.2	Nr	96 h	NOECg	nom	318	Miao et al. 2005
Ulva reticulata (adult)	$CuCl_2$	Diluted natural seawater	S	25	Nr	Nr	Nr	20	7 d	NOECg	nom	8.9	Mamboya et al., 2009
Ulva reticulate *(adult)*	$CuCl_2$	Diluted natural seawater	S	25	Nr	Nr	Nr	25	7 d	NOECg	nom	7.9	Mamboya et al., 2009
Ulva reticulata *(adult)*	$CuCl_2$	Diluted natural seawater	S	25	Nr	Nr	Nr	30	7 d	NOECg	nom	18.0	Mamboya et al., 2009
Ulva reticulata *(adult)*	$CuCl_2$	Diluted natural seawater	S	25	Nr	Nr	Nr	35	7 d	NOECg	nom	4.0	Mamboya et al., 2009
Ulva reticulata *(adult)*	$CuCl_2$	Diluted natural seawater	S	25	Nr	Nr	Nr	40	7 d	NOECg	nom	1.1	Mamboya et al., 2009

Nr – not reported; $CuSO_4$ – copper sulphate; $CuCl_2$- copper chloride; S – static test; R- renewal test; F-flow through test; art – artificial; nat – natural; est – estimated; meas- measured; HA – humic acids; d – day; w-week,; h-hour; NOEC – non observed effect concentration; EC10 – 10 % population effect concentration; nom – nominal; sg - g – growth; b – biomass; gr – growth rate; ger – germination; ger t g – germination tube growth.

Table 14. Chronic NOEC/EC10 values for invertebrates. High quality chronic NOEC values are in bold.

Organisms & lifestage	Test compound	Test water	Test	Temp (ºC)	Cu backg. (µg/L)	DOC (mg/L)	pH	Salinity (g/L)	Test duration	Criterion	Chemical analysis	NOEC (µg/L)	Reference
Acropora tenuis (larvae)	$CuCl_2$	Nat. seawater	S	Nr	0.63 (meas)	2.0(est)	Nr	Nr	48 h	NOECsettl	meas	**17.3**	Reichelt-Brushett and Harrison, 2000
Aiptasia sp (polyps)	$CuSO_4$	Nat. seawater	S	24	1.1(est)	2.0(est)	8.3	34	8 w	NOECpop g	meas	70	Kaiser et al., 2004
Allorchestes compressa (1 d old juveniles)	$CuSO_4$	Nat. seawater	F	19	0.3(meas)	2.0(est)	8	31	4 w	LOECg, b	meas	9.5	Ahsanullah and Williams 1991
Argopecten irradians (adult)	$CuCl_2$	Nat. seawater	F	14 (8-18)	1.8(meas)	2.0(est)	Nr	29-32	56 d	NOECspaw	meas	>10.2	Zaroogian and Johnston, 1983
Artemia franciscana (cysts)	$CuCl_2$	Art seawater	S	25	0.2(meas)	0.48(meas)	7.8 – 8.1	Nr	48 h	NOECh	meas	**6.6**	Brix et al., 2006
Artemia salina Linn (eggs)	$CuSO_4$	Art seawater	Nr	Nr	0.5(est)	0.3(est)	Nr	30	-	NOEChat	nom	5000	Rao and, Latheef, 1989
Artemia salina Linn (juveniles)	$CuSO_4$	Art seawater	Nr	Nr	0.5(est)	0.3(est)	Nr	30	15 d	EC10g	nom	100	Rao and, Latheef, 1989
Busycon canaliculatum	$CuCl_2$	Nat. seawater	R	13-22	3(meas)	2.0(est)	Nr	Nr	54 d	NOECm	nom	100	Betzer and Yevich, 1975
Campanularia flexuosa	Copper	Filtered nat. seawater	R	25	0.5(meas)	2.0(est)	Nr	25°C	14 d	LOECg	nom	10	Stebbing, 1976
Cancer anthonyi (embryo)	$CuCl_2$	Filtered nat. seawater	R every working day	Nr	1.7(meas)	2.0(est)	7.8	34	7 d	NOECm	nom	10	McDonald et al., 1988
Cancer anthonyi (embryo)	$CuCl_2$	filtered nat. seawater	R every working day	Nr	1.7(meas)	2.0(est)	7.8	34	11 d	NOECm	nom	10	McDonald et al., 1988
Carcinus maenas (intermoult)	$CuSO_4$	Filtered nat. seawater	S R	15	1.1(est)	2.0(est)	Nr	35	28 d	LC10m	nom	273.7	Lundebye and Depledge, 1998
Carcinus maenass (juvenile)	Nr	Art seawater	R twice weekly	10	6.0 (meas)	0.3(est)	Nr	33	21 d	NOECm	nom	1000	Rainbow, 1985
Ciona intestinalis (fertilized embryos)	$CuCl_2$	Art seawater	S	18–23	0.5(est)	0.3(est)	7.4–8.8	34	20 h	NOECemb dev	nom	16	Bellas et al., 2004
Ciona intestinalis (fertilized embryos)	$CuCl_2$	Art seawater	S	18–23	0.5(est)	0.3(est)	7.4–8.8	34	20 h	NOEClarv attach	nom	32	Bellas et al., 2004

Table 14 (cont). Chronic NOEC/EC10 values for invertebrates. High quality chronic NOEC values are in bold.

Organisms & lifestage	Test compound	Test water	Test	Temp (ºC)	Cu backg. (µg/L)	DOC (mg/L)	pH	Salinity (g/L)	Test duration	Criterion	Chemical analysis	NOEC (µg/L)	Reference
Cirriformia spirabrancha (adult)	$CuSO_4$	Nat seawater	S R	10	1.1(est)	2.0(est)	Nr	29	34 d	NOECm, g	nom	20	Millanovich et al.,1976
Crassostrea virginica (adults)	Nr	Nat seawater	F	20	1.1(est)	2.0(est)	8	31	20 w	NOECacc	nom	25	Shuster and Pringle, 1969
Crassostrea virginica (adults)	Nr	Nat. seawater	F	20	1.1(est)	2.0(est)	8	31	20 w	NOECm,g	nom	50	Shuster and Pringle, 1969
Crassostrea virginica (larvae)	$CuCl_2$	Filtered nat seawater	R every 24 hours	25	13.4 (meas)	2.0(est)	Nr	24	14 d	LC10m	nom	12.6	Calabrese et al., 1977
Crassostrea virginica (larvae)	$CuCl_2$	Filtered nat seawater	R every 24 hours	24	13.4(meas)	2.0(est)	Nr	24	14 d	EC10g	nom	14.8	Calabrese et al., 1977
Crassostreas gigas (embryo)	$CuCl_2$	Nat seawater+ 0.1 mg DOC/L, added as HA	F	21 ± 1	2.8(meas)	2.19(meas)	8.0 - 8.2	31.1 - 34.2	24 h	NOECdev	meas	**10.89**	Brooks, 2006b
Crassostreas gigas (embryo)	$CuCl_2$	natural seawater+ 0.81 mg DOC/L, added as HA	F	21 ± 1	2.5(meas)	3.36(meas)	8.0 - 8.2	31.1 - 34.2	24 h	NOECdev	meas	**10.42**	Brooks, 2006b
Crassostreas gigas (embryo)	$CuCl_2$	natural seawater+ 1.02 mg DOC/L, added as HA	F	21 ± 1	3.0(meas)	3.36(meas)	8.0 - 8.2	31.1 - 34.2	24 h	NOECdev	meas	**12.83**	Brooks, 2006b
Crassostreas gigas (embryo)	$CuCl_2$	Nat seawater+ 1.85 mg DOC/L, added as HA	F	21 ± 1	3.6(meas)	3.88(meas)	8.0 - 8.2	31.1 - 34.2	24 h	NOECdev	meas	**19.53**	Brooks, 2006b
Crassostreas gigas (embryo)	$CuCl_2$	Nat seawater+ 2.77 mg DOC/L, added as HA	F	21 ± 1	1.1(meas)	4.66(meas)	8.0 - 8.2	31.1 - 34.2	24 h	NOECdev	meas	**28.19**	Brooks, 2006b

Table 14 (cont). Chronic NOEC/EC10 values for invertebrates. High quality chronic NOEC values are in bold.

Organisms & lifestage	Test compound	Test water	Test	Temp (ºC)	Cu backg. (µg/L)	DOC (mg/L)	pH	Salinity (g/L)	Test duration	Criterion	Chemical analysis	NOEC (µg/L)	Reference
Crassostreas gigas (embryo)	$CuCl_2$	Nat seawater+ 3.13 mg DOC/L, added as humic acids	F	21 ± 1	3.2(meas)	5.19(meas)	8.0 - 8.2	31.1 - 34.2	24 h	NOECdev	meas	47.13	Brooks, 2006b
Ctenodrilus serratus (adults)	$CuSO_4$	Nat seawater	Nr	not reported	1.1(est)	2.0(est)	Nr	Nr	21 d	NOECr	Nr	500	Reish and Carr, 1978
Echinogammarus perlotti (juvenile)	Nr	Art seawater	R twice weekly	10	6.0(meas)	0.3(est)	Nr	33	21 d	NOECm	nom	100	Rainbow and White, 1989
Echinometra mathaei (sperm)	$CuCl_2$	Filtered nat seawater	S	Not reported	1.1(est)	2.0(est)	Nr	34	60 min	NOECfer	nom	5	Ringwood, 1992
Eirene Viridula (Hydroid)	$CuSO_4$	Filtered nat seawater	S	20 - 30	1.1(est)	2.0(est)	7.9 - 8.2	30	mo	NOECmor changes	nom	30	Karbe, 1972
Elminius modestus (juvenile)	Nr	Art seawater	R twice weekly	10	6.0(meas)	0.3(est)	Nr	33	28 da	NOECm	nom	6	Rainbow and White, 1989
Elminius modestus (juvenile)	Nr	Art seawater	R days 3, 7, 11, 16	10	6.0(meas)	0.3(est)	Nr	33	21 d	NOECm	nom	316	Rainbow, 1985
Eudistylia vancouveri (larvae)	$CuCl_2$	Nat seawater	F	8.2	0.3(meas)	2.0(est)	7.8	30.4	35 d	NOECg	nom	6.1	Young et al., 1979
Eurytemora affinis (< 24h)	$CuCl_2$	Nat estuarine water	Semi- S	25±2	<3(meas)	2.0(est)	7.9 - 8.8	14 - 17	8 d	NOECm, fec, mat	meas	51.1	Hall, 1997
Gammarus duebeni (15-21 mm)	$CuSO_4$	Diluted sea water	S R	11	0.55(est)	1.0(est)	Nr	15.5	7 d	NOECswim	nom	30	Lawrence and Poulter, 1998
Goniastrea aspera (larvae)	$CuCl_2$	Nat seawater	S	Nr	1.2(meas)	2.0(est)	Nr	Nr	72 h	NOECm	meas	14.2	Reichelt-Brushett and Harrison, 2004
Hydra littoralis	$CuCl_2$	Art seawater	S R	Nr	0.5(est)	0.3(est)	Nr	Nr	11 d	NOECr	nom	2.5	Stebbing and Pomroy, 1978
Isognomon californicum (larvae)	$CuCl_2$	Filtered nat seawater	S	Nr	1.1(est)	2.0(est)	Nr	34	48 h	NOECdev	nom	5	Ringwood, 1992

Table 14 (cont). Chronic NOEC/EC10 values for invertebrates. High quality chronic NOEC values are in bold.

Organisms & lifestage	Test compound	Test water	Test	Temp (ºC)	Cu backg. (µg/L)	DOC (mg/L)	pH	Salinity (g/L)	Test duration	Criterion	Chemical analysis	NOEC (µg/L)	Reference
llyanassa obsoleta Say (larvae)	Nr	Filtered nat seawater	S	21	1.1(est)	2.0(est)	8	Nr	Until ph I polar lobe constriction	NOECabn dev	nom	6.3	Conrad, 1988
Lobophytum compactum (eggs/sperm)	$CuCl_2$	Nat seawater	S	Nr	Nr	2.0(est)	Nr	Nr	5 h	NOECfer	meas	**36**	Reichelt-Brushett et al., 2005
Mercenaria mercenaria (larvae)	$Cu(NO_3)_2$	Art seawater	S	24	1(meas)	0.5(est)	8.0 – 8.5	26.5	96 h	NOECdev	meas	**7**	LaBreche et al., 2002
Mercenaria mercenaria (larvae)	$CuCl_2$	Filtered nat seawater	R every 24 hours	24	13.4(meas)	2.0(est)	Nr	24	8-10 d	LC10m	nom	6.2	Calabrese et al., 1977
Mercenaria mercenaria (larvae)	$CuCl_2$	Filtered nat seawater	R every 24 hours	24	13.4(meas)	2.0(est)	Nr	24	8-10 d	EC10g	nom	5.5	Calabrese et al., 1977
Mylilus edulis (larvae)	$CuCl_2$	Filtered nat seawater	R every 2/3 day	15	1.1(est)	2.0(est)	Nr	32	15 d	EC10shell g	nom	13.9	Beaumont et al., 1987
Mylilus edulis (larvae)	$CuCl_2$	Filtered nat seawater	R every 2/3 day	15	1.1(est)	2.0(est)	Nr	32	15 d	LC10m	nom	91.5	Beaumont et al., 1987
Mysidopsis bahia (larvae)	$CuCl_2$	Nat seawater	F	20-25	2.9(meas)	2.0(est)	Nr	30	35 d	NOECm	meas	77	Lussier et al., 1985
Mysidopsis bahia (larvae)	$CuCl_2$	Nat seawater	F	20-25	2.9(meas)	2.0(est)	Nr	30	35 d	NOECr	meas	38	Lussier et al., 1985
Mytilus edulis (1.0-1.5 cm individuals)	$CuCl_2$	Filtered seawater	Daily R	Nr	2.0 – 2.4(meas)	2.0(meas)	Nr	Nr	10 d	NOECg,r	meas	**6**	Redpath, 1985
Mytilus edulis (2 months, 4.5 mm)	$CuCl_2$	Nat seawater	F	2.6 to 24	3.0(meas)	2.0(est)	Nr	25	21 mo	NOECg	meas	7.9	Calabrese et al., 1984
Mytilus edulis (adult)	$CuCl_2$	Filtered nat seawater	F	3.5-13.8	2-4 (meas)	2.0(est)	Nr	27	126 d	NOECm	nom	10	Nelson et al., 1988
Mytilus edulis (embryo)	$CuCl_2$	Nat seawater	F	13	1.8(meas)	1.51(meas)	8.3	32	48 h	NOECdev	meas	**6.2**	Brooks, 2006c
Mytilus edulis (larvae)	$CuCl_2$	Filtered nat seawater	S R	Nr	3(meas)	2.0(est)	Nr	Nr	Various life-stage exposure	NOECs, dev	meas	10.3	Hoare et al., 1995

Table 14 (cont). Chronic NOEC/EC10 values for invertebrates. High quality chronic NOEC values are in bold.

Organisms & lifestage	Test compound	Test water	Test	Temp (ºC)	Cu backg. (µg/L)	DOC (mg/L)	pH	Salinity (g/L)	Test duration	Criterion	Chemical analysis	NOEC (µg/L)	Reference
Mytilus galloprovincialis (embryo)	$CuSO_4$	Filtered seawater	S	15	0.6(meas)	0.9(meas)	Nr	Nr	48 h	NOECdev	meas	**5.9**	Rosen, 2005
Mytilus galloprovincialis (embryo)	$CuSO_4$	Filtered seawater	S	15	1.5(meas)	0.9(meas)	Nr	Nr	48 h	NOECdev	meas	**7.5**	Rosen, 2005
Mytilus galloprovincialis (embryo)	$CuSO_4$	Filtered seawater	S	15	0.7(meas)	1.5(meas)	Nr	Nr	48 h	NOECdev	meas	**9.2**	Rosen, 2005
Mytilus galloprovincialis (embryo)	$CuSO_4$	Filtered seawater	S	15	1.0(meas)	0.9(meas)	Nr	Nr	48 h	NOECdev	meas	**9.7**	Rosen, 2005
Mytilus trossolus (embryo)	$CuCl_2$	Filtered nat seawater	S	20	1.5(meas)	4.0(meas)	7.96	29	48 h	EC20emb dev	meas	2.7	Nadella et al., 2009
Mytilus trossolus (embryo)	$CuCl_2$	Filtered nat seawater	S	20	1.5(meas)	4.0(meas)	7.50	16.5	48 h	EC20emb dev	meas	2.9	Nadella et al., 2009
Neanthes arenaceodentata (3-4 w larvae)	$CuCl_2$	Filtered nat seawater	F	Nr	2±1(meas)	2.0(meas)	Nr	32	28 d	NOECg	meas	**13.5**	Pesch et al., 1986
Neanthes arenaceodentata (3-4 w larvae)	$CuCl_2$	Filtered nat seawater	F	Nr	2±1(meas)	2.0(meas)	Nr	32	28 d	NOECg	meas	**12.1**	Pesch et al., 1986
Nereis diversicolor (adult)	$CuSO_4$	Diluted nat seawater	Daily R	13	0.55(est)	1.0(est)	Nr	20	34.5 d	NOECs	nom	100	Bryan and Hummerstone, 1971
Nereis diversicolor (adult)	$CuSO_4$	Diluted nat seawater	Daily R	13	0.55(est)	1.0(est)	Nr	20	37 d	NOECs	nom	150	Bryan and Hummerstone, 1971
Ophryotrocha diadema (adults)	$CuSO_4$	Nat seawater	Nr	Nr	1.1(est)	2.0(est)	Nr	Nr	28 d	NOECr	Nr	1,000	Reish and Carr, 1978
Palaemon elegans (35-50 mm)	Nr	Art seawater (Tropic Marin Neu)	S R	Nr	6.0(meas)	0.3(est)	Nr	Nr	21 d	NOECs	nom	316	White and Rainbow, 1982

Table 14 (cont). Chronic NOEC/EC10 values for invertebrates. High quality chronic NOEC values are in bold.

Organisms & lifestage	Test compound	Test water	Test	Temp (ºC)	Cu backg. (µg/L)	DOC (mg/L)	pH	Salinity (g/L)	Test duration	Criterion	Chemical analysis	NOEC (µg/L)	Reference
Palaemon elegans (juvenile)	Nr	Art seawater	R twice weekly	10	6.0(meas)	0.3(est)	Nr	33	21 d	NOECm	nom	316	Rainbow and White, 1989
Palaemonetes pugio (embryos: 3-15 d old)	$CuCl_2$	Filtered nat seawater	S	27	1.1(est)	2.0(est)	7.0-7.8		12 d	NOECemb length	nom	100	Rayburn and Fisher, 1999
Pandalus danae (larvae)	$CuSO_4$	Nat seawater	F	8.7-10.3	0.47(meas)	2.0(est)	7.9-9.7	29.8-30.6	>42 d	NOECm	meas	**9.9**	Young et al., 1979
Pandalus danae (larvae)	$CuSO_4$	Nat seawater	F	8.7-10.3	0.47(meas)	2.0(est)	7.9-9.7	29.8-30.6	>42 d	NOECdev	meas	**9.9**	Young et al., 1979
Paracentrotus lividus (embryo)	$CuCl_2$	Nat seawater	S	18	<0.4(meas)	1.83(meas)	8.2 – 8.3	34.4	48 h	NOECdev	meas	**8.8**	Hurd, 2006b
Paracentrotus lividus (embryo)	$CuCl_2$	Nat seawater	S	20	0.32 – 1.45(meas)	2.0(est)	8.1	35	48 h	NOECdev	meas	**16.5**	Lorenzo et al., 2006
Penaeus mergulensis (juvenile)	Copper	Nat seawater	F	27	<1(meas)	2.0(est)	Nr	20	14 d	NOECg	meas	**33**	Ahsanullah and Ying, 1995
Penaeus monodon (juvenile)	Copper	Nat seawater	F	27	<1(meas)	2.0(est)	Nr	20	14 d	NOECg	meas	**145**	Ahsanullah and Ying, 1995
Phyllodoce maculata (adult)	$CuSO_4$	Nat seawater	S R	10	1.1(est)	2.0(est)	Nr	35	21 d	NOECs	nom	70	McLusky and Phillips, 1975
Placopecten magellanicus (adult)	$CuSO_4$	Nat seawater	F	6.6	2.5-3.4(meas)	2.0(est)	Nr	25	8 w	NOECgon dev	meas	**10**	Gould et al., 1988
Protothaca staminea (5.2 to 5.8 cm total length)	$CuCl_2$	Nat seawater	F	12.3	0.35(meas)	2.0(est)	8.1	32	30 d	NOECm	meas	**18**	Roesijadi, 1980
Saccostrea commercialis (eyed larvae)	$CuCl_2$	Filtered nat seawater	R every working day	28	1.1(est)	2.0(est)	7	30	5 d	EC10set r	nom	8.8	Nell and Holliday, 1986
Spisula solidissima (young)	$CuCl_2$	Filtered nat seawater	F	3.5-13.8	2-4(meas)	2.0(est)	Nr	26	126 d	NOECm	nom	2	Nelson et al., 1988
Tisbe battagliai (<24 h)	$CuCl_2$	Nat seawater	Semi-S	20 ± 1	2.0(meas)	2.79(meas)	8.1-8.4	35	21 d	NOECs	meas	**18**	Williams and Hayfield, 2006

Table 14 (cont). Chronic NOEC/EC10 values for invertebrates. High quality chronic NOEC values are in bold.

Organisms & lifestage	Test compound	Test water	Test	Temp (ºC)	Cu backg. (µg/L)	DOC (mg/L)	pH	Salinity (g/L)	Test duration	Criterion	Chemical analysis	NOEC (µg/L)	Reference
Tisbe battagliai (<24 h)	$CuCl_2$	Nat seawater	Semi-S	20 ± 1	2.0(meas)	2.79(meas)	8.1-8.4	35	21 d	NOECdev	meas	**18**	Williams and Hayfield, 2006
Tisbe battagliai (<24 h)	$CuCl_2$	Nat seawater	Semi-S	20 ± 1	2.0(meas)	2.79(meas)	8.1-8.4	35	21 d	NOECr	meas	**18**	Williams and Hayfield, 2006
Tisbe furcata (life cycle)	$CuSO_4$	Nat seawater	S R	15	Nr	2.0(est)	8	34	100 d	NOECs, r	meas	**19.1**	Bechmann, 1994

Nr – not reported; $CuSO_4$ – copper sulphate; $CuCl_2$ - copper chloride; S – static test; R- renewal test; F-flow through test; art – artificial; nat – natural; est – estimated; meas-measured; HA – humic acids; d – day; w-week,; h-hour; mo - month; NOEC – non observed effect concentration; EC10 – 10 % population effect concentration; nom – nominal; sg - g – growth; b – biomass; acc – accumulation; s – survival; r – reproduction; hatc – hatching success; dev – development; gon dev – gonad development; fec – fecundity; mat – maturation; m – mortality; Settl – settlement success; fer – fertilization; emb – embryonic; larv attach – larval attachment; pop – population; spaw – spawning; abn – abnormal; mor – morphological; swim –swimming activity;

Table 15. Accepted NOEC values for marine fish

Organisms & lifestage	Test compound	Test water	Test	Temp (ºC)	Cu backg. (µg/L)	DOC (mg/L)	pH	Salinity (g/L)	Test duration	Criterion	Chemical analysis	NOEC (µg/L)	Reference
Atherinops affinis (early blastula embryo)	$CuCl_2$	Filtered nat seawater	S	21	<3 (meas)	2.0 (est)	7.1-7.7	33	12 d	NOECemb abn	meas	(123)	Anderson et al., 1991
Atherinops affinis (early blastula embryo)	$CuCl_2$	Filtered nat seawater	S	21	<3(meas)	2.0 (est)	7.1-7.7	33	12 d	NOEChatc	meas	(123)	Anderson et al., 1991
Atherinops affinis (early blastula embryo)	$CuCl_2$	Filtered nat seawater	S	21	<3(meas)	2.0 (est)	7.1-7.7	33	12 d	NOECyoung abn	meas	63	Anderson et al., 1991
Atherinops affinis (early blastula embryo)	$CuCl_2$	Filtered nat seawater	S	21	<3(meas)	2.0 (est)	7.1-7.7	33	12 d	NOECemb abn	meas	(115)	Anderson et al., 1991
Atherinops affinis (early blastula embryo)	$CuCl_2$	Filtered nat seawater	S	21	<3(meas)	2.0 (est)	7.1-7.7	33	12 d	NOEChatc	meas	(115)	Anderson et al., 1991
Atherinops affinis (early blastula embryo)	$CuCl_2$	Filtered nat seawater	S	21	<3(meas)	2.0 (est)	7.1-7.7	33	12 d	NOECyoung abn	meas	68	Anderson et al., 1991
Atherinops affinis (early blastula embryo)	$CuCl_2$	Filtered nat seawater	S	21	<3(meas)	2.0 (est)	7.1-7.7	33	12 d	NOECemb abn	meas	55	Anderson et al., 1991
Atherinops affinis (early blastula embryo)	$CuCl_2$	Nat seawater	S	21	<3(meas)	2.0 (est)	7.1-7.7	33	12 d	NOEChatc	meas	55	Anderson et al., 1991
Atherinops affinis (early blastula embryo)	$CuCl_2$	Nat seawater	S	21	<3(meas)	2.0 (est)	7.1-7.7	33	12 d	NOECyoung abn	meas	55	Anderson et al., 1991
Cyprinodon variegates (egg)	$CuCl_2$	Nat seawater	F	25	<0.4(meas)	1.19 (meas)	8.0-8.3	23.5-27	7 d	NOEChatc	meas	(109)	Hurd, 2006a
Cyprinodon variegates (embryo-larval stage)	$CuCl_2$	Nat seawater	F	25	<0.4(meas)	1.19 (meas)	8.0-8.3	23.5-27	32 d	NOECs	meas	(109)	Hurd, 2006a
Cyprinodon variegates (embryo-larval stage)	$CuCl_2$	Nat seawater	F	25	<0.4(meas)	1.19 (meas)	8.0-8.3	23.5-27	32 d	NOECemb dev w	meas	57.8	Hurd, 2006a
Cyprinodon variegates (embryo-larval stage)	$CuCl_2$	Nat seawater	F	25	<0.4(meas)	1.19 (meas)	8.0-8.3	23.5-27	32 d	NOECemb dev l	meas	57.8	Hurd, 2006a

Note: NOEC values in parentheses are not included in the derivation of a species mean NOEC, because they are not the most sensitive biological endpoint for the species

NOEC – non observed effect concentration; $CuCl_2$ - copper chloride; S – static test; F-flow through test; nat – natural; est – estimated; meas-measured; d – days; emb abn – embryo abnormalities; hatc – hatching; abn – abnormalities; s- survival; dev- development; w – weight; l-length.

6.2.5. Normalization of chronic toxicity values for copper availability

The toxicity database showed large variations in chronic toxicity within the same species. The most important parameter to explain this intra-species variability has been shown to be DOC. Therefore, the copper availability in marine waters is assessed from the relationship between DOC and copper toxicity.

Copper effects -DOC relationships were established and compared for a range of marine organisms: *Mytilus edulis* (Mollusca), *Fucus vesiculosus* (Chromophycota), *Crassostreas gigas* (Mollusca), *Mytilus galloprovincialis (*Mollusca), *Dendraster excentricus* (Echinodermata), *Strongylocentrotus purpuratus* (Echinodermata). The data demonstrate that there were no statistical differences between the observed copper effects-DOC relationships among taxonomic groups. Therefore, in this RA, all chronic toxicity values were normalized to a range of DOC values, 0.2-2 mg/L, using the approach $\mathbf{EC_{50} = 11.53 * DOC^{0.53}}$ derived by Arnold et al. (2005). This correlation is based on acute toxicity (EC_{50}) but since this correlation is an external mechanism it can be applied to EC_{10} or NOEC values and within this RA it was considered to be a justified approach to provide a protective PNEC.

The copper risk assessment for marine waters is based on a total risk approach with the incorporation of DOC normalization.

The normalized NOEC species geometric mean values for 3 different DOC scenario's for high quality data that were used to derive PNEC for the marine environment are provided in Table 16.

Table 16. Normalized species geometric mean NOECs for high quality data

Species	**Taxonomic group**	**NOEC 0.2 mg/L DOC**	**NOEC 0.5 mg/L DOC**	**NOEC 2.0 mg/L DOC**	**Number NOECs used**
Phaeodactylum tricornutum	Diatom	1.06	1.86	4.36	2
Skeletonema costatum	Diatom	1.37	2.41	5.63	1
Mytilus edulis	Mollusc	1.61	2.83	6.63	2
Pandalus danae	Crustacea	2.41	4.23	9.90	1
Macrocystis pyrifera	Macroalgae	2.43	4.27	10.00	2
Placopecten magellanicus	Mollusc	2.43	4.27	10.00	1
Crassostreas gigas	Mollusc	2.57	4.50	10.54	6
Mytilus galloprovincialis	Mollusc	2.91	5.11	11.96	4
Paracentrotus lividus	Echinoderm	3.01	5.29	12.38	2
Neanthes arenaceodentata	Annelid	3.11	5.46	12.78	2
Goniastrea aspera	Cnidaria	3.46	6.07	14.20	1
Tisbe battagliai	Crustacea	3.57	6.27	14.67	3
Artemia franciscana	Crustacea	3.86	6.77	15.84	1
Mercenaria mercenaria	Mollusc	3.99	7.00	16.39	1

Table 16 (cont.). Normalized species geometric mean NOECs for high quality data

Species	**Taxonomic group**	**NOEC 0.2 mg/L DOC**	**NOEC 0.5 mg/L DOC**	**NOEC 2.0 mg/L DOC**	**Number NOECs used**
Acropora tenuis	Cnidaria	4.21	7.39	17.30	1
Prototheca staminea	Mollusc	4.38	7.69	18.00	1
Fucus vesiculosis	Macroalgae	4.45	7.80	18.26	5
Tisbe furcata	Crustacea	4.65	8.16	19.10	1
Penaeus mergulensis	Crustacea	8.03	14.10	33.00	1
Lobophytum compactum	Cnidaria	8.76	15.38	36.00	1
Eurytemora affinis	Crustacea	12.44	21.83	51.10	1
Atherinopsis affinis	Fish	14.35	25.19	58.96	5
Cyprinodon variegatus	Fish	19.35	33.95	79.48	2
Penaeus monodon	Crustacea	35.30	61.94	145.00	1

6.2.6. Derivation of the Predicted No Effect Concentration marine waters ($PNEC_{marine}$)

Three DOC scenario's have been selected and the HC_{5-50} were calculated using the statistical extrapolation method.
HC_{5-50} values derived from the high quality dataset for DOC of 2.0 mg/L scenario range between 4.4 µg Cu/L using the log-normal distribution and 5.2 µg Cu/L using the Best-fit. The HC_{5-50} value derived from the semi-parametric Kernel Density Estimation was 4.8 µg Cu/L.

Evaluation of the HC_{5-50} values derived was undertaken with several sensitivity analysis:

- using only NOECs/EC10s from "truly filtered" systems;
- inclusion of the lower quality NOEC/EC10 values;
- considering varying DOC quality.

Based on the statistical uncertainty and sensitivity analysis it was concluded that an HC_{5-50} value around 5 µg Cu/L (4.8 µg Cu/L from semi-parametric statistics and 5.2 µg Cu/L for the best fitting) is a robust HC_{5-50} determination. The sensitivity analysis shows that the uncertainty around this value is very low.

The derived HC_{5-50} values are close to copper concentrations in control media and above reported copper background concentrations in open oceans. This therefore gives confidence to the proposed HC_{5-50} values but cautions to the use of an unnecessary assessment factor on the derived HC_{5-50} values. Nevertheless, since a high quality mesocosm study was not found, an assessment factor of 2 has been applied to the HC_{5-50}. TCNES agreed that this assessment factor could in future be reduced if the HC_{5-50} could be validated with reliable, high quality mesocosm data.

6.2.7. Summary and final derivation of the $PNEC_{marine}$

Considering that:

- the large amount of high quality single species chronic NOEC values for a wide variety of taxonomic groups
- the knowledge on the mechanism of action of copper
- the robustness of the DOC normalization
- the small statistical uncertainty around the HC_{5-50}
- the overestimation of copper toxicity in laboratory non-equilibrated compared to natural systems due to limited Cu-DOC binding
- the use of the total risk approach
- the marine natural open ocean background levels and copper levels observed in control media
- the essentiality of copper and the homeostatic capacity of aquatic organisms

it was concluded that the organic carbon normalized HC_{5-50} values for marine scenarios are robust and ecologically relevant and are proposed as PNECs for marine waters.

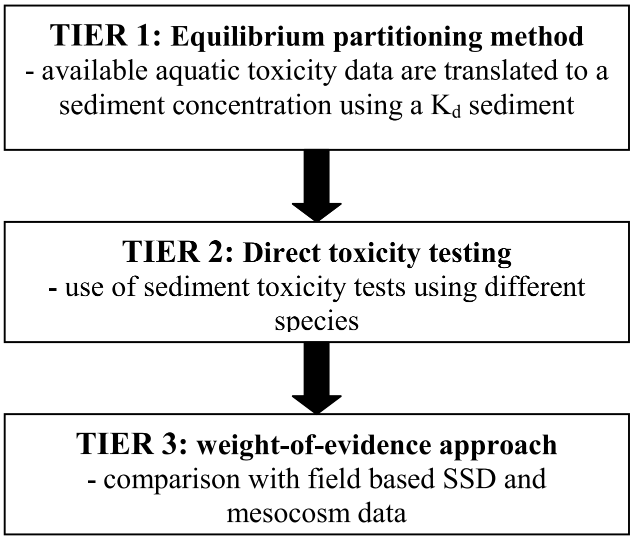
Therefore, the HC_{5-50} derived from the best-fitting distribution (5.2 µg Cu/L) was retained to derive the $PNEC_{marine}$. An assessment factor of 2 was applied to the HC_{5-50} value in the absence of a high quality mesocosm/field data and therefore, a **$PNEC_{marine}$** of **2.6 µg Cu/L** was carried forward for risk characterization.

6.3. Freshwater sediment toxicity

6.3.1. General approach

The TGD (TGD, 2003) proposes a tiered approach in assessing sediment toxicity. In a first tier the equilibrium partitioning method (EP) is used as a screening method. In case of concern in Tier 1, a second tier compares the results from EP with results of whole sediment toxicity tests.

Figure 1. Tiered approach proposed for assessing sediment toxicity



Metal toxicity in sediments mainly occurs via pore water exposure and thus the equilibrium partitioning method can be used for metals. Therefore, in a first tier, $PNEC_{sediment}$ for copper were derived using the available aquatic SSDs for copper which are translated to a sediment HC_{5-50} through the equilibrium partitioning approach. In a second tier, the HC_{5-50} sediment is derived from the ecotoxicity data. In a third tier, values obtained from mesocosms and field data are evaluated and compared to the 2 other tiers derived HC_{5-50}.

6.3.2. Tier 1: $PNEC_{sediment(EP)}$ using the aquatic effects dataset and the equilibrium partitioning method

In accordance with the TGD, the concentration in freshly deposited sediment is taken as the PEC for sediments and thus properties of suspended matter should be used for the PEC calculations. The $PNEC_{sediment\ EP}$ should be calculated using the PNEC aquatic and the sediment/water partitioning coefficients as input (TGD, 2003).

For copper, the application of the EP approach was performed in two steps:
(i) using the median Kd values from monitoring data
(ii) using Kd values calculated by the WHAM speciation model.

EP approach, using the median Kd values, obtained from monitoring data

Seven typical scenario's have been chosen for the aquatic compartment and HC_{5-50} were calculated using the statistical extrapolation method. HC_{5-50} values from log-normal based SSDs were between 7.8 and 27.7 µg Cu/L and 7.8 to 22.1 µg Cu/L when the best-fitting approach was used. The differences in freshwater HC_{5-50} values are related to differences in physico-chemical characteristics of the surface waters.
The scenario-specific $HC_{5-50sediment\ (EP)}$ values were calculated from the scenario-specific aquatic HC_{5-50} values and the application of the EU median K_d suspended solids and the median K_d sediment.

Using the median Kd suspended solids and the EP method, an $HC_{5-50\ sediment}$ range between 236 and 823 mg Cu/kg dry weight for $HC_{5-50\ aquatic}$ of 7.8 to 27.7 µg Cu/L When using the log-normal aquatic SSD fitting, and between 236 to 668 mg Cu/kg dry weight when using the aquatic HC_{5-50} with the best fitting approach.

Considering a suspended solid organic carbon fraction of **0.1** (TGD, 2003), the organic carbon based $HC_{5-50\ sediment}$ range between 2359 and 8227 mg Cu/kg OC (log normal aquatic SSD fitting) and between 2359 and 6684 mg Cu/kg OC (best fitting of the aquatic SSD).

Similarly, if the EU median K_d sediment is used, than $HC_{5-50\ sediment(EP\ sed)}$ range from 190 and 664 mg Cu/kg dry weight (log normal fitting of the aquatic SSD), and between 190 and 538 mg Cu/kg dry weight (best fitting of the aquatic SSD) are obtained. Considering a sediment organic carbon fraction of **0.05** (TGD, 2003), $HC_{5-50\ sediment}$ range between 3808 and 13278 mg Cu/kg OC (log normal aquatic SSD fitting) and between 3808 and 10789 mg Cu/kg OC (best fitting of the aquatic SSD) are obtained.

The organic carbon based $HC_{5-50\ sediment\ (EP\ Sed)}$ are thus slightly higher (a factor 1.6) higher than the organic carbon based $HC_{5-50\ sediment\ (EP\ SS)}$. This difference may be related to additional sulfide binding sites, present in settled sediments.

Equilibrium partition method using Kd values calculated using the WHAM model

The fraction of copper that is bound to organic carbon under different environmental conditions was derived using the WHAM (Winderemere Humic Aqueous Model) speciation model. This model assumes that the organic carbon is the most important fraction of the particulate phase for binding copper. A summary of the results using the WHAM model shows that $HC_{5-50sediment}$ WHAM vary between 1833 mg Cu/kg OC to 4183 mg Cu/kg OC, depending on the scenario.

The OC normalized $HC_{5\text{-}50sediment}$ WHAM values are lower than the $HC_{5\text{-}50sediment\ EP\ sed}$ values. This difference is likely to be that the WHAM model only considers binding to OC and other binding sites exist.

