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Impact of soil properties on critical concentrations of cadmium, lead, copper, zinc
and mercury in soil and soil solution in view of ecotoxicological effects

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1 Introduction

Use of critical metal loads in assessing the risk of metal inputs

Concern about the input of metals to terrestrial ecosystems is related to: (i) the ecotoxicological impact on soil organisms and plants (e.g. Bringmark et al. 1998; Palmborg et al. 1998) and also on aquatic organisms due to runoff to surface water and (ii) the uptake via food chains into animal tissues and products, which may result in health effects on animals and humans (e.g. Clark 1989). Effects on soil organisms, including micro-organisms/macromycetes and soil fauna, such as nematodes and earthworms, are reduced species diversity, abundance and biomass and changes in microbe mediated processes (e.g. Bengtsson and Tranvik 1989; Giller et al. 1998; Vig et al. 2003). Effects on vascular plants are reduced development and growth of roots and shoots (toxicity symptoms), elevated concentrations of starch and total sugar, decreased nutrient contents in foliar tissues (physiological symptoms) and decreased enzymatic activity (biochemical symptoms) (e.g. Prasad 1995; Das et al. 1997). A review of these phytotoxic effects is given by Balsberg-Påhlsson (1989). Effects on aquatic organisms, including algae, crustacea and fish, include effects on gill function (e.g. Sola et al. 1995), nervous systems (e.g. Baatrup 1991), and growth and reproduction rates (e.g. Mance 1987). Environmental quality standards or critical limits (often also denoted as predicted No effect Concentrations or PNECs) for metals in soils and surface waters related to those effects serve as a guide in the environmental risk assessment process for those substances.

Next to effects on soil organisms, metals may be transferred in food chains to cause effects on animals and humans (secondary poisoning). This may affect (i) humans by reducing food quality of crops and animal products and (ii) animal health through the accumulation in organs of cattle, birds and mammals (secondary poisoning). Heavy metal accumulation in food chains is specifically considered important with respect to cadmium (Cd) and mercury (Hg), and to a lesser extent for lead (Pb), for all of which no biological functions are known (e.g. Clark 1989). The only exception known is that Cd appears to be essential under Zn-limiting conditions for one marine diatom (Lee et al. 1995).

One risk assessment approach, used successfully in international negotiations on the reduction of atmospheric deposition of pollutants, is to determine the maximum load of constant atmospheric pollution that causes no or tolerable damage (“long-term acceptable load” or “critical load”). A major advantage of this method is that it can be used to optimise the protection of the environment for a given international investment in pollution control by minimising the difference between present loads and critical loads on a regional scale. A major difficulty is the quantification of the relationship between atmospheric emission, deposition and environmental effects.

The method to calculate critical loads of metals is based on the balance of all relevant metal fluxes in and out of a considered ecosystem in a (distant) future steady state situation. First approaches were described in Manuals for calculation of critical loads of heavy metals in terrestrial ecosystems (De Vries and Bakker 1998) and aquatic ecosystems (De Vries et al. 1998). These methods were discussed at various international workshops (e.g. Gregor et al. 1997; Gregor et al. 1999). An important

development in the calculation and mapping of heavy metals were the results of a first preliminary European mapping exercise on critical loads related to ecotoxicological effects of Cd and Pb (Hettelingh et al. 2002) using a guidance document provided by De Vries et al. (2002). In the most recent manual, the critical load of a metal is simply calculated as the sum of tolerable outputs from the considered system in terms of net metal uptake by plants and metal leaching/runoff (De Vries et al. 2005). These fluxes depend on the receptor considered and the related critical limits for heavy metals.

Relevant receptors and related critical limits

With respect to risks on terrestrial ecosystems, a distinction can be made between risks/effects on the health of: (i) soil organisms/processes and plants (primary ecotoxicological risks) and (ii) animals, including both domestic and wild animals and humans that use ground water for drinking water or that consume crops, meat or fish (secondary poisoning). A description of major pathways of metals in terrestrial ecosystems, including the link with aquatic ecosystems, is given in Figure 1.

<Table 1>

Relevant receptors in terrestrial ecosystems, distinguishing arable land, grassland and non-agricultural land (forest, heath lands) are presented in Table 1. Possible effects on soil organisms and plants (phytotoxicity) and terrestrial fauna are of concern in all types of ecosystems. Food quality criteria are, however, of relevance for arable land and grassland (limits for animal food), whereas possible secondary poisoning effects on animals are relevant in grassland (cattle) and non-agricultural land (wild animals).