Summary and conclusion

From the different $HC_{5\text{-}50sediment}$ values calculated the lowest values are retained and represent the worst-case scenario. Therefore, the $HC_{5\text{-}50sediment}$ retained are:

$HC_{5\text{-}50sediment\ (EP\ WHAM)}$: 1833 mg Cu/kg OC
$HC_{5\text{-}50sediment\ (EP\ sed)}$: 3808 mg Cu/kg OC
$HC_{5\text{-}50sediment\ (EP\ SS)}$: 2358 mg Cu/kg OC

6.3.3. Tier 2: $PNEC_{sediment\ (benthic\ SSD)}$, from sediment ecotoxicity data

Results sediment toxicity data

Data on chronic tests resulting in NOECs are summarized in Table 17. Chronic toxicity results (n=106) for 6 different sediment organisms were compiled for the Cu RA. More recent data (n= 9) was found in the literature and was included in the table, however they were not included for the PNEC derivation.
The selected NOEC values range between 18.3 and 1856 mg Cu/kg dry weight for *Tubifex tubifex* (Guent University, 2004).

Influence of organic carbon and AVS

A large variability was observed in the reported effect levels that could possibly be due to different sediment characteristics such as the acid volatile sulfide (AVS) and the organic carbon. Both AVS and OC affect copper bioavailability and if the database is used without any correction it would lead to erroneous PNEC value for freshwater sediments.

The AVS content extracted from the literature varied between 0.05 and 58.6 mmol/kg and is compared with AVS data reported for other countries. There is limited information available, but an extensive database is available for the Flemish region in Belgium with an average AVS value of 0.088 mmol/kg dry weight (n=200; Vangheluwe et al., 2005). Recently, Burton (2007) investigated AVS concentrations of pristine waters from 10 countries and nine eco-regions in Europe. AVS concentrations ranged from 0.004 µmol/g dry weight to 44 µmol/g dry weight with an average value of 2.5 µmol/g dry weight.

The OC content varied between 0.5 and 24.8 %. The organic carbon concentrations in European countries range between 0.006 (= 0.6 % OC) and 0.09 (= 9 % OC). The TGD default value for organic carbon is 0.05 (= 5 % OC).

Selection of toxicity values for PNEC derivation

It was not feasible to normalize the database for AVS content. Therefore, NOEC values generated from sediments with an AVS concentration higher than the 10th percentile of the AVS concentration (0.77 mmol/kg dry weight) derived from the Flemish dataset were rejected. In order to reduce variability due to the different OC contents in sediment samples, each NOEC value was corrected for the OC fraction using the formula

$$NOEC_{OC,\ normalized} = \frac{NOEC_{total}}{fOC}$$

with $NOEC_{total}$ (mg Cu/kg dry weight), f_{OC} = fraction organic carbon and $NOEC_{OC}$, normalised (mg/g OC). NOEC values corrected for OC content are also summarized in Table 17.

Therefore, for the PNEC derivation, NOEC values were normalized to OC content and only low AVS sediments were accepted.

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Table 17. NOEC values and sediment parameters for sediment dwelling organisms. NOECs used for PNEC derivation are in bold.

ORGANISM	TEST TYPE	TEST COMPOUND	TEST SEDIMENT	OC (%)	EXPOSURE TIME	CRITERION	RESULT (mg Cu/kg dw)	RESULT NORMALIZED TO OC (mg Cu/kg dw)	REFERENCE
Tubifex tubifex	S	$CuSO_4$	art (Sala Bolognese)	1.41	28-d	NOECr	**67.25**	47.7	Vecchi et al., 1999
Tubifex tubifex	S	$CuSO_4$	art (Sala Bolognese)	1.41	28-d	NOECs	**67.25**	47.7	Vecchi et al., 1999
Tubifex tubifex	S	$CuSO_4$	lake (Maggiore)	1.56	28-d	NOECr	**231.7**	148.5	Vecchi et al., 1999
Tubifex tubifex	S	$CuSO_4$	art (Ca Bosco+food supplement)	1.03	28-d	NOECr	**62.64**	60.8	Vecchi et al., 1999
Tubifex tubifex	S	$CuSO_4$	lake (Maggiore)	1.56	28-d	NOECs	**385.8**	247.3	Vecchi et al., 1999
Tubifex tubifex	S	$CuSO_4$	art (Ca Bosco+food supplement)	1.03	28-d	NOECs	**101.4**	98.4	Vecchi et al., 1999
Tubifex tubifex	S	$CuSO_4$	art (Ca Bosco-food supplement)	1.05	28-d	NOECs	**69.1**	65.8	Vecchi et al., 1999
Tubifex tubifex	R	$CuCl_2$	art (OECD substrate; AVS 0.05 mmol/kg)	2.62	28-d	NOECs	**138.5**	52.9	Ghent University, 2004
Tubifex tubifex	R	$CuCl_2$	art (OECD substrate; AVS 0.05 mmol/kg)	2.62	28-d	NOECr	**79.3**	30.3	Ghent University, 2004
Tubifex tubifex	R	$CuCl_2$	art (OECD substrate; AVS 0.05 mmol/kg)	2.62	28-d	NOECg	**79.3**	30.3	Ghent University, 2004
Tubifex tubifex	R	$CuCl_2$	art (OECD substrate; AVS 8.04 mmol/kg)	3.33	28-d	NOECs	988.3		Ghent University, 2004
Tubifex tubifex	R	$CuCl_2$	art (OECD substrate; AVS 8.04 mmol/kg)	3.33	28-d	NOECr	459.2		Ghent University, 2004
Tubifex tubifex	R	$CuCl_2$	art (OECD substrate; AVS 8.04 mmol/kg)	3.33	28-d	NOECg	163		Ghent University, 2004
Tubifex tubifex	R	$CuCl_2$	art (OECD substrate; AVS 14.39 mmol/kg)	3.33	28-d	NOECs	937		Ghent University, 2004
Tubifex tubifex	R	$CuCl_2$	art (OECD substrate; AVS 0.59 mmol/kg)	9.81	28-d	NOECs	**580.9**	59.2	Ghent University, 2004
Tubifex tubifex	R	$CuCl_2$	art (OECD substrate; AVS 0.59 mmol/kg)	9.81	28-d	NOECr	**580.9**	59.2	Ghent University, 2004
Tubifex tubifex	R	$CuCl_2$	art (OECD substrate; AVS 0.59 mmol/kg)	9.81	28-d	NOECg	**580.9**	59.2	Ghent University, 2004
Tubifex tubifex	R	$CuCl_2$	art (OECD substrate; AVS 5.43 mmol/kg)	9.81	28-d	NOECs	1267		Ghent University, 2004

Table 17. (cont.) NOEC values and sediment parameters for sediment dwelling organisms. NOECs used for PNEC derivation are in bold.

ORGANISM	TEST TYPE	TEST COMPOUND	TEST SEDIMENT	OC (%)	EXPOSURE TIME	CRITERION	RESULT (mg Cu/kg dw)	RESULT NORMALIZED TO OC (mg Cu/kg dw)	REFERENCE
Tubifex tubifex	R	$CuCl_2$	art (OECD substrate; AVS 5.43 mmol/kg)	9.81	28-d	NOECr	1037		Ghent University, 2004
Tubifex tubifex	R	$CuCl_2$	art (OECD substrate; AVS 5.43 mmol/kg)	9.81	28-d	NOECg	1036.5		Ghent University, 2004
Tubifex tubifex	R	$CuCl_2$	art (OECD substrate; AVS 15.15 mmol/kg)	9.81	28-d	NOECs	1357		Ghent University, 2004
Tubifex tubifex	R	$CuCl_2$	art (OECD substrate; AVS 15.15 mmol/kg)	9.81	28-d	NOECr	480.9		Ghent University, 2004
Tubifex tubifex	R	$CuCl_2$	art (OECD substrate; AVS 15.15 mmol/kg)	9.66	28-d	NOECg	271.6		Ghent University, 2004
Tubifex tubifex	R	$CuCl_2$	Natural Brakel (AVS 0.27 mmol/kg)	2.83	28-d	NOECs	**54**	19.1	Ghent University, 2004
Tubifex tubifex	R	$CuCl_2$	Natural Brakel (AVS 0.27 mmol/kg)	2.83	28-d	NOECr	**18.3**	6.5	Ghent University, 2004
Tubifex tubifex	R	$CuCl_2$	Natural Brakel (AVS 0.27 mmol/kg)	2.83	28-d	NOECg	**18.3**	6.5	Ghent University, 2004
Tubifex tubifex	R	$CuCl_2$	Natural Kraenepoel (AVS 0.28 mmol/kg)	2.12	28-d	NOECs	**95.3**	45.0	Ghent University, 2004
Tubifex tubifex	R	$CuCl_2$	Natural Kraenepoel (AVS 0.28 mmol/kg)	2.12	28-d	NOECr	**56.1**	26.5	Ghent University, 2004
Tubifex tubifex	R	$CuCl_2$	Natural Kraenepoel (AVS 0.28 mmol/kg)	2.12	28-d	NOECg	**32.2**	15.2	Ghent University, 2004
Tubifex tubifex	R	$CuCl_2$	Natural Kraenepoel 2 (AVS 0.10 mmol/kg)	1.96	28-d	NOECr	**98.3**	50.2	Ghent University, 2004
Tubifex tubifex	R	$CuCl_2$	Natural Kraenepoel 2 (AVS 0.10 mmol/kg)	1.96	28-d	NOECg	**53**	27.0	Ghent University, 2004
Tubifex tubifex	R	$CuCl_2$	Natural Leuven (AVS 56.4 mmol/kg)	24.8	28-d	NOECr	1856		Ghent University, 2004
Tubifex tubifex	R	$CuCl_2$	Natural Leuven (AVS 56.4 mmol/kg)	24.8	28-d	NOECg	1855.6		Ghent University, 2004
Tubifex tubifex	S	$CuCl_2$	Lake Erie reference sed Longpoint	0.5 (TOC)	28-d	NOECs	237.8		Milani et al., 2003

Table 17. (cont.) NOEC values and sediment parameters for sediment dwelling organisms. NOECs used for PNEC derivation are in bold

ORGANISM	TEST TYPE	TEST COMPOUND	TEST SEDIMENT	OC (%)	EXPOSURE TIME	CRITERION	RESULT (mg Cu/kg dw)	RESULT NORMALIZED TO OC (mg Cu/kg dw)	REFERENCE
Tubifex tubifex	S	$CuCl_2$	Lake Erie reference sed Longpoint	0.5 (TOC)	28-d	NOECs	**246.9**	493.8	Milani et al., 2003
Tubifex tubifex	S	$CuCl_2$	Lake Erie reference sed Longpoint	0.5 (TOC)	28-d	NOECs	**270.5**	541.0	Milani et al., 2003
Tubifex tubifex	R	$CuCl_2$	art (OECD substrate; AVS 0.06 mmol/kg)	2.6	28-d	NOECs	**138**	255.6	Roman et al., 2007
Tubifex tubifex	R	$CuCl_2$	art (OECD substrate; AVS 0.06 mmol/kg)	2.6	28-d	NOECg	**78.3**	258.0	Roman et al., 2007
Tubifex tubifex (juveniles/adult)	R	$CuCl_2$	art (OECD substrate; AVS 0.06 mmol/kg)	2.6	28-d	NOECr	**78.3**	541.0	Roman et al., 2007
Tubifex tubifex (cocoons/adult)	R	$CuCl_2$	art (OECD substrate; AVS 0.06 mmol/kg)	2.6	28-d	NOECr	**78.3**	53.1	Roman et al., 2007
Hyalella azteca	R	$CuCl_2$	art (OECD substrate; AVS 0.05 mmol/kg)	2.62	28-d	NOECg	**53.2**	20.3	Ghent University, 2004
Hyalella azteca	R	$CuCl_2$	art (OECD substrate; AVS 4.87 mmol/kg)	3.29	28-d	NOECs	292.5		Ghent University, 2004
Hyalella azteca	R	$CuCl_2$	art (OECD substrate; AVS 4.87 mmol/kg)	3.29	28-d	NOECg	292.5		Ghent University, 2004
Hyalella azteca	R	$CuCl_2$	art (OECD substrate; AVS 12.33 mmol/kg)	3.29	28-d	NOECs	582.6		Ghent University, 2004
Hyalella azteca	R	$CuCl_2$	art (OECD substrate; AVS 0.27 mmol/kg)	9.66	28-d	NOECs	**337.6**	34.9	Ghent University, 2004
Hyalella azteca	R	$CuCl_2$	art (OECD substrate; AVS 0.27 mmol/kg)	9.66	28-d	NOECg	**538.6**	55.8	Ghent University, 2004
Hyalella azteca	R	$CuCl_2$	art (OECD substrate; AVS 5.30 mmol/kg)	9.66	28-d	NOECs	739.5		Ghent University, 2004
Hyalella azteca	R	$CuCl_2$	art (OECD substrate; AVS 5.30 mmol/kg)	9.66	28-d	NOECg	492.7		Ghent University, 2004
Hyalella azteca	R	$CuCl_2$	art (OECD substrate; AVS 8.97 mmol/kg)	9.66	28-d	NOECs	849.5		Ghent University, 2004
Hyalella azteca	R	$CuCl_2$	art (OECD substrate; AVS 8.97 mmol/kg)	9.66	28-d	NOECg	512.2		Ghent University, 2004

Table 17. (cont.) NOEC values and sediment parameters for sediment dwelling organisms. NOECs used for PNEC derivation are in bold

ORGANISM	TEST TYPE	TEST COMPOUND	TEST SEDIMENT	OC (%)	EXPOSURE TIME	CRITERION	RESULT (mg Cu/kg dw)	RESULT NORMALIZED TO OC (mg Cu/kg dw)	REFERENCE
Hyalella azteca	R	$CuCl_2$	Natural Brakel (AVS 0.18 mmol/kg)	2.83	28-d	NOECs	**171**	60.4	Ghent University, 2004
Hyalella azteca	R	$CuCl_2$	Natural Kraenepoel (AVS 0.28 mmol/kg)	2.12	28-d	NOECs	**141**	66.5	Ghent University, 2004
Hyalella azteca	R	$CuCl_2$	Natural Kraenepoel-1 sed (AVS 0.28 mmol/kg)	2.12	28-d	NOECg	**21.8**	10.3	Ghent University, 2004
Hyalella azteca	R	$CuCl_2$	Natural Kraenepoel-2 sed (AVS 0.10 mmol/kg)	1.96	28-d	NOECs	**140**	71.4	Ghent University, 2004
Hyalella azteca	R	$CuCl_2$	Natural Kraenepoel-2 sed (AVS 0.10 mmol/kg)	1.96	28-d	NOECg	**49.9**	25.5	Ghent University, 2004
Hyalella azteca	R	$CuCl_2$	Natural Leuven (AVS 58.6 mmol/kg)	18.9	28-d	NOECs	3158		Ghent University, 2004
Hyalella azteca	R	$CuCl_2$	Natural Leuven (AVS 58.6 mmol/kg)	18.9	28-d	NOECg	1531		Ghent University, 2004
Hyalella azteca	R	$CuCl_2$	Natural Ijzer sed (AVS 18.25 mmol/kg)	6.48	28-d	NOECs	1495		Ghent University, 2004
Hyalella azteca	S	$CuCl_2$	Lake Erie reference sed Longpoint	0.5 (TOC)	28-d	NOECs	**59.3**	118.6	Milani et al., 2003
Hyalella azteca	S	$CuCl_2$	Lake Erie reference sed Longpoint	0.5 (TOC)	28-d	NOECs	**66.9**	133.8	Milani et al., 2003
Hyalella azteca	S	$CuCl_2$	Lake Erie reference sed Longpoint	0.5 (TOC)	28-d	NOECg	**155.1**	310.2	Milani et al., 2003
Hyalella azteca	S	$CuCl_2$	Lake Erie reference sed Longpoint	0.5 (TOC)	28-d	NOECg	**59.3**	118.6	Milani et al., 2003
Hyalella azteca	S	$CuCl_2$	Lake Erie reference sed Longpoint	0.5 (TOC)	28-d	NOECg	**66.9**	133.8	Milani et al., 2003
Hyalella azteca	S	$CuCl_2$	Lake Erie reference sed Longpoint	0.5 (TOC)	28-d	NOECg	**52.3**	104.6	Milani et al., 2003
Hyalella azteca	R	$CuCl_2$	art (OECD substrate; AVS 0.06 mmol/kg)	2.6	28-d	NOECg	**53.2**	20.5	Roman et al., 2007

Table 17. (cont.) NOEC values and sediment parameters for sediment dwelling organisms. NOECs used for PNEC derivation are in bold

ORGANISM	TEST TYPE	TEST COMPOUND	TEST SEDIMENT	OC (%)	EXPOSURE TIME	CRITERION	RESULT (mg Cu/kg dw)	RESULT NORMALIZED TO OC (mg Cu/kg dw)	REFERENCE
Hexagenia spp	S	$CuCl_2$	Lake Erie reference sed Longpoint	0.5 (TOC)	28-d	NOECs	**39.2**	78.4	Milani et al., 2003
Hexagenia spp	S	$CuCl_2$	Lake Erie reference sed Longpoint	0.5 (TOC)	28-d	NOECs	**33.9**	67.8	Milani et al., 2003
Hexagenia spp	S	$CuCl_2$	Lake Erie reference sed Longpoint	0.5 (TOC)	21-d	NOECs	**44.9**	89.8	Milani et al., 2003
Hexagenia spp	S	$CuCl_2$	Lake Erie reference sed Longpoint	0.5 (TOC)	21-d	NOECg	**23.4**	46.8	Milani et al., 2003
Hexagenia spp	S	$CuCl_2$	Lake Erie reference sed Longpoint	0.5 (TOC)	21-d	NOECg	**29.2**	58.4	Milani et al., 2003
Hexagenia spp	S	$CuCl_2$	Lake Erie reference sed Longpoint	0.5 (TOC)	21-d	NOECg	**44.9**	89.8	Milani et al., 2003
Chironomus riparius	R	$CuCl_2$	Natural Ijzer sed (AVS 18.25 mmol/kg)	6.48	28-d	NOECg	244.8		Ghent University, 2004
Chironomus riparius	R	$CuCl_2$	art (OECD substrate; AVS 0.05 mmol/kg)	2.62	28-d	NOECs	**59.5**	22.7	Ghent University, 2004
Chironomus riparius	R	$CuCl_2$	art (OECD substrate; AVS 0.05 mmol/kg)	2.62	28-d	NOECe	**59.5**	22.7	Ghent University, 2004
Chironomus riparius	R	$CuCl_2$	art (OECD substrate; AVS 0.05 mmol/kg)	2.62	28-d	NOECg	**89.2**	34.0	Ghent University, 2004
Chironomus riparius	R	$CuCl_2$	art (OECD substrate; AVS 4.02 mmol/kg)	3.33	28-d	NOECs	589.3		Ghent University, 2004
Chironomus riparius	R	$CuCl_2$	art (OECD substrate; AVS 4.02 mmol/kg)	3.33	28-d	NOECe	318		Ghent University, 2004
Chironomus riparius	R	$CuCl_2$	art (OECD substrate; AVS 4.02 mmol/kg)	3.33	28-d	NOECg	318		Ghent University, 2004
Chironomus riparius	R	$CuCl_2$	art (OECD substrate; AVS 16.21 mmol/kg)	3.33	28-d	NOECs	553.6		Ghent University, 2004
Chironomus riparius	R	$CuCl_2$	art (OECD substrate; AVS 16.21 mmol/kg)	3.33	28-d	NOECe	553.6		Ghent University, 2004
Chironomus riparius	R	$CuCl_2$	art (OECD substrate; AVS 16.21 mmol/kg)	3.33	28-d	NOECg	553.6		Ghent University, 2004

Table 17. (cont.) NOEC values and sediment parameters for sediment dwelling organisms. NOECs used for PNEC derivation are in bold

ORGANISM	TEST TYPE	TEST COMPOUND	TEST SEDIMENT	OC (%)	EXPOSURE TIME	CRITERION	RESULT (mg Cu/kg dw)	RESULT NORMALIZED TO OC (mg Cu/kg dw)	REFERENCE
Chironomus riparius	R	$CuCl_2$	art (OECD substrate; AVS 0.30 mmol/kg)	9.81	28-d	NOECs	**292**	29.8	Ghent University, 2004
Chironomus riparius	R	$CuCl_2$	art (OECD substrate; AVS 0.30 mmol/kg)	9.81	28-d	NOECe	**292**	29.8	Ghent University, 2004
Chironomus riparius	R	$CuCl_2$	art (OECD substrate; AVS 0.30 mmol/kg)	9.81	28-d	NOECg	**505.9**	51.6	Ghent University, 2004
Chironomus riparius	R	$CuCl_2$	art (OECD substrate; AVS 4.05 mmol/kg)	9.81	28-d	NOECs	934.1		Ghent University, 2004
Chironomus riparius	R	$CuCl_2$	art (OECD substrate; AVS 4.05 mmol/kg)	9.81	28-d	NOECe	934.1		Ghent University, 2004
Chironomus riparius	R	$CuCl_2$	art (OECD substrate; AVS 4.05 mmol/kg)	9.81	28-d	NOECg	452.6		Ghent University, 2004
Chironomus riparius	R	$CuCl_2$	art (OECD substrate; AVS 12.60 mmol/kg)	9.81	28-d	NOECs	1417		Ghent University, 2004
Chironomus riparius	R	$CuCl_2$	art (OECD substrate; AVS 12.60 mmol/kg)	9.81	28-d	NOECe	1417		Ghent University, 2004
Chironomus riparius	R	$CuCl_2$	art (OECD substrate; AVS 12.60 mmol/kg)	9.81	28-d	NOECg	1417		Ghent University, 2004
Chironomus riparius	R	$CuCl_2$	Natural Brakel (AVS 0.15 mmol/kg)	2.83	28-d	NOECs	**177.1**	62.6	Ghent University, 2004
Chironomus riparius	R	$CuCl_2$	Natural Brakel (AVS 0.15 mmol/kg)	2.83	28-d	NOECg	**75.4**	26.6	Ghent University, 2004
Chironomus riparius	R	$CuCl_2$	Natural Kraenepoel-1 sed (AVS 0.28 mmol/kg)	2.12	28-d	NOECs	**54.2**	25.6	Ghent University, 2004
Chironomus riparius	R	$CuCl_2$	Natural Kraenepoel-1 sed (AVS 0.28 mmol/kg)	2.12	28-d	NOECg	**54.4**	25.7	Ghent University, 2004
Chironomus riparius	R	$CuCl_2$	Natural Kraenepoel-2 sed (AVS 0.10 mmol/kg)	19.6	28-d	NOECs	**85.4**	4.4	Ghent University, 2004
Chironomus riparius	R	$CuCl_2$	Natural Kraenepoel-2 sed (AVS 0.10 mmol/kg)	1.96	28-d	NOECg	**55.5**	28.3	Ghent University, 2004
Chironomus riparius	R	$CuCl_2$	Natural Ijzer sed (AVS 15.57 mmol/kg)	6.48	28-d	NOECs	2113		Ghent University, 2004

Table 17. (cont.) NOEC values and sediment parameters for sediment dwelling organisms. NOECs used for PNEC derivation are in bold

ORGANISM	TEST TYPE	TEST COMPOUND	TEST SEDIMENT	OC (%)	EXPOSURE TIME	CRITERION	RESULT (mg Cu/kg dw)	RESULT NORMALIZED TO OC (mg Cu/kg dw)	REFERENCE
Chironomus riparius	R	$CuCl_2$	Natural Ijzer sed (AVS 15.57 mmol/kg)	6.97	28-d	NOECe	1320		Ghent University, 2004
Chironomus riparius	R	$CuCl_2$	Natural Ijzer sed (AVS 15.57 mmol/kg)	6.97	28-d	NOECg	776.5		Ghent University, 2004
Chironomus riparius	R	$CuCl_2$	art (OECD substrate; AVS 0.06 mmol/kg)	2.6	28-d	NOECg	**89.2**	34.3	Roman et al., 2007
Chironomus riparius	R	$CuCl_2$	art (OECD substrate; AVS 0.06 mmol/kg)	2.6	28-d	NOECe	**59.5**	22.9	Roman et al., 2007
Lumbriculus variegatus	R	$CuCl_2$	art (OECD substrate; AVS 0.05 mmol/kg)	2.62	28-d	NOECb	**80.5**	30.7	Ghent University, 2004
Lumbriculus variegatus	R	$CuCl_2$	Natural Kraenepoel-2 sed (AVS 0.10 mmol/kg)	1.96	28-d	NOECb	**91.8**	46.8	Ghent University, 2004
Lumbriculus variegatus	R	$CuCl_2$	Natural Ijzer sed (AVS 16.50 mmol/kg)	6.97	28-d	NOECb	416.3	59.7	Ghent University, 2004
Lumbriculus variegatus	R	$CuCl_2$	art (OECD substrate; AVS 0.06 mmol/kg)	2.6	28-d	NOECs	**114**	43.8	Roman et al., 2007
Lumbriculus variegatus	R	$CuCl_2$	art (OECD substrate; AVS 0.06 mmol/kg)	2.6	28-d	NOECb	**80.5**	31.0	Roman et al., 2007
Lumbriculus variegatus	R	$CuCl_2$	art (OECD substrate; AVS 0.06 mmol/kg)	2.6	28-d	NOECr	**80.5**	31.0	Roman et al., 2007
Gammarus pulex	R	$CuCl_2$	art (OECD substrate; AVS 0.05 mmol/kg)	2.62	35-d	NOECs	**94.7**	36.1	Ghent University, 2004
Gammarus pulex	R	$CuCl_2$	art (OECD substrate; AVS 0.05 mmol/kg)	2.62	35-d	NOECg	**94.7**	36.1	Ghent University, 2004
Gammarus pulex	R	$CuCl_2$	Natural Brakel (AVS 0.21 mmol/kg)	2.83	35-d	NOECs	**97.4**	34.4	Ghent University, 2004
Gammarus pulex	R	$CuCl_2$	Natural Brakel (AVS 0.21 mmol/kg)	2.83	35-d	NOECg	**30.6**	10.8	Ghent University, 2004
Gammarus pulex	R	$CuCl_2$	Natural Ijzer sed (AVS 17.50 mmol/kg)	6.48	35-d	NOECs	1268		Ghent University, 2004
Gammarus pulex	R	$CuCl_2$	Natural Ijzer sed (AVS 17.50 mmol/kg)	6.97	35-d	NOECg	789		Ghent University, 2004

Table 17. (cont.) NOEC values and sediment parameters for sediment dwelling organisms. NOECs used for PNEC derivation are in bold.

ORGANISM	TEST TYPE	TEST COMPOUND	TEST SEDIMENT	OC (%)	EXPOSURE TIME	CRITERION	RESULT (mg Cu/kg dw)	RESULT NORMALIZED TO OC (mg Cu/kg dw)	REFERENCE
Gammarus pulex	R	$CuCl_2$	art (OECD substrate; AVS 0.06 mmol/kg)	2.6	35-d	NOECs	**94.7**	36.4	Roman et al., 2007
Gammarus pulex	R	$CuCl_2$	art (OECD substrate; AVS 0.06 mmol/kg)	2.6	35-d	NOECg	**94.7**	36.4	Roman et al., 2007

NOEC – no observed effect concentration; S-static test; R-renewal test; OC-organic carbon; art – artificial; d-days; r – reproduction; s-survival; g-growth; e-emergence; AVS -acid volatile sulphide; $CuCl_2$- copper chloride; $CuSO_4$-copper sulphate.

$HC_{5\text{-}50}$ Derivation approach using sediments effect data (SSD approach)

Since a large database is available for copper effects on sediment organisms, the $PNEC_{freshwater\ sediment}$ can be derived using the statistical approach method.
In the Cu RA, the species mean NOEC values were used for the PNEC derivation.
To evaluate toxicity using the statistical extrapolation method, the median 5th percentile (HC_5) of the best fitting SSD has been calculated and the best-fit distribution is a beta distribution. The log normal distribution was also found relevant and therefore also evaluated.

Best fit

An $HC_{5\text{-}50sediment\ benthic\ SSD}$ was calculated as 2021 mg Cu/kg OC. According to the TGD (TGD, 1996) a standard sediment in the EU contains 5% of OC and therefore:

$HC_{5\text{-}50\ normalized,\ 5\%OC} = HC_{5\text{-}50OC\ norm}$ x 0.05= 101 mg Cu/kg dry weight

Log normal distribution

An $HC_{5\text{-}50sediment\ benthic\ SSD}$ was calculated as 1741 mg Cu/kg OC. According to the TGD (TGD, 1996) a standard sediment in the EU contains 5% of OC and therefore:

$HC_{5\text{-}50normalized,\ 5\%OC} = HC_{5\text{-}50OC\ norm}$ x 0.05= 87.1 mg Cu/kg dry weight

Conclusions

These two calculated $HC_{5\text{-}50}$ values are similar and will be carried forward to the PNEC derivation.

$HC_{5\text{-}50sediment\ benthic\ SSD\ (best\text{-}fit)}$: 2021 mg Cu/kg dry weight
$HC_{5\text{-}50sediment\ benthic\ SSD\ (log\text{-}normal)}$: 1741 mg Cu/kg dry weight

Comparison of the $HC_{5\text{-}50}$ values calculated from sediment and soil ecotoxicity data

Finally, $HC_{5\text{-}50sed\ (benthic\ SSD)}$ were compared to $HC5\text{-}50_{sed\ (soil\ SSD)}$ and were similar. The average OC normalized $HC_{5\text{-}50sediment\ (soil\ SSD)}$ is 2601 mg Cu/kg OC, similar to somewhat above (not significant) the $HC_{5\text{-}50sediment\ (benthic\ SSD)}$: 1741 and 2021 mg Cu/kg OC. This analysis therefore adds further weight of evidence to the $HC_{5\text{-}50sediment\ (benthic\ SSD)}$.

6.3.4. Tier 3: Sediment threshold values obtained from mesocosms and field studies

For Tier 3, NOEC values obtained from mesocosm/field studies were compared to $HC_{5\text{-}50sediment}$ calculated using the different approaches and NOEC values were found to be above the $HC_{5\text{-}50}$ value. The mesocosms therefore demonstrate that the $HC_{5\text{-}}$

$_{50sediment\ (benthic\ SSD)}$ are protective for a wide range of benthic organisms, tested in a variety of conditions and including multi-exposure routes.

6.3.5. Summary and conclusions

Calculated $HC_{5\text{-}50\ sediment}$ using the different approaches are summarized in Table 18.

Table 18. Summary of the $HC_{5\text{-}50\ sediment}$ values calculated using the different approaches

Approaches	$HC_{5\text{-}50}$ and 95% confidence interval (mg Cu/kg OC)
EP-WHAM	1833 (1434-2040)
EP-Kd SS	2359 (1162-3599)
EP-Kd sed	3808 (1876-5806)
Sed SSD-best fit (low AVS)	2021 (1960-2115)
Sed SSD-log normal (low AVS)	1741 (989-2086)
Mesocosm/field SSD log normal	3007 (2021-3776)

Comparison between $HC_{5\text{-}50}$ and background levels

The PNEC was compared to copper background levels in Europe that vary between 1.7 and 59 mg/kg dry weight. These values are below the PNEC value.

Comparison between $HC_{5\text{-}50}$ and essentiality levels

No data are available on the copper deficiency of sediment dwelling organisms. Considering however that the $HC_{5\text{-}50\ sediment\ benthic\ SSD}$ are similar to the $HC_{5\text{-}50\ sediment\ EP}$, as for the aquatic compartment, caution is needed with the use of unnecessary AF on the $HC_{5\text{-}50}$.

Conclusions

From this analysis it is concluded that the $HC_{5\text{-}50sediment\ (benthic\ SSD)}$ obtained from the sediment ecotoxicity data and obtained from best fitting (2021 mg Cu/kg organic carbon) or log normal distributions (1741 mg Cu/kg organic carbon) will protect benthic organisms from copper exposures under toxic conditions.

Considering that:

- the large amount of high quality single species and multi-species chronic NOEC values for a wide variety of taxonomic groups
- the knowledge on the mechanism of action of copper
- the robustness of the OC normalization
- the small statistical uncertainty around the $HC_{5\text{-}50}$

- the validation of the OC predicted HC_{5-50} values for mesocosms threshold values, protective to the structure and functioning of the ecosystems and representing lotic and lentic systems of varying sensitivity
- the use of the total risk approach
- the EU natural background levels
- the essentiality of copper and the homeostatic capacity of living organisms

A **$PNEC_{freshwater\ sediment}$** of **87 mg/kg dry weight for a OC fraction of 0.05** derived from the log normal distribution was carried out as the basic safe threshold value for sediments.

6.4. $PNEC_{marine\ sediments}$ derivation

There are no NOEC data available from direct toxicity sediment exposures of copper. The $PNEC_{marine}$ of 2.6 µg Cu/L was used in an equilibrium partitioning approach. The partitioning behaviour of copper between dissolved and particulate phases is essential to derive the $PNEC_{marine\ sediment}$.
The median copper K_d values derived from literature search within this RA were 131826 L/kg for marine waters and 56234 L/kg for estuarine waters.

The partitioning method thus resulted in a **$PNEC_{estuarine\ sediments}$ of 144 mg Cu/kg dw** and **$PNEC_{marine\ sediments}$ 338 mg Cu/kg dw** (suspended solids method). These PNECs were used for the risk characterisation.

7. TERRESTRIAL ENVIRONMENT

5.1. Results chronic toxicity data for soil organisms

The copper terrestrial effects database contains a large number of high quality chronic NOEC/EC_{10} values (252 chronic NOECs for 19 species and microbial processes). For the terrestrial compartment, the effects assessment of copper was based on NOEC/EC_{10} collected for soil organisms.

7.1.1. Toxicity data for higher plants

Data on chronic single species toxicity tests resulting in NOEC values for plants and accepted for the PNEC derivation are summarized in Table 19. NOEC values range from 18 mg Cu/kg for *Hordeum vulgare* to 698 mg Cu/kg for *Lycopersicon esculentum*.

7.1.2. Toxicity data for invertebrates

Data on chronic single-species toxicity tests resulting in NOEC values for plants and accepted for PNEC derivation are summarized in Table 20. NOEC values range from 8.4 mg Cu/kg for *Eisenia andrei* cocoon reproduction to 1460 mg Cu/kg for *Folsomia candida* reproduction. The NOEC value of 8.4 mg Cu/kg found for *Eisenia andrei* is below the limit for essentiality.

7.1.3. Toxicity data for microorganisms

Data on chronic microbial toxicity resulting in NOEC values are summarized in Table 21. These tests are on m icrobial processes and therefore they are multi-species tests. In the total risk approach, NOEC values range from 30 mg Cu/kg (glucose respiration) to 2402 mg Cu/kg (maize respiration).

Table 19. NOEC values and soil parameters for higher plants (accepted studies)

ORGANISM	TEST COMPOUND	TEST MEDIUM	PH	OM (%)	CLAY (%)	CEC	Cb (mg/kg dw)	EQ. TIME (d)	DURATION (d)	CRITERION	ADDED NOEC (mg/kg dw)	TOTAL NOEC (mg/kg dw)	REFERENCE
Polygonum (Fallopia) convolvulus	$CuSO_4$	field soil: clay sand	6.4	1.7	11.1	9.2	12	11	105	NOECmo	125	137	Kjaer and Elmegaard, 1996
Polygonum convolvulus	$CuSO_4$	field soil: clay sand	6.4	1.7	11.1	9.2	12	11	34	NOECy-tp	200	212	Kjaer and Elmegaard, 1996
Polygonum convolvulus	$CuSO_4$	field soil: clay sand	6.4	1.7	11.1	9.2	12	11	34	NOECr	200	212	Kjaer and Elmegaard, 1996
Polygonum convolvulus	$CuSO_4$	field soil: clay sand	6.4	1.7	11.1	9.2	12	11	105	NOECsb	200	212	Kjaer and Elmegaard, 1996
Polygonum convolvulus	$CuSO_4$	field soil: Hygum site	6.7	4.5	13.8	15.7	22	84	35	NOECy-st	200	222	Pedersen et al., 2000a
Polygonum convolvulus	$CuSO_4$	field soil: Hygum site	6.7	4.5	13.8	15.7	22	85	35	NOECy-l	200	222	Pedersen et al., 2000a
Avena sativa	$Cu(Ac)_2$	Clay soil	5.6	1.6	12	*8.7*	6	Nr	150	NOECy-g	200	206	De Haan et al., 1985
Avena sativa	$Cu(Ac)_2$	Clay soil	5.4	2.4	40	*24.7*	7	Nr	150	NOECy-g	200	207	De Haan et al., 1985
Avena sativa	$Cu(Ac)_2$	Clay soil	5.2	3.2	58	*34.8*	58	Nr	150	NOECy-g	200	258	De Haan et al., 1985
Avena sativa	$Cu(Ac)_2$	Sandy soil	5	3.4	4	*6*	4	Nr	150	NOECy-g	200	204	De Haan et al., 1985
Avena sativa	$Cu(Ac)_2$	Sandy soil	5.4	6.8	5	*11.3*	19	Nr	150	NOECy-g	200	219	De Haan et al., 1985
Lolium perenne	$Cu(NO_3)_2$	Loamy soil	7.5	3.1	12.8	*14*	*10.7*	Nr	102	NOECy-s	95.3	106	Jarvis, 1978
Lolium perenne	$Cu(NO_3)_2$	Loamy soil	7.5	3.1	12.8	*14*	*10.7*	Nr	102	NOECy-r	95.3	106	Jarvis, 1978
Hordeum vulgare	$CuSO_4$	Forest soil	7.6	3.8	8	12.4	17.2	0	14	NOECg-s	304.8	322	Ali et al., 2004
Hordeum vulgare	$CuSO_4$	Forest soil	7.6	3.8	8	12.4	17.2	0	14	NOECg-r	20.2	37.4	Ali et al., 2004
Hordeum vulgare	$CuSO_4$	Forest soil	7.6	3.8	8	12.4	17.2	0	14	NOECse	111.8	129	Ali et al., 2004
Hordeum vulgare	$CuCl_2$	Sandy loam Nottingham	3.4	8.3	13	6.7	17	7	4	EC10rl	58	75	Rothamsted research, 2004
Hordeum vulgare	$CuCl_2$	Loamy sand Houthalen	3.4	3.2	5	1.9	2	7	4	EC10rl	16	18	Rothamsted research, 2004
Hordeum vulgare	$CuCl_2$	Loamy sand Rhydtalog	4.2	20.7	13	15.2	14	7	4	NOECrl	30	44	Rothamsted research, 2004
Hordeum vulgare	$CuCl_2$	Sandy clay loam Zegveld	4.7	37.3	24	35.3	70	7	4	NOECrl	80	150	Rothamsted research, 2004
Hordeum vulgare	$CuCl_2$	Loamy sand Kovlinge I	7.8	2.6	7	2.4	6	7	4	NOECrl	45	51	Rothamsted research, 2004
Hordeum vulgare	$CuCl_2$	Sandy clay Souli I	4.8	0.7	38	11.2	31	7	4	NOECrl	77	108	Rothamsted research, 2004
Hordeum vulgare	$CuCl_2$	Sandy loam Kovlinge II	5.1	3.8	9	4.7	8	7	4	NOECrl	37	45	Rothamsted research, 2004

Table 19 (cont.). NOEC values and soil parameters for higher plants (accepted studies)

ORGANISM	TEST COMPOUND	TEST MEDIUM	PH	OM (%)	CLAY (%)	CEC	Cb (mg/kg dw)	EQ. TIME (d)	DURATION (d)	CRITERION	ADDED NOEC (mg/kg dw)	TOTAL NOEC (mg/kg dw)	REFERENCE
Hordeum vulgare	$CuCl_2$	Loamy sand Montpellier	5.2	1.2	9	2.5	5	7	4	EC10rl	38	43	Rothamsted research, 2004
Hordeum vulgare	$CuCl_2$	Clay Aluminosa	5.4	1.4	51	22.6	21	7	4	NOECrl	252	273	Rothamsted research, 2004
Hordeum vulgare	$CuCl_2$	Sandy clay loam Woburn	6.4	7	21	23.4	22	7	4	NOECrl	144	166	Rothamsted research, 2004
Hordeum vulgare	$CuCl_2$	Silt loam Ter Munck	6.8	1.6	15	8.9	22	7	4	NOECrl	55	77	Rothamsted research, 2004
Hordeum vulgare	$CuCl_2$	Silty clay loam Vault de Lugny	7.3	2.3	38	26.2	21	7	4	NOECrl	154	175	Rothamsted research, 2004
Hordeum vulgare	$CuCl_2$	Silty clay loam Rots	7.4	2	27	20	14	7	4	NOECrl	47	61	Rothamsted research, 2004
Hordeum vulgare	$CuCl_2$	Clay Souli II	7.4	4.2	46	36.3	34	7	4	EC10rl	120	154	Rothamsted research, 2004
Hordeum vulgare	$CuCl_2$	Silt loam Marknesse	7.5	2	26	20.1	18	7	4	NOECrl	37	55	Rothamsted research, 2004
Hordeum vulgare	$CuCl_2$	Loam Barcelona	7.5	2.4	21	14.3	88	7	4	NOECrl	77	165	Rothamsted research, 2004
Hordeum vulgare	$CuCl_2$	Clay Bercy	7.5	2.4	50	23.5	31	7	4	NOECrl	44	75	Rothamsted research, 2004
Hordeum vulgare	$CuCl_2$	Sandy clay Hygum	5.4	3.3	23	6.7	21	7	4	NOECrl	114	135	Rothamsted research, 2004
Hordeum vulgare	$CuCl_2$	Sand Woburn salt	6.5	1.7	8	8.4	13	7	4	NOECrl	44	57	Rothamsted research, 2004
Lycopersicum esculentum	$CuCl_2$	Sandy loam Nottingham	3.4	8.3	13	6.7	17	7	28	NOECy-s	19	36	Rothamsted research, 2004
Lycopersicum esculentum	$CuCl_2$	Loamy sand Rhydtalog	4.2	20.7	13	15.2	14	7	28	NOECy-s	357	371	Rothamsted research, 2004
Lycopersicum esculentum	$CuCl_2$	Sandy clay loam Zegveld	4.7	37.3	24	35.3	70	7	28	NOECy-s	628	698	Rothamsted research, 2004
Lycopersicum esculentum	$CuCl_2$	Loamy sand Kovlinge I	4.8	2.6	7	2.4	6	7	28	NOECy-s	85	91	Rothamsted research, 2004
Lycopersicum esculentum	$CuCl_2$	Sandy clay Souli I	4.8	0.7	38	11.2	31	7	28	NOECy-s	43	74	Rothamsted research, 2004
Lycopersicum esculentum	$CuCl_2$	Sandy loam Kovlinge II	5.1	3.8	9	4.7	8	7	28	NOECy-s	197	205	Rothamsted research, 2004
Lycopersicum esculentum	$CuCl_2$	Clay Aluminosa	5.4	1.4	51	22.6	21	7	28	NOECy-s	176	197	Rothamsted research, 2004

Table 19 (cont.). NOEC values and soil parameters for higher plants (accepted studies)

ORGANISM	TEST COMPOUND	TEST MEDIUM	PH	OM (%)	CLAY (%)	CEC	Cb (mg/kg dw)	EQ. TIME (d)	DURATION (d)	CRITERION	ADDED NOEC (mg/kg dw)	TOTAL NOEC (mg/kg dw)	REFERENCE
Lycopersicum esculentum	$CuCl_2$	Sandy clay loam Woburn	6.4	7	21	23.4	22	7	28	NOECy-s	91	113	Rothamsted research, 2004
Lycopersicum esculentum	$CuCl_2$	Silt loam Ter Munck	6.8	1.6	15	8.9	22	7	28	NOECy-s	198	220	Rothamsted research, 2004
Lycopersicum esculentum	$CuCl_2$	Silty clay loam Vault de Lugny	7.3	2.3	38	26.2	21	7	28	NOECy-s	311	332	Rothamsted research, 2004
Lycopersicum esculentum	$CuCl_2$	Silty clay loam Rots	7.4	2	27	20	14	7	28	NOECy-s	660	674	Rothamsted research, 2004
Lycopersicum esculentum	$CuCl_2$	Clay Souli II	7.4	4.2	46	36.3	34	7	28	NOECy-s	628	662	Rothamsted research, 2004
Lycopersicum esculentum	$CuCl_2$	Silt loam Marknesse	7.5	2	26	20.1	18	7	28	NOECy-s	227	245	Rothamsted research, 2004
Lycopersicum esculentum	$CuCl_2$	Loam Barcelona	7.5	2.4	21	14.3	88	7	28	NOECy-s	315	403	Rothamsted research, 2004
Lycopersicum esculentum	$CuCl_2$	Clay Brecy	7.5	2.4	50	23.5	31	7	28	NOECy-s	100	131	Rothamsted research, 2004
Lycopersicum esculentum	$CuCl_2$	Loam Guadalajara	7.5	0.6	25	16.9	7	7	28	NOECy-s	313	320	Rothamsted research, 2004
Lycopersicum esculentum	$CuCl_2$	Sandy clay Hygum	5.4	3.3	23	6.7	21	7	28	NOECy-s	106	127	Rothamsted research, 2004
Lycopersicum esculentum	$CuCl_2$	Loamy sand Wageningen D	5	0.3	9	1.9	19	7	28	NOECy-s	71	90	Rothamsted research, 2004
Lycopersicum esculentum	$Cu(HO)_2$	Loamy fine sand (thermic Typic Paleudult)	5.9-6.5	2.7	9	*9.2*	*10.7*	14	42	NOECy-s	175	*185.7*	Rhoads et al., 1989
Lycopersicum esculentum	$Cu(HO)_2$	Loamy fine sand (thermic Typic Paleudult)	6.5-6.6	2.7	9	*9.6*	*10.7*	14	42	NOECy-s	350	*360.7*	Rhoads et al., 1989
Lycopersicum esculentum	$Cu(HO)_2$	Loamy fine sand (thermic Typic Paleudult)	7.1-7.4	2.7	9	*10.5*	*10.7*	14	42	NOECy-s	350	*360.7*	Rhoads et al., 1989
Senecio vulgaris	$CuSO_4$	Regolithic acid	4.1	1.9	17.5	10.1	158	28	>105	LC10m	67	225	Brun et al., 2003
Senecio vulgaris	$CuSO_4$	Regolithic acid	4.1	1.9	17.5	10.1	158	28	>105	EC10r	28	186	Brun et al., 2003

Table 19 (cont.). NOEC values and soil parameters for higher plants (accepted studies)

ORGANISM	TEST COMPOUND	TEST MEDIUM	PH	OM (%)	CLAY (%)	CEC	Cb (mg/kg dw)	EQ. TIME (d)	DURATION (d)	CRITERION	ADDED NOEC (mg/kg dw)	TOTAL NOEC (mg/kg dw)	REFERENCE
Senecio vulgaris	$CuSO_4$	Regolithic acid	4.1	1.9	17.5	10.1	158	28	>105	EC10se	181	339	Brun et al., 2003
Poa annua	$CuSO_4$	Regolithic acid	4.1	1.9	17.5	10.1	158	28	210	LC10m	379	537	Brun et al., 2003
Poa annua	$CuSO_4$	Regolithic acid	4.1	1.9	17.5	10.1	158	28	210	EC10r	42	200	Brun et al., 2003
Poa annua	$CuSO_4$	Regolithic acid	4.1	1.9	17.5	10.1	158	28	210	EC10se	158	316	Brun et al., 2003
Andryala integrifolia	$CuSO_4$	Regolithic acid	4.1	1.9	17.5	10.1	158	28	>175	LC10m	76	234	Brun et al., 2003
Andryala integrifolia	$CuSO_4$	Regolithic acid	4.1	1.9	17.5	10.1	158	28	>175	EC10se	78	236	Brun et al., 2003
Hypochoeris radicata	$CuSO_4$	Regolithic acid	4.1	1.9	17.5	10.1	158	28	196	LC10m	192	350	Brun et al., 2003
Hypochoeris radicata	$CuSO_4$	Regolithic acid	4.1	1.9	17.5	10.1	158	28	196	EC10r	192	350	Brun et al., 2003
Hypochoeris radicata	$CuSO_4$	Regolithic acid	4.1	1.9	17.5	10.1	158	28	196	EC10se	181	339	Brun et al., 2003

NOEC- no observed effect concentration; NOEC indices: m = mortality; y = yield (based on root (r), shoot (s), leaves (l), stem (st), grain (g), tubers (tub) or total plant (tp) dry weight); rep = reproductive dry matter; sb = seed biomass; se=seedling emergence; rl = root length.
NR-not reported

Estimated background copper concentrations and CEC are indicated in italics.

*measured concentration-Cb
** If the CEC was missing from a test with plants/invertebrates/micro-organisms, then it was estimated from % clay, pH and %organic matter using an experimentally derived regression model: CEC=(30+4.4 pH)*clay/100+(-34.66+29.72 pH)*OM/100; the clay is the % clay in the soil (Helling et al., 1964; regression based on CEC measured at various pH values on 60 different soils; CEC refers to the soil pH).

Table 20. NOEC values and soil parameters for soil invertebrates (accepted studies)

ORGANISM	TEST COMPOUND	TEST MEDIUM	PH	OM (%)	CLAY (%)	CEC	Cb (mg/kg dw)	EQ. TIME (d)	DURATION (d)	CRITERION	ADDED NOEC (mg/kg dw)	TOTAL NOEC (mg/kg dw)	REFERENCE
Cognetia sphagnetorum	$CuCl_2$	LUFA 2.2+peat+fungus	4.1	66	5.1	*60.6*	*10.7*	0	35	NOECg	63	73.7	Augustsson and Rundgren, 1998
Cognetia sphagnetorum	$CuCl_2$	LUFA 2.2+peat+algae	4.1	66	5.1	*60.6*	*10.7*	0	63	NOECg	441	451.7	Augustsson and Rundgren, 1998
Cognetia sphagnetorum	$CuCl_2$	LUFA 2.2+peat+algae	4.1	66	5.1	*60.6*	*10.7*	0	42	NOECg	312	322.7	Augustsson and Rundgren, 1998
Cognetia sphagnetorum	$CuCl_2$	LUFA 2.2+peat+algae	4.1	66	5.1	*60.6*	*10.7*	0	70	NOECf	455	465.7	Augustsson and Rundgren, 1998
Eisenia andrei	$CuCl_2$	OECD soil	6.2	10	20	*15.1*	*3.2*	0	84	NOECg	56	59.2	Van Dis et al., 1988
Eisenia andrei	$CuCl_2$	OECD soil	6.3-7.1	10	20	*16.6*	*3.2*	0	28	NOECr-cp	120	123.2	Van Gestel et al., 1989
Eisenia andrei	$CuCl_2$	OECD soil	6.2	10	20	*15.1*	6.1	0	84	NOECg	56	62	Van Gestel et al., 1991
Eisenia andrei	$CuCl_2$	Forest soil	5.6	<1	4	*2.9*	*3.7*	3	28	NOECm	*188	192	Svendsen and Weeks, 1997a
Eisenia andrei	$CuCl_2$	Forest soil	5.6	<1	4	*2.9*	*3.7*	3	28	NOECr-cp	*188	192	Svendsen and Weeks, 1997a
Eisenia andrei	Cu salt	OECD soil	6	10	20	*14.5*	*3.2*	0	28	NOECr-cp	100	103.2	Kula and Larink, 1997
Eisenia andrei	Cu salt	OECD soil	6	10	20	*14.5*	*3.2*	0	28	NOECr-jp	100	103.2	Kula and Larink, 1997
Eisenia andrei	Cu salt	LUFA 2.2	5.8	3.9	5.1	*8.3*	*5.2*	0	28	NOECr-cp	3.2	8.4	Kula and Larink, 1997
Eisenia fetida	$Cu(NO_3)_2$	OECD soil	6.3	10	20	*15.4*	2.4	0	56	NOECm	200	202.4	Spurgeon et al., 1994
Eisenia fetida	$Cu(NO_3)_2$	OECD soil	6.3	10	20	*15.4*	2.4	0	56	NOECr-cp	10	12.4	Spurgeon et al., 1994
Eisenia fetida	$Cu(NO_3)_2$	OECD soil	6.1	10	20	*14.8*	3.2	NR	21	NOECr-cp	29	32.3	Spurgeon and Hopkin, 1995
Eisenia fetida	$Cu(NO_3)_2$	OECD soil	6.1	10	20	*14.8*	3.2	NR	21	NOECg	725	728.2	Spurgeon and Hopkin, 1995
Eisenia fetida	$Cu(NO_3)_2$	OECD soil	6.1	10	20	*14.8*	3.2	NR	14	NOECm	293	296.2	Spurgeon and Hopkin, 1995
Eisenia fetida	$CuCl_2$	Sandy clay	6.5-7.0	3.9-5.5	13-16	*16.6*	15	1	21	NOECg	700	715	Scott-Fordsman et al., 2000a
Eisenia fetida	$CuCl_2$	Sandy clay	6.5-7.0	3.9-5.5	13-16	*16.6*	15	1	21	NOECr	100	115	Scott-Fordsman et al., 2000a
Eisenia fetida	$CuCl_2$	Loamy sand Gudow	3	8.2	7	5.8	2	7	28	NOECr	177	179	University of Ghent, 2004
Eisenia fetida	$CuCl_2$	Sandy loam Nottingham	3.4	8.3	13	6.7	17	7	28	NOECr	93.6	110.6	University of Ghent, 2004
Eisenia fetida	$CuCl_2$	Sandy clay loam Zegveld	4.7	37.3	24	35.3	70	7	28	NOECr	56.4	126	University of Ghent, 2004
Eisenia fetida	$CuCl_2$	Loamy sand Kovlinge	4.8	2.6	7	2.4	6	7	28	NOECr	48.2	54	University of Ghent, 2004
Eisenia fetida	$CuCl_2$	Sandy clay Souli	4.8	0.7	38	11.2	31	7	28	NOECr	179	210	University of Ghent, 2004

Table 20 (cont.). NOEC values and soil parameters for soil invertebrates (accepted studies)

ORGANISM	TEST COMPOUND	TEST MEDIUM	PH	OM (%)	CLAY (%)	CEC	Cb (mg/kg dw)	EQ. TIME (d)	DURATION (d)	CRITERION	ADDED NOEC (mg/kg dw)	TOTAL NOEC (mg/kg dw)	REFERENCE
Eisenia fetida	$CuCl_2$	Sandy loam Kovlinge	5.1	3.8	9	4.7	8	7	28	NOECr	86.8	95	University of Ghent, 2004
Eisenia fetida	$CuCl_2$	Loamy sand Montpellier	5.2	1.2	9	2.5	5	7	28	NOECr	54.9	60	University of Ghent, 2004
Eisenia fetida	$CuCl_2$	Sandy clay loam Woburn	6.4	7	21	23.4	22	7	28	NOECr	177	199	University of Ghent, 2004
Eisenia fetida	$CuCl_2$	Silt loam Ter Munck	6.8	1.6	15	8.9	22	7	28	ED10r	91.8	114	University of Ghent, 2004
Eisenia fetida	$CuCl_2$	Silty clay loam Vault de Lugny	7.3	2.3	38	26.2	21	7	28	NOECr	303	324	University of Ghent, 2004
Eisenia fetida	$CuCl_2$	Silty clay loam Rots	7.4	2	27	20	14	7	28	NOECr	289	303	University of Ghent, 2004
Eisenia fetida	$CuCl_2$	Clay Souli	7.4	4.2	46	36.3	34	7	28	NOECr	287	321	University of Ghent, 2004
Eisenia fetida	$CuCl_2$	Silt loam Marknesse	7.5	2	26	20.1	18	7	28	NOECr	153	171	University of Ghent, 2004
Eisenia fetida	$CuCl_2$	Clay Brecy	7.5	2.4	50	23.5	31	7	28	NOECr	164	195	University of Ghent, 2004
Eisenia fetida	$CuCl_2$	Sandy clay Hygum	5.4	3.3	23	6.7	21	7	28	NOECr	91.6	112.6	University of Ghent, 2004
Eisenia fetida	$CuCl_2$	LUFA 2.2	5			7.88	5.7	7	28	NOEC	81.9	87.6	University of Ghent, 2004
Eisenia fetida	$CuCl_2$	OECD soil	6.45			16.74	2.3	7	28	NOEC	186	188	University of Ghent, 2004
Eisenia fetida	$CuCl_2$	LUFA 2.2	5			7.88	5.7	7	28	NOEC	154	159	University of Ghent, 2004
Folsomia candida	$Cu(NO_3)_2$	OECD soil	6	10	20	*14.5*	*3.2*	2	28	NOECr	200	203.2	Sandifer and Hopkin, 1996
Folsomia candida	$Cu(NO_3)_2$	OECD soil	5	10	20	*11.5*	*3.2*	2	28	NOECm	40	43.2	Sandifer and Hopkin, 1996
Folsomia candida	$Cu(NO_3)_2$	OECD soil	5	10	20	*11.5*	*3.2*	2	28	NOECr	200	203.2	Sandifer and Hopkin, 1996
Folsomia candida	$Cu(NO_3)_2$	OECD soil	4.5	10	20	*10*	*3.2*	2	28	NOECr	1000	1003.2	Sandifer and Hopkin, 1996
Folsomia candida	$Cu(NO_3)_2$	OECD soil	6	10	20	*14.5*	*3.2*	2	28	NOECr	200	203.2	Sandifer and Hopkin, 1997

Table 20 (cont.). NOEC values and soil parameters for soil invertebrates (accepted studies)

ORGANISM	TEST COMPOUND	TEST MEDIUM	PH	OM (%)	CLAY (%)	CEC	Cb (mg/kg dw)	EQ. TIME (d)	DURATION (d)	CRITERION	ADDED NOEC (mg/kg dw)	TOTAL NOEC (mg/kg dw)	REFERENCE
Folsomia candida	$Cu(NO_3)_2$	OECD soil	6	10	20	*14.5*	*3.2*	2	42	NOECr	200	203.2	Sandifer and Hopkin, 1997
Folsomia candida	$Cu(NO_3)_2$	OECD soil	6	10	20	*14.5*	*3.2*	2	28	NOECm	1000	1003.2	Sandifer and Hopkin, 1997
Folsomia candida	$Cu(NO_3)_2$	OECD soil	6	10	20	*14.5*	*3.2*	2	42	NOECm	1000	1003.2	Sandifer and Hopkin, 1997
Folsomia candida	$CuCl_2$	LUFA 2.2	5.8	3.9	5.1	8.3	5.2	0	21	NOECg	200	205.2	Rundgren and Van Gestel, 1998
Folsomia candida	$CuCl_2$	LUFA 2.2	5.8	3.9	5.1	8.3	5.2	0	21	NOECr	400	405.2	Rundgren and Van Gestel, 1998
Folsomia candida	$CuCl_2$	OECD soil	6	10	20	14.5	3.2	0	56	NOECg	800	803.2	Rundgren and Van Gestel, 1998
Folsomia candida	$CuCl_2$	OECD soil	6	10	20	14.5	3.2	0	56	NOECr	400	403.2	Rundgren and Van Gestel, 1998
Folsomia candida	$CuCl_2$	OECD soil	6	10	20	14.5	3.2	7	28	NOECri	796.8	800	Herbert et al., 2004
Folsomia candida	$CuCl_2$	Sandy loam Nottingham	3.4	8.3	13	6.7	17	7	28	NOECr	174	191	Ghent University, 2004
Folsomia candida	$CuCl_2$	Loamy sand Houthalen	3.4	3	5	1.9	2	7	28	NOECr	28.2	31	Ghent University, 2004
Folsomia candida	$CuCl_2$	Loamy sand Rhydtalog	4.2	20.7	13	15.2	14	7	28	NOECr	279	293	Ghent University, 2004
Folsomia candida	$CuCl_2$	Sandy clay loam Zegveld	4.7	37.3	24	35.3	70	7	28	EDr	1390	1460	Ghent University, 2004
Folsomia candida	$CuCl_2$	Loamy sand Kovlinge	4.8	2.6	7	2.4	6	7	28	NOECr	55.5	61.5	Ghent University, 2004
Folsomia candida	$CuCl_2$	Sandy clay Souli	4.8	0.7	38	11.2	31	7	28	NOECr	53.1	84.1	Ghent University, 2004
Folsomia candida	$CuCl_2$	Loamy sand Montpellier	5.2	1.2	9	2.5	5	7	28	NOECr	172	177	Ghent University, 2004

Table 20 (cont.). NOEC values and soil parameters for soil invertebrates (accepted studies)

ORGANISM	TEST COMPOUND	TEST MEDIUM	PH	OM (%)	CLAY (%)	CEC	Cb (mg/kg dw)	EQ. TIME (d)	DURATION (d)	CRITERION	ADDED NOEC (mg/kg dw)	TOTAL NOEC (mg/kg dw)	REFERENCE
Folsomia candida	$CuCl_2$	Clay Aluminosa	5.4	1.4	51	22.6	21	7	28	NOECr	276	297	Ghent University, 2004
Folsomia candida	$CuCl_2$	Sandy clay loam Woburn	6.4	7	21	23.4	22	7	28	NOECr	244	266	Ghent University, 2004
Folsomia candida	$CuCl_2$	Silt loam Ter Munck	6.8	1.6	15	8.9	22	7	28	NOECr	237	259	Ghent University, 2004
Folsomia candida	$CuCl_2$	Silty clay loam Vault de Lugny	7.3	2.5	38	26.2	21	7	28	NOECr	534	555	Ghent University, 2004
Folsomia candida	$CuCl_2$	Silty clay loam Rots	7.4	2	27	20	14	7	28	NOECr	160	174	Ghent University, 2004
Folsomia candida	$CuCl_2$	Clay Souli	7.4	4.2	46	36.3	34	7	28	NOECr	887	921	Ghent University, 2004
Folsomia candida	$CuCl_2$	Silt loam Marknesse	7.5	2	26	20.1	18	7	28	NOECr	453	471	Ghent University, 2004
Folsomia candida	$CuCl_2$	Loam Barcelona	7.5	2.4	21	14.3	88	7	28	NOECr	139	227	Ghent University, 2004
Folsomia candida	$CuCl_2$	Clay Bercy	7.5	2.4	50	23.5	31	7	28	NOECr	632	663	Ghent University, 2004
Folsomia candida	$CuCl_2$	Loam Guadalajara	7.5	0.6	25	16.9	7	7	28	NOECr	538	545	Ghent University, 2004
Folsomia candida	$CuCl_2$	Sandy clay Hygum	5.4	3.3	23	6.7	21	7	28	NOECr	493	511	Ghent University, 2004
Folsomia candida	$CuCl_2$	Loamy sand Wageningen A	4.3	2.2	9	1.2	19	7	28	NOECr	27.9	45.4	Ghent University, 2004
Folsomia candida	$CuCl_2$	Loamy sand Wageningen D	5	2.3	9	1.9	19	7	28	NOECr	48	65.4	Ghent University, 2004
Folsomia candida	$CuCl_2$	Sandy clay Souli	4.8	0.7	38	11.2	31	7	28	NOECr	53.1	84.1	Ghent University, 2004
Folsomia candida	$CuCl_2$	Sand Woburn cake	6.5	0.3	8	11.6	35	7	28	NOECr	132	167	Ghent University, 2004

Table 20 (cont.). NOEC values and soil parameters for soil invertebrates (accepted studies)

ORGANISM	TEST COMPOUND	TEST MEDIUM	PH	OM (%)	CLAY (%)	CEC	Cb (mg/kg dw)	EQ. TIME (d)	DURATION (d)	CRITERION	ADDED NOEC (mg/kg dw)	TOTAL NOEC (mg/kg dw)	REFERENCE
Folsomia fimetaria	$CuCl_2$	LUFA 2.2	5.5	3.91	5	*7.8*	*5.2*	1	21	NOECm	800	805.2	Scott-Fordsman et al., 1997
Folsomia fimetaria	$CuCl_2$	LUFA 2.2	5.5	3.91	5	*7.8*	*5.2*	1	21	NOECg	542	547.2	Scott-Fordsman et al., 1997
Folsomia fimetaria	$CuCl_2$	LUFA 2.2	5.5	3.91	5	*7.8*	*5.2*	1	21	NOECg	845	850.2	Scott-Fordsman et al., 1997
Folsomia fimetaria	$CuCl_2$	LUFA 2.2	5.5	3.91	5	*7.8*	*5.2*	1	21	NOECg	400	405.2	Scott-Fordsman et al., 1997
Folsomia fimetaria	$CuCl_2$	Sandy clay	6.5-7.0	3.9-5.5	13-16	*16.6*	*15*	1	21	NOECm	1000	1015	Scott-Fordsman et al., 2000b
Folsomia fimetaria	$CuCl_2$	Sandy clay	6.5-7.0	3.9-5.5	13-16	*16.6*	*15*	1	21	NOECm	600	615	Scott-Fordsman et al., 2000b
Folsomia fimetaria	$CuCl_2$	Sandy clay	6.5-7.0	3.9-5.5	13-16	*16.6*	*15*	1	21	NOECm	1000	1015	Scott-Fordsman et al., 2000b
Folsomia fimetaria	$CuCl_2$	Sandy clay	6.5-7.0	3.9-5.5	13-16	*16.6*	*15*	1	21	NOECg	1000	1015	Scott-Fordsman et al., 2000b
Folsomia fimetaria	$CuCl_2$	Sandy clay	6.5-7.0	3.9-5.5	13-16	*16.6*	*15*	1	21	NOECg	1000	1015	Scott-Fordsman et al., 2000b
Folsomia fimetaria	$CuCl_2$	Sandy clay	6.5-7.0	3.9-5.5	13-16	*16.6*	*15*	1	21	NOECg	1000	1015	Scott-Fordsman et al., 2000b
Folsomia fimetaria	$CuCl_2$	Sandy clay	6.5-7.0	3.9-5.5	13-16	*16.6*	*15*	1	21	NOECr	400	415	Scott-Fordsman et al., 2000b
Folsomia fimetaria	$CuSO_4$	Sandy clay Hygum	6.7	4.5	13.8	*15.6*	19	0	21	EC10r	122	141	Pedersen et al., 2000b
Folsomia fimetaria	$CuSO_4$	Sandy clay Hygum	6.7	4.5	13.8	*15.6*	19	1	21	EC10r	698	717	Pedersen et al., 2001
Folsomia fimetaria	$CuSO_4$	Sandy clay Hygum	6.7	4.5	13.8	*15.6*	19	7	21	EC10r	776	795	Pedersen et al., 2001
Folsomia fimetaria	$CuSO_4$	Sandy clay Hygum	6.7	4.5	13.8	*15.6*	19	35	21	EC10r	888	907	Pedersen et al., 2001
Folsomia fimetaria	$CuSO_4$	Sandy clay Hygum	6.7	4.5	13.8	*15.6*	19	84	21	EC10r	648	667	Pedersen et al., 2001

Table 20(cont.) NOEC values and soil parameters for soil invertebrates (accepted studies)

ORGANISM	TEST COMPOUND	TEST MEDIUM	PH	OM (%)	CLAY (%)	CEC	Cb (mg/kg dw)	EQ. TIME (d)	DURATION (d)	CRITERION	ADDED NOEC (mg/kg dw)	TOTAL NOEC (mg/kg dw)	REFERENCE
Folsomia fimetaria	$CuSO_4$	Sandy clay Hygum	6.7	4.5	13.8	*15.6*	19	NR	21	EC10r	688	707	Pedersen et al., 2001
Hypoaspis aculeifer	$CuCl_2$	LUFA 2.2	5.8	3.9	5.1	*8.3*	*5.2*	0	21	NOECr	174	179.2	Krogh and Axelsen, 1998
Isotoma viridis	$CuCl_2$	LUFA 2.2	5.8	3.9	5.1	*8.3*	*5.2*	0	56	NOECg	50	55.2	Rundgren and Van Gestel, 1998
Isotoma viridis	$CuCl_2$	OECD soil	6	10	20	*14.59*	*3.2*	0	56	NOECg	400	403.2	Rundgren and Van Gestel, 1998
Lumbricus rubellus	$CuCl_2$	Sandy loam	7.3	8	17	*25.3*	12	0	84	NOECm	150	162	Ma, 1982
Lumbricus rubellus	$CuCl_2$	Loamy sand	4.8	5.7	2	*7.2*	14	0	42	NOECr	*40	54	Ma, 1984
Lumbricus rubellus	$CuCl_2$	Loamy sand	4.8	5.7	2	*7.2*	14	0	42	NOEClb	*40	54	Ma, 1984
Lumbricus rubellus	$CuCl_2$	Loamy sand	4.8	5.7	2	*7.2*	14	0	42	NOECg	*117	131	Ma, 1984
Lumbricus rubellus	$CuCl_2$	Loamy sand	4.8	5.7	2	*7.2*	14	0	42	NOECm	*117	131	Ma, 1984
Lumbricus rubellus	$CuCl_2$	Calcareous sandy loam	7.3	3.4	17	*16.9*	13	0	42	NOEClb	*50	63	Ma, 1984
Lumbricus rubellus	$CuCl_2$	Calcareous sandy loam	7.3	3.4	17	*16.9*	13	0	42	NOECm	*123	136	Ma, 1984
Lumbricus rubellus	$CuCl_2$	Forest soil	5.6	<1	4	*2.9*	3	5	110	NOECg	*73	76	Svendsen and Weeks, 1997b
Lumbricus rubellus	$CuCl_2$	Forest soil	5.6	<1	4	*2.9*	3	5	110	NOECm	*150	153	Svendsen and Weeks, 1997b
Lumbricus rubellus	$CuCl_2$	Clay loam	7.2-7.8	9.6-9.95	41	*44.2*	14.4	14	294	NOECg	139.6	154	Spurgeon et al., 2004
Plectus acuminatus	$CuCl_2$	OECD soil	5.5	10	20	*13*	3.2	5h	21	NOECr-jp	32	35.2	Kammenga et al., 1996
Platynothrus peltifer	$CuCl_2$	LUFA 2.2	5.8	3.9	5.1	*8.3*	*5.2*	0	70-d	NOECr-jp	63	68.2	Van Gestel and Doornekamp, 1998

Table 20 (cont.) NOEC values and soil parameters for soil invertebrates (accepted studies)

ORGANISM	TEST COMPOUND	TEST MEDIUM	PH	OM (%)	CLAY (%)	CEC	Cb (mg/kg dw)	EQ. TIME (d)	DURATION (d)	CRITERION	ADDED NOEC (mg/kg dw)	TOTAL NOEC (mg/kg dw)	REFERENCE
Platynothrus peltifer	$CuCl_2$	LUFA 2.2	5.8	3.9	5.1	*8.3*	*5.2*	0	70-d	NOECr-jp	63	68.2	Van Gestel and Doornekamp, 1998
Platynothrus peltifer	$CuCl_2$	LUFA 2.2	5.8	3.9	5.1	*8.3*	*5.2*	0	70-d	NOECr-jp	63	68.2	Van Gestel and Doornekamp, 1998

NOEC- no observed effect concentration; NOEC indices: m: mortality, r: reproduction (based on cocoon production (cp), juvenile production (jp)); h: hatching success, g: growth, ab: abundance, f: fragmentation, lb: litter breakdown, mi: maturity index; ri: Instantaneous rate of population increase.

Estimated background copper concentrations and CEC are indicated in italics.

Cb- measured concentration

If the CEC was missing from a test with plants/invertebrates/micro-organisms, then it was estimated from % clay, pH and %organic matter using an experimentally derived regression model: CEC=(30+4.4 pH)*clay/100+(-34.66+29.72 pH)*OM/100; the clay is the % clay in the soil (Helling et al., 1964; regression based on CEC measured at various pH values on 60 different soils; CEC refers to the soil pH).