For most of the receptors or compartments indicated in Table 1, critical limits have been defined related to ecotoxicological or human-toxicological risks, such as:

- Soil: critical limits related to effects on soil organisms (micro-organisms and soil invertebrates) and plants ($\text{mg}\cdot\text{kg}^{-1}$).
- Plants/terrestrial fauna: critical limits in plant tissue, animal products (meat) or target organs, such as kidney, related to effects on plants and/or animals and on humans by consumption (food quality criteria) ($\text{mg}\cdot\text{kg}^{-1}$).
- Ground water: critical limits in drinking water related to effects on humans by consumption ($\mu\text{g}\cdot\text{l}^{-1}$).
- Humans: acceptable daily intake or ADI ($\mu\text{g}\cdot\text{kg}^{-1}\cdot\text{d}^{-1}$). This dose is the quantity of a compound to which man can be orally exposed, on the basis of body weight, without experiencing adverse effects on health.

Critical limits related to ecotoxicological effects on soil organisms and plants are limited to soil, whereas critical limits related to human-toxicological risks are mainly accounted for by food quality criteria for metals in food crops, animal products (cows/sheep), fish and drinking water (ground water) consumed by them. A final critical limit can be based on the most sensitive receptor.

Need of critical limits for metals in soil and soil solution as a function of soil properties

In view of general risk assessment, there is a need for critical limits for metals in soil. Such limits, based on laboratory studies with plants and soil organisms (soil microbiota and soil invertebrates), are mostly related to total metal contents, either in

the humus layer or the mineral soil (Bååth 1989; Bengtsson and Tranvik 1989; Tyler 1992; Witter 1992). The same is true for effects by secondary poisoning on terrestrial fauna (e.g. Ma and van der Voet 1993; Jongbloed et al. 1994). Furthermore, limits are still often expressed as one value for a soil or transferred by a simple weighting procedure with organic and clay content that is not based on ecotoxicological assessments.

The use of a single soil metal concentration as a critical limit for ecotoxicological effects upon soil organisms has been criticised (Allen 1993) since it does not account for observed variations in the toxicity of cationic metals among soils of differing chemistry (e.g. Spurgeon and Hopkin 1996). These variations in toxicity are believed to arise since for many organisms uptake and consequent toxicity of metals occurs via the soil solution (e.g. Ritchie and Sposito). Specifically, the free metal ion (FMI) in soil solution (e.g. Cu^{2+} , Zn^{2+} , Cd^{2+} , Pb^{2+}) is believed to be the form that is available for interactions with organisms (Lanno et al. 1999). This rationale is based on the principle of the free ion activity model (FIAM) (Morel 1983; Campbell 1995) and the Biotic Ligand Model (BLM) (Di Toro et al. 2001; Santore et al. 2001), as discussed in the methodological section. The evidence that soil properties such as soil organic matter content, clay content and specifically pH do affect the bioavailability and toxicity of metals in biota (e.g. Spurgeon and Hopkin 1996; Van Gestel and Koolhaas 2004), is hardly accounted for in the critical limits assessment.

Since effects on micro organisms, plants and, to a large extent, also to invertebrates occur through the soil solution, in particular by the free metal ions, an approach to set critical limits for FMI is in particularly appropriate to evaluate the risks of effects.

It enables the consideration of the chemistry of soils (and soil solution) and their influence on the toxicity of metals. Furthermore, in view of critical load assessments for terrestrial ecosystems, there is a need for critical metal concentrations in soil solution since the critical metal leaching rate is the most important term in deriving critical loads. Since metal concentrations in soil solution are hardly ever measured, such concentrations need to be derived from critical metal concentrations in the soil with so-called transfer functions, which relate the partitioning of (free) metal ion concentrations in soil solution and metal concentrations in the solid phase with soil properties.

Aim and contents of this paper

The aim of this paper is to derive critical concentrations for Cd, Pb, Cu, Zn and Hg in soil and soil solution in view of impacts on soil organisms/soil processes (see the solid arrows in Figure 1) while considering the effect of soil properties.. The critical concentrations include: (i) reactive and total metal concentrations in soils and (ii) free metal ion concentrations and total metal concentrations in soil solution. First we present the methodologies used to derive those concentrations based on available ecotoxicological research data on impacts on soil organisms and plants in terrestrial ecosystems. We then present results obtained for Cd, Pb, Cu and Zn, followed by a critical evaluation of the assumptions related to the derivation and use of these critical limits. A separate section is related to Hg. In a subsequent paper (De Vries et al. 2006), an overview is given of critical limits of Cd, Pb and Hg in view of the impacts on human health and on animal health due to potential accumulation in the food chain, with a focus on food quality aspects.