Table 21. NOEC values, soil parameters, and microbial processes for soil microorganisms (accepted studies)

MICROBIAL PROCESS	TEST COMPOUND	TEST MEDIUM	PH	OM (%)	CLAY (%)	CEC	Cb (mg/kg dw)	DURATION (d)	ADDED NOEC (mg/kg dw)	TOTAL NOEC (mg/kg dw)	REFERENCE
Respiration	$CuCl_2$	Sand	7.7	1.6	2	4.4	4	490	150	154	Doelman and Haanstra, 1984
Respiration	$CuCl_2$	Sandy peat	4.3	12.8	5	14.5	5.5	574	400	406	Doelman and Haanstra, 1984
N-mineralization	$CuSO_4$	Sandy loam	5.9	3.4	16	13.8	33	21	100	133	Quraishi and Cornfield, 1973
Nitrification	$CuSO_4$	Sandy loam	5.9	3.4	16	13.8	33	21	100	133	Quraishi and Cornfield, 1973
Nitrification	$CuSO_4$	Sandy loam	7.3	3.4	16	16.3	33	21	100	133	Quraishi and Cornfield, 1973
Ammonification (aerobic)	$CuSO_4$	Sandy loam	7.1	3.4	17	16.5	33	21	1000	1033	Premi and Cornfield, 1969
Nitrification	$CuSO_4$	Sandy loam	7.1	3.4	17	16.5	33	21	1000	1033	Premi and Cornfield, 1969
Glutamic acid decomposition	$CuCl_2$	Silty loam	7.4	2.4	19	16.5	22	540	55	77	Haanstra and Doelman, 1984
Glutamic acid decomposition	$CuCl_2$	Clay	6.8	3.2	60	41.6	52	540	55	107	Haanstra and Doelman, 1984
Glutamic acid decomposition	$CuCl_2$	Sandy peat	4.3	12.8	5	14.5	5.5	540	400	406	Haanstra and Doelman, 1984
Microbial biomass C	$Cu(NO_3)_2$	Grassland soil	6.3	10.1	29.8	61.4	32	49	118	150	Speir et al., 1999
Microbial biomass N	$Cu(NO_3)_2$	Grassland soil	6.3	10.1	29.8	61.4	32	49	468	500	Speir et al., 1999
N-mineralization	$Cu(NO_3)_2$	Grassland soil	6.3	10.1	29.8	61.4	32	49	268	300	Speir et al., 1999
Substrate induced respiration	$Cu(NO_3)_2$	Loam	6.1	20.4	32	48.5	10.7	7	635	645.7	Speir et al., 1999
Substrate induced respiration	$Cu(NO_3)_2$	Silt loam	6.3	13.8	2.5	22.7	10.7	7	635	645.7	Speir et al., 1999
Nitrification	$CuCl_2$	Sandy loam Nottingham	3.4	8.3	13	6.7	17	28	200	217	University of Leuven, 2004
Nitrification	$CuCl_2$	Sandy clay loam Zegveld	4.7	37.3	24	35.3	70	4	1200	1270	University of Leuven, 2004
Nitrification	$CuCl_2$	Loamy sand Kovlinge I	4.8	2.6	7	2.4	6	28	25	31	University of Leuven, 2004
Nitrification	$CuCl_2$	Sandy clay Souli I	4.8	0.7	38	11.2	31	28	25	56	University of Leuven, 2004

Table 21 (cont.). NOEC values, soil parameters, and microbial processes for soil microorganisms (accepted studies)

MICROBIAL PROCESS	TEST COMPOUND	TEST MEDIUM	PH	OM (%)	CLAY (%)	CEC	Cb (mg/kg dw)	DURATION (d)	ADDED NOEC (mg/kg dw)	TOTAL NOEC (mg/kg dw)	REFERENCE
Nitrification	$CuCl_2$	Sandy loam Kovlinge II	5.1	3.8	9	4.7	8	14	50	58	University of Leuven, 2004
Nitrification	$CuCl_2$	Clay Aluminosa	5.4	1.4	51	22.6	21	28	100	121	University of Leuven, 2004
Nitrification	$CuCl_2$	Sandy clay loam Woburn	6.4	7.0	21	23.4	22	4	300	322	University of Leuven, 2004
Nitrification	$CuCl_2$	Silt loam Ter Munck	6.8	1.6	15	8.9	22	7	200	222	University of Leuven, 2004
Nitrification	$CuCl_2$	Silty clay loam Vault de Lugny	7.3	2.3	38	26.2	21	4	800	821	University of Leuven, 2004
Nitrification	$CuCl_2$	Silty clay loam Rots	7.4	2.0	27	20	14	7	400	414	University of Leuven, 2004
Nitrification	$CuCl_2$	Clay Souli II	7.4	4.2	46	36.3	34	14	600	634	University of Leuven, 2004
Nitrification	$CuCl_2$	Silt loam Marknesse	7.5	2.0	26	20.1	18	7	800	818	University of Leuven, 2004
Nitrification	$CuCl_2$	Loam Barcelona	7.5	2.4	21	14.3	88	11	300	388	University of Leuven, 2004
Nitrification	$CuCl_2$	Clay Brecy	7.5	2.4	50	23.5	31	4	400	431	University of Leuven, 2004
Nitrification	$CuCl_2$	Loam Guadalajara	7.5	0.6	25	16.9	7	7	52	59	University of Leuven, 2004
Nitrification	$CuCl_2$	Sandy clay Hygum	5.4	3.3	23	6.7	21	14	127	148	University of Leuven, 2004
Nitrification	$CuCl_2$	Loamy sand Wageningen D	5	2.3	9	1.9	19	18	65	84	University of Leuven, 2004
Nitrification	$CuCl_2$	Sand Woburn salt	6.5	0.2	8	8.4	13	14	100	113	University of Leuven, 2004
Nitrification	$CuCl_2$	Sand Woburn cake	6.5	0.3	8	11.6	35	14	50	85	University of Leuven, 2004
Glucose respiration	$CuCl_2$	Loamy sand Gudow	3	8.2	7	5.8	2	4	1200	1202	University of Leuven, 2004

Table 21 (cont.). NOEC values, soil parameters, and microbial processes for soil microorganisms (accepted studies)

MICROBIAL PROCESS	TEST COMPOUND	TEST MEDIUM	PH	OM (%)	CLAY (%)	CEC	Cb (mg/kg dw)	DURATION (d)	ADDED NOEC (mg/kg dw)	TOTAL NOEC (mg/kg dw)	REFERENCE
Glucose respiration	$CuCl_2$	Sandy loam Nottingham	3.4	8.3	13	6.7	17	4	150	167	University of Leuven, 2004
Glucose respiration	$CuCl_2$	Loamy sand Houthalen	3.4	3.0	5	1.9	2	4	50	52	University of Leuven, 2004
Glucose respiration	$CuCl_2$	Loamy sand Rhydtalog	4.2	20.7	13	15.2	14	4	600	614	University of Leuven, 2004
Glucose respiration	$CuCl_2$	Sandy clay loam Zegveld	4.7	37.3	24	35.3	70	4	100	170	University of Leuven, 2004
Glucose respiration	$CuCl_2$	Loamy sand Kovlinge I	4.8	2.6	7	2.4	6	4	25	31	University of Leuven, 2004
Glucose respiration	$CuCl_2$	Sandy clay Souli I	4.8	0.7	38	11.2	31	4	100	131	University of Leuven, 2004
Glucose respiration	$CuCl_2$	Sandy loam Kovlinge II	5.1	3.8	9	4.7	8	4	50	58	University of Leuven, 2004
Glucose respiration	$CuCl_2$	Loamy sand Montpellier	5.2	1.2	9	2.5	5	4	25	30	University of Leuven, 2004
Glucose respiration	$CuCl_2$	Clay Aluminosa	5.4	1.4	51	22.6	21	4	400	421	University of Leuven, 2004
Glucose respiration	$CuCl_2$	Sandy clay loam Woburn	6.4	7.0	21	23.4	22	4	300	321	University of Leuven, 2004
Glucose respiration	$CuCl_2$	Silt loam Ter Munck	6.8	1.6	15	8.9	22	4	50	72	University of Leuven, 2004
Glucose respiration	$CuCl_2$	Silty clay loam Vault de Lugny	7.3	2.3	38	26.2	21	4	102	123	University of Leuven, 2004
Glucose respiration	$CuCl_2$	Silty clay loam Rots	7.4	2.0	27	20	14	4	200	214	University of Leuven, 2004
Glucose respiration	$CuCl_2$	Clay Souli II	7.4	4.2	46	36.3	34	4	89	123	University of Leuven, 2004
Glucose respiration	$CuCl_2$	Silt loam Marknesse	7.5	2.0	26	20.1	18	4	23	41	University of Leuven, 2004
Glucose respiration	$CuCl_2$	Loam Barcelona	7.5	2.4	21	14.3	88	4	300	388	University of Leuven, 2004

Table 21 (cont.). NOEC values, soil parameters, and microbial processes for soil microorganisms (accepted studies)

MICROBIAL PROCESS	TEST COMPOUND	TEST MEDIUM	PH	OM (%)	CLAY (%)	CEC	Cb (mg/kg dw)	DURATION (d)	ADDED NOEC (mg/kg dw)	TOTAL NOEC (mg/kg dw)	REFERENCE
Glucose respiration	$CuCl_2$	Clay Brecy	7.5	2.4	50	23.5	31	4	200	231	University of Leuven, 2004
Glucose respiration	$CuCl_2$	Loam Guadalajara	7.5	0.6	25	16.9	7	4	50	57	University of Leuven, 2004
Glucose respiration	$CuCl_2$	Sandy clay Hygum	5.4	3.3	23	6.7	21	4	170	191	University of Leuven, 2004
Glucose respiration	$CuCl_2$	Loamy sand Wageningen A	4.3	2.2	9	1.2	19	4	12	31	University of Leuven, 2004
Glucose respiration	$CuCl_2$	Loamy sand Wageningen D	5	2.3	9	1.9	19	4	25	44	University of Leuven, 2004
Glucose respiration	$CuCl_2$	Sand Woburn salt	6.5	0.2	8	8.4	13	4	100	113	University of Leuven, 2004
Glucose respiration	$CuCl_2$	Sand Woburn cake	6.5	0.3	8	11.6	35	4	27	62	University of Leuven, 2004
Maize respiration	$CuCl_2$	Loamy sand Gudow	3	8.2	7	5.8	2	28	2400	2402	University of Leuven, 2004
Maize respiration	$CuCl_2$	Sandy loam Nottingham	3.4	8.3	13	6.7	17	28	1200	1217	University of Leuven, 2004
Maize respiration	$CuCl_2$	Loamy sand Rhydtalog	4.2	20.7	13	15.2	14	28	1200	1214	University of Leuven, 2004
Maize respiration	$CuCl_2$	Sandy clay loam Zegveld	4.7	37.3	24	35.3	70	28	300	370	University of Leuven, 2004
Maize respiration	$CuCl_2$	Loamy sand Kovlinge I	4.8	2.6	7	2.4	6	28	50	56	University of Leuven, 2004
Maize respiration	$CuCl_2$	Sandy clay Souli II	4.8	0.7	38	11.2	31	28	200	231	University of Leuven, 2004
Maize respiration	$CuCl_2$	Sandy loam Kovlinge II	5.1	3.8	9	4.7	8	28	100	108	University of Leuven, 2004
Maize respiration	$CuCl_2$	Loamy sand Montpellier	5.2	1.2	9	2.5	5	28	50	55	University of Leuven, 2004
Maize respiration	$CuCl_2$	Clay Aluminosa	5.4	1.4	51	22.6	21	28	400	421	University of Leuven, 2004

Table 21 (cont.). NOEC values, soil parameters, and microbial processes for soil microorganisms (accepted studies)

MICROBIAL PROCESS	TEST COMPOUND	TEST MEDIUM	PH	OM (%)	CLAY (%)	CEC	Cb (mg/kg dw)	DURATION (d)	ADDED NOEC (mg/kg dw)	TOTAL NOEC (mg/kg dw)	REFERENCE
Maize respiration	$CuCl_2$	Sandy clay loam Woburn	6.4	7.0	21	23.4	22	28	150	172	University of Leuven, 2004
Maize respiration	$CuCl_2$	Silt loam Ter Munck	6.8	1.6	15	8.9	22	28	50	72	University of Leuven, 2004
Maize respiration	$CuCl_2$	Silty clay loam Vault de Lugny	7.3	2.3	38	26.2	21	28	400	421	University of Leuven, 2004
Maize respiration	$CuCl_2$	Clay Souli II	7.4	4.2	46	36.3	34	28	600	634	University of Leuven, 2004
Maize respiration	$CuCl_2$	Silt loam Marknesse	7.5	2.0	26	20.1	18	28	150	168	University of Leuven, 2004
Maize respiration	$CuCl_2$	Loam Barcelona	7.5	2.4	21	14.3	88	28	150	238	University of Leuven, 2004
Maize respiration	$CuCl_2$	Loamy sand Wageningen A	4.3	2.2	9	1.2	19	28	51	70	University of Leuven, 2004
Maize respiration	$CuCl_2$	Loamy sand Wageningen D	5	2.3	9	1.9	19	28	83	102	University of Leuven, 2004
Maize respiration	$CuCl_2$	Sand Woburn cake	6.5	0.3	8	11.6	35	28	100	135	University of Leuven, 2004

NOEC- no observed effect concentration;

Estimated background copper concentrations and CEC are indicated in italics.

If the CEC was missing from a test with plants/invertebrates/micro-organisms, then it was estimated from % clay, pH and %organic matter using an experimentally derived regression model: CEC=(30+4.4 pH)*clay/100+(-34.66+29.72 pH)*OM/100; the clay is the % clay in the soil (Helling et al., 1964; regression based on CEC measured at various pH values on 60 different soils; CEC refers to the soil pH).

7.1.4. Normalization of chronic toxicity values for copper bioavailability

Toxicity data for soil organisms was found to be very variable and research results showed that differences in toxicity can be attributed to differences in bioavailability due to soil properties and to differences in ageing and application mode and rate. Regarding the bioavailability of Cu in soils, two factors on the ecotoxicity of Cu to soil organisms are apparent:

- Toxicity is highly dependent on soil type
- Toxicity is highly dependent on time

For the risk assessment of Cu in the terrestrial environment, these two factors have to be taken into account to assess Cu bioavailability.

7.1.5. Regression models

Regression models were applied to the database to predict copper toxicity to terrestrial organisms and the soil parameter that best explained variability in copper toxicity was the CEC. Therefore, the regression models were applied to the database and significantly reduced variability and allow the derivation of meaningful geometric mean NOEC/EC_{10} values for each endpoint. Normalized NOEC/EC_{10} geometric mean are summarized in Table 22.

Table 22. Normalized geometric mean NOEC/EC_{10} values following the application of regression models.

	Non-normalised	Normalised
Plants		
Hordeum vulgare – root elongation (n=20)	15.3	6.0
Lycopersicon esculentum – growth (n=21)	24.1	10.8
Avena sativa – yield grain (n=5)	1.1	2.9
Invertebrates		
Eisenia andrei – reproduction (n=4)	1.9*	4.7*
Eisenia fetida – reproduction (n=23)	10.3*	10.0*
Folsomia candida – reproduction (n=28)	48.5	16.3
Folsomia fimetaria – reproduction	6.8	6.8
Isotoma viridis – growth (n=2)	7.3	4.5
Cognettia sphagnetorum – growth (n=3)	6.5	6.5
Lumbriculus rubellus – litter breakdown (n=2)	1.2	1.4

Table 22 (cont.). Normalized geometric mean NOEC/EC_{10} values following the application of regression models.

	Non-normalised	Normalised
Microbial functions		
Microbial biomass (n=2)	3.6	3.6
Nitrification (n=22)	63.3	18.7
Substrate induced respiration (n=26)	72.9**	15.8**
Maize induced respiration (n=18)	45.9	14.9
Respiration (n=2)	13.9	12.7
Glutamic acid decomposition (n=3)	6.1	8.0
N-mineralisation (n=2)	2.4	2.0

*: without the toxicity data from Kula & Larink (1998); **: based on EC_{10} values

7.1.6. Leaching-ageing factor

Following the addition of Cu to soils, several reactions may occur that change the concentration of Cu in the soil pore water and the fraction of added Cu available to organisms. Ageing is defined as the slow reactions that occur after soluble Cu is added to soil and after initial partitioning of Cu between solution and solid phases in soil, defined as occurring in the first 24 hours following Cu addition.

It has been concluded that there are sufficient reasons to assume that the toxicity under field conditions is less than under laboratory conditions, and a reasonable worst case generic leaching/ageing of 2.0 is proposed for all soils. This factor is based on the 25 percentile of an extensive ecotoxicity dataset and is supported by mechanistic data. This generic leaching-ageing factor will be used on all individual $NOEC_{add}$ values of tests starting within 120 days after spiking to generate aged $NOEC_{add}$ values. For $NOEC_{add}$ values of tests in soils that have equilibrated for more than 120 days after spiking, the leaching/ageing factor is 1.0.

For the normalization of the ecotoxicity data first the leaching/ageing factor was applied to the $NOEC_{add}$ values, which represent NOEC values from the database corrected for the background Cu concentration (or the background concentration was subtracted from NOEC measured values or NOEC nominal values were used). Secondly, the Cu background concentration was added to the NOEC values corrected for leaching/ageing factor and NOEC values were sorted into 6 different groups representing EU soils using relevant regression models. Normalised NOEC/EC_{10} values used for PNEC derivation are summarized in Table 23.

Table 23. Individual aged/normalised NOEC values for the different soil scenarios

Species sensitivity	Normalised NOEC (mg/kg)	Species sensitivity	Normalised NOEC (mg/kg)	Species sensitivity	Normalised NOEC (mg/kg)	Species sensitivity	Normalised NOEC (mg/kg)	Species sensitivity	Normalised NOEC (mg/kg)	Species sensitivity	Normalised NOEC (mg/kg)
Sweden – Acid Sandy soil		**The Netherlands – Loamy soil**		**The Netherlands – Peaty soil**		**Germany – Acid Sandy soil**		**Greece - Clay soil**		**Spain – loamy soil**	
Denitrification	20.0	P. acuminatus	86.3	P. acuminatus	119.4	P. acuminatus	42.9	P. acuminatus	121.3	P. acuminatus	66.6
P. acuminatus	25.2	Glutamic acid	109.2	E. andrei	189.9	Denitrification	52.9	E. andrei	193.1	Glutamic acid	98.5
N-mineralisation	25.8	E. andrei	137.3	L. rubellus	201.1	N-mineralisation	68.1	L. rubellus	204.4	E. andrei	106.0
P. peltifer	40.0	L. rubellus	145.3	H. vulgare	305.8	E. andrei	68.3	Respiration	246.5	L. rubellus	112.2
E. andrei	40.1	Respiration	149.3	C. sphagnetorum	310.2	L. rubellus	72.3	Glutamic acid	259.3	Denitrification	118.2
L. rubellus	42.5	Microbial biomass	154.5	E. fetida	340.9	H. vulgare	90.6	MR	268.3	Microbial biomass	139.3
H. vulgare	48.1	MR	162.5	Denitrification	343.3	P. peltifer	96.4	H. vulgare	311.8	N-mineralisation	152.0
Glutamic acid	59.3	Denitrification	189.7	L. perenne	378.7	C. sphagnetorum	111.5	C. sphagnetorum	315.3	H. vulgare	152.8
L. perenne	59.6	H. vulgare	207.8	N-mineralisation	441.5	L. perenne	112.2	E. fetida	346.6	C. sphagnetorum	173.1
C. sphagnetorum	65.6	C. sphagnetorum	224.2	S. vulgaris	502.8	E. fetida	122.6	Denitrification	353.7	L. perenne	189.2
Nitrification	66.3	N-mineralisation	244.0	P. peltifer	523.9	Glutamic acid	139.0	Microbial biomass	366.9	E. fetida	190.2
I. viridis	67.7	SIR	244.1	P. annua	568.6	S. vulgaris	148.9	L. perenne	386.1	P. peltifer	199.5
E. fetida	72.1	E. fetida	246.4	P. convolvulus	660.2	I. viridis	163.1	N-mineralisation	454.9	SIR	220.1
S. vulgaris	79.1	L. perenne	257.4	A. integrifolia	728.3	P. annua	168.4	S. vulgaris	512.7	S. vulgaris	251.2

Table 23 (cont.). Individual aged/normalised NOEC values for the different soil scenarios

Species sensitivity	Normalised NOEC (mg/kg)	Species sensitivity	Normalised NOEC (mg/kg)	Species sensitivity	Normalised NOEC (mg/kg)	Species sensitivity	Normalised NOEC (mg/kg)	Species sensitivity	Normalised NOEC (mg/kg)	Species sensitivity	Normalised NOEC (mg/kg)
Sweden – Acid Sandy soil		**The Netherlands – Loamy soil**		**The Netherlands – Peaty soil**		**Germany – Acid Sandy soil**		**Greece - Clay soil**		**Spain – loamy soil**	
Microbial biomass	83.9	P. peltifer	306.2	A. sativa	792.7	Nitrification	175.2	P. peltifer	538.3	P. annua	284.0
L. esculentum	85.3	S. vulgaris	341.7	Glutamic acid	864.9	P. convolvulus	195.5	SIR	579.6	Respiration	299.5
P. annua	89.5	P. annua	386.5	I. viridis	886.7	Microbial biomass	196.7	P. annua	579.7	MR	326.0
P. convolvulus	103.9	P. convolvulus	448.8	L. esculentum	1117.4	L. esculentum	205.5	P. convolvulus	673.2	P. convolvulus	329.8
H. aculeifer	107.7	A. integrifolia	495.0	Nitrification	1135.9	A. integrifolia	215.7	A. integrifolia	742.6	I. viridis	337.6
A. integrifolia	114.6	I. viridis	518.2	H. radicata	1221.7	A. sativa	234.8	A. sativa	808.3	A. integrifolia	363.8
F. candida	118.8	A. sativa	538.8	Microbial biomass	1223.7	H. aculeifer	259.5	I. viridis	911.0	Nitrification	391.1
A. sativa	124.8	Nitrification	627.7	H. aculeifer	1410.5	F. candida	286.2	L. esculentum	1148.0	A. sativa	396.0
SIR	132.5	L. esculentum	652.9	F. candida	1555.8	SIR	310.7	Nitrification	1170.4	L. esculentum	425.4
F. fimetaria	174.1	H. aculeifer	824.2	SIR	1933.3	H. radicata	361.8	H. radicata	1245.7	H. aculeifer	537.0
H. radicata	192.3	H. radicata	830.4	Respiration	1999.9	F. fimetaria	419.6	H. aculeifer	1449.2	F. candida	592.3
Ammonification	262.9	F. candida	909.2	MR	2176.5	Ammonification	694.4	F. candida	1598.5	H. radicata	610.3
Respiration	268.6	F. fimetaria	1333.0	F. fimetaria	2281.1	Respiration	2125.9	F. fimetaria	2343.7	F. fimetaria	868.5
MR	292.3	Ammonification	2487.9	Ammonification	4502.5	MR	2313.7	Ammonification	4639.0	Ammonification	1550.2

7.1.7. Derivation of the Predicted No Effect Concentration terrestrial compartment ($PNEC_{soil}$)

Derivation of HC5-50 values

A Species Sensitivity Distributions (SSD) was constructed using the normalised NOEC/EC_{10} data. Using the SSD fitting model, the median fifth percentile (HC_5) was derived using the log-normal model and the best-fit models for a range of EU soil types. The latter gives the smallest uncertainty around the HC_5.
HC_{5-50} values calculated for the different soil types are presented in Table 24.

Table 24. HC_{5-50} derived from the SSD best fitting distribution

Scenario	HC_{5-50} (mg/kg) using the best fit distribution	HC_{5-50}(mg/kg) using the log-normal distribution
Acid sandy soil - Sweden *	20.4 *	25.3 *
Loamy soil - The Netherlands	89.6	**87.7**
Peaty soil - The Netherlands	172.8	**172.8**
Acid sandy soil – Germany*	47.6 *	38.9 *
Clay soil - Greece	142.4	**141.5**
Loamy soil - Spain *	73.1	**78.9**

* CEC < 10P of the CEC in EU soils

The HC_{5-50} values ranged between 20.4 and 172.8 mg Cu/kg dw for the defined soil types using the best-fit model and between 25.3and 172.8 mg Cu/kg dw using the log-normal model.

PNEC derivation for the terrestrial compartment

Based on the above uncertainty analysis it can be concluded that the available database and models allow for the derivation of an HC_{5-50}, which is protective for the terrestrial environment. The application of an AF = 1 is therefore proposed on the HC_{5-50} derived with the statistical extrapolation method. This provides a robust and ecological relevant PNEC to be retained for the risk characterisation. PNEC values for soil types with physico-chemical properties **within the 10-90 percentile** bounderies of the EU conditions vary between 73.1 and 172.8 mg Cu /kg dw (statistical extrapolation method using the best fit distribution) and between 78.9 and 172.8 mg Cu/kg dw (statistical extrapolation method using the log-normal distribution).
For the risk characterization, the **PNECsoil** derived from the log-normal distribution have been carried forward and are between **78.9 and 172.8 mg Cu/kg dw**.

8. REGIONAL RISK CHARACTERIZATION

8.1. Introduction

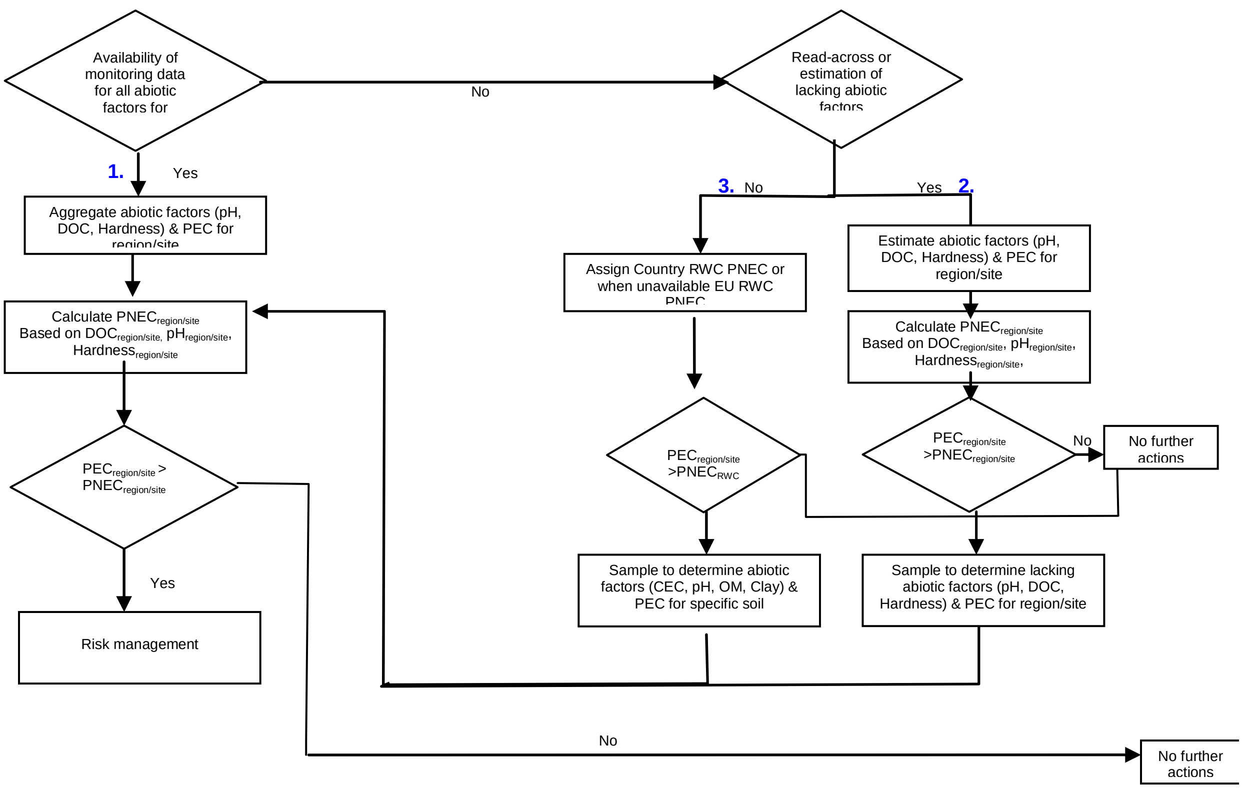
Copper is an essential nutrient and natural copper levels available for plants, animals and microorganisms are dependent on the natural geological and physico-chemical properties of the environment. This risk characterization used a total risk approach that includes the background copper concentration and anthropogenic emissions.

For the risk characterization, PNECs previously calculated for the different environmental compartments, the PEC values based on measured concentrations or models and the corresponding PEC/PNEC values for the environmental compartments surface water, sediment and soil are calculated.
The risk characterization used the available information on bioavailability in a step-wise approach.

8.1.1. Aquatic environment

The risk characterization used the available information on bioavailability in a step-wise approach. The proposed step-wise approach methodology for risk characterization for the aquatic environment is presented in Figure 2 and then described in more detail below.

Figure 2. Step-wise approach for the aquatic environment risk characterization



Water compartment

Step-wise approach 1: paired PEC/PNECs

For regional monitoring sites, where measured copper concentrations as well as measured data on abiotic parameters including pH, DOC, and hardness are available, Bio-Ligand model (BML) normalised PNECs are calculated. For each paired set of monitoring data, the copper concentrations are then compared to BLM-PNECs. This allowed deriving region-specific cumulative frequency distributions of the risk characterization ratio (RCR) and thus an evaluation of the probability of risk for the region considered. The region-specific risk ratio is then further calculated in analogy to the TGD methodology for the PEC-regional derivations:

- where for each site within a region data are available over time, the 90th P for each site is derived and the average of the risk ratio's across the sites within a region is calculated;
- where for each site within a region data have been taken only once the 90th P of the risk ratio's across the sites within a region is calculated.

Step-wise approach 2: estimation of the PNECs for the site

The regional risk characterization is carried out by comparing the regional PEC with the range of PNECs obtained from uncoupled data for the same region or similar region.

Step-wise approach 3: use of the worst-case PNEC value for Europe

Site-specific PEC values are compared with the reasonable worst-case PNEC value for Europe.

Sediment compartment

For the sediment compartment a similar approach was taken.

Step-wise approach 1: This approach was used when detailed data on OC and AVS of the region and region specific PNECs could be calculated and compared with the PEC for the region. The risks for the region can then be calculated from comparing the $PEC_{AVS\ normalised}$ and the $PNEC_{normalised,\ OC\ site\ specific}$ accounting for site specific information on the OC and AVS content using the following equation:

$$RCR = \frac{PEC_{AVSnormalized}}{PNEC_{normalized,\,OC(5\%)} \times \frac{fOC_{site}}{0.05}}$$

For the regional assessment, data from the AVS-SEM monitoring campaigns, allowed to assess the copper fraction not bound to AVS and this assessment was included in the regional RCR.

Step-wise approach 2: no step-wise approach 2 was carried out

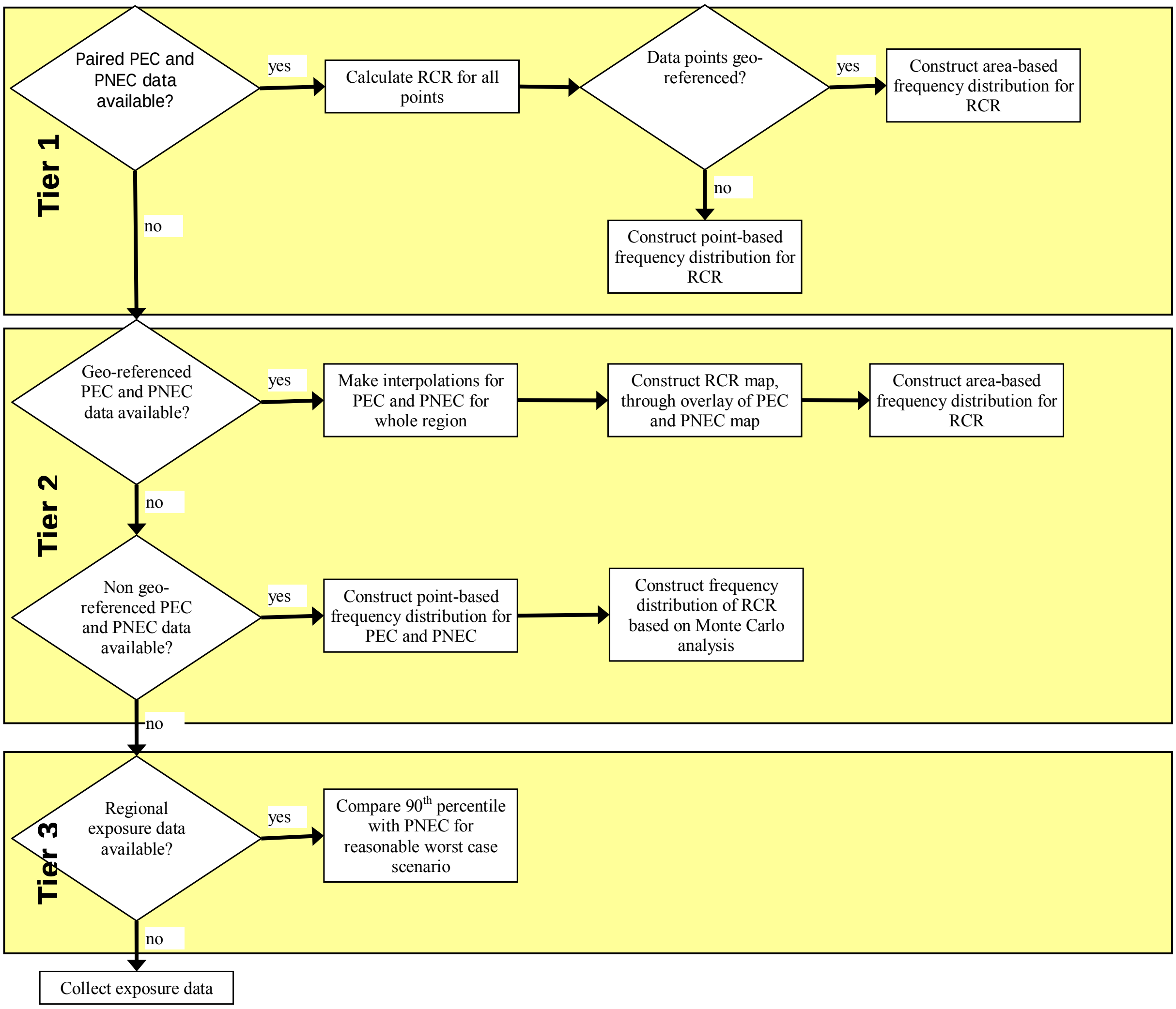
Step-wise approach 3: For the regional risk characterization under step-wise approach 3, two options were applied:

- **Option 1**: *risk characterization on the basis of the local additions only from the site (added risk approach)*- this approach can be used if it has been proven that at a regional scale copper in sediment is bound to sediment sulphides and is therefore not available.
- **Option 2**: *use of the default bioavailability scenario to the regional exposure data* – in case that region-specific data are lacking the use of conservative default AVS value could be considered and the RCR derived (PEC sediment-AVS default)/default PNEC. In this case a default OC of 5%OC (freshwater) and a default AVS of 0.62 µmol/kg dry weight was used.

8.1.2. Soil compartment

Bioavailability of copper is also implemented in a step-wise approach similar to the aquatic compartment method. The proposed step-wise approach methodology for risk characterization for the soil compartment is presented in Figure 3 and then described in more detail below.

Figure 3. Step-wise approach for the soil compartment risk characterization



Step-wise approach 1: The frequency distribution of RCR values is based on a database where both PEC and PNEC data are available.

Step-wise approach 2: In case PEC and PNEC data are available which are from different locations (non-paired data), this information can be combined to yield a frequency distribution of RCR values

Step-wise approach 3: Where not-geo-referenced PEC data are available for a region but insufficient data to assess the PNEC of a region the regional risk assessment is based on a comparison of the 90th percentile of the PEC of that region with the reasonable worst case PNEC for Europe.

8.2. Summary of the RWC-ambient PECs derived for Europe

The RWC –ambient Cu concentrations in different environmental compartments for different European Union conuntries are summarized in Table 25.

Table 25. Summary of the regional Cu concentrations based on measured data

COMPARTMENT	Unit	RWC-ambient PEC	Countries
Aquatic			
Freshwater median (min; max)	µg/L	**2.9** (0.5; 4.7)	B, Dk, Fi, G, Ir, P, Nl, Sw, UK, Sp, A
Freshwater sediment median (min; max)	mg/kg dw	**67.5** (45.8; 88.3)	B, Fr, Sw, Nl, Sp
Marine water median (min; max)	µg/L	**1.1** (0.8; 2.7)	B, Dk, Nl, No, Sw, UK
Marine sediment median (min; max)	mg/kg dw	**16.1** (4.2; 55.3)	B, Dk, G, Ir, Nl, No, Sw, UK
Soil			A, B, Fi, Fr, G, Ir, It, Nl, No, Sw, Sp
Forest soil median (min; max)	mg/kg dw	**24.4** (7.3; 40.2)	
Agricultural soil median (min; max)	mg/kg dw	**31.2** (16.5; 57.4)	
Grassland soil median (min; max)	mg/kg dw	**32.8** (28.0; 44.0)	

8.3. Risk characterization for the aquatic compartment

8.3.1. Freshwater compartment

Dissolved ambient Cu concentrations in European surface waters typically range from 0.5 µg/L (Denmark) to 4.7 µg/L (Ireland).

In the step-wise approach 1 assessment, where the site-specific values of the abiotic factors that control Cu bioavailability for toxicity are available, the normalised PNECs for the particular region were calculated. Where available, a normalised site-specific $HC_{5\text{-}50}$ value was derived using the Cu-BLM. Data on physico-chemical properties and dissolved Cu concentrations on a site-level are available for the Waloon region, Germany, the UK, Sweden, The Netherlands, Spain and France. These data allowed the calculation of a $HC_{5\text{-}50}$ value for each data point available. The risk ratio was then calculated for each specific data point, **RCR=Cu_{diss}/$HC_{5\text{-}50}$**. A cumulative frequency distribution was performed with the 90th percentile RCR values for all data points. The median RCR value was calculated and the risk was assessed.

For the regions without the step-wise approach 1 information, PNEC values determined from other dataset for the same region or from similar regions were used for the risk characterization and an estimated $HC_{5\text{-}50}$ was calculated. The risk ratio was calculated using **RCR=Median RWC PEC/ Median $HC_{5\text{-}50}$**.

Using both these approaches, RCR were calculated for each region/country and are summarized in Table 26.

Table 26. RCR calculated for the different regions for the freshwater compartment and approach used.

Country - region	RCR	% sites with median RCR>1 (approach used)
Belgium - Walloon	0.07	None (Step-wise approach 1)
Germany –Elbe Germany-Rhine	0.17 0.21	None (Step-wise approach 1)
UK - England	0.45	4 (Step-wise approach 1)
Sweden	0.1	3 (Step-wise approach 1)
The Netherlands	0.1	1
Spain	0.59	None (Step-wise approach 1)
France	0.4 to 0.54	None (Step-wise approach 1)
Austria	0.17	None (Step-wise approach 1)
Belgium - Flanders	0.12	Very low probability (Step-wise approach 2)
Denmark	0.03	None (Step-wise approach 2)
Finland	0.05	None (Step-wise approach 2)
Ireland (COMMPS)	0.55	None (Step-wise approach 2)
Northern Ireland	0.55	Very low probability (Step-wise approach 2)
Portugal	0.16-0.23	Very low probability (Step-wise approach 2)

From the step-wise approach 1 and 2 analysis, it was concluded that copper does not pose a regional risk to the aquatic compartment. Regional risk ratio ranged from 0.03 to 0.55. Considering all individual sites, RCR>1 are only rarely expected and in very localized situations.

8.3.2. Marine waters

Exposure data were obtained for the coastal areas of Belgium, the Netherlands, Norway, Denmark, Sweden and UK sampled between 1984 and 2005. The median of the 90th percentiles of copper in marine waters was 1.1 µg/L. A PNEC of 2.6 µg Cu/L was retained from the effects assessment. Regional RCR for the marine environment are presented in Table 27.

Table 27. RCR calculated for marine waters

Country	90th percentile PEC ($\mu g\ Cu_{diss}/L$)	RCR (PEC/PNEC) (PNEC – 2.6 µg Cu/L)
Belgium	0.8	0.3
Denmark	1.1	0.4
The Netherlands	1.1	0.4
Norway	1.1	0.4
Sweden	1.4	0.5
UK	2.7	1.0
Median	**1.1**	0.4

The marine RCR ranged from 0.3 to 1.0 when all the data was considered. Considering only the more recent data, RCR <0.5. The RCR median was 0.4 and it was concluded that there is no regional risk from copper exposure to the marine coastal zone.

8.3.3. Freshwater sediments

Risk characterization without AVS correction

The ambient sediment concentrations without AVS correction were used to calculate the RCR and results are reported in Table 28. RCR values show that even without AVS correction there is no risk for benthic organisms, with the exception of a potential risk for The Netherlands.

Table 28. Derived RWC-ambient sediment PECs for different European countries and RCR

Country	RWC-ambient PEC mg Cu/kg	RCR (PNEC: 87 MG CU/KG)
Belgium	75.4	0.87
France - average	46.8	0.54
France – Artois-Picardie	47.6	0.55
France – Rhone-Mediterranean area	45.8	0.53
Sweden	52.2	0.60
The Netherlands - waterbase	88.3	1.01
Spain- COMMPS	79.0	0.91

Risk characterization with AVS correction

The RCR for sediments can be refined using the SEM-AVS approach. SEM-AVS databases that represent regional conditions are available for Belgium (Flanders), UK, Finland, The Netherlands, Spain and Serbia and allowed to perform a regional risk characterization for these regions. The data showed that for the different countries and up to the 90th percentile of the SEM-AVS data no measurable bioavailable copper is expected to occur. Therefore, it was concluded that at a regional scale, copper is bound to AVS and presents no risk to sediments from the previously mentioned countries.

8.3.4. Marine sediments

From the effects section, a marine PNEC value calculated for the estuarine and marine sediments was 144 mg Cu/kg dw and 338 mg Cu/kg dw, respectively.

Sediment concentrations were obtained for the coastal zones of Belgium, Denmark, Germany, Ireland, the Netherlands, Norway, Sweden and the UK. In Table 29, an overview of the RWC-ambient PEC values and calculated RCR for the different countries was calculated.

Table 29. Country specific RWC-ambient PEC values and RCR 90th percentile for different European countries

Country	RWC-ambient PEC (mg Cu/kg dw)	RCR estuarine sed (PNEC: 144 mg Cu/kg dw)	RCR marine sed (PNEC: 338 mg Cu/kg dw)
Belgium	4.2	0.03	0.01
Denmark	33.6	0.23	0.06
Germany	18.5	0.13	0.03
Ireland	11.9	0.08	0.02
The Netherlands	6.2	0.04	0.01
Norway	55.3	0.38	0.10
Sweden	27.1	0.19	0.05
UK	12.8	0.09	0.04
Median	**15.65**	**0.11**	**0.04**

The region-specific RCR values are all below 1 with a median value of 0.11 for estuarine sediments and 0.04 for the marine sediments. It was concluded that no regional risks are expected for marine sediments.

8.4. Risk characterization for the soil compartment

The methodology used for the risk characterization at the regional scale depends on the information that is available for a region or country. As for the other compartments, the step-wise approach 1 will result in a more accurate estimate for regional risk assessment whereas higher step-wise approaches are used when there is lack of data. The result of both step-wise approaches 1 and 2 was a frequency distribution of the risk characterization ratios.

In a step-wise approach 1, the frequency distribution was based on a database that for the same site both PEC and PNEC were available (paired data). RCR were calculated for all points and if data points were geo-referenced, an area-based frequency distribution for RCR was performed, if not, a point-based frequency distribution was performed. The step-wise approach 1 could only be used for The Netherlands, Spain, England and Wales.

The step-wise approach 2 was used when paired PEC and PNEC data were not available. If geo-referenced PEC and PNEC data were available for one region, interpolations were made for the region and a RCR map was constructed by overlaying the PEC and PNEC map. Finally an area-based frequency distribution for RCR was performed. If geo-referenced PEC and PNEC data were not available, a point-based frequency distribution for PEC and PNEC was performed that resulted in a frequency distribution of RCR based on a Monte-Carlo analysis.
This approach was used for Finland, Sweden, Norway, Germany, France, Austria, Italy, Belgium, and Ireland.

Step-wise approach 3 was not used since there were no countries with exposure data but no available PNEC data.

The 90th percentile risk characterization ratios calculated for the different European countries for the soil compartment are summarized in Table 30.

Table 30. Summary of the 90th percentile RCR calculated for different European countries and approach used

Country	Cu 90th percentile RCR	
	Step-wise approach 1	**Step-wise approach 2***
Austria		0.37
Belgium		0.37
Finland		0.12-0.27
France		0.39
Germany		0.28
Ireland		0.24
Italy		0.77
The Netherlands	0.32 (point-based) 0.23 (area-based)	
Norway		0.22-0.37
Spain	0.51 (point-based)	0.43
Sweden		0.08-0.17
England and Wales	0.34 (point-based) 0.25 (area-based)	

* area-based and Monte-Carlo based

For the different European countries, all 90th percentile RCR values were below 1and therefore no risk is predicted for Cu toxicity in soils at the regional scale.

8.5. Final conclusion on the regional risk characterization

For all compartments:

Conclusion (ii): there is no need to further information and/or testing and no need for risk reduction measures beyond those that are being applied already.

9. OPINIONS ON THE ENVIRONMENTAL PART OF THE RISK ASSESSMENT

9.1. Opinion by the Technical Committee on New and Existing Substances (TC NES)

Comments were received from the following Member States: Italy, the Netherlands, the UK, Sweden, Denmark, France, Spain and Poland. Conclusions were that the voluntary risk assessment was conducted according to the methodology in the Technical Guidance Documents for the risk assessment of existing substances (TGD). The principles of the TGD were expanded by implementation of the Biotic Ligand Model (BLM)-concept. On the assumption that the information presented is correct and that the methodology applied is appropriate, the conclusions drawn by the voluntary risk assessment are plausible and supported by the majority of the TC NES. Two Member States did not support the application of an assessment factor of 1 for the derivation of the $PNEC_{freshwater}$, $PNEC_{sediment}$ and $PNEC_{soil}$.One Member State had concerns on the conclusions of the risk characterization.

9.2. Opinion by the Scientific Committee on Health and Environmental Risks (SCHER)

The comments generated by SCHER are that the general quality of the risk assessment is very good and that some of the procedures used are innovative and scientifically sound. The theoretical approaches used are found to be appropriate and generally well applied.
However, some issues present some weaknesses and some points would require further clarification such as:

- The selection of the freshwater toxicity data;
- Possible increased sensitivity for some species due to adaptation/acclimatation to low copper background values;
- Additional evaluations for physico-chemical properties of agricultural soils should be incorporated.

Regarding the risk characterization at the regional level, it is the opinion of the SCHER that the above-presented issues are not likely to substancially affect the quantitative results reported. Therefore, the proposed conclusions on risk characterization can be accepted.

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1. INTRODUCTION

The rapporteur for the risk evaluation of zinc metal and zinc compounds was the Ministry of Housing, Spatial Planning and the Environment (VROM) in consultation with the Ministry of Social Affairs and Employment (SZW) and the Ministry of Public Health Welfare and Sport (VWS). The scientific work on the zinc risk assessment report was prepared by the Netherlands organization for Applied Scientific research (TNO) and the National Institute of Public Health and Environment (RIVM). The final report was finalized in May 2008.

Opinions on the performance and risk characterization of this risk assessment from the Scientific Committee on Health and Environmental Risks (SCHER) are summarized within the present report.

The Technical Guidance Document (TGD) does not provide detailed information on how to deal with elements that have a natural background concentration in the environment such as zinc. Therefore, in this risk assessment (RA) the **added risk approach** has been used. Therefore, both the Predicted Environmental Concentrations (PECs) and Predicted No Effect Concentrations (PNECs) have been determined on the basis of the added amount of zinc, resulting in a PEC_{add} and $PNEC_{add}$. The use of this approach implies that only the anthropogenic amount of a substance (the amount added to the natural background concentration) is considered relevant for the effect assessment of that substance.

In the present RA, the use of the added risk approach implies that the PEC_{add} values have been calculated from zinc emissions due to anthropogenic activities. By focusing only on the anthropogenic part of zinc, the problem of the great variety of natural background concentrations of zinc in the different geographic regions is eliminated. Within this RA it was realized that comparison between calculated PEC_{add} with measured environmental concentrations must take into account that the measured values include both natural background and anthropogenic concentrations.

In the environmental effects assessment, the use of the added risk approach implies that the $PNEC_{add}$ has been derived from toxicity data based on the added amount of zinc in the tests. Therefore, the $PNEC_{add}$ is the maximum permissible addition to the background concentration.

In the environmental risk characterization, the use of the added risk approach implies the evaluation of the $PEC_{add}/PNEC_{add}$ ratios. When measured environmental concentrations are used in the risk characterization, either the background concentration was subtracted from the measured environmental concentration or the background concentration was added to the $PNEC_{add}$.

2. OVERALL RESULTS FOR THE REGIONAL ENVIRONMENTAL RISK ASSESSMENT FOR ZINC METAL AND OTHER ZINC COMPOUNDS

The risk assessment was performed separately for the compounds presented in Table 1. Regional risk characterization for all zinc compounds was assessed in the risk assessment for zinc metal.

Table 1. Zinc compounds

Coumpound	IUPAC name	CAS number	EINEC NUMBER
Zn	Zinc metal	7440-66-6	231-175-3
ZnO	Zinc oxide	1314-13-2	215-222-5
$Zn(C_{18}H_{35}O_2)_2$	Zinc distearate	557-05-1 and 91051-01-3	209-151-9 and 293-049-4
$ZnCl_2$	Zinc chloride	7646-85-7	231-592-0
$ZnSO_4$	Zinc sulphate	7733-02-0	231-793-3
$O_8P_2Zn_3$	Trizinc bis(*ortho*-phosphate)	7779-90-0	231-944-3

Possible conclusions for the risk assessment were:

Conclusion (i) There is a need for further information and/or testing.
Conclusion (ii) There is at present no need for further information and/or testing and no need for risk reduction measures beyond those which are being applied already.
Conclusion (iii) There is a need for limiting the risk; risk reduction measures which are already being applied shall be taken into account.

The regional environmental risk characterization concluded that some measured or calculated zinc concentrations in surface waters and sediments alongside motorways in the EU exceeded the corresponding $PNEC_{add}$ (**Conclusion (i)**). Due to a number of uncertainties, additional information is needed to refine this part of the risk assessment.
For the aquatic environment a **conclusion (iii)** was drawn. For the aquatic compartment, a conclusion (iii) was drawn because the $PNEC_{add\ water}$ was exceeded in some regional waters in the EU. For sediments, in some EU regions there was a potential risk for sediment-dwelling organims.
Risks related to zinc accumulation in regional soils of zinc and zinc compounds are not expected and therefore a **conclusion (ii)** was drawn for agricultural soils.

3. ENVIRONMENTAL FATE

3.1. Introduction

In freshwater and seawater, zinc can occur in both suspended and dissolved forms and is partitioned over a number of chemical species. In freshwater, it can be divided as hydrated zinc ions, zinc ions complexed by organic ligands (humic and fulvic acids), zinc oxy ions and zinc adsorbed to solid matter.

3.2. Degradation

Metals do not degrade in the environment according to the Organization for Economic Cooperation and Development (OECD, 1998). However, metals can be transformed by environmental processes to either increase or decrease the availability of toxic species.

3.3. Adsorption

The behaviour of zinc in the different environment compartments is affected by adsorption to soil, sediments, and suspended matter.

3.3.1. Aquatic environment

In the aquatic compartment, the speciation of zinc is very complex and is highly dependent on abiotic factors, including pH, (dissolved) organic matter content, redox potential, etc.
A literature review was performed on the partitioning of zinc in the aquatic environment and the following partition coefficients have been derived for Zn metal and Zn compounds:

- Partition coefficient in suspended matter (Venema, 1994):
  Kp_{susp} = 110,000 l/kg (log Kp_{susp} = 5.04)

- Partition coefficient in sediment (Venema, 1994):
  Kp_{sed} = 73,000 l/kg (log Kp_{sed} = 4.86)

3.3.2. Terrestrial environment

In soils, zinc interacts with various soil surfaces and strongly adsorbs to oxides and hydroxides, silica, calcium carbonate, clay particles and organic matter and the sorption tends to increase with increasing pH.
A literature review was performed on the partitioning of zinc in the terrestrial environment and the following partition coefficient has been derived for Zn metal and Zn compounds and was used in this RA because it is based on the part of metals that can actually exchange and it is assumed in equilibrium with the water phase:

- Partition coefficient in soil
  $LogKp_{soil}$= 2.2 (Buchter et al., 1989)

4. EXPOSURE ASSESSMENT

In accordance with the TGD, it was assumed that the individual zinc compounds are all transformed into the ionic species. Another assumption was that all emissions are diffuse. The regional exposure assessment included the industrial and diffuse emissions of all zinc compounds.
In the regional exposure assessment, regional PEC_{add} values were calculated for the Netherlands as representative EU region and also for a theoretical EU region. The Netherlands was chosen as a representative region because the most recent data on environmental zinc emissions are available and according to the TGD, the Netherlands corresponds with that of a EU-region (40000km^2). The PEC_{add} values for the NL-region were calculated from the environmental zinc emissions in the Netherlands and additionally PEC_{add} values were calculated from the total EU zinc emissions. Emission data were available for the Netherlands (1999), Belgium (1995), Sweden (1990-1995), Germany (1998) and UK (1999 and 2000).
The calculated regional PEC_{add} values to which the natural background concentrations have been added were compared to monitoring data for regional zinc concentrations.

4.1. Aquatic environment

4.1.1. $PEC_{add, water}$ derivation

PEC_{add} were calculated using emission data for the Netherlands and also for theoretical EU-region using the total zinc emissions for the EU. Derived PEC_{add} for the aquatic environment are provided in table 2.

Table 2. Calculated PEC_{add} values using zinc emission data for the Netherlands and a theoretical EU-region

Calculated PEC_{add}	**EU-region**	**The Netherlands**
$PEC_{add, water}$ (total Zn; µg/L)	16.8* 27.0**	12.2* 20.0**
$PEC_{add, sediment}$ (mg/kg ww)	268	194
$PEC_{add, sediment}$ (mg/kg dw)	696	504

* $C_{suspended\ matter}$ 15 mg/L and $Kp_{susp\ matter/water}$ 110 000 L/kg
** $C_{suspended\ matter}$ 30 mg/L and $Kp_{susp\ matter/water}$ 110 000 L/kg

Comparison between the calculated $PEC_{add, water}$ values and regional measured data for zinc in surface waters show that values are similar. The measured data for the river Meuse were substantially higher than the calculated $PEC_{add, water}$. In other EU regions, measured zinc concentrations in surface waters (90th percentile values) exceeded the calculated $PEC_{add, water}$ in several regions in France and Germany and in the Flanders region. On the other hand, the 90th percentile concentration in Swedish waters was lower than the calculated PEC_{add}. In sediments, comparisons between sediment monitoring data and calculated $PEC_{add, sediment}$ also showed that measured concentrations exceeded the calculated $PEC_{add, sediment}$.

4.1.2. Ambient and natural background concentrations

Ambient concentrations include the total concentration due to the natural background plus the imission of zinc diffuse sources of human origin. Natural concentrations are defined as the concentration present due to natural sources only.
The concentrations of zinc in seawater and fresh surface water are dependent on natural conditions and it is almost impossible to experimentally determine a natural background concentration in Europe. Therefore, background concentrations were not measured but estimated or determined with other methods. In a number of EU countries it was concluded that there were several estimates on background concentrations of zinc in fresh waters that ranged from 2.5 to 12 µg total Zn/L. In the Zn RA, a pragmatic approach was followed rather than selecting one particular background value by using the lower limit of 3 µg total Zn/Land the upper limit of 12 µg total Zn/L for correcting the available EU monitoring data in the risk characterization.
In sediments, currently available natural background data are more or less in the same order of magnitude and range from 70 to 175 mg Zn/kg dw. Based on the data of several EU-regions, the value of 140 mg Zn/kg dw was used as a natural background for correcting the EU sediment monitoring data.

4.2. Terrestrial environment

4.2.1. $PEC_{add, soil}$ derivation

As for the aquatic environment, $PEC_{add, soil}$ were calculated using emission data for the Netherlands and also for theoretical EU-region using the total zinc emissions for the EU. Derived $PEC_{add, soil}$ for the terrestrial environment are provided in Table 3.

Table 3. Calculated $PEC_{add, soil}$ values using zinc emission data for the Netherlands and a theoretical EU-region

Calculated PEC_{add}	EU-region	The Netherlands
PEC_{add}, agricultural soil (mg/kg ww)	57	57
PEC_{add}, agricultural soil (mg/kg dw)	64	64
PEC_{add}, natural soil (mg/kg ww)	0.9	0.5
PEC_{add}, natural soil (mg/kg dw)	1.0	0.6
PEC_{add}, industrial soil (mg/kg ww)	86	38
PEC_{add}, industrial soil (mg/kg dw)	97	43

The zinc concentration in soils are strongly related to the soil type. A comparison between the calculated $PEC_{add, agricultural soil}$ with monitoring data for agricultural soils was performed in the regional risk characterization.

4.2.2. Ambient and natural background concentrations

The natural zinc concentrations in soils are highly variable and dependent on the native soil material and soil characteristics, especially clay and organic matter content (Cleven et al., 1993; WHO, 1996). From the available data for a number of EU

countries, it is clear that there is a large variation in the natural zinc background concentrations and thus it is extremely difficult to quantify. As a screening tool, data for background zinc concentrations in the Netherlands was used for estimating background concentrations for other EU countries. The data on zinc background concentrations in Dutch soils range from 20-45 mg/kg in sand soils, 55-140 mg/kg in peat soils and 70-150 mg/kg in clay soils.
In the Zinc RA, available soil monitoring data was only used in the risk characterization when a correction with the natural zinc background concentrations typical for that soil type was possible.

5. EFFECTS ASSESSMENT

5.1. General approach

The added risk approach has been used in this risk assessment on zinc. The added approach implies that the PNEC is derived from toxicity data that are based on the added zinc concentration in the tests resulting in an added Predicted No Effect Concentration ($PNEC_{add}$).

To assess the environmental effects of zinc to organisms from different environmental compartments a large amount of literature data are available that includes acute and chronic exposure scenarios. Since a wide amount of reliable data is available, chronic effects have been used to derive Predicted No Effect Concentrations (PNECs) for all compartments.
To assess the effects of zinc to the different organisms:

- Only chronic effects were used to derive $PNEC_{add}$ for all compartments;
- All papers were evaluated for relevance and reliability in accordance with Technical Guidance Document (TGD) principles;
- No Observed Effect Concentrations (NOECs) or 10% Effect Concentration (EC10) were used to derive $PNEC_{add}$;
- Zinc specific characteristics such as bioavailability and essentiality were integrated in the assessment.

5.2. Specific characteristics for zinc

5.2.1. Essentiality

Zinc is an essential element, which implies that organisms will have a minimum requirement for zinc and a maximum concentration at which zinc will be toxic. For each species and for all essential elements an “optimal concentration range for essential elements” (OCEE) is required for normal function. This OCEE is determined by the natural bioavailable concentration range of that essential element in the species natural habitat. However, if the concentration range is too high, the element becomes toxic.The use of the added risk approach implies that there is no risk of deficiency at the PNEC since the $PNEC_{add}$ derived in this approach is defined as the maximum permissible addition to the background concentration.

5.2.2. Bioavailability

For metals it is important to define the actual or bioavailable concentration. Due to a number of processes, zinc will be present in different forms, some of which are more bioavailable than others, therefore affecting its toxicity to organisms. Several abiotic factors may change zinc bioavailability, such as pH and hardness for the water compartment and organic matter, clay particles and oxides and hydroxides for the terrestrial compartment.

According to the Guidelines from the Technical Guidance Document (TGD, 1996; TGD revisions, 2003) a study is accepted or rejected based on both reliability and relevance of the data for environmental risk assessment.
For the aquatic environment, toxicity data on algae, invertebrates and fish for fresh and marine waters and sediments are from single-species that study endpoints including growth, reproduction and mortality.
For the terrestrial environment, toxicity data on invertebrates and plants are from single-species tests that study endpoints such as survival, growth and/or reproduction. Data on microorganisms are from tests in which microbe-mediated soil processes were studied (e.g. C- and N- mineralization). These tests are multiple species tests because these processes reflect the action of many species in soil microbial communities.

5.3. Selection of ecotoxicological data

5.3.1. Reliability

Standardised tests by organizations such as the OECD and USEPA were considered highly reliable when test methodology, performance and data reporting were included. Non-standardised tests were accepted but require a thorough check on their compliance with reliability criteria.

Type of test

In this risk assessment (RA) only chronic tests with reliable endpoints were considered. Chronic exposure is defined as >4 days for all invertebrates and fish. For organisms including unicellular algae and other microorganisms (bacteria, protozoa) an exposure of 4 days already covers one or more generations, thus chronic NOEC values for exposure times of less than 4 days may be derived for these organisms. On the other hand, for organisms that have a long generation time (e.g. fish) an exposure time of just over four days was considered much to short to derive a chronic NOEC. For PNEC derivation a full life-cycle test was preferred. However, results from tests that were more limited than a full life-cycle test could be used.

Concentration effect relationships

In all chronic test studies, clear dose-response should be observed. Since effect concentrations are statistically derived, information on statistics should be used as data criterion. However, if data include sufficient details to perform appropriate statistics that permit to derive reliable NOEC/EC_{10} values, the data has been retained. EC_{10} values have been considered equivalent to NOEC. If values are visually derived the data was considered unreliable.
Only studies that include a control and at least two Zn concentrations were accepted for this risk assessment. The exception was the work from Tabatabai and co-workers in which only one concentration was used resulting in effect, but considered LOEC. Although it was not possible to check the concentration-effect relationship, the results of these tests were used to derive the NOEC provided the percentage inhibition at the LOEC was below 30%.

Chemical analysis

All aquatic and terrestrial toxicity data used in this RA are expressed as zinc, not as the test compound, because zinc itself is considered to be the causative factor of toxicity.
Results from aquatic toxicity studies were expressed as either actual (measured) concentration of zinc, which included the background concentration of zinc, or as the nominal (added) concentration. Because of the use of the added risk approach in this RA, results based on actual concentrations were corrected for the background concentration of zinc, based in the fact that only the added concentration of zinc is relevant for toxicity.
Almost all results from terrestrial toxicity were expressed as the nominal concentration in soil; actual concentrations were only reported in a few studies.
Analysis of exposure concentrations, recommended in most guidelines (OECD) was considered an important criterion. The major issue is whether the exposures concentrations were maintained over the course of the test. Actual exposure concentrations were only determined in a few studies that indicated that the exposure concentrations were usually adequately maintained in renewal test systems. For static systems, data on actual versus nominal concentration are usually not available and since most tests were performed using renewal and flow-through test systems, the analysis of exposure concentrations has not been used as selection criterion.

5.3.2. Relevance

According to the TGD not all data considered reliable can be used for risk assessment. Because of the difficulties to compare different NOECs from different data with different endpoints, only chronic toxicity data from studies in which survival, filtration rate, reproduction, growth and per capita rate of increase were retained for the invertebrates and fish. For algae the only relevant endpoint used for PNEC derivation was growth.

Aquatic environment

Abiotic factors can influence speciation, bioavailability and toxicity of zinc.
In the revised TGD (2003) different PNECs are introduced for freshwater and marine waters. However, this RA follows the "old" TGD (1996) that only aimed at freshwater and only provides guidance for deriving a freshwater PNEC.
Therefore, for the aquatic environment, water characteristics have been taken into account for freshwater selection of data. Both natural and artificial water were accepted if chemical characteristics are similar to the ranges that would be found in natural fresh/marine waters. Water characteristics that have been taken into account for freshwater data selection were pH, hardness and zinc background concentrations with the following boundaries:

pH: minimum value:6
maximum value: 9
Hardness: minimum value: 24 mg/L (as $CaCO_3$)
Maximum value: 250 mg/L (as $CaCO_3$)
Background zinc concentration: minimum value for soluble zinc: around 1 μg/L.

It is noted that these criteria do not cover all European aquatic systems. For example waters from Scandinavia have much lower hardness and therefore a soft water $PNEC_{add}$ has also been derived in addition to the $PNEC_{add,\ aquatic}$.
It is also noted that some references do not contain data on the background concentration of zinc in the test water and in some cases data on pH and hardness are also lacking. Hence, the limits imposed for the 3 parameters would significantly reduce the dataset, which would not be practical. Therefore, it was decided that:

- If data are reported for the three parameters, the selection criteria was used;
- When no data was reported:
  - Tests conducted in artificial waters were excluded if there were no data on pH and hardness values
  - Tests conducted in natural waters were maintained unless there were clear indications that the 3 parameters strongly deviated from real environmental conditions.

A further selection criterion was used only for two studies, Heijerick et al (2003) and De Schamphelaere et al (2003) in which different combinations were used for the different parameters, pH, hardness and dissolved organic carbon (DOC). For only these two studies an upper limit of 2 mg/L DOC was selected for artificial waters.

Terrestrial environment

In soils, abiotic factors that influence the speciation of zinc and might therefore influence bioavailabilituy andf toxicity were the clay content, the organic matter content and the pH. However, these abiotic factors were not used in a stringent matter for data selection. The background zinc concentration has not been used for data selection because of the lack of data on background zinc concentrations in most test soils. The following has been decided on the use of soil type and major soil characteristics:

- EU soils – All tests in EU soils have been accepted, regardless wether or not there are data on the soil type and the major characteristics. The data was only rejected if one or more of the parameters strongly deviated from real environmental conditions, which was nos not the case for any of the studies.
- Non-EU soils:
  - if there was available data on soil parameters, studies have only been accepted if they fall in the range of EU-soils.
  - if there was not data o soil parameters or zinc background concentrations the relevance of the test has been judged on case by case basis.
- Artificial soils – If there are data for background concentration and soil parameters, values need to be in the range of EU soils. if no data is reported on soil parameters the tests were not accepted unless it was OECD artificial soil.
- Only tests that were performed in more or less freshly-spiked soils, i.e. soils in which the test was strated within some weeks after spiking and ended 6 months after spiking, as tests in aged soils might underestimate the toxicity. Based on this, the results of a number of microbial tests have been rejected.

5.4. PNEC derivation

5.4.1. Approach toxicity assessment for organisms

For the $PNEC_{add}$ derivation only the most reliable ecotoxicity data from standard and non-standardised tests were incorporated in the risk assessment. In the effect assessment chronic NOEC/EC_{10} values are used rather than 50% Effect Concentration (EC_{50}) values to derive PNEC values. Acute effect values were not considered in this report. Ecotoxicity data was selected according to reliability and relevance as stated above.

5.4.2. Method used for the derivation of NOEC values

The methods used for the derivation of NOEC values are the same as outlined in the TGD (1996; revisions, 2003). They were real NOEC values or were derived from effect concentrations.
When possible, real NOEC values were derived from the data reported:

Statistical analysis – the NOEC is the highest concentration showing no statistical effect compared to the control. Significance level is $p=0.05$ (optional, the $p=0.01$ level is reported instead of the $p=0.05$). There also need to be a clear concentration effect-response relationship.

If the real NOEC value could not be derived the following procedure was used:

- If the EC_{10} values were available, the NOEC was set at this value, on condition that the value fell within the concentration range.
- In more recent data there was the preference for the ECx (where x is a low effect between 5 and 20%) instead of the NOEC. In those studies the EC_{10} was used if no NOEC was reported.
- Furthermore, if the individual data were reported, a number of EC_{10} values were calculated.
- The NOEC was derived from the Lowest Observed Effect Concentration (LOEC) using the following extrapolation factors:
    - NOEC=LOEC/2 in case inhibition was >10% but <20%
    - NOEC=LOEC/3 in case inhibition >10% and < 30%.

5.4.3. Method used for the aggregation of NOEC data

- If for one species several chronic NOEC values based on the same endpoint were available, they were averaged by calculating the geometric mean, resulting in a "species mean" NOEC. NOEC values should be from equivalent tests and same exposure time. Nevertheless, NOEC derived from tests with a short exposure time may be used together with NOEC values derived from longer exposure time if the data indicated that a sensitive life stage was tested.
- If for one species there were several NOECs derived for different endpoints, then the lowest value was selected (the most sensitive endpoint). The lowest value was determined on the basis of the geometric mean if more than one NOEC value was reported. The most sensitive endpoint per species is further used as input in the species sensitivity distribution (SSD).

- In some cases NOEC values for different life stages for a specific organism were reported. If it is evident that a life stage is more sensitive, then the result for the most sensitive life stage was selected.

5.4.4. Derivation of PNEC values using statistical extrapolation methods

The PNECs for the different compartments were calculated from the chronic NOEC data extracted from the different databases. For the derivation of $PNEC_{add}$ the results of the toxicity tests were corrected, if possible, for background zinc concentration.

PNEC values were derived using the two ecotoxicological extrapolation methods, both described in the TGD:

- The PNEC was calculated from the lowest acute LC_{50} or EC_{50} or preferably from the lowest NOEC/EC_{10} using assessment factors that depended on the available toxicity data (TGD-Chapter 3)
- In case the chronic database is sufficiently large, the PNEC was calculated by means of statistical extrapolation, using all available NOECs values as input (TGD chapter 3, appendix V).

In the TGD, the first extrapolation method is preferred and it is recommended to use statistical extrapolation as a supplementary approach. However, when large amounts of ecotoxicity data are available, the statistical approach is being preferred for the derivation of PNEC.

In a London workshop on the use of statistical extrapolation for the derivation of PNEC values, some recommendations were made to calculate PNEC values provided that chronic database meet certain requirements (EC, 2001).

- General requirements: at least 10 NOEC values and preferably 15 values are available for different species.
- Taxonomic requirements: at least 8 taxonomic groups, using the EPA list of 8 groups required for the derivation of the final chronic value (PNEC equivalent) as a starting point.
- Distribution function: the log-normal distribution (the methods of Wagner and Løkke (1991) and Aldenberg and Jaworska (2000)) and the log-logistic distribution (Aldenberg and Slob, 1993) are pragmatic choices because of its mathematical properties. Several other approaches could be used to derive variability distributions and percentiles from parametric (e.g. log-normal, Weibull distributions) and non-parametric methods. To select the most appropriate distribution function for the available data, both statistical (e.g. Kolmogorov-Smirnov, Andersen-Darling tests) and visual (e.g. Q-Q plots) goodness-of-fit techniques were used. To select the most appropriate distribution for a given data set, goodness of fit statistics (software BestFit, Palisade Inc.) were used. Goodness of fit tests are formal statistic tests of the hypothesis that the data represents an independent sample from an assumed distribution. These tests compare the actual data and the theoretic distribution considered. The Andersen-Darling test is preferred since it emphasizes tail values. This test is a quadratic statistic that measures the vertical discrepancy in a cumulative distribution function-type probability plot and is sensitive to departures of the distributions in the tails (Stephens, 1982). The calculated

goodness-of-fit statistic measures how good the fit is and is used by comparing the values to the goodness-of-fit of other distributions. Additionally, critical values are calculated and used to determine if a fitted distribution should be accepted or rejected at a specific level of confidence. Usually, a significant level of 0.05 is used, and implies that a value of the test-statistic below the 95th percentile of distribution for the statistic is acceptable and leads to the inability to reject the hypothesis.

- Level of protection: the 5th percentile value with 50% (HC_{5-50}) confidence should be used
- Uncertainty considerations: Depending on the database and the confidence limits for that database, and assessment factor (AF) should be applied on the 5th percentile value and therefore PNEC= 5th percentile value/AF. This AF should be between 1 and 5. To determine the size of AF the following points are mentioned:
    - The overall quality of the database and endpoints covered (e.g. if all the data are generated from real chronic studies covering sensitive life stages);
    - The diversity and representativeness of the taxonomic groups covered by the database;
    - The mode of action of the chemical;
    - Statistical uncertainties around 5th percentile estimate (as reflected in the goodness-of-fit or the size of confidence interval);
    - Comparisons between field and mesocosms studies and the 5th percentile and mesocosm/field studies to evaluate the laboratory to field extrapolation.

6. EFFECTS ASSESSMENT - AQUATIC ENVIRONMENT

6.1. Results freshwater toxicity

The zinc aquatic effects database contains a large number of chronic NOEC values (161 chronic NOECs for 18 species). For the freshwater compartment, the effects assessment of zinc was based on NOECs collected for freshwater organisms.
Data on chronic toxicity tests resulting in NOEC values for freshwater algae, invertebrates and fish are summarized in Tables 4, 5 and 6, respectively. Some recent studies (grey) were found in the literature and were added to the tables. However, these chronic NOEC values were not included in the PNEC derivation in the zinc RA.

6.1.1. Toxicity data for freshwater algae

In the Zn RA, 26 chronic studies reporting the NOEC for freshwater algae/higher plants for two species were found and used for $PNEC_{add}$ derivation. The species mean NOEC for freshwater algae/higher plants was 17 µg/L Zn for *Pseudokircherniella subcapitata* (endpoint growth; geometric mean of 25 test values) and 60 µg/L Zn for *Cladophora glomerata* (endpoint growth; only one test value).

6.1.2. Toxicity data for freshwater invertebrates

In the Zn RA, 61 chronic studies reporting NOEC for 10 single-species freshwater invertebrates were found and used for $PNEC_{add}$ derivation. The species mean NOEC for freshwater invertebrates range from 37 µg Zn /L (measured concentration) for the crustacean *Ceriodaphnia dubia* (endpoint reproduction; 13 test values) to 137 µg Zn /L (measured concentration) for the insect *Chironomus tentans* (1 test result).
More recent chronic toxicity test studies were found in the literature and the database has now 70 NOEC values reported. However, these NOEC values were not included in the PNEC derivation in this RA.

6.1.3. Toxicity data for freshwater fish

In the Zn RA, 74 chronic studies reporting NOEC for 6 single-species of freshwater fish were found and used for $PNEC_{add}$ derivation. The "species mean" NOEC values for freshwater fish range from 44 µg Zn/L for *Jordanella floridae* (endpoint growth; geometric mean of 2 test values) to 660 µg Zn/L Zn for *Brachydanio rerio* (endpoint hatching; 9 test results).
More recent chronic toxicity test studies were found in the literature and the database has now 78 NOEC values reported. However, these NOEC values were not included in the PNEC derivation in this RA.

Table 4. NOEC measured values and physico-chemical parameters for freshwater algae/higher plants (accepted studies).

ORGANISM (CODE)	TEST TYPE	TEST COMPOUND	TEST WATER	PH	HARDNESS	EXPOSURE TIME	CRITERION	RESULT µg Zn /L	REFERENCE
Pseudokirchneriella subcapitata	S	Zn powder	art.(OECD no EDTA)	7.4	24	3-d	NOECg	**50**	Van Woensel, 1994
Pseudokirchneriella subcapitata	S	ZnO (EPM-grade)	art.(OECD no EDTA)	7.5	24	3-d	NOECg	**24**	Van Ginneken, 1994
Pseudokirchneriella subcapitata (code:Na-2.7 mM)	S	$ZnCl_2$	art.(OECD no EDTA)	7.5	24	3-d	NOECg	**5.4**	De Schamphelaere et al., 2003
Pseudokirchneriella subcapitata (code:Ca-1.0 mM)	S	$ZnCl_2$	art.(OECD no EDTA)	7.5	112	3-d	NOECg	**5.2**	De Schamphelaere et al., 2003
Pseudokirchneriella subcapitata (code:Ca-1.5 mM)	S	$ZnCl_2$	art.(OECD no EDTA)	7.5	162	3-d	NOECg	**5.5**	De Schamphelaere et al., 2003
Pseudokirchneriella subcapitata (code:Ca-2.0 mM)	S	$ZnCl_2$	art.(OECD no EDTA)	7.5	212	3-d	NOECg	**5.5**	De Schamphelaere et al., 2003
Pseudokirchneriella subcapitata (code:Mg-0.5 mM)	S	$ZnCl_2$	art.(OECD no EDTA)	7.5	62	3-d	NOECg	**5.2**	De Schamphelaere et al., 2003
Pseudokirchneriella subcapitata (code:Mg-1.0 mM)	S	$ZnCl_2$	art.(OECD no EDTA)	7.5	112	3-d	NOECg	**8.6**	De Schamphelaere et al., 2003
Pseudokirchneriella subcapitata (code:Mg-1.5 mM)	S	$ZnCl_2$	art.(OECD no EDTA)	7.5	162	3-d	NOECg	**7.7**	De Schamphelaere et al., 2003
Pseudokirchneriella subcapitata(code:Mg-2.0 mM)	S	$ZnCl_2$	art.(OECD no EDTA)	7.5	212	3-d	NOECg	**8.5**	De Schamphelaere et al., 2003
Pseudokirchneriella subcapitata (code:Na-3.2 mM)	S	$ZnCl_2$	art.(OECD no EDTA)	7.5	24	3-d	NOECg	**6.8**	De Schamphelaere et al., 2003
Pseudokirchneriella subcapitata (code:Na-3.7 mM)	S	$ZnCl_2$	art.(OECD no EDTA)	7.5	24	3-d	NOECg	**7.9**	De Schamphelaere et al., 2003
Pseudokirchneriella subcapitata (code:Na-4.7 mM)	S	$ZnCl_2$	art.(OECD no EDTA)	7.5	24	3-d	NOECg	**7.4**	De Schamphelaere et al., 2003
Pseudokirchneriella subcapitata (code:Na-7.2 mM)	S	$ZnCl_2$	art.(OECD no EDTA)	7.5	24	3-d	NOECg	**4.9**	De Schamphelaere et al., 2003
Pseudokirchneriella subcapitata (code:pH-6.2)	S	$ZnCl_2$	art.(OECD no EDTA)	6.2	24	3-d	NOECg	**124**	De Schamphelaere et al., 2003

Table 4 (cont.). NOEC measured values and physico-chemical paramenters for freshwater algae/higher plants (accepted studies)

ORGANISM (CODE)	TEST TYPE	TEST COMPOUND	TEST WATER	PH	HARDNESS	EXPOSURE TIME	CRITERION	RESULT µg Zn /L	REFERENCE
Pseudokirchneriella subcapitata (code:pH-6.8)	S	$ZnCl_2$	art.(OECD no EDTA)	6.8	24	3-d	NOECg	**74**	De Schamphelaere et al., 2003
Pseudokirchneriella subcapitata (code:pH-7.1)	S	$ZnCl_2$	art.(OECD no EDTA)	7.1	24	3-d	NOECg	**41**	De Schamphelaere et al., 2003
Pseudokirchneriella subcapitata (code:pH-7.4)	S	$ZnCl_2$	art.(OECD no EDTA)	7.4	24	3-d	NOECg	**15**	De Schamphelaere et al., 2003
Pseudokirchneriella subcapitata (code:pH-7.7)	S	$ZnCl_2$	art.(OECD no EDTA)	7.4	24	3-d	NOECg	**15**	De Schamphelaere et al., 2003
Pseudokirchneriella subcapitata (code:pH-7.8)	S	$ZnCl_2$	art.(OECD no EDTA)	7.7	24	3-d	NOECg	**10**	De Schamphelaere et al., 2003
Pseudokirchneriella subcapitata (code:Brisy-R)	S	$ZnCl_2$	art.(OECD no EDTA)	7.8	24	3-d	NOECg	**9.4**	De Schamphelaere et al., 2003
Pseudokirchneriella subcapitata (code:Brisy-N)	S	$ZnCl_2$	river (DOC: 2.9 mg/L)	6.2	28	3-d	NOECg	**58**	De Schamphelaere et al., 2003
Pseudokirchneriella subcapitata (code:Voyon-R)	S	$ZnCl_2$	river (DOC: 2.5 mg/L)	6.3	27	3-d	NOECg	**91**	De Schamphelaere et al., 2003
Pseudokirchneriella subcapitata (code:Markemeer-R)	S	$ZnCl_2$	river (DOC: 3.7 mg/L)	6.4	27	3-d	NOECg	**72.9**	De Schamphelaere et al., 2003
Pseudokirchneriella subcapitata (code:Ankeveen-R)	S	$ZnCl_2$	river (DOC: 5.9 mg/L)	8	239	3-d	NOECg	**27**	De Schamphelaere et al., 2003
Cladophora glomerata (1 cm fragments)	S	-	art.	8.4	>35	3-d	NOECg	**60** (added)	Whitton, 1967

NOEC – No Observed Effect Concentration; S – static; g- growth; d- day; w- week; art-artificial

Table 5. NOEC nominal (added) values and physico-chemical parameters for freshwater invertebrates (accepted studies)

ORGANISM (LIFESTAGE / SIZE)	TEST TYPE	TEST COMPOUND	TEST WATER	PH	HARDNESS	EXPOSURE TIME	CRITERION	RESULT µg Zn /L	REFERENCE
Ceriodaphnia dubia (<1d)	R	-	river (N)	6	81	1-w	NOECr	**25**	Belanger and Cherry, 1990
Ceriodaphnia dubia (<1d)	R	-	river (N)	8	81	1-w	NOECe,r	**25**	Belanger and Cherry, 1990
Ceriodaphnia dubia (<1d)	R	-	river (N)	9	81	1-w	NOECr	**25**	Belanger and Cherry, 1990
Ceriodaphnia dubia (<1d)	R	-	river (A)	6	118	1-w	NOECe,r	**40**	Belanger and Cherry, 1990
Ceriodaphnia dubia (<1d)	R	-	river (A)	8	118	1-w	NOECr	**50**	Belanger and Cherry, 1990
Ceriodaphnia dubia (<1d)	R	-	river (A)	9	118	1-w	NOECe,r	**45**	Belanger and Cherry, 1990
Ceriodaphnia dubia (<1d)	R	-	river (C)	6	168	1-w	NOECe,r	**29**	Belanger and Cherry, 1990
Ceriodaphnia dubia (<1d)	R	-	river (C)	8	168	1-w	NOECr	**50**	Belanger and Cherry, 1990
Ceriodaphnia dubia (<1d)	R	-	river (C)	9	168	1-w	NOECe,r	**33**	Belanger and Cherry, 1990
Ceriodaphnia dubia (3 d)	R	$ZnCl_2$	river	8.0	169	4-d	NOECe,r	**50**	Masters et al., 1991
Ceriodaphnia dubia (3 d)	R	$ZnCl_2$	river	8.0	169	4-d	NOECe,s	**50**	Masters et al., 1991
Ceriodaphnia dubia (3 d)	R	$ZnCl_2$	river	8.0	169	4-d	NOECe,r	**14**	Masters et al., 1991
Ceriodaphnia dubia (3 d)	R	$ZnCl_2$	river	8.0	169	4-d	NOECe,s	**50**	Masters et al., 1991
Ceriodaphnia dubia (<1d)	R	$ZnCl_2$	river	8.0	169	7-d	NOECe,r	**50**	Masters et al., 1991
Ceriodaphnia dubia (<1d)	R	$ZnCl_2$	river	8.0	169	7-d	NOECe,s	**29**	Masters et al., 1991
Ceriodaphnia dubia (<1d)	R	$ZnCl_2$	river	8.0	169	7-d	NOECe,r	**100**	Masters et al., 1991
Ceriodaphnia dubia (<1d)	R	$ZnCl_2$	river	8.0	169	7-d	NOECe,s	**100**	Masters et al., 1991
Chironomos tentans (newly hatched larvae)	R	$ZnCl_2$	lake	7.7	45	8-w	NOECs,g,e,r	**137**	Sibley et al., 1996
Daphnia magna (<1d)	R	$ZnCl_2$	well	7.5	52	21-d	NOECr,s	**97** (actual)	Chapman et al., 1980
Daphnia magna (<1d)	R	$ZnCl_2$	well	7.7	104	21-d	NOECr,s	**43** (actual)	Chapman et al., 1980
Daphnia magna (<1d)	R	$ZnCl_2$	well	8.4	211	21-d	NOECr,s	**42** (actual)	Chapman et al., 1980
Daphnia magna (<1d)	R	$ZnSO_4.7H_2O$	pond	8.4	52	7-w	NOECr,e	**31**	Paulaskis and Winner, 1988
Daphnia magna (<1d)	R	$ZnSO_4.7H_2O$	pond (+DOC:0.75 mg/L)	8.4	52	7-w	NOECr,e	**33**	Paulaskis and Winner, 1988

Table 5 (cont.). NOEC nominal (added) values and physico-chemical parameters for freshwater invertebrates (accepted studies)

ORGANISM (LIFESTAGE / SIZE)	TEST TYPE	TEST COMPOUND	TEST WATER	PH	HARDNESS	EXPOSURE TIME	CRITERION	RESULT µg Zn /L	REFERENCE
Daphnia magna (<1d)	R	$ZnSO_4.7H_2O$	pond (+DOC:1.5 mg/L)	8.4	52	7-w	NOECr	**84**	Paulaskis and Winner, 1988
Daphnia magna (<1d)	R	$ZnSO_4.7H_2O$	pond	8.3	102	7-w	NOECr	**83**	Paulaskis and Winner, 1988
Daphnia magna (<1d)	R	$ZnSO_4.7H_2O$	pond	8.3	197	7-w	NOECr	**159**	Paulaskis and Winner, 1988
Daphnia magna (<1d)	R	$ZnSO_4.7H_2O$	Pond (+DOC:1.5 mg/L)	8.3	197	7-w	NOECr	**208**	Paulaskis and Winner, 1988
Daphnia magna (<1d)	R	$ZnCl_2$	lake	7.7	45	3-w	NOECr,e	**35**	Biesinger and Christensen, 1972
Daphnia magna (<1d)	R	$ZnCl_2$	lake	7.7	45	3-w	NOECr	**74**	Biesinger et al., 1986
Daphnia magna (<1d)	R	$ZnCl_2$	lake	8.1	225	3-w	NOECg	**37**	Enserik et al., 1991
Daphnia magna (<1d)	R	$ZnCl_2$	lake	8.1	225	3-w	NOECr,s	**310**	Enserik et al., 1991
Daphnia magna	R	$ZnCl_2$	lake	8.1	225	17-d	NOECr,s-e	**420**	Enserik et al., 1991
Daphnia magna (< 2d)	R		lake	7.7	65	3-w	NOECr,s	**100**	Münzinger and Monicelli, 1991
Daphnia magna (< 2d)	R		lake	7.7	65	3-w	NOECr,s	**100**	Münzinger and Monicelli, 1991
Daphnia magna (< 2d)	R		lake	7.7	65	3-w	NOECr,e	**25**	Münzinger and Monicelli, 1991
Daphnia magna (< 2d)							NOECs	**100**	Münzinger and Monicelli, 1991
Daphnia magna (<1 d; code: CA-0.25; MG-0.25; NA-2)	R	$ZnCl_2$	art.	6.6	50	3-w	NOECr,s	**82** (actual)	De Schamphelaere et al., 2003
Daphnia magna (<1 d; CA-05)	R	$ZnCl_2$	art.	6.6	75	3-w	NOECr,s	**50** (actual)	De Schamphelaere et al., 2003
Daphnia magna (<1 d; CA-1)	R	$ZnCl_2$	art.	6.6	125	3-w	NOECr,s	**54** (actual)	De Schamphelaere et al., 2003
Daphnia magna (<1 d; CA-2)	R	$ZnCl_2$	art.	6.6	225	3-w	NOECr,s	**92** (actual)	De Schamphelaere et al., 2003
Daphnia magna (<1 d; MG-05)	R	$ZnCl_2$	art.	6.6	75	3-w	NOECr,s	**48** (actual)	De Schamphelaere et al., 2003
Daphnia magna (<1 d; MG-1)	R	$ZnCl_2$	art.	6.6	125	3-w	NOECr,s	**152** (actual)	De Schamphelaere et al., 2003

Table 5 (cont.). NOEC nominal (added) values and physico-chemical parameters for freshwater invertebrates (accepted studies)

ORGANISM (LIFESTAGE / SIZE)	TEST TYPE	TEST COMPOUND	TEST WATER	PH	HARDNESS	EXPOSURE TIME	CRITERION	RESULT µg Zn /L	REFERENCE
Daphnia magna (<1 d; MG-1.5)	R	$ZnCl_2$	art.	6.6	175	3-w	NOECr,s	**155** (actual)	De Schamphelaere et al., 2003
Daphnia magna (<1 d; MG-2)	R	$ZnCl_2$	art.	6.6	225	3-w	NOECr,s	**156** (actual)	De Schamphelaere et al., 2003
Daphnia magna (<1 d; NA-6)	R	$ZnCl_2$	art.	6.6	50	3-w	NOECr,s	**143** (actual)	De Schamphelaere et al., 2003
Daphnia magna (<1 d; NA-9)	R	$ZnCl_2$	art.	6.6	50	3-w	NOECr,s	**136** (actual)	De Schamphelaere et al., 2003
Daphnia magna (<1 d; NA-12)	R	$ZnCl_2$	art.	6.6	50	3-w	NOECr,s	**143** (actual)	De Schamphelaere et al., 2003
Daphnia magna (<1d)	R	dissolved Zn	art	7.2	33.2	3-w	NOECr	155 (actual)	De Schamphelaere et al., 2005
Daphnia magna (<1d; Code: Ankeveen)	R	dissolved Zn	river (DOC:17.3 mg/L)	6.8	12.3	3-w	NOECr	491 (actual)	De Schamphelaere et al. 2005
Daphnia magna (<1d - code: Bihain)	R	dissolved Zn	river (DOC:5.37 mg/L)	6	6.9	3-w	NOECr	62.6 (actual)	De Schamphelaere et al. 2005
Daphnia magna (<1d - code:Brisy)	R	dissolved Zn	river (DOC:2.53 mg/L)	7.3	13.6	3-w	NOECr	94.5 (actual)	De Schamphelaere et al. 2005
Daphnia magna (<1d code:Markermeer)	R	dissolved Zn	river (DOC:7.49 mg/L)	8	127	3-w	NOECr	244 (actual)	De Schamphelaere et al. 2005
Daphnia magna (<1d - code:Regge)	R	dissolved Zn	river (DOC:9.87 mg/L)	8	165	3-w	NOECr	251 (actual)	De Schamphelaere et al. 2005
Daphnia magna (<1d - code:Rhine)	R	dissolved Zn	River (DOC:2.30 mg/L)	8.2	159	3-w	NOECr	143 (actual)	De Schamphelaere et al. 2005
Daphnia magna (<1d - code:Voyon)	R	dissolved Zn	river (DOC:4.17 mg/L)	8.4	125	3-w	NOECr	72.7 (actual)	De Schamphelaere et al. 2005
Daphnia magna (Code: S4)	R	$ZnCl_2$	art (DOC: 2 mg/L)	7.25	240	3-w	NOECr	209 (actual)	Heijerick et al., 2003

Table 5 (cont.). NOEC nominal (added) values and physico-chemical parameters for freshwater invertebrates (accepted studies)

ORGANISM (LIFESTAGE / SIZE)	TEST TYPE	TEST COMPOUND	TEST WATER	PH	HARDNESS	EXPOSURE TIME	CRITERION	RESULT µg Zn /L	REFERENCE
Dreissena polymorpha (length 1.6-2.0 cm)	R	$ZnCl_2$	lake	7.9	270 (Ca)	10-w	NOECf	**100**	Kraak et al., 1994
Dreissena polymorpha (length 1.6-2.0 cm)	R	$ZnCl_2$	lake	7.9	270 (Ca)	10-w	NOECs	**400**	Kraak et al., 1994
Dreissena polymorpha (length 1.6-2.0 cm)	R	$ZnCl_2$	lake	7.9	270 (Ca)	10-w	NOECg	≥ 1400	Kraak et al., 1994
Ephydatia fluviatilis	S	$ZnCl_2$	art (M4)	8	250	7-d	NOECd	**43**	Van de Vyver, 2001
Ephydatia muelleri	S	$ZnCl_2$	art (M4)	8	250	7-d	NOECd	**43**	Van de Vyver, 2001
Eunapius fragilis	S	$ZnCl_2$	art (M4)	8	250	7-d	NOECd	**43**	Van de Vyver, 2001
Hyalella azteca (<1 w)	R		tap	7.9-8.6	130	10-w	NOECr,s	**42**	Borgmann et al., 1993
Hyalella azteca (<1 w)	R		tap	7.9-8.6	130	10-w	NOECg	> 316	Borgmann et al., 1993
Hyalella azteca (<1 w)	S	$ZnCl_2$	tap	7.9-8.6	130	4-w	NOECs	**166** (actual)	Borgmann and Norwood, 1997
Hyalella azteca (<1 w)	S	$ZnCl_2$	tap	7.9-8.6	130	4-w	NOECs	**49**	Borgmann and Norwood, 1997
Hyalella azteca (<1 w)	S	$ZnCl_2$	tap	7.9-8.6	130	4-w	NOECg	≥ 208 (actual)	Borgmann and Norwood, 1997
Hyalella azteca (<1 w)	S	$ZnCl_2$	tap	7.9-8.6	130	4-w	NOECg	≥ 91	Borgmann and Norwood, 1997
Potamopyrgus jenkinsi (juveniles (length 1.7 cm)	R	$ZnCl_2$	lake	8	160 (Ca)	16-w	NOECg	**75**	Dorgelo et al., 1995
Spongilla lacustris	S	$ZnCl_2$	art (M4)	8	250	7-d	NOECd	**65**	Van de Vyver, 2001

NOEC – No Observed Effect Concentration; S – static; R-renewal; g- growth; r- reproduction; d-development effects in sponges (measured cell aggregation, settlement and formation of functional sponges); e – emergence; f- filtration rate; d- day; w- week; art-artificial.

Table 6. NOEC nominal values and physico-chemical parameters for freshwater fish (accepted studies)

ORGANISM (LIFESTAGE / SIZE)	TEST TYPE	TEST COMPOUND	TEST WATER	PH	HARDNESS	EXPOSURE TIME	CRITERION	RESULT µg Zn /L	REFERENCE
Brachydanio rerio (eggs<4h)	R	$ZnSO_4.7H_2O$	art.	7.5	100	2-w	NOECh	**2900**	Dave et al., 1987
Brachydanio rerio (eggs<4h)	R	$ZnSO_4.7H_2O$	art.	7.5	100	2-w	NOECs	5800	Dave et al., 1987
Brachydanio rerio (eggs<4h)	R	$ZnSO_4.7H_2O$	art.	7.5	100	2-w	NOECh	**180**	Dave et al., 1987
Brachydanio rerio (eggs<4h)	R	$ZnSO_4.7H_2O$	art.	7.5	100	2-w	NOECs	5800	Dave et al., 1987
Brachydanio rerio (eggs<4h)	R	$ZnSO_4.7H_2O$	art.	7.5	100	2-w	NOECh	**720**	Dave et al., 1987
Brachydanio rerio (eggs<4h)	R	$ZnSO_4.7H_2O$	art.	7.5	100	2-w	NOECs	5800	Dave et al., 1987
Brachydanio rerio (eggs<4h)	R	$ZnSO_4.7H_2O$	art.	7.5	100	2-w	NOECh	**180**	Dave et al., 1987
Brachydanio rerio (eggs<4h)	R	$ZnSO_4.7H_2O$	art.	7.5	100	2-w	NOECs	5800	Dave et al., 1987
Brachydanio rerio (eggs<4h)	R	$ZnSO_4.7H_2O$	art.	7.5	100	2-w	NOECh	**180**	Dave et al., 1987
Brachydanio rerio (eggs<4h)	R	$ZnSO_4.7H_2O$	art.	7.5	100	2-w	NOECs	2900	Dave et al., 1987
Brachydanio rerio (eggs<4h)	R	$ZnSO_4.7H_2O$	art.	7.5	100	2-w	NOECh	**180**	Dave et al., 1987
Brachydanio rerio (eggs<4h)	R	$ZnSO_4.7H_2O$	art.	7.5	100	2-w	NOECs	5800	Dave et al., 1987
Brachydanio rerio (eggs<4h)	R	$ZnSO_4.7H_2O$	art.	7.5	100	2-w	NOECh	**2900**	Dave et al., 1987
Brachydanio rerio (eggs<4h)	R	$ZnSO_4.7H_2O$	art.	7.5	100	2-w	NOECs	2900	Dave et al., 1987
Brachydanio rerio (eggs<4h)	R	$ZnSO_4.7H_2O$	art.	7.5	100	2-w	NOECh	<720	Dave et al., 1987

Table 6 (cont.). NOEC nominal values and physico-chemical parameters for freshwater fish (accepted studies)

ORGANISM (LIFESTAGE / SIZE)	TEST TYPE	TEST COMPOUND	TEST WATER	PH	HARDNESS	EXPOSURE TIME	CRITERION	RESULT µg Zn /L	REFERENCE
Brachydanio rerio (eggs<4h)	R	$ZnSO_4.7H_2O$	art.	7.5	100	2-w	NOECs	5800	Dave et al., 1987
Brachydanio rerio (eggs<4h)	R	$ZnSO_4.7H_2O$	art.	7.5	100	2-w	NOECh	**2900**	Dave et al., 1987
Brachydanio rerio (eggs<4h)	R	$ZnSO_4.7H_2O$	art.	7.5	100	2-w	NOECs	11500	Dave et al., 1987
Brachydanio rerio (eggs<4h)	R	$ZnSO_4.7H_2O$	art.	7.5	100	2-w	NOECh	**1400**	Dave et al., 1987
Brachydanio rerio (eggs<4h)	R	$ZnSO_4.7H_2O$	art.	7.5	100	2-w	NOECs	11500	Dave et al., 1987
Cottus bairdi (mottled sculpin)	F	$ZnSO_4.7H_2O$	tap	7.5	154	30-d	NOECs	172 (actual)	Brinkman and Woodling, 2005
Cottus bairdi (mottled sculpin)	F	$ZnSO_4.7H_2O$	tap	7.38	46.3	30-d	NOECs	16 (actual)	Woodling et al., 2002
Jordanella floridae (larvae)	F	$ZnSO_4.7H_2O$	lake	7.5	44	14-w	NOECg	**26** (actual)	Spehar, 1976
Jordanella floridae (larvae)	F	$ZnSO_4.7H_2O$	lake	7.5	44	14-w	NOECs	51 (actual)	Spehar, 1976
Jordanella floridae (larvae)	F	$ZnSO_4.7H_2O$	lake	7.5	44	14-w	NOECr,h	≥ 85 (actual)	Spehar, 1976
Jordanella floridae (larvae)	F	$ZnSO_4.7H_2O$	lake	7.5	44	14-w	NOECg,r	**75** (actual)	Spehar, 1976
Jordanella floridae (larvae)	F	$ZnSO_4.7H_2O$	lake	7.5	44	14-w	NOECs	139 (actual)	Spehar, 1976
Jordanella floridae (larvae)	F	$ZnSO_4.7H_2O$	lake	7.5	44	14-w	NOECh	≥ 139 (actual)	Spehar, 1976
Oncorhynchus mykiss (eyed eggs)	F	$ZnSO_4.7H_2O$	tap	6.8	26	~ 2years	NOECs	**130**	Sinley et al., 1974
Oncorhynchus mykiss (eyed eggs)	F	$ZnSO_4.7H_2O$	tap	6.8	26	~ 2years	NOECg	≥ 535	Sinley et al., 1974

Table 6 (cont.). NOEC nominal values and physico-chemical parameters for freshwater fish (accepted studies)

ORGANISM (LIFESTAGE / SIZE)	TEST TYPE	TEST COMPOUND	TEST WATER	PH	HARDNESS	EXPOSURE TIME	CRITERION	RESULT µg Zn /L	REFERENCE
Oncorhynchus mykiss "fish" unexposed eggs)	F	$ZnSO_4.7H_2O$	tap	6.8	26	25-d	NOECs	**25**	Sinley et al., 1974
Oncorhynchus mykiss (eggs)	F	$ZnCl_2$	well	7	27	72-d	NOECs	**440** (actual)	Cairns and Garton, 1982
Oncorhynchus mykiss (early juveniles-5-6w, code: RF-B)	F	$ZnCl_2$	art.	7.5	30	30-d	NOECs	31.5 (actual)	De Schamphelaere et al., 2004
Oncorhynchus mykiss (early juveniles-5-6w, code:MG-B)	F	$ZnCl_2$	art.	7.5	30	30-d	NOECs	48 (actual)	De Schamphelaere et al., 2004
Oncorhynchus mykiss (early juveniles-5-6w, code: RF-B; MG-B)	F	$ZnCl_2$	art.	7.5	30	30-d	NOECs	**39** (actual)	De Schamphelaere et al., 2003
Oncorhynchus mykiss (early juveniles-5-6w, code: RF-NA-5)	F	$ZnCl_2$	art.	7.5	30	30-d	NOECs	**95** (actual)	De Schamphelaere et al., 2003
Oncorhynchus mykiss (early juveniles-5-6w, code: MG-0.2)	F	$ZnCl_2$	art.	7.7	45	30-d	NOECs	**45** (actual)	De Schamphelaere et al., 2003
Oncorhynchus mykiss (early juveniles-5-6w, code: MG-1)	F	$ZnCl_2$	art.	7.7	139	30-d	NOECs	**151** (actual)	De Schamphelaere et al., 2003
Oncorhynchus mykiss (early juveniles-5-6w, code: MG-2)	F	$ZnCl_2$	art.	7.7	229	30-d	NOECs	**159** (actual)	De Schamphelaere et al., 2003
Oncorhynchus mykiss (early juveniles-5-6w, code: PH-6.5)	F	$ZnCl_2$	art.	6.7	29	30-d	NOECs	**256** (actual)	De Schamphelaere et al., 2003

Table 6 (cont.). NOEC nominal values and physico-chemical parameters for freshwater fish (accepted studies)

ORGANISM (LIFESTAGE / SIZE)	TEST TYPE	TEST COMPOUND	TEST WATER	PH	HARDNESS	EXPOSURE TIME	CRITERION	RESULT µg Zn /L	REFERENCE
Oncorhynchus mykiss (early juveniles-5-6w, code: PH-7.5)	F	$ZnCl_2$	art.	7.6	28	30-d	NOECs	**157** (actual)	De Schamphelaere et al., 2003
Oncorhynchus mykiss (early juveniles-5-6w, code: CA-2)	F	$ZnCl_2$	art.	7.9	190	30-d	NOECs	**974** (actual)	De Schamphelaere et al., 2003
Oncorhynchus mykiss (early juveniles-5-6w, code: ANK)	F	$ZnCl_2$	ditch (DOC:23 mg/L)	7.8	104	30-d	NOECs	**771** (actual)	De Schamphelaere et al., 2003
Oncorhynchus mykiss (early juveniles-5-6w, code: MAR)	F	$ZnCl_2$	lake (DOC:6.2 mg/L)	8.1	176	30-d	NOECs	**696** (actual)	De Schamphelaere et al., 2003
Oncorhynchus mykiss (early juveniles-5-6w, code: VOY)	F	$ZnCl_2$	river (DOC:3.9 mg/L)	6.8	28	30-d	NOECs	**324** (actual)	De Schamphelaere et al., 2003
Oncorhynchus mykiss (early juveniles-5-6w, code: BIH)	F	$ZnCl_2$	river (DOC:4.3 mg/L)	6.2	23	30-d	NOECs	**370** (actual)	De Schamphelaere et al., 2003
Phoxinus phoxinus (mature)	F	$ZnNO_3.4H_2O$	tap	7.5	70	5-m	NOECs,g	130 (actual)	Bengtsson, 1974
Phoxinus phoxinus (yearlings)	F	$ZnNO_3.4H_2O$	tap	7.5	70	5-m	NOECs,g	**50** (actual)	Bengtsson, 1974
Pimephales promelas (eggs<1d)	F	$ZnSO_4.7H_2O$	lake	7.7	47	32-d	NOECs	129 (actual)	Norberg-King, 1989
Pimephales promelas (eggs<1d)	F	$ZnSO_4.7H_2O$	lake	7.7	47	32-d	NOECg	≥ 129 (actual)	Norberg-King, 1989
Pimephales promelas (newly hatched larvae)	R	$ZnSO_4.7H_2O$	lake	7.7	47	7-d	NOECg	128 (actual)	Norberg-King, 1989
Pimephales promelas (newly hatched larvae)	R	$ZnSO_4.7H_2O$	lake	7.7	47	7-d	NOECs	≥ 128 (actual)	Norberg-King, 1989

Table 6 (cont.). NOEC nominal values and physico-chemical parameters for freshwater fish (accepted studies)

ORGANISM (LIFESTAGE / SIZE)	TEST TYPE	TEST COMPOUND	TEST WATER	PH	HARDNESS	EXPOSURE TIME	CRITERION	RESULT µg Zn /L	REFERENCE
Pimephales promelas (newly hatched larvae)	F	$ZnSO_4.7H_2O$	lake	7.7	47	7-d	NOECs,g	117 (actual)	Norberg-King, 1989
Pimephales promelas (newly hatched larvae)	F	$ZnSO_4.7H_2O$	lake	7.7	47	7-d	NOECg	129 (actual)	Norberg-King, 1989
Pimephales promelas (newly hatched larvae)	F	$ZnSO_4.7H_2O$	lake	7.7	47	7-d	NOECs	≥ 129 (actual)	Norberg-King, 1989
Pimephales promelas (newly hatched larvae)	F	$ZnSO_4.7H_2O$	lake	7.7	47	7-d	NOECs,g	277 (actual)	Norberg-King, 1989
Pimephales promelas (newly hatched larvae)	R	$ZnSO_4.7H_2O$	lake	7.7	47	7-d	NOECs,g	291 (actual)	Norberg-King, 1989
Pimephales promelas (newly hatched larvae)	R	$ZnSO_4.7H_2O$	lake	7.7	47	5-d	NOECg	128 (actual)	Norberg-King, 1989
Pimephales promelas (newly hatched larvae)	R	$ZnSO_4.7H_2O$	lake	7.7	47	5-d	NOECs	≥ 128 (actual)	Norberg-King, 1989
Pimephales promelas (newly hatched larvae)	R	$ZnSO_4.7H_2O$	lake	7.7	47	5-d	NOECs	117 (actual)	Norberg-King, 1989
Pimephales promelas (newly hatched larvae)	R	$ZnSO_4.7H_2O$	lake	7.7	47	5-d	NOECg	≥ 117 (actual)	Norberg-King, 1989
Pimephales promelas (newly hatched larvae)	R	$ZnSO_4.7H_2O$	lake	7.7	48	7-d	NOECs	85 (actual)	Norberg and Mount, 1985
Pimephales promelas (newly hatched larvae)	R	$ZnSO_4.7H_2O$	lake	7.7	48	7-d	NOECg	184 (actual)	Norberg and Mount, 1985
Pimephales promelas (embryos)	R	$ZnSO_4.7H_2O$	art	7	100	6-d	NOEC d	120 (actual)	Dawson et al., 1988
Pimephales promelas (eggs <1 d)	F	$ZnSO_4.7H_2O$	lake	7 to 8	46	± 8-min	NOECr	**78** (actual)	Benoit and Holcombe 1978
Pimephales promelas (eggs <1 d)	F	$ZnSO_4.7H_2O$	lake	7 to 8	46	± 8-min	NOECs,h,d	145 (actual)	Benoit and Holcombe 1978

Table 6 (cont.). NOEC nominal values and physico-chemical parameters for freshwater fish (accepted studies)

ORGANISM (LIFESTAGE / SIZE)	TEST TYPE	TEST COMPOUND	TEST WATER	PH	HARDNESS	EXPOSURE TIME	CRITERION	RESULT µg Zn /L	REFERENCE
Pimephales promelas (eggs <1 d)	F	$ZnSO_4.7H_2O$	lake	7 - 8	46	± 8-min	NOECm	295 (actual)	Benoit and Holcombe 1978
Pimephales promelas (eggs <1 d)	F	$ZnSO_4.7H_2O$	lake	7 - 8	46	± 8-min	NOEC g	≥ 575 (actual)	Benoit and Holcombe 1978
Salvenilus fontinalis (yearlings)	F	$ZnSO_4.7H_2O$	lake	7.0-7.7	45	3-yr	NOECh	**530** (actual)	Holcombe et al., 1979
Salvenilus fontinalis (yearlings)	F	$ZnSO_4.7H_2O$	lake	7.0-7.7	45	3-yr	NOECs,g,r	≥ 1360 (actual)	Holcombe et al., 1979
Salvenilus fontinalis (eggs 6h)	F	$ZnSO_4.7H_2O$	lake	7.2-7.9	45	>12-w	NOECs	720 (actual)	Holcombe et al., 1979
Salvenilus fontinalis (eggs 6h)	F	$ZnSO_4.7H_2O$	lake	7.2-7.9	45	>12-w	NOECg	≥ 2060 (actual)	Holcombe et al., 1979
Salvenilus fontinalis (newly hatched larvae)	F	$ZnSO_4.7H_2O$	lake	7.2-7.9	45	12-w	NOECs	720 (actual)	Holcombe et al., 1979
Salvenilus fontinalis (newly hatched larvae)	F	$ZnSO_4.7H_2O$	lake	7.2-7.9	45	12-w	NOECg	≥ 2060 (actual)	Holcombe et al., 1979
Salvenilus fontinalis (newly hatched larvae)	F	$ZnSO_4.7H_2O$	lake	7.2-7.9	45	> 12-w	NOECs	1370 (actual)	Holcombe et al., 1979
Salvenilus fontinalis (newly hatched larvae)	F	$ZnSO_4.7H_2O$	lake	7.2-7.9	45	> 12-w	NOECg	≥ 2060 (actual)	Holcombe et al., 1979
Salvenilus fontinalis (larvae 4-w)	F	$ZnSO_4.7H_2O$	lake	7.2-7.9	45	8-w	NOECs	720 (actual)	Holcombe et al., 1979
Salvenilus fontinalis (larvae 4-w)	F	$ZnSO_4.7H_2O$	lake	7.2-7.9	45	8-w	NOECg	≥ 2060 (actual)	Holcombe et al., 1979

NOEC – No Observed Effect Concentration; F- flow-through; R-renewal; g- growth; r- reproduction; d-development; s-survival; h-hatching; d- day; w- week; min- minutes; art-artificial.

6.1.4. Abiotic factors influencing the aquatic toxicity of zinc in freshwater

Physico-chemical water characteristic such as hardness, pH, DOC and zinc background concentration influences the chemical speciation of zinc in water and thus may influence bioavailability and toxicity.
Toxicity of metals is assumed to be inversely related to hardness. However it was concluded that there is a poor basis to correct PNEC based on one of the water chemistry properties. Therefore, the biotic ligand model (BLM) that incorporated various mitigation factors was used to take into account bioavailability of zinc in surface waters.

Background concentration

According to the metallo-region concept, adaptation to natural background levels and also to test conditions may influence the sensitivity to metals. An increase in tolerance towards zinc has been observed for *Daphnia magna*, for *Raphidocelis subcapitata* and *Chlorella vulgaris* when cultured in laboratory under varying zinc concentrations (Muyssen and Janssen, 2001b). From the selected studies to derive PNEC, all background concentrations were plotted against NOEC values to evaluate a possible relationship between background concentrations and toxicity. However, there was not a clear trend and it was concluded that there is a too poor basis to derive background dependent PNEC values for fresh water.

6.1.5. Derivation of the Predicted No Effect Concentration surface waters ($PNEC_{freshwater}$)

HC5-50 derived from statistical extrapolation and assessment factor

The use of statistical extrapolation was preferred for the derivation of a $PNEC_{add}$ rather than the use of an assessment factor on the lowest NOEC. In accordance with the Workshop recommendation, the 5^{th} percentile value (HC_{5-50}) with an assessment factor between 1 and 5 was applied. A species sensitivity distribution was performed using the "species mean" NOEC values and when using a log-normal distribution the resulting value was 15.6 µg Zn/L in freshwater.
Based on the available data an assessment factor smaller than 5 and above 1 was used for several reasons:

- There is a relative large database and a small difference between the 50% confidence and the 95% confidence limits that would support an AF lower than 5;
- The median 5% percentile values calculated with the log-normal and the log-logistic distribution functions are nearly equal which would suggest that there is no need of an AF.
- The median value of 15.6 µg Zn/L might no be protective enough for some species as there were NOEC values below this value for two species. Therefore an AF bigger than one but below 5 is supported.

- In some ecosystem or field studies effects were found below the median 5% percentile of 15.6 µg Zn/L. Therefore an AF bigger than 1 and lower than 5 is supported.

6.1.6. Final derivation of the $PNEC_{add, freshwater}$

The use of statistical extrapolation using all NOECs in the ecotoxicity database was preferred for the $PNEC_{add}$ derivation.

The median 5% percentile value of 15.6 µg Zn/L using an AF of 2 because of the above reasons resulted in a **$PNEC_{add}$ of 7.8 µg Zn/L for freshwater**. In the risk characterization, this $PNEC_{add}$ was also used for saltwater.

For soft waters (hardness < 24mg/L) this $PNEC_{add, freshwater}$ was considered not protective enough and therefore a $PNEC_{add, soft water}$ was also derived for surface waters where hardness is below 24 mg/L. Therefore the $PNEC_{add, soft water}$ was derived from the generic $PNEC_{add, freshwater}$ by dividing this value by a "water effect ratio"(WER). The WER, defined as the NOEC derived from the test performed in the medium hardness water divided by the NOEC derived from the original soft water, was calculated for each test of 6 available tests. From these WERs, the arithmetic mean was calculated and resulted in WER value of 2.5.
The use of the arithmetic mean WER of 2.5 and the generic $PNEC_{add, freshwater}$ of 7.8 µg Zn/L resulted in a **$PNEC_{add, freshwater}$ soft waters of 3.1 µg Zn/L.**

6.2. Chronic toxicity data for marine organisms

The zinc marine effects database contains a number of chronic NOEC values (48 chronic NOECs for 28 species). For the marine compartment, the effects assessment of zinc was based on NOECs collected for saltwater organisms.
Data on chronic toxicity tests resulting in NOEC values for freshwater algae/higher plants and invertebrates are summarized in Tables 7 and 8, respectively.

6.2.1. Toxicity data for marine algae

In the Zn RA, 33 chronic studies reporting the NOEC for saltwater algae/higher plants for 15 species were found. The species mean NOEC for saltwater algae/higher plants range from 10 µg/L Zn for *Chaetoceros compressum, Schroederella schroederi* and *Thalassiosira rotula*(endpoint growth) and 2700 µg/L Zn for *Phaeodactilum tricornutum* (endpoint growth; 3 test values).

6.2.2. Toxicity data for marine invertebrates

In the Zn RA, 15 chronic studies reporting NOEC for 12 single-species saltwater invertebrates were found. The species mean NOEC for saltwater invertebrates range from 10 µg Zn /L (measured concentration) for the echinoderm *Arbacia lixula* (endpoint reproduction; 1 test value) to 1000 µg Zn /L for the mollusc *Scrobicularia plana* (endpoint survival; 1 test result).

6.2.3. PNEC$_{add}$, saltwater derivation

Within this RA, PNEC$_{add, saltwater}$ has not been derived. Although there were sufficient NOEC values for saltwater organisms to apply statistical extrapolation and a 5% percentile value of 6.1 μg Zn/L saltwater was calculated. This value was considered too unreliable to derive a saltwater PNEC$_{add}$, because the saltwater NOEC values were not updated and checked for reliability based on the criteria used for freshwater. Therefore, for risk characterization, the PNEC$_{add}$ derived for freshwater was applied for both freshwater and saltwater.

Table 7. NOEC values (added) and physico-chemical parameters for saltwater algae/higher plants (accepted studies)

ORGANISM (LIFESTAGE / SIZE)	TEST TYPE	TEST COMPOUND	TEST WATER	SALINITY ˚/00	EXPOSURE TIME	CRITERION	RESULT µg Zn /L	REFERENCE
Amphidinium carteri	S	$ZnSO_4$	art sw	-	9-d	NOECg	**100**	Break et al., 1976
Asterionella japonica (clone AST C2 or N1.1)	S	$ZnSO_4$	nat sw	35	3-d	NOECg	**7**	Fisher and Frood, 1980
Asterionella japonica (clone AST C2 or N1.1)	S	$ZnSO_4$	nat sw	35	3-d	NOECg	**20**	Fisher and Frood, 1980
Asterionella japonica (clone AST C4)	S	$ZnSO_4$	nat sw	35	3-d	NOECg	**40**	Fisher and Frood, 1980
Asterionella japonica (clone AST N1.1)	S	$ZnSO_4$	nat sw	35	3-d	NOECg	**30**	Fisher and Jones, 1981
Asterionella japonica (clone AST N1.1)	S	$ZnSO_4$	nat sw	35	3-d	NOECg	**7**	Fisher and Frood, 1980
Asterionella japonica (clone AST N1.1)	S	$ZnSO_4$	nat sw	35	3-d	NOECg	**7**	Fisher and Frood, 1980
Asterionella japonica (clone AST N1.1)	S	$ZnSO_4$	nat sw	35	3-d	NOECg	**20**	Fisher and Frood, 1980
Chaetoceros compressum	S	$ZnSO_4$	nat sw	35	3-d	NOECg	**10**	Fisher and Frood, 1980
Gymnodinium splendens	S	$ZnSO_4$	nat sw	32	5-w	NOECg	**500**	Kayser, 1977
Laminaria hyperborea	R	$ZnSO_4$	nat sw		4-w	NOECg	**100**	Hopkins and Kain, 1971
Nitzschia closterium	S	$ZnSO_4$	nat sw	35	3-d	NOECg	**40**	Fisher and Frood, 1980
Nitzschia closterium	S	$ZnSO_4$	nat sw	35	3-d	NOECg	**10**	Fisher and Frood, 1980
Phaeodactilum tricornutum	F	$ZnCl_2$	nat sw	-	2-w	NOECg	**10000**	Jensen et al., 1974
Phaeodactilum tricornutum	S	$ZnSO_4$	art sw	-	10-d	NOECg	**4000**	Braek et al., 1976
Phaeodactilum tricornutum	S	$ZnSO_4$	art sw	-	10-d	NOECg	**500**	Braek et al., 1976
Prorocentrum micans	S	$ZnSO_4$	nat sw	32	5-w	NOECg	**100**	Kayser, 1977
Rhizosolenia spp	S	-	nat sw	-	12-24 h	NOECg	**15**	Davies and Sleep, 1979
Schroederella schroederi	S	$ZnSO_4$	nat sw	32	11-d	NOECg	**10**	Kayser, 1977
Scrippsiella faeroense	S	$ZnCl_2$	nat sw	32	7-w	NOECg	**100**	Kayser, 1977
Skeletonema costatum	-	-	-	-	10/14-d	NOECg	**200**	MARITOX 9761

Table 7 (cont.). NOEC values (added) and physico-chemical parameters for saltwater algae/higher plants (accepted studies)

ORGANISM (LIFESTAGE / SIZE)	TEST TYPE	TEST COMPOUND	TEST WATER	SALINITY °/00	EXPOSURE TIME	CRITERION	RESULT µg Zn /L	REFERENCE
Skeletonema costatum	-	-	-	-	10/14-d	NOECg	**50**	MARITOX 9761
Skeletonema costatum (clone skel-0)	S	$ZnSO_4$	art sw	-	10-d	NOECg	**100**	Braek et al., 1976
Skeletonema costatum (clone skel-5)	F	$ZnSO_4$	nat sw	-	2-w	NOECg	**25**	Jensen et al., 1974
Skeletonema costatum (clone skel-5)	S	$ZnSO_4$	art sw	-	10-d	NOECg	**50**	Braek et al., 1976
Skeletonema costatum (clone skel-C6)	S	$ZnSO_4$	nat sw	35	3-d	NOECg	**30**	Fisher and Frood, 1980
Skeletonema costatum (clone skel-C7)	S	$ZnSO_4$	nat sw	35	3-d	NOECg	**20**	Fisher and Frood, 1980
Skeletonema costatum (clone skel-C7)	S	$ZnSO_4$	nat sw	35	3-d	NOECg	**7**	Fisher and Frood, 1980
Skeletonema costatum (clone skel-C7)	S	$ZnSO_4$	nat sw	35	3-d	NOECg	**7**	Fisher and Frood, 1980
Thalassiosira guillardii	-	-	-	-	10/14-d	NOECg	**200**	MARITOX 9761
Thalassiosira pseudonana	F	$ZnCl_2$	nat sw	-	14-d	NOECg	**100**	Jensen et al., 1974
Thalassiosira pseudonana	S	$ZnSO_4$	art sw	-	9-d	NOECg	**200**	Braek et al., 1976
Thalassiosira rotula	S	$ZnSO_4$	nat sw	32	14-d	NOECg	**10**	Kayser, 1977

NOEC – No Observed Effect Concentration; S – static; F-flowthrough; g- growth; nat- natural; art-artificial; sw-saltwater; d- day; w- week;

Table 8. NOEC values (added) and physico-chemical parameters for saltwater invertebrates (accepted studies)

ORGANISM (LIFESTAGE / SIZE)	TEST TYPE	TEST COMPOUND	TEST WATER	SALINITY °/00	EXPOSURE TIME	CRITERION	RESULT µg Zn /L	REFERENCE
Arbacia lixula	-	-	-	-	4-d	NOECr	**10**	MARITOX 51385
Arbacia lixula	-	-	-	-	20-d	NOECs	**1000**	MARITOX 51385
Calianassa australiensis	-	-	-	-	14-d	NOECs	**440**	MARITOX 15338
Capitella capitata	-	-	-	-	25/40-d(?)	NOECr	**320**	MARITOX 51618
Crassostera gigas	R	$ZnSO_4$	nat sw	29	5-d	NOECd,g	**50**	Brereton et al. 1973
Ctenodrilus serratus	S	$ZnSO_4.7H_2O$	nat sw	-	3-w	NOECs,r	**100**	Reish and Carr, 1978
Ctenodrilus serratus	-	-	-	-	28/31-d	NOECr	**100**	MARITOX 51618
Eirene viridula	R	$ZnSO_4$	nat sw	30	3-mo	NOECmc	**300**	Karbe, 1972
Haliotis refescens	-	-	-	-	9-d	NOECr	**19**	MARITOX 50173
Holmesimysis costata (9-d old juveniles)	R	$ZnSO_4.7H_2O$	nat sw	35	7-w	NOECs,g	**18**	Martin et al., 1989
Mercenaria mercenaria (2 d larvae)	R	$ZnCl_2$	nat sw	24	8-d	NOECs,g	**50**	Calabrese et al., 1977
Mysidopsis bahia	-	-	-	-		NOECr	**120**	MARITOX 51549
Nereis arenaceodentata	-	-	-	-	4-mo (?)	NOECr	**100**	MARITOX 51618
Scrobicularia plana (length 4-5 cm)	R	$Zn(NO_3)_2$	nat sw	31	14-d	NOECs	**1000**	Akberali et al., 1981

NOEC – No Observed Effect Concentration; S – static; R-renewal; g- growth; r- reproduction; s- survival; d-development; mc – morphological changes; nat-natural; art-artificial; sw-saltwater; d- day; w- week; mo- month.

6.3. Freshwater sediment toxicity

According to the TGD, the PNEC for sediment ($PNEC_{add,sediment}$) can be derived from sediment toxicity data for benthic organisms. In the absence of toxicity data for benthic organisms, the PNEC for sediment may be calculated using the equilibrium partitioning (EP) method. In this Zn RA this method was used for comparison.

6.3.1. Results for freshwater sediment toxicity

Limited data is available for freshwater sediment systems with Zn-spiked sediments. Chronic toxicity data results for zinc toxicity for benthic organisms are summarized in Table 9. NOEC values (added) were only available for three invertebrate species, *Tubifex tubifex*, *Hyalella azteca* and *Chironomus tentans*.

6.3.2. $PNEC_{add,sediment}$ using the sediment toxicity data for benthic organisms

For benthic invertebrates only four useful chronic NOEC values were available: one for the oligochaete *Tubifex tubifex* (1101 mg/kg dw), two for the insect *Chironomus tentans* (609 and 795 mg/kg dw) and one for the crustacean *Hyalella azteca* (488 mg/kg dw). These NOEC values are expressed as the added Zn- concentration. These data are too limited to apply statistical extrapolation. Thus the $PNEC_{add,sediment}$ has been derived from the lowest chronic NOEC which is the NOEC for *Hyalella azteca* of 488 mg/kg dw. These three benthic species represent three taxonomic groups of invertebrates with different living conditions and therefore, according to the TGD, an assessment factor of 10 should be used on the lowest chronic NOEC, resulting in a $PNEC_{add,sediment}$ of 49 mg/kg dw.

6.3.3. $PNEC_{add,sediment}$ using the equilibrium partitioning method

The EP-method used for the derivation of the $PNEC_{add,sediment}$ has limitations because of the following assumptions:

- Bioavailability, bioaccumulation and toxicity are closely related to the pore water concentration;
- Equilibrium exists between the chemical sorbed to the particulate sediment and the pore water and that these concentrations are related to a partition coefficient;
- Sensitivity distributions for aquatic and benthic organisms are equal.

As with the calculation of the PEC_{add} for sediment, the properties of suspended matter were used to calculate the $PNEC_{add,sediment}$, that is $PNEC_{add,sediment}$= $PNEC_{add,suspended\ matter}$. This resulted on a $PNEC_{add,sediment}$of 187 mg/kg wet weight (ww) as follows:

1.1. $K_{susp-water}$:

$$Fwater_{susp} + (Fsolid_{susp} \times Kp_{susp} \times RHO_{solid}) = 27501$$

1.2. $PNEC_{add,sed}$= $PNEC_{add,susp}$:

$$(K_{susp\text{-}water}/ RHO_{susp}) \ \times PNEC_{add,aquatic} = 187 \text{ mg/kg ww}$$

where:

$K_{susp\text{-}water}$ - volumetric suspended matter/water partition coefficient (110)
$Fwater_{susp}$ – volume fraction water in suspended matter (0.9)
$Fsolid_{susp}$ - volume fraction solids in suspended matter (0.1)
Kp_{susp} – suspended matter/ water partition coefficient
RHO_{solid} – density of the solid fraction (2500 kg/m^3)
RHO_{susp} – bulk density of wet suspended matter fraction (1150 kg/m^3)
$PNEC_{add,sed}$ – Predicted No Effect Concentration in sediment (mg/kg wet sed)
$PNEC_{add,susp}$ - Predicted No Effect Concentration in suspended matter (mg/kg wet suspended matter)
$PNEC_{add,aquatic}$ - Predicted No Effect Concentration in water (7.8 µg/L)

6.3.4. Conclusion on $PNEC_{add,sediment}$

Based on all data, preference was given to the $PNEC_{add,\ sediment}$ based on the sediment toxicity data for benthic organisms. Therefore, the **$PNEC_{add,\ sediment}$ of 49 mg/kg dw** which is equivalent to 11 mg/kg wet weight.

In the risk characterization, the above $PNEC_{add,\ sed}$ was used for both the freshwater and marine environment as no $PNEC_{add,\ sed}$ could be derived for the marine environment. For saltwater benthic organisms no chronic toxicity data for zinc-spiked sediments are available.

Table 9. NOEC values (added) and physico-chemical parameters for sediment dwelling-organisms (accepted studies)

ORGANISM (LIFESTAGE / SIZE)	TEST TYPE	TEST COMPOUND	SEDIMENT	FRACTION OC	CLAY (%)	TEMP. ˚C	EXPOSURE TIME	CRITERION	RESULT (mg/kg dw)	REFERENCE
Tubifex tubifex (adults)	S	$ZnCl_2$	pond sediment	0.01-0.02	-	23	4-w	NOECr	**1101**	Farrar and Bridges, 2003
Tubifex tubifex (adults)	S	$ZnCl_2$	pond sediment	0.01-0.02	-	23	4-w	NOECs	2576	Farrar and Bridges, 2003
Hyalella azteca (1-w old)	R	$ZnCl_2$	stream sediment	0.02	8	23	6-w	NOECs	**488**	Nguyen et al., 2005
Hyalella azteca (1-w old)	R	$ZnCl_2$	stream sediment	0.02	8	23	4-w	NOECg	>978	Nguyen et al., 2005
Hyalella azteca (1-w old)	R	$ZnCl_2$	stream sediment	0.02	8	23	6-w	NOECr	>978	Nguyen et al., 2005
Chironomus tentans (newly hatched larvae)	R	$ZnCl_2$	lake sediment	-	-	23	8-w	NOECs,g,e,r	**795**	Sibley et al., 1996
Chironomus tentans (<1-d old)	R	$ZnCl_2$	pond sediment	0.01	-	23	3-w	NOECg	**609**	Farrar and Bridges, 2002,2003
Chironomus tentans (<1-d old)	R	$ZnCl_2$	pond sediment	0.01	-	23	3-w	NOECs	2390	Farrar and Bridges, 2002,2003

NOEC – No Observed Effect Concentration; S – static; R-renewal; g- growth; r- reproduction; s- survival; e-emergence; d- day; w- week.

7. TERRESTRIAL COMPARTMENT

7.1. Results chronic toxicity data for soil organisms

The zinc terrestrial effects database contains a large number of chronic NOEC/EC10 values (200 NOEC/EC10 for 20 species and 17 microbe-mediated soil processes). For the terrestrial environment, the effects assessment of zinc was based on NOEC/EC10s collected for soil organisms. Data on chronic toxicity tests resulting in NOEC/EC10 for higher plants, soil invertebrates and microbe-mediated processes are summarized in Tables 10, 11 and 12, respectively. No recent studies were found in the literature.

7.1.1. Toxicity data for higher plants

In the Zn RA, 49 chronic studies reporting NOEC/EC10 for soil higher plants for 16 species were found in the literature but only 31 NOEC/EC10 were used for $PNEC_{add}$ derivation. The species mean NOEC for higher plants ranged from 45 mg Zn/kg dry weight for *Trifolium pratense* (endpoint yeld based on weigh of the roots; 6 test values) to 200 mg Zn/kg dry weight for *Avena sativa* (endpoint yeld; 3 test values).

7.1.2. Toxicity for soil invertebrates

In the Zn RA, 100 chronic studies reporting NOEC/EC10 for soil invertebrates for 4 species were found in the literature, but only 43 NOEC/EC10 were used for $PNEC_{add}$ derivation. The species mean NOEC for soil invertebrates ranged from 280 mg Zn/kg dry weight for *Eisenia fetida* (endpoint reproduction based on the number of cocoons; 25 test values) to 600 mg Zn/kg dry weight for *Aporrectodea caliginosa* (endpoint reproduction based on the number of cocoons; 1 test value).

7.1.3. Toxicity for soil microbe-mediated processes

In the Zn RA, 151 chronic studies reporting NOEC/EC10 values for soil microbe-mediated processes for 17 microbial processes were found in the literature but only 97 NOEC/EC10 values were used for $PNEC_{add}$ derivation.

Table 10. Estimated NOEC values used for $PNEC_{add}$ derivation for higher plants and physico-chemical parameters for soils (accepted studies)

Organism	Test compound	**Soil type**	**pH**	OM (%)	**Clay (%)**	**Temp ˚C**	**Exp time**	**Criterion**	**NOEC (mg Zn/kg dw)**	**NOEC (added) used for $PNEC_{add}$**	Reference
Allium cepa	$ZnSO_4.7H_2O$	clay loam	8.3	0.5	24	-		NOECy(p)	200	200	Dang et al., 1990
Avena sativa	$Zn(Ac)_2$	loamy soil	5.6	2	12	-	5-mo	NOECy(gr)	100	100	De Haan et al., 1985
Avena sativa	$Zn(Ac)_2$	loamy soil	5.4	2	40	-	5-mo	NOECy(gr)	200	200	De Haan et al., 1985
Avena sativa	$Zn(Ac)_2$	sandy loam	5	3	4	-	5-mo	NOECy(gr)	200	200	De Haan et al., 1985
Avena sativa	$Zn(Ac)_2$	sandy loam	5.4	7	5	-	5-mo	NOECy(gr)	400	400	De Haan et al., 1985
Beta vulgaris	$Zn(NO_3)_2.\ 6H_2O$	silt loam	7.5	-	-	26-31	42-d	NOECy(p)	300	300	Boawn and Rasmussen, 1971
Hordeum vulgare	$ZnCl_2$	sandy loam	5.6	8	13	14-17	48-d	NOECy(s)	10	33	Luo and Rimmer, 1995
Hordeum vulgare	$ZnCl_2$	sandy loam	5.6	8	13	14-17	48-d	NOECy(r)	>100		Luo and Rimmer, 1995
Hordeum vulgare	$ZnSO_4.7H_2O$	sandy loam	7.8	1	-	-	45-d	NOECy(r)	50		Aery and Jagetiya, 1997
Hordeum vulgare	$ZnSO_4.7H_2O$	sandy loam	7.8	1	-	-	45-d	EC10y(r)	215	215	Aery and Jagetiya, 1997
Hordeum vulgare	$ZnSO_4.7H_2O$	sandy loam	7.8	1	-	-	45-d	NOECy(s)	250		Aery and Jagetiya, 1997
Hordeum vulgare	$ZnSO_4.7H_2O$	sandy loam	7.8	1	-	-	45-d	EC10y(s)	1450		Aery and Jagetiya, 1997
Hordeum vulgare	$Zn(NO_3)_2.\ 6H_2O$	silt loam	7.5	-	-	26-30	33-d	NOECy(p)	100	100	Boawn and Rasmussen, 1971
Lactuca sativa	$Zn(NO_3)_2.\ 6H_2O$	silt loam	7.5	-	-	26-30	40-d	NOECy(p)	400	400	Boawn and Rasmussen, 1971
Lycopersicon esculentum	$Zn(NO_3)_2.\ 6H_2O$	silt loam	7.5	-	-	26-31	-	NOECy(p)	400	400	Boawn and Rasmussen, 1971
Medicago sativa	$Zn(NO_3)_2.\ 6H_2O$	silt loam	7.5	-	-	26-30	67-d	NOECy(p)	300	300	Boawn and Rasmussen, 1971
Pisum sativum	$Zn(NO_3)_2.\ 6H_2O$	silt loam	7.5	-	-	26-31		NOECy(p)	400	400	Boawn and Rasmussen, 1971
Sorghum bicolor	$Zn(NO_3)_2.\ 6H_2O$	silt loam	7.5	-	-	26-30	35-d	NOECy(p)	100	100	Boawn and Rasmussen, 1971
Sorghum bicolor	$Zn(NO_3)_2.\ 6H_2O$	silt loam	7.5	-	-	26-30	35-d	NOECy(p)	200	200	Boawn and Rasmussen, 1971

Table 10 (cont.). Estimated NOEC values used for $PNEC_{add}$ derivation for higher plants and physico-chemical parameters for soils (accepted studies)

Organism	Test compound	**Soil type**	**pH**	OM (%)	**Clay (%)**	**Temp °C**	**Exp time**	**Criterion**	**NOEC (mg Zn/kg dw)**	**NOEC (added) used for $PNEC_{add}$**	Reference
Spinacea oleracea	$Zn(NO_3)_2. 6H_2O$	silt loam	7.5	-	-	26-31		NOECy(p)	200	200	Boawn and Rasmussen, 1971
Trifolium pratense	$ZnCl_2$	art soil (OECD)	6.2	10	20	18-24	24-d	NOECy(r,s)	100	100	Van der Hoeven and Henzen 1994a, b
Trifolium pratense	$ZnCl_2$	art soil (OECD)	6.2	10	20	18-24	24-d	EC10y(r)	113		Van der Hoeven and Henzen 1994a, b
Trifolium pratense	$ZnCl_2$	art soil (OECD)	6.2	10	20	18-24	24-d	EC10y(s)	133		Van der Hoeven and Henzen 1994a, b
Trifolium pratense	$ZnCl_2$	art soil (OECD)	6.2	10	20	18-24	24-d	NOECy(r)	84	84	Van der Hoeven and Henzen 1994a, b
Trifolium pratense	$ZnCl_2$	art soil (OECD)	6.2	10	20	18-24	24-d	EC10y(r)	84		Van der Hoeven and Henzen 1994a, b
Trifolium pratense	$ZnCl_2$	art soil (OECD)	6.2	10	20	18-24	24-d	NOECy(s)	150		Van der Hoeven and Henzen 1994a, b
Trifolium pratense	$ZnCl_2$	art soil (OECD)	6.2	10	20	18-24	24-d	EC10y(s)	130		Van der Hoeven and Henzen 1994a, b
Trifolium pratense	$ZnCl_2$	sand	5	5(?)	13(?)	19-27	25-d	NOECy(r,s)	32	32	Van der Hoeven and Henzen 1994b, b
Trifolium pratense	$ZnCl_2$	sand (PANH)	5.3	2	2	19-24	25-d	NOECy(r,s)	32	32	Van der Hoeven and Henzen 1994b
Trifolium pratense	$ZnCl_2$	sand (PANH)	5.3	2	2	19-24	25-d	NOECgerm	180		Van der Hoeven and Henzen 1994b
Trifolium pratense (1994)	$ZnCl_2$	sand (PANH)	5.3	2	2	19-24	25-d	EC10y(s)	30		Hoofman and Henzen, 1996
Trifolium pratense (1994)	$ZnCl_2$	sand (PANH)	5.3	2	2	19-24	25-d	EC10y(r)	24		Hoofman and Henzen, 1996
Trifolium pratense (1995a)	$ZnCl_2$	sand (PANH)	5.3	2	2	20	25-d	NOECy(r,s)	32	32	Hoofman and Henzen, 1996

Table 10 (cont.). Estimated NOEC values used for $PNEC_{add}$ derivation for higher plants and physico-chemical parameters for soils (accepted studies)

Organism	Test compound	**Soil type**	**pH**	OM (%)	**Clay (%)**	**Temp °C**	**Exp time**	**Criterion**	**NOEC (mg Zn/kg dw)**	**NOEC (added) used for $PNEC_{add}$**	Reference
Trifolium pratense (1995a)	$ZnCl_2$	sand (PANH)	5.3	2	2	20	25-d	NOECgerm	320		Hoofman and Henzen, 1996
Trifolium pratense (1995b)	$ZnCl_2$	sand (PANH)	5.3	2	2	20	25-d	NOECy(r,s)	32	32	Hoofman and Henzen, 1996
Trifolium pratense (1995b)	$ZnCl_2$	sand (PANH)	5.3	2	2	20	25-d	NOECgerm	320		Hoofman and Henzen, 1996
Trigonella poenumgraceum	$ZnSO_4.7H_2O$	clay loam	8.3	0.5	24		8-w	NOECy(p)	200	200	Dang et al., 1990
Triticum vulgare	$Zn(NO_3)_2.\ 6H_2O$	silt loam	7.5	-	-	26-31	33-d	NOECy(p)	200	200	Boawn and Rasmussen, 1971
Vicia sativa	$ZnCl_2$	sand	5	5(?)	13(?)	19-24	24-d	NOECy(r)	32	32	Van der Hoeven and Henzen, 1994c
Vicia sativa	$ZnCl_2$	sand	5	5(?)	13(?)	19-24	24-d	NOECy(s)	100		Van der Hoeven and Henzen, 1994c
Vigna mungo	$ZnSO_4.7H_2O$	-	6.2	-	-	-	45-d	NOECy(r,st)	100	100	Kalyanaraman and Sivagurunathan, 1993
Vigna mungo	$ZnSO_4.7H_2O$	-	6.2	-	-	-	45-d	EC10y(r)	155		Kalyanaraman and Sivagurunathan, 1993
Vigna mungo	$ZnSO_4.7H_2O$	-	6.2	-	-	-	45-d	EC10y(st)	162		Kalyanaraman and Sivagurunathan, 1993
Vigna mungo	$ZnSO_4.7H_2O$	-	6.2	-	-	-	45-d	NOECy(l)	150		Kalyanaraman and Sivagurunathan, 1993
Zea mays	$ZnSO_4.7H_2O$	sandy loam (without P)	4.9	3	16	-	6-w	NOECy(s)	83	83	MacLean, 1974
Zea mays	$Zn(NO_3)_2.\ 6H_2O$	silt loam	7.5	-	-	26-30	28-d	NOECy(p)	300	300	Boawn and Rasmussen, 1971
Zea mays	$Zn(NO_3)_2.\ 6H_2O$	silt loam	7.5	-	-	26-30	28-d	NOECy(p)	200	200	Boawn and Rasmussen, 1971

Table 10 (cont.). Estimated NOEC values used for $PNEC_{add}$ derivation for higher plants and physico-chemical parameters for soils (accepted studies)

Organism	Test compound	**Soil type**	**pH**	OM (%)	**Clay (%)**	**Temp ˚C**	**Exp time**	**Criterion**	**NOEC (mg Zn/kg dw)**	**NOEC (added) used for $PNEC_{add}$**	Reference
Zea mays	$Zn(NO_3)_2 . 6H_2O$	silt loam	7.5	-	-	26-30	28-d	NOECy(p)	300	300	Boawn and Rasmussen, 1971
Zea mays	$Zn(NO_3)_2 . 6H_2O$	silt loam	7.5	-	-	26-30	28-d	NOECy(p)	200	200	Boawn and Rasmussen, 1971

NOEC – No Observed Effect Concentration;y(r)- yield based on weight of the roots; y(g)- yield based on weight of grains; y(l)- yield based on weight of the leaves; y(p)- yield based on weight of whole plants; y(s)- yield based on weight of shoots; germ – germination; d- day; mo-month.

Table 11. Estimated NOEC values used for $PNEC_{add}$ derivation for soil invertebrates and physico-chemical parameters for soils (accepted studies)

Organism (lifestage/size)	Test compound	Soil type	pH	OM (%)	Clay (%)	Temp °C	Exp time	Criterion	NOEC (mg Zn/kg dw)	NOEC (added) used for $PNEC_{add}$	Reference
Aporrectodea caliginosa (adults)	$ZnSO_4$		7.1	22		25	8-w	NOECr©	600	600	Khalil et al., 1996
Aporrectodea caliginosa (adults)	$ZnSO_4$		7.1	22		25	8-w	EC10r©	568		Khalil et al., 1996
Aporrectodea caliginosa (adults)	$ZnSO_4$		7.1	22		25	8-w	NOECs	>1600		Khalil et al., 1996
Eisenia andrei (adults)	$ZnCl_2$	art soil (OECD)	6	10	20	20	21-d	NOECr(c,j)	320	320	Van Gestel et al., 1993
Eisenia andrei (adults)	$ZnCl_2$	art soil (OECD)	6	10	20	20	21-d	NOECg(f)	>1000		Van Gestel et al., 1993
Eisenia fetida (adults)	$Zn(NO_3)_2$	art soil (OECD)	6	8	8	20	2-w	EC10g	300		Neuhauser et al., 1985
Eisenia fetida (adults)	$Zn(NO_3)_2$	art soil (OECD)	6	10	20	15	21-d	NOECr(c)	350	350	Spurgeon et al., 1997
Eisenia fetida (adults)	$Zn(NO_3)_2$	art soil (OECD)	6	10	20	15	14-d	NOECs	1200		Spurgeon et al., 1997
Eisenia fetida (adults)	$Zn(NO_3)_2$	art soil (OECD)	6	10	20	20	21-d	NOECr(c)	350		Spurgeon et al., 1997
Eisenia fetida (adults)	$Zn(NO_3)_2$	art soil (OECD)	6	10	20	20	14-d	NOECs	1200		Spurgeon et al., 1997
Eisenia fetida (adults)	$ZnCl_2$	art soil (OECD)	6.1	10	20	20	14-d	NOECs	442		Spurgeon and Hopkin, 1995
Eisenia fetida (adults)	$ZnCl_2$	art soil (OECD)	6.1	10	20	20	21-d	NOECr(c)	237		Spurgeon and Hopkin, 1995
Eisenia fetida (adults)	$ZnCl_2$	art soil (OECD)	6.1	10	20	20	21-d	NOECg(f)	>400		Spurgeon and Hopkin, 1995
Eisenia fetida (adults)	$Zn(NO_3)_2$	art soil (OECD)	6.3	10	20	20	56-d	NOECs	289		Spurgeon et al., 1994
Eisenia fetida (adults)	$Zn(NO_3)_2$	art soil (OECD)	6.3	10	20	20	56-d	NOECr(c)	199	199	Spurgeon et al., 1994
Eisenia fetida (adults)	$Zn(NO_3)_2$	art soil (OECD)	6	5	20	20	21-d	NOECs	274		Spurgeon and Hopkin, 1996
Eisenia fetida (adults)	$Zn(NO_3)_2$	art soil (OECD)	6	5	20	20	21-d	NOECr(c)	97	97	Spurgeon and Hopkin, 1996
Eisenia fetida (adults)	$Zn(NO_3)_2$	art soil (OECD)	6	10	20	20	21-d	NOECs	702		Spurgeon and Hopkin, 1996
Eisenia fetida (adults)	$Zn(NO_3)_2$	art soil (OECD)	6	10	20	20	21-d	NOECr(c)	553	553	Spurgeon and Hopkin, 1996
Eisenia fetida (adults)	$Zn(NO_3)_2$	art soil (OECD)	6	15	20	20	21-d	NOECs	1048		Spurgeon and Hopkin, 1996
Eisenia fetida (adults)	$Zn(NO_3)_2$	art soil (OECD)	6	15	20	20	21-d	NOECr(c)	484	484	Spurgeon and Hopkin, 1996
Eisenia fetida (adults)	$Zn(NO_3)_2$	art soil (OECD)	5	5	20	20	21-d	NOECs	366		Spurgeon and Hopkin, 1996
Eisenia fetida (adults)	$Zn(NO_3)_2$	art soil (OECD)	5	5	20	20	21-d	NOECr(c)	85	85	Spurgeon and Hopkin, 1996
Eisenia fetida (adults)	$Zn(NO_3)_2$	art soil (OECD)	5	10	20	20	21-d	NOECs	256		Spurgeon and Hopkin, 1996

Table 11 (cont.). Estimated NOEC values used for $PNEC_{add}$ derivation for soil invertebrates and physico-chemical parameters for soils (accepted studies)

Organism (lifestage/size)	Test compound	**Soil type**	**pH**	OM (%)	**Clay (%)**	**Temp ˚C**	**Exp time**	**Criterion**	**NOEC (mg Zn/kg dw)**	**NOEC (added) used for $PNEC_{add}$**	Reference
Eisenia fetida (adults)	$Zn(NO_3)_2$	art soil (OECD)	5	10	20	20	21-d	NOECr(c)	183	183	Spurgeon and Hopkin, 1996
Eisenia fetida (adults)	$Zn(NO_3)_2$	art soil (OECD)	5	15	20	20	21-d	NOECs	368		Spurgeon and Hopkin, 1996
Eisenia fetida (adults)	$Zn(NO_3)_2$	art soil (OECD)	5	15	20	20	21-d	NOECr(c)	414	414	Spurgeon and Hopkin, 1996
Eisenia fetida (adults)	$Zn(NO_3)_2$	art soil (OECD)	4	5	20	20	21-d	NOECs	197		Spurgeon and Hopkin, 1996
Eisenia fetida (adults)	$Zn(NO_3)_2$	art soil (OECD)	4	5	20	20	21-d	NOECr(c)	115	115	Spurgeon and Hopkin, 1996
Eisenia fetida (adults)	$Zn(NO_3)_2$	art soil (OECD)	4	10	20	20	21-d	NOECs	168		Spurgeon and Hopkin, 1996
Eisenia fetida (adults)	$Zn(NO_3)_2$	art soil (OECD)	4	10	20	20	21-d	NOECr(c)	161	161	Spurgeon and Hopkin, 1996
Eisenia fetida (adults)	$Zn(NO_3)_2$	art soil (OECD)	4	15	20	20	21-d	NOECs	184		Spurgeon and Hopkin, 1996
Eisenia fetida (adults)	$Zn(NO_3)_2$	art soil (OECD)	4	15	20	20	21-d	NOECr(c)	223	223	Spurgeon and Hopkin, 1996
Eisenia fetida (adults)	$ZnCl_2$	loamy sand (Gudow)	3	9	7	20	28-d	NOECr(c)	180	180	Lock et al., 2003
Eisenia fetida (adults)	$ZnCl_2$	loamy sand (Gudow)	3	9	7	20	28-d	EC10r	130		Lock et al., 2003
Eisenia fetida (adults)	$ZnCl_2$	loamy sand (Houthalen)	3.4	3	5	20	28-d	NOECr(c)	100	100	Lock et al., 2003
Eisenia fetida (adults)	$ZnCl_2$	loamy sand (Houthalen)	3.4	3	5	20	28-d	EC10 r(c)	96		Lock et al., 2003
Eisenia fetida (adults)	$ZnCl_2$	sandy clay loam (Zegveld)	4.7	40	24	20	28-d	NOECr(c)	1000	1000	Lock et al., 2003
Eisenia fetida (adults)	$ZnCl_2$	sandy clay loam (Zegveld)	4.7	40	24	20	28-d	EC10 r(c)	1150		Lock et al., 2003
Eisenia fetida (adults)	$ZnCl_2$	? (Rhydtalog)	4.8	13		20	28-d	NOECr(c)	320	320	Lock et al., 2003
Eisenia fetida (adults)	$ZnCl_2$	? (Rhydtalog)	4.8	13		20	28-d	EC10 r(c)	486		Lock et al., 2003
Eisenia fetida (adults)	$ZnCl_2$	sandy clay (Souli I)	4.8	1	38	20	28-d	NOECr(c)	560	560	Lock et al., 2003
Eisenia fetida (adults)	$ZnCl_2$	sandy clay (Souli I)	4.8	1	38	20	28-d	EC10 r(c)	503		Lock et al., 2003

Table 11 (cont.). Estimated NOEC values used for $PNEC_{add}$ derivation for soil invertebrates and physico-chemical parameters for soils (accepted studies)

Organism (lifestage/size)	Test compound	**Soil type**	**pH**	OM (%)	**Clay (%)**	**Temp ˚C**	**Exp time**	**Criterion**	**NOEC (mg Zn/kg dw)**	**NOEC (added) used for $PNEC_{add}$**	Reference
Eisenia fetida (adults)	$ZnCl_2$	sandy loam (Kovlinge)	5.1	4	9	20	28-d	NOECr(c)	320	320	Lock et al., 2003
Eisenia fetida (adults)	$ZnCl_2$	sandy loam (Kovlinge)	5.1	4	9	20	28-d	EC10 r(c)	243		Lock et al., 2003
Eisenia fetida (adults)	$ZnCl_2$	? (De Meern)	5.2	17		20	28-d	NOECr(c)	560	560	Lock et al., 2003
Eisenia fetida (adults)	$ZnCl_2$	? (De Meern)	5.2	17		20	28-d	EC10 r(c)	747		Lock et al., 2003
Eisenia fetida (adults)	$ZnCl_2$	? (Zeveren)	5.7	6		20	28-d	NOECr(c)	1000	1000	Lock et al., 2003
Eisenia fetida (adults)	$ZnCl_2$	? (Zeveren)	5.7	6		20	28-d	EC10 r(c)	1040		Lock et al., 2003
Eisenia fetida (adults)	$ZnCl_2$	sandy clay loam (Woburn)	6.4	7	21	20	28-d	NOECr(c)	560	560	Lock et al., 2003
Eisenia fetida (adults)	$ZnCl_2$	sandy clay loam (Woburn)	6.4	7	21	20	28-d	EC10r(c)	629		Lock et al., 2003
Eisenia fetida (adults)	$ZnCl_2$	silt loam (Ter Munck)	6.8	2	15	20	28-d	NOECr(c)	180	180	Lock et al., 2003
Eisenia fetida (adults)	$ZnCl_2$	silt loam (Ter Munck)	6.8	2	15	20	28-d	EC10r(c)	79		Lock et al., 2003
Eisenia fetida (adults)	$ZnCl_2$	silt loam (Marknesse)	7.5	2	26	20	28-d	NOECr(c)	180	180	Lock et al., 2003
Eisenia fetida (adults)	$ZnCl_2$	silt loam (Marknesse)	7.5	2	26	20	28-d	EC10r(c)	122		Lock et al., 2003
Eisenia fetida (adults)	$ZnCl_2$	loam (Guadalajara)	7.5	1	25	20	28-d	NOECr(c)	560	560	Lock et al., 2003
Eisenia fetida (adults)	$ZnCl_2$	loam (Guadalajara)	7.5	1	25	20	28-d	EC10r(c)	346		Lock et al., 2003
Folsomia candida (10-d juveniles)	$ZnCl_2$	art soil (OECD)	6	10	20	18	4-w	NOECg(d,f)	565		Smit and van Gestel, 1998
Folsomia candida (10-d juveniles)	$ZnCl_2$	art soil (OECD)	6	10	20	18	4-w	NOECr(j)	366	366	Smit and van Gestel, 1998

Table 11 (cont.). Estimated NOEC values used for $PNEC_{add}$ derivation for soil invertebrates and physico-chemical parameters for soils (accepted studies)

Organism (lifestage/size)	Test compound	Soil type	pH	OM (%)	Clay (%)	Temp ˚C	Exp time	Criterion	NOEC (mg Zn/kg dw)	NOEC (added) used for $PNEC_{add}$	Reference
Folsomia candida (10-d juveniles)	$ZnCl_2$	art soil (OECD)	6	10	20	18	4-w	EC10g(f)	736		Smit and van Gestel, 1998
Folsomia candida (10-d juveniles)	$ZnCl_2$	art soil (OECD)	6	10	20	18	4-w	EC10r(j)	267		Smit and van Gestel, 1998
Folsomia candida (10-d juveniles)	$ZnCl_2$	sand (PAHN)	6	2	2	19	4-w	NOECg(d,f)	275		Smit and van Gestel, 1998
Folsomia candida (10-d juveniles)	$ZnCl_2$	sand (PAHN)	6	2	2	19	4-w	NOECr(j)	275	275	Smit and van Gestel, 1998
Folsomia candida (10-d juveniles)	$ZnCl_2$	sand (PAHN)	6	2	2	19	4-w	EC10g(f)	136		Smit and van Gestel, 1998
Folsomia candida (10-d juveniles)	$ZnCl_2$	sand (PAHN)	6	2	2	19	4-w	EC10r(j)	113		Smit and van Gestel, 1998
Folsomia candida (10-d juveniles)	$ZnCl_2$	sand (perc.)	6	2	2	18	4-w	NOECg(d,f)	436		Smit and van Gestel, 1998
Folsomia candida (10-d juveniles)	$ZnCl_2$	sand (perc.)	6	2	2	18	4-w	NOECr(j)	314	314	Smit and van Gestel, 1998
Folsomia candida (10-d juveniles)	$ZnCl_2$	sand (perc.)	6	2	2	18	4-w	EC10g(f)	284		Smit and van Gestel, 1998
Folsomia candida (10-d juveniles)	$ZnCl_2$	sand (perc.)	6	2	2	18	4-w	EC10r(j)	334		Smit and van Gestel, 1998
Folsomia candida (adults)	$Zn(NO_3)_2$	art soil (OECD)	6	10	20	20	4-w	NOECs	3000		Sandifer and Hopkin, 1996
Folsomia candida (adults)	$Zn(NO_3)_2$	art soil (OECD)	6	10	20	20	4-w	NOECr(j)	620	620	Sandifer and Hopkin, 1996
Folsomia candida (adults)	$Zn(NO_3)_2$	art soil (OECD)	5	10	20	20	4-w	NOECs	6500		Sandifer and Hopkin, 1996
Folsomia candida (adults)	$Zn(NO_3)_2$	art soil (OECD)	5	10	20	20	4-w	NOECr(j)	300	300	Sandifer and Hopkin, 1996
Folsomia candida (adults)	$Zn(NO_3)_2$	art soil (OECD)	4.5	10	20	20	4-w	NOECs	300		Sandifer and Hopkin, 1996
Folsomia candida (adults)	$Zn(NO_3)_2$	art soil (OECD)	4.5	10	20	20	4-w	NOECr(j)	300	300	Sandifer and Hopkin, 1996
Folsomia candida (adults)	$Zn(NO_3)_2$	art soil (OECD)	6	10	20	15	6-w	NOECs	300		Sandifer and Hopkin, 1997
Folsomia candida (adults)	$Zn(NO_3)_2$	art soil (OECD)	6	10	20	15	6-w	NOECr(j)	300	300	Sandifer and Hopkin, 1997

Table 11 (cont.). Estimated NOEC values used for $PNEC_{add}$ derivation for soil invertebrates and physico-chemical parameters for soils (accepted studies)

Organism (lifestage/size)	Test compound	**Soil type**	**pH**	OM (%)	**Clay (%)**	**Temp ˚C**	**Exp time**	**Criterion**	**NOEC (mg Zn/kg dw)**	**NOEC (added) used for $PNEC_{add}$**	Reference
Folsomia candida (10-d juveniles)	$ZnCl_2$	art soil (OECD)	6	10	20	20	6-w	EC10g(f)	840		Van Gestel and Hensbergen, 1997
Folsomia candida (10-d juveniles)	$ZnCl_2$	art soil (OECD)	6	10	20	20	4-w	EC10r(j)	399	399	Van Gestel and Hensbergen, 1997
Folsomia candida (10-d juveniles)	$ZnCl_2$	art soil (OECD)	6	10	20	20	6-w	EC10r(j)	423		Van Gestel and Hensbergen, 1997
Folsomia candida (10-d juveniles)	$ZnCl_2$	loamy sand (Houthalen)	3.4	3	5	20	28-d	NOECr(j)	32	32	Lock et al., 2003
Folsomia candida (10-d juveniles)	$ZnCl_2$	loamy sand (Houthalen)	3.4	3	5	20	28-d	EC10r(j)	30		Lock et al., 2003
Folsomia candida (10-d juveniles)	$ZnCl_2$	sandy clay (Zegveld)	4.7	40	24	20	28-d	NOECr(j)	1000	1000	Lock et al., 2003
Folsomia candida (10-d juveniles)	$ZnCl_2$	sandy clay (Zegveld)	4.7	40	24	20	28-d	EC10r(j)	520		Lock et al., 2003
Folsomia candida (10-d juveniles)	$ZnCl_2$	? (Rhydtalog)	4.8	13		20	28-d	NOECr(j)	320	320	Lock et al., 2003
Folsomia candida (10-d juveniles)	$ZnCl_2$	? (Rhydtalog)	4.8	13		20	28-d	EC10r(j)	88		Lock et al., 2003
Folsomia candida (10-d juveniles)	$ZnCl_2$	sandy clay (Souli I)	4.8	1	38	20	28-d	NOECr(j)	100	100	Lock et al., 2003
Folsomia candida (10-d juveniles)	$ZnCl_2$	sandy clay (Souli I)	4.8	1	38	20	28-d	EC10r(j)	63		Lock et al., 2003
Folsomia candida (10-d juveniles)	$ZnCl_2$	? (De Meern)	5.2	17		20	28-d	NOECr(j)	300	300	Lock et al., 2003
Folsomia candida (10-d juveniles)	$ZnCl_2$	? (De Meern)	5.2	17		20	28-d	EC10r(j)	303		Lock et al., 2003
Folsomia candida (10-d juveniles)	$ZnCl_2$	clay (Aluminusa)	5.4	1	51	20	28-d	NOECr(j)	320	320	Lock et al., 2003

Table 11 (cont.). Estimated NOEC values used for $PNEC_{add}$ derivation for soil invertebrates and physico-chemical parameters for soils (accepted studies)

Organism (lifestage/size)	Test compound	**Soil type**	**pH**	OM (%)	**Clay (%)**	**Temp ˚C**	**Exp time**	**Criterion**	**NOEC (mg Zn/kg dw)**	**NOEC (added) used for $PNEC_{add}$**	Reference
Folsomia candida (10-d juveniles)	$ZnCl_2$	clay (Aluminusa)	5.4	1	51	20	28-d	EC10r(j)	209		Lock et al., 2003
Folsomia candida (10-d juveniles)	$ZnCl_2$	? (Zeveren)	5.7	6		20	28-d	NOECr(j)	320	320	Lock et al., 2003
Folsomia candida (10-d juveniles)	$ZnCl_2$	? (Zeveren)	5.7	6		20	28-d	EC10r(j)	89		Lock et al., 2003
Folsomia candida (10-d juveniles)	$ZnCl_2$	silty clay loam (Rots)	7.4	2	27	20	28-d	NOECr(j)	560	560	Lock et al., 2003
Folsomia candida (10-d juveniles)	$ZnCl_2$	silty clay loam (Rots)	7.4	2	27	20	28-d	EC10r(j)	588		Lock et al., 2003
Folsomia candida (10-d juveniles)	$ZnCl_2$	clay (Souli II)	7.4	4	46	20	28-d	NOECr(j)	1000	1000	Lock et al., 2003
Folsomia candida (10-d juveniles)	$ZnCl_2$	clay (Souli II)	7.4	4	46	20	28-d	EC10r(j)	1210		Lock et al., 2003
Folsomia candida (10-d juveniles)	$ZnCl_2$	loam (Guadalajara)	7.5	1	25	20	28-d	NOECr(j)	320	320	Lock et al., 2003
Folsomia candida (10-d juveniles)	$ZnCl_2$	loam (Guadalajara)	7.5	1	25	20	28-d	EC10r(j)	139		Lock et al., 2003

NOEC – No Observed Effect Concentration; EC10 – Effect concentration for 10% of the population; g- growth; g(d)-growth based on dry weight; g(f)-growth based on fresh weight; r- reproduction; r (c)- reproduction based on the number of cocoons; r(j)-reproduction based on the number of juveniles; s-survival;f – feeding activity; ; w- week.

Table 12. Estimated NOEC values used for $PNEC_{add}$ derivation for soil microbe-mediated processes and physico-chemical parameters for soils (accepted studies)

Microbial process	Test compound	Soil type	pH	OM (%)	Clay (%)	Temp ˚C	Exp time	Criterion	NOEC (mg Zn/kg dw)	NOEC (added) used for $PNEC_{add}$	Reference
Acetate induced respiration	$ZnCl_2$	sand (Flevopolder)	7.4	1	1	10	18-h	EC10	303	303	Van Beelen et al., 1994
Acetate induced respiration	$ZnCl_2$	sand (Flevopolder)	7.4	1	1	10	18-h	IC10	0.7		Van Beelen et al., 1994
Amidase	$ZnSO_4$	clay	7.5		18	28	12-w	NOEC	200	200	Hemida et al., 1997
Amidase	$ZnSO_4$	sand	7.4		2	28	12-w	NOEC	200	200	Hemida et al., 1997
Ammonification	$ZnSO_4$	sandy loam	7.1	3	17	30	3-w	NOEC	1000	1000	Premi and Cornfield, 1969
Arylsulphatase	$ZnSO_4$	clay loam (Nicollet)	6.2	5	29		30-min	EC(20%)	1640	820	Al-Khafaji and Tatabatai, 1979
Arylsulphatase	$ZnSO_4$	clay loam (Harps)	7.8	6	30		30-min	EC10	140	140	Haanstra and Doelman, 1991
Arylsulphatase	$ZnSO_4$	clay (Webster)	5.8	4	23		30-min	NOEC	164	164	Haanstra and Doelman, 1991
Arylsulphatase	$ZnSO_4$	silty clay (Okoboji)	7.4	9	34		30-min	EC(17%)	1640	820	Haanstra and Doelman, 1991
Arylsulphatase	$ZnCl_2$	sand	7.7	2	2	20	6-w	EC10	105	105	Haanstra and Doelman, 1991
Arylsulphatase	$ZnCl_2$	sand	7.7	2	2	20	1.5 yr	EC10	311		Haanstra and Doelman, 1991
Arylsulphatase	$ZnCl_2$	sandy loam	5.1	6	9	20	6-w	EC10	728	728	Haanstra and Doelman, 1991
Arylsulphatase	$ZnCl_2$	sandy loam	5.1	6	9	20	1.5 yr	EC10	800		Haanstra and Doelman, 1991
Arylsulphatase	$ZnCl_2$	silty loam	7.4	2	19	20	6-w	EC10	151	151	Haanstra and Doelman, 1991
Arylsulphatase	$ZnCl_2$	silty loam	7.4	2	19	20	1.5 yr	EC10	2704		Haanstra and Doelman, 1991
Arylsulphatase	$ZnCl_2$	clay	6.8	3	60	20	6-w	EC10	2353	2353	Haanstra and Doelman, 1991
Arylsulphatase	$ZnCl_2$	clay	6.8	3	60	20	1.5 yr	EC10	1014		Haanstra and Doelman, 1991
Arylsulphatase	$ZnCl_2$	sandy peat	4.3	13	5	20	1.5 yr	EC10	7930		Haanstra and Doelman, 1991
Dehydrogenase	$ZnSO_4$	sand	6.9	3		20	3-mo	EC10	76	76	Maliszewska et al., 1985
Dehydrogenase	$ZnSO_4$	alluvial soil	7.1	2		20	3-mo	NOEC	500	500	Maliszewska et al., 1985

Table 12 (cont.). Estimated NOEC values used for $PNEC_{add}$ derivation for soil microbe-mediated processes and physico-chemical parameters for soils (accepted studies)

Microbial process	Test compound	**Soil type**	**pH**	OM (%)	**Clay (%)**	**Temp ˚C**	**Exp time**	**Criterion**	**NOEC (mg Zn/kg dw)**	**NOEC (added) used for $PNEC_{add}$**	Reference
Dehydrogenase	$ZnSO_4$	(unenriched)		2		27	24-h	NOEC	30		Rogers and Li, 1985
Dehydrogenase	$ZnSO_4$	(unenriched)		2		27	24-h	EC10	145	145	Rogers and Li, 1985
Dehydrogenase	$ZnSO_4$	(+1% alfafa)		2		27	24-h	NOEC	30		Rogers and Li, 1985
Dehydrogenase	$ZnSO_4$	(+1% alfafa)		2		27	24-h	EC10	48	48	Rogers and Li, 1985
Denitrification	$Zn(NO_3)_2$	silt loam	6.8	3	28	28	3-w	NOEC	100	100	Bollag and Barabasz, 1979
Glucose respiration	$ZnCl_2$	sandy clay	6.7	2	4	28	96-h	NOEC	300	300	Ohya et al., 1985
Glucose respiration	$ZnSO_4$	sandy loam	5.7	1	14	20	9-w	NOEC	80	80	Stadelmann and Santschi-Fuhrimann, 1987
Glucose respiration	$ZnCl_2$	loamy sand (Gudow)	3	9	7	20	3-d	NOEC	240	240	Smolders et al., 2003
Glucose respiration	$ZnCl_2$	loamy sand (Gudow)	3	9	7	20	3-d	EC10	256		Smolders et al., 2003
Glucose respiration	$ZnCl_2$	loamy sand (Houthalen)	3.4	3	5	20	3-d	NOEC	30	30	Smolders et al., 2003
Glucose respiration	$ZnCl_2$	loamy sand (Houthalen)	3.4	3	5	20	3-d	EC10	33		Smolders et al., 2003
Glucose respiration	$ZnCl_2$	? (Rhydtalog)	4.8	13		20	3-d	NOEC	800	800	Smolders et al., 2003
Glucose respiration	$ZnCl_2$	? (Rhydtalog)	4.8	13		20	3-d	EC10	780		Smolders et al., 2003
Glucose respiration	$ZnCl_2$	sandy clay (Souli I)	4.8	1	38	20	3-d	NOEC	100	100	Smolders et al., 2003
Glucose respiration	$ZnCl_2$	sandy clay (Souli I)	4.8	1	38	20	3-d	EC10	70		Smolders et al., 2003
Glucose respiration	$ZnCl_2$	sandy loam (Kovlinge II)	5.1	4	9	20	3-d	NOEC	400	400	Smolders et al., 2003

Table 12 (cont.). Estimated NOEC values used for $PNEC_{add}$ derivation for soil microbe-mediated processes and physico-chemical parameters for soils (accepted studies)

Microbial process	Test compound	**Soil type**	**pH**	OM (%)	**Clay (%)**	**Temp °C**	**Exp time**	**Criterion**	**NOEC (mg Zn/kg dw)**	**NOEC (added) used for $PNEC_{add}$**	Reference
Glucose respiration	$ZnCl_2$	sandy loam (Kovlinge II)	5.1	4	9	20	3-d	EC10	124		Smolders et al., 2003
Glucose respiration	$ZnCl_2$	? (De Meern)	5.2	17		20	3-d	NOEC	1300	1300	Smolders et al., 2003
Glucose respiration	$ZnCl_2$	? (De Meern)	5.2	17		20	3-d	EC10	1238		Smolders et al., 2003
Glucose respiration	$ZnCl_2$	clay (Aluminusa)	5.4	1	51	20	3-d	NOEC	600	600	Smolders et al., 2003
Glucose respiration	$ZnCl_2$	clay (Aluminusa)	5.4	1	51	20	3-d	EC10	549		Smolders et al., 2003
Glucose respiration	$ZnCl_2$	? (Zeveren)	5.7	6		20	3-d	NOEC	1400	1400	Smolders et al., 2003
Glucose respiration	$ZnCl_2$	? (Zeveren)	5.7	6		20	3-d	EC10	227		Smolders et al., 2003
Glucose respiration	$ZnCl_2$	sandy clay loam (Wolburn)	6.4	7	21	20	3-d	NOEC	300	300	Smolders et al., 2003
Glucose respiration	$ZnCl_2$	sandy clay loam (Wolburn)	6.4	7	21	20	3-d	EC10	653		Smolders et al., 2003
Glucose respiration	$ZnCl_2$	silt loam (Ter Munck)	6.8	2	15	20	3-d	NOEC	50	50	Smolders et al., 2003
Glucose respiration	$ZnCl_2$	silt loam (Ter Munck)	6.8	2	15	20	3-d	EC10	111		Smolders et al., 2003
Glucose respiration	$ZnCl_2$	silty clay loam (Rots)	7.4	2	27	20	3-d	NOEC	100	100	Smolders et al., 2003
Glucose respiration	$ZnCl_2$	silty clay loam (Rots)	7.4	2	27	20	3-d	EC10	211		Smolders et al., 2003
Glucose respiration	$ZnCl_2$	clay (Souli II)	7.4	4	46	20	3-d	NOEC	100	100	Smolders et al., 2003

Table 12 (cont.). Estimated NOEC values used for $PNEC_{add}$ derivation for soil microbe-mediated processes and physico-chemical parameters for soils (accepted studies)

Microbial process	Test compound	**Soil type**	**pH**	OM (%)	**Clay (%)**	**Temp ˚C**	**Exp time**	**Criterion**	**NOEC (mg Zn/kg dw)**	**NOEC (added) used for $PNEC_{add}$**	Reference
Glucose respiration	$ZnCl_2$	clay (Souli II)	7.4	4	46	20	3-d	EC10	189		Smolders et al., 2003
Glucose respiration	$ZnCl_2$	silt loam (Marknesse)	7.5	2	26	20	3-d	NOEC	100	100	Smolders et al., 2003
Glucose respiration	$ZnCl_2$	silt loam (Marknesse)	7.5	2	26	20	3-d	EC10	179		Smolders et al., 2003
Glucose respiration	$ZnCl_2$	loam (Guadalajara)	7.5	1	25	20	3-d	NOEC	100	100	Smolders et al., 2003
Glucose respiration	$ZnCl_2$	loam (Guadalajara)	7.5	1	25	20	3-d	EC10	95		Smolders et al., 2003
Glutamic acid decomposition	$ZnCl_2$	humic sand (Wageningen)	5.5	4		22?	2-d	NOEC	100	100	Posthuma et al., 1998
Glutamic acid decomposition	$ZnCl_2$	sand (Budel ref soil #11)	3.4	4	12	22?	2-d	NOEC	100	100	Posthuma et al., 1998
Glutamic acid decomposition	$ZnCl_2$	sand	4.9	2	3	22?	2-d	NOEC	30	30	Notenboom and Postuma, 1995
Glutamic acid decomposition	$ZnCl_2$	sand	6	2	3	22?	2-d	NOEC	55	55	Posthuma et al., 1998
Maize respiration	$ZnCl_2$	loamy sand (Gudow)	3	9	7	20	28-d	NOEC	120	120	Smolders et al., 2003
Maize respiration	$ZnCl_2$	loamy sand (Gudow)	3	9	7	20	28-d	EC10	78		Smolders et al., 2003
Maize respiration	$ZnCl_2$	sandy clay loam (Zegveld)	4.7	40	24	20	28-d	NOEC	200	200	Smolders et al., 2003

Table 12 (cont.). Estimated NOEC values used for $PNEC_{add}$ derivation for soil microbe-mediated processes and physico-chemical parameters for soils (accepted studies)

Microbial process	Test compound	**Soil type**	**pH**	OM (%)	**Clay (%)**	**Temp ˚C**	**Exp time**	**Criterion**	**NOEC (mg Zn/kg dw)**	**NOEC (added) used for $PNEC_{add}$**	Reference
Maize respiration	$ZnCl_2$	sandy clay loam (Zegveld)	4.7	40	24	20	28-d	EC10	38		Smolders et al., 2003
Maize respiration	$ZnCl_2$	? (Rhydtalog)	4.8	13		20	28-d	NOEC	469	469	Smolders et al., 2003
Maize respiration	$ZnCl_2$	? (Rhydtalog)	4.8	13		20	28-d	EC10	160		Smolders et al., 2003
Maize respiration	$ZnCl_2$	sandy loam (Kovlinge)	5.1	4	9	20	28-d	NOEC	50	50	Smolders et al., 2003
Maize respiration	$ZnCl_2$	sandy loam (Kovlinge)	5.1	4	9	20	28-d	EC10	30		Smolders et al., 2003
Maize respiration	$ZnCl_2$	? (De Meern)	5.2	17		20	28-d	NOEC	1300	1300	Smolders et al., 2003
Maize respiration	$ZnCl_2$	? (De Meern)	5.2	17		20	28-d	EC10	817		Smolders et al., 2003
Maize respiration	$ZnCl_2$	? (Zeveren)	5.7	6		20	28-d	NOEC	1400	1400	Smolders et al., 2003
Maize respiration	$ZnCl_2$	? (Zeveren)	5.7	6		20	28-d	EC10	1068		Smolders et al., 2003
Maize respiration	$ZnCl_2$	silt loam (Ter Munck)	6.8	2	15	20	28-d	NOEC	38	38	Smolders et al., 2003
Maize respiration	$ZnCl_2$	silt loam (Ter Munck)	6.8	2	15	20	28-d	EC10	18		Smolders et al., 2003
Maize respiration	$ZnCl_2$	silty clay loam (Rots)	7.4	2	27	20	28-d	NOEC	150	150	Smolders et al., 2003
Maize respiration	$ZnCl_2$	silty clay loam (Rots)	7.4	2	27	20	28-d	EC10	76		Smolders et al., 2003
Maize respiration	$ZnCl_2$	clay (Souli II)	7.4	4	46	20	28-d	NOEC	600	600	Smolders et al., 2003

Table 12 (cont.). Estimated NOEC values used for $PNEC_{add}$ derivation for soil microbe-mediated processes and physico-chemical parameters for soils (accepted studies)

Microbial process	Test compound	**Soil type**	**pH**	OM (%)	**Clay (%)**	**Temp ˚C**	**Exp time**	**Criterion**	**NOEC (mg Zn/kg dw)**	**NOEC (added) used for $PNEC_{add}$**	Reference
Maize respiration	$ZnCl_2$	clay (Souli II)	7.4	4	46	20	28-d	EC10	636		Smolders et al., 2003
Maize respiration	$ZnCl_2$	silt loam (Marknesse)	7.5	2	26	20	28-d	NOEC	150	150	Smolders et al., 2003
Maize respiration	$ZnCl_2$	silt loam (Marknesse)	7.5	2	26	20	28-d	EC10	122		Smolders et al., 2003
Maize respiration	$ZnCl_2$	loam (Guadalajara)	7.5	1	25	20	28-d	NOEC	300	300	Smolders et al., 2003
Maize respiration	$ZnCl_2$	loam (Guadalajara)	7.5	1	25	20	28-d	EC10	183		Smolders et al., 2003
Nitrate reductase	$ZnSO_4$	sand	7.4		2		12-w	EC10	34	67	Hemida et al., 1997
Nitrification	$ZnSO_4$	clay loam (Harps)	7.8	6	30	30	10-d	EC(24%)	327	109	Liang and Tabatabai, 1977
Nitrification	$ZnSO_4$	sandy loam	7.1	3	17	30	3-w	NOEC	100	100	Premi and Cornfield, 1969
Nitrification	$ZnSO_4$	clay loam (Decatur)	5.5	2	28	30	7-w	NOEC	100	100	Wilson, 1977
Nitrification	$ZnSO_4$	sandy loam (Cecil)	6.2	2	8	30	7-w	NOEC	100	100	Wilson, 1977
Nitrification	$ZnSO_4$	loamy sand (Leefield)	5.1	1	2	30	7-w	NOEC	50	50	Wilson, 1977
Nitrification	$ZnCl_2$	sandy clay loam (Zegveld)	4.7	40	24	20	7-d	NOEC	400	400	Smolders et al., 2003
Nitrification	$ZnCl_2$	sandy clay loam (Zegveld)	4.7	40	24	20	7-d	EC10	506		Smolders et al., 2003

Table 12 (cont.). Estimated NOEC values used for $PNEC_{add}$ derivation for soil microbe-mediated processes and physico-chemical parameters for soils (accepted studies)

Microbial process	Test compound	Soil type	pH	OM (%)	Clay (%)	Temp °C	Exp time	Criterion	NOEC (mg Zn/kg dw)	NOEC (added) used for $PNEC_{add}$	Reference
Nitrification	$ZnCl_2$	? (Rhydtalog)	4.8	13		20	7-d	NOEC	257	257	Smolders et al., 2003
Nitrification	$ZnCl_2$	? (Rhydtalog)	4.8	13		20	7-d	EC10	517		Smolders et al., 2003
Nitrification	$ZnCl_2$	sandy clay (Souli I)	4.8	1	38	20	28-d	NOEC	50	50	Smolders et al., 2003
Nitrification	$ZnCl_2$	sandy clay (Souli I)	4.8	1	38	20	28-d	EC10	77		Smolders et al., 2003
Nitrification	$ZnCl_2$	sandy loam (Kovlinge)	5.1	4	9	20	14-d	NOEC	50	50	Smolders et al., 2003
Nitrification	$ZnCl_2$	sandy loam (Kovlinge)	5.1	4	9	20	14-d	EC10	51		Smolders et al., 2003
Nitrification	$ZnCl_2$	? (De Meern)	5.2	17		20	4-d	NOEC	424	424	Smolders et al., 2003
Nitrification	$ZnCl_2$	? (De Meern)	5.2	17		20	4-d	EC10	436		Smolders et al., 2003
Nitrification	$ZnCl_2$	clay (Aluminusa)	5.4	1	51	20	14-d	NOEC	38	38	Smolders et al., 2003
Nitrification	$ZnCl_2$	clay (Aluminusa)	5.4	1	51	20	14-d	EC10	43		Smolders et al., 2003
Nitrification	$ZnCl_2$	? (Zeveren)	5.7	6		20	7-d	EC10	206	206	Smolders et al., 2003
Nitrification	$ZnCl_2$	sandy clay loam (Wolburn)	6.4	7	21	20	4-d	NOEC	75	75	Smolders et al., 2003
Nitrification	$ZnCl_2$	sandy clay loam (Wolburn)	6.4	7	21	20	4-d	EC10	241		Smolders et al., 2003

Table 12 (cont.). Estimated NOEC values used for $PNEC_{add}$ derivation for soil microbe-mediated processes and physico-chemical parameters for soils (accepted studies)

Microbial process	Test compound	Soil type	pH	OM (%)	Clay (%)	Temp ˚C	Exp time	Criterion	NOEC (mg Zn/kg dw)	NOEC (added) used for $PNEC_{add}$	Reference
Nitrification	$ZnCl_2$	silt loam (Ter Munck)	6.8	2	15	20	4-d	NOEC	150	150	Smolders et al., 2003
Nitrification	$ZnCl_2$	silt loam (Ter Munck)	6.8	2	15	20	4-d	EC10	113		Smolders et al., 2003
Nitrification	$ZnCl_2$	silty clay loam (Rots)	7.4	2	27	20	4-d	NOEC	300	300	Smolders et al., 2003
Nitrification	$ZnCl_2$	silty clay loam (Rots)	7.4	2	27	20	4-d	EC10	336		Smolders et al., 2003
Nitrification	$ZnCl_2$	clay (Souli II)	7.4	4	46	20	23-d	NOEC	150	150	Smolders et al., 2003
Nitrification	$ZnCl_2$	clay (Souli II)	7.4	4	46	20	23-d	EC10	542		Smolders et al., 2003
Nitrification	$ZnCl_2$	silt loam (Marknesse)	7.5	2	26	20	4-d	NOEC	300	300	Smolders et al., 2003
Nitrification	$ZnCl_2$	silt loam (Marknesse)	7.5	2	26	20	4-d	EC10	262		Smolders et al., 2003
Nitrification	$ZnCl_2$	loam (Guadalajara)	7.5	1	25	20	10-d	NOEC	75	75	Smolders et al., 2003
Nitrification	$ZnCl_2$	loam (Guadalajara)	7.5	1	25	20	10-d	EC10	87		Smolders et al., 2003
N-mineralization	$ZnSO_4$	loam (Webster)	5.8	4	23	30	3-w	EC(14%)	327	164	Liang and Tabatabai, 1977
N-mineralization	$ZnSO_4$	silty clay (Judson)	6.6	5	45	30	3-w	EC(12%)	327	164	Liang and Tabatabai, 1977
N-mineralization	$ZnSO_4$	clay loam (Harps)	7.8	6	30	30	3-w	EC(15%)	327	164	Liang and Tabatabai, 1977

Table 12 (cont.). Estimated NOEC values used for $PNEC_{add}$ derivation for soil microbe-mediated processes and physico-chemical parameters for soils (accepted studies)

Microbial process	Test compound	Soil type	pH	OM (%)	Clay (%)	Temp ˚C	Exp time	Criterion	NOEC (mg Zn/kg dw)	NOEC (added) used for $PNEC_{add}$	Reference
N-mineralization	$ZnSO_4$	silty clay (Okoboji)	7.4	9	34	30	3-w	EC(14%)	327	164	Liang and Tabatabai, 1977
N-mineralization	$ZnSO_4$	silt loam (+1% sludge+1% alfafa)	6.9	2	44	25	3-mo	NOEC	100	100	Chang and Broadbent, 1981
N-mineralization	$ZnSO_4$	(forest)	3.4	8	10	20	7-w	EC(30%)	700	233	Necker and Kunze, 1986
Phosphatase	$ZnSO_4$		4.7			22	1-h	EC10	508	508	Svenson, 1986
Phosphatase	ZnCl2	sandy loam	5.1	6	9	20	6-w	EC10	1341	1341	Doelman and Haanstra, 1989
Phosphatase	ZnCl2	sandy loam	5.1	6	9	20	1.5 yr	EC10	570		Doelman and Haanstra, 1989
Phosphatase	ZnCl2	silty loam	7.4	2	19	20	6-w	EC10	2623	2623	Doelman and Haanstra, 1989
Phosphatase	ZnCl2	silty loam	7.4	2	19	20	1.5 yr	EC10	300		Doelman and Haanstra, 1989
Phosphatase		clay	6.8	3	60	20	6-w	EC10	160	160	Doelman and Haanstra, 1989
Phosphatase		clay	6.8	3	60	20	1.5 yr	EC10	36		Doelman and Haanstra, 1989
Phosphatase	$ZnSO_4$	loam (Webster)	5.8	4	23		30-min	NOEC	164	164	Juma and Tabatabai, 1977
Phosphatase	$ZnSO_4$	silty clay (Okoboji)	7.4	9	34		30-min	NOEC	164	164	Juma and Tabatabai, 1977
Phytase	$ZnSO_4$		4.7			22	1-h	NOEC	590	590	Svenson, 1986
Pyrophosphatase	$ZnSO_4$	loam (Clarion)	4.6	3	24		30-min	NOEC	1640	1640	Stott et al., 1985
Pyrophosphatase	$ZnSO_4$	clay loam (Nicollet)	6.2	5	29		30-min	NOEC	1640	1640	Stott et al., 1985
Pyrophosphatase	$ZnSO_4$	clay loam (Okoboji)	7.4	9	34		30-min	NOEC	1640	1640	Stott et al., 1985
Respiration	$ZnSO_4$	silt loam (+1% sludge+1% alfafa)	6.9	2	44	25	3-mo	EC10	12	17	Chang and Broadbent, 1981
Respiration	$ZnSO_4$	silt loam (Crider)	6.7	3	27	20	45-d	NOEC	33	110	Lighthart et al., 1983
Respiration	$ZnSO_4$	? (Rifle)	6.2	64		20	45-d	NOEC	327	327	Lighthart et al., 1983
Respiration	$ZnSO_4$	clay (Toledo)	7	6	51	20	45-d	NOEC	33	165	Lighthart et al., 1983

Table 12 (cont.). Estimated NOEC values used for $PNEC_{add}$ derivation for soil microbe-mediated processes and physico-chemical parameters for soils (accepted studies)

Microbial process	Test compound	Soil type	pH	OM (%)	Clay (%)	Temp ˚C	Exp time	Criterion	NOEC (mg Zn/kg dw)	NOEC (added) used for $PNEC_{add}$	Reference
Respiration	$ZnSO_4$	silt loam (Walla Walla)	7.2	2	21	20	45-d	NOEC	33	110	Lighthart et al., 1983
Respiration	$ZnSO_4$	sandy loam(Sharpsburg)	8.2	5	11	20	45-d	NOEC	3	17	Lighthart et al., 1983
Respiration	$ZnCl_2$	sandy loam (+1% straw)	5.2	2	8	22	4-w	NOEC	50	50	Saviozzi et al., 1995
Urease	$ZnSO_4$	loam (Webster)	5.8	4	23	37	30-min	EC(23%)	327	109	Tabatabai, 1977
Urease	$ZnSO_4$	clay loam (Harps)	7.8	6	30	37	30-min	NOEC	33		Tabatabai, 1977
Urease	$ZnSO_4$	clay loam (Harps)	7.8	6	30	37	30-min	EC10	52	52	Tabatabai, 1977
Urease	$ZnSO_4$	silty clay (Okoboji)	7.4	9	34	37	30-min	NOEC	33		Tabatabai, 1977
Urease	$ZnSO_4$	silty clay (Okoboji)	7.4	9	34	37	30-min	EC10	64	64	Tabatabai, 1977
Urease	$ZnCl_2$	sand	7.7	2	2	20	6-w	EC10	70	70	Doelman and Haanstra, 1986
Urease	$ZnCl_2$	sand	7.7	2	2	20	1.5 yr	EC10	160		Doelman and Haanstra, 1986
Urease	$ZnCl_2$	sandy loam	5.1	6	9	20	6-w	EC10	30	30	Doelman and Haanstra, 1986
Urease	$ZnCl_2$	sandy loam	5.1	6	9	20	1.5 yr	EC10	1		Doelman and Haanstra, 1986
Urease	$ZnCl_2$	silty loam	7.4	2	19	20	6-w	EC10	30	30	Doelman and Haanstra, 1986
Urease	$ZnCl_2$	clay	6.8	3	60	20	6-w	EC10	460	460	Doelman and Haanstra, 1986
Urease	$ZnCl_2$	clay	6.8	3	60	20	1.5 yr	EC10	8		Doelman and Haanstra, 1986
Urease	$ZnCl_2$	sandy peat	4.3	13	5	20	6-w	EC10	5		Doelman and Haanstra, 1986

NOEC- No Observed Effect Concentration; EC10 – Effect concentration for 10% of the population; w-week; d-days; min-minutes; yr-year

7.1.4. $PNEC_{add, soil}$ derivation

Both the tests on terrestrial species (plants and invertebrates) as well as as the tests on microbe-mediated processes can be used to derive PNEC for the terrestrial compartment. In this RA it was proposed to treat them separately since tests on microbe-mediated processes usually pertain to multiple species tests, whereas the statistical extrapolation method apply to single-species tests only.
Regarding abiotic characteristics, the soil is less homogeneous than the water and based on this and also because a wide range of NOEC values for microbe-mediated processes tested in different soils were available, the use of the geometric mean NOEC values for either microbe-mediated processes or species was considered less appropriate. Thus, preference was given to the use of individual NOEC values from the different tests. Therefore, the use of statistical extrapolation using individual NOEC values was used to derive $PNEC_{add, soil}$.

The use of statistical extrapolation method for individual NOECs for both microbe-mediated processes or species resulted in in median 5% percentile values ranging from 27 to 38 mg Zn/kg dw and 31 to 52 mg Zn/kg dw, respectively.

7.1.5. Overall conclusion on $PNEC_{add, soil}$

In conclusion, the statistical extrapolation resulted in a **$PNEC_{add, soil}$ of 26 mg Zn/kg dw** soil derived from the median 5th percentile val;ue (52 mg Zn/kg dw) for species and applying an assessment factor of 2. This $PNEC_{add, soil}$ is just below the value derived from the data for microbe-mediated processes (27 mg Zn/kg dw).

8. REGIONAL RISK CHARACTERIZATION

8.1. General

The use of the added risk approach implied that in the risk characterization the added Predicted Environmental Concentration (PEC_{add}s) in the various environmental compartments was compared with the corresponding added Predicted No Effect Concentration ($PNEC_{add}$s). In case measured environmental concentrations were used in the risk characterization, either the natural background concentration had to subtracted from the measured environmental concentration (resulting in a traditional $PEC_{add}/PNEC_{add}$ ratio) or the natural background concentration had to be added to the $PNEC_{add}$ (resulting in a traditional PEC/PNEC ratio). Finally, a correction for bioavailability was carried out in the risk characterization stage. For the scenarios were the uncorrected PEC values held a PEC/PNEC ratio above 1, a bioavailability correction was made for surface water, sediment and soil.
The regional exposure assessment consisted of both a modelled approach (SimpleBox/EUSES) based on regional emission data and actual zinc monitoring data in the environment.

8.1.1. Aquatic environment

Water compartment

The calculated $PEC_{add,\ water}$ amount to 12.2 and 16.8 μg/L for the NL-region and the EU-region respectively. Using the $PNEC_{add,\ water}$ of 21 μg/L (total; defaultof 15 mg/L suspended matter) resulted in a PEC/PNEC ratios of 0.6 (NL-region) and 0.8 (EU-region). These PEC/PNEC ratios refer to values without an additional correction for bioavailability in surface water. In the regional risk characterization preference was given to monitoring data, which were considered representative and valid and only measured data for the period after 1995 was used in the zinc RA.

Using recent monitoring data for the Netherlands and the EU indicated that the PNEC was exceeded in a number of surface waters, when no bioavailability correction was performed. Therefore, for those regional waters where abiotic parameters were available (pH, DOC and hardness), the Bio-Ligand Model were applied for bioavailability correction. However, even after correction for bioavailability, in most cases PEC/PNEC ratios remained above 1. This was the case for the river Meuse (Netherlands and Belgium), Flanders, Wallon Provences, various German rivers and the French region. Overall, a **conclusion iii** was drawn for the regional scale as in a number of EU areas tre measured surface water concentration of zinc exceeded the PNEC. This conclusion includes correction for bioavailability of zinc in surface water.

Sediment compartment

The calculated regional concentrations ($PEC_{add\ sediment}$) of zinc in sediment were 504 mg/kg dw for the NL-region and 696 mg/kg dw for the EU-region, excluding a natural background level of 140 mg/kg dw. Monitoring data for sediments was available for the Netherlands, France, Germany, Sweden, Norway, and Belgium. Regional PEC/PNEC ratios based on both calculated and measured data pointed to a potential risk for sediment-dwelling organisms. With the exception of Northern Sweden, all data (after subtraction of zinc natural background concentration of 140 mg/kg dw for measured data) were much higher than the $PNEC_{add\ sediment}$ of 49 ,g/kg dw. This conclusion was based without any further correction for zinc bioavailability in sediment (SEM/AVS method). However, the bioavailability correction could only be applied to the region of Flanders since this is the only region that had zinc sediment measurements with a corresponding SEM/AVS. For all the other regions where no information of SEM/AVS was available a default correction value of 0.5 for the PEC could be applied. However, even with an additional factor of 0.5 for nearly all data the PEC/PNEC ratios were still above 1. Therefore a **conclusion iii** was drawn for sediment at a regional scale.

8.1.2. Soil compartment

Non-agricultural soils

In the Netherlands and other EU countries there are a number of areas that are highly contaminated with zinc due to industrial activities. Contaminations are mostly due to historical emissions from zinc smelters, etc. In the zinc RA it was ddecided not to pay further attention to regions affected by historical pollution.

Agricultural soils

The regional $PEC_{add\ soil}$ in agricultural soil was calculated based on the diffuse zinc emissions to soils. Manure application is by far the major contributor of these soil emissions. The $PEC_{add,\ agricultural\ soil}$ was 64 mg/kg dw for both the NL-region and EU-region. Comparing these PEC_{add} with the $PNEC_{add}$ for soil based on the micro-organimks (26 mg/kg dw) resulted in a $PEC_{add}/PNEC_{add}$ ratio of 2.5. Zinc bioavailability in soil was corrected by using a generic lab-to-field correction factor of 3 for ageing resulted in a $PEC_{add}/PNEC_{add}$ ratio of 0.8.
Measured data of zinc oin agricultural soils come from the Alterra study (De Vries et al., 2004) since this is the more recent data. These data is also representative of other North-Western countries having similar intensive agriculture activities. Inputs of zinc via manure application in the Netherlands might be among the highest in Europe, however it do not deviate a lot from other EU countries due to the fact that inputs from sludge are much higher in most other countries. In the Alterra study, the present and future zinc concentrations were compared to the critical zinc limit in soil. This critical limit in soil was based on the current $PNEC_{add}$ of 26 mg/kg dw and the bioavailability corrections of the calculated PEC_{add} values by using the generic ageing related lab-to-field correction factor of 3 and also soil-specific bioavailability corrections.
Diffuse zinc emissions to agricultural soil result in a zinc accumulation in several EU areas with intensive agricultural activities. On the basis of the outcomes of the Alkterra study it was concluded that current animal manure application rates on land will result in an exceedance of the critical zinc concentrations in soil. However, the time period for reaching these critical zinc concentration in agricultural soils was estimated to be long. On average and depending on the soil type, it will take 100 to 500 years for grassland and 300 to 900 years for arable land. If the EU-standard for nitrogen application on agricultural land is applied this time scales would be

significantly enhanced. This study was based on the situation for the Netherlands but this scenario is representative (realistic worst-case) for regions in the European Union. Overall, a **conclusion ii** was drawn for agricultural soils at a regional scale and it no risks are expected for zinc in agricultural soils.

9. OPINIONS ON THE ENVIRONMENTAL PART OF THE RISK ASSESSMENT

9.1. Opinion by the Scientific Committee on Health and Environmental Risks (SCHER)

The main concern of the SCHER is the use of the added risk approach in the zinc and zinc compounds RAs, since this approach should only be used if a region specific realistic natural background can be established. In the Zn RA it has not been done since it was very difficult to establish a region-specific background and it is the opinion of SCHER that the use of a range of Zn natural background concentrations applicable to the whole EU was not useful for risk characterization.
Another concern was the use of the model predicting environmental concentrations of zinc. SCHER opinion is that the PECs derived by a modified version of EUSES was not helpful since modifications were substantial and therefore there was a concern on the use of this model as a key element of the risk assessment.
Another major concern for the zinc risk assessment was correction for bioavailability. SCHER opinion is that the Biotic Ligand Models (BLM) applied to account for bioavailability should not be applied on the exposure side if other options are available and thus there was a concern that adjustments made could have a serious impact on the effects assessment; bioavailability adjustments made to indicidual species endpoints could alter the shape of the SSD curve. In general, the zinc RA took bioavailability into account through the use of bioavailability factors (BioF), which was considered problematic by SCHER since these BioF and the resulting risk characterization ratio was dependent on the choice of the reference water to establish the BioF. Within the RA it was unclear if this reference water reflected an EU wide realistic worst case scenario and how it was established.
Another concern was on the effects assessment for both the aquatic and terrestrial compartment. SCHER accepted the relevance and reliability criteria are important for the selection of the data in environmental RA, but the use of background concentration as a relevance criterion was complicated by the possibility of natural adaptation/acclimatation responses. Therefore it might be argued that inclusion of the data from organisms from low background concentrations is overly conservative because it excludes natural adaptation/acclimatation that are natural processes. Exclusion of data from organisms from high background concentrations might be critisised fro the same reasons. Both these adjustments were made in the Zn RA on the grounds of both relevance and conservativism. It is the opinion of SCHER that the topic on background mediation for effects endpoints and its implications should have been treated more explicitly and consistently within the zinc and zinc compounds RAs.
Throughout the RA careful and detailed consideration was given to variability in measured exposure and effects data and in partition coefficients. However, it is the opinion of SCHER that the information was obscured in the RA by the use of averages, worst cases and ranges and that given the current availability of methodology distributions could have been used more effectively in probabilistic assessments.
Finally, another concern was the derivation of risk characterizations ratios from the Zn and Zn compounds RAs. These are predominantly based on North European data

and it is the SCHER opinion that there might be significant differences in Southern European countries. These differences cover geochemistry, climatic conditions and ecology.

In conclusion, it was SCHER opinion that in general the RAs on zinc and zinc compounds gave detailed consideration to variability in measured exposure and effects data but that the information was lost by the use of averages, worst cases and ranges. It was also concluded that with appropriate PECs and measured environmental concentrations a total risk approach could have been contemplated. Overall, the uncertainties on the risk characterization ratios and the RAs conclusions derived from them were problematic.

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