2 Methodological approach

2.1 General approach

Our approach to derive critical limits for Cd, Pb, Cu and Zn for soil and soil solution as a function of soil properties is based on the standard OECD (Organisation for Economic Co-operation and Development) approach for calculating Maximum Permissible Concentrations (MPC's) or critical limits of substances in the soil (OECD 1989). The toxicity data refer to No Observed Effects Concentration (NOECs) or Lowest Observed Effects Concentration (LOECs) for metals in soils or surface water, based on chronic toxicity tests. From a range of NOEC data an HC_p is derived from the "species sensitivities distribution" (SSD), being the hazardous concentration at which p% of the species in an ecosystem is potentially affected, or 100-p % is protected. In line with the OECD approach, a concentration of a certain compound was considered hazardous when the probability of selecting a species with a NOEC below this concentration equals 5 %. This implies that theoretically 95 % of the species within an ecosystem are protected. Using this method, the 95% protection level calculated with 50% confidence is regarded as the maximum permissible concentration ($MPC = HC_5$).

The use of critical total metal concentrations in soil solution requires NOEC data for soil solution that are either directly based on measurements or derived from NOEC soil data. Since NOEC data on free ionic Cd, Pb, Cu and Zn concentrations in soil solution are hardly available, the derivation of critical limit functions for metals in solution was based on NOEC and EC_{10} endpoint from: (i) organisms which are

exposed to the metal via the soil solution (plants, micro-organisms and soft bodied soil invertebrates), (ii) accompanied by data on soil properties (pH and organic matter content) to allow the calculation of dissolved concentrations by using transfer functions and (iii) evaluated by a statistical approach deriving limits based on a 95% protection level. Related critical reactive soil concentrations were derived in the same procedure as a function of pH and organic matter content.

In the approach it is assumed that apart from the hard bodied invertebrates, where soil ingestion is the major intake route, soil solution is the major pathway for metal impacts on all soil organisms and plants. This assumption is certainly valid for plants and micro-organisms and for invertebrates living in soil water, such as nematodes, but is also a reliable assumption for soft bodied invertebrates living in soil, such as earthworms (e.g. Saxe et al. 2001). The use of transfer functions is based on the assumption that effects data from ecotoxicological investigations in laboratory can be related to a “reactive” heavy metal concentration in the soil, since the heavy metal applied in such tests is in a well available form.

Unlike standard statistical extrapolation methods, used to derive an HC_p , our approach is not based on the assumption that the SSD in natural ecosystems approximates a postulated statistical frequency distribution such as a log logistic or log normal distribution (Aldenberg and Slob 1993; Aldenberg and Jaworska 2000). Instead we used an alternative approach called bootstrapping, presented by Newman et al. (2000), requiring no a priori assumed statistical distribution of the data. Briefly, the dataset of toxicity endpoints was repeatedly sampled and an HC_5 for each sample taken as the 5th percentile. The number of data points sampled was the same as the

number in the whole data set, but individual data points could be sampled more than once, thus each sample was slightly different from all the others. Calculation of MPCs with different confidence levels was possible by taking different percentiles of the sample HC5s. For example, the median (50% ile) and 5% ile of all sampled HC5s was taken to be the MPC with 50% and 95% confidence level, respectively. Critical limits for Cd, Pb using the data of Klepper and Van de Meent (1997), calculated with the log-logistic and bootstrap methods, are presented in Table 2.

<Table 2>

Below we describe the in more detail the (i) Transfer functions that were used to derive critical total metal concentrations in soil and soil solution from NOEC soil data (Section 2.2) and the approach that was used to include impacts of soil properties on critical free, reactive and total metal concentrations in soil and soil solution (Section 2.3).

2.2 Use of transfer functions to derive critical free and total metal concentrations in soil and soil solution

Transfer functions describing the partitioning between metals soil and soil solution were used needed to calculate critical limits for free metal ion (FMI) activities from soil toxicity data (assumed to be related to reactive soil metal contents). They were also used to re-calculate critical reactive or critical total metal contents for different soil conditions. The various transfer functions used in this study are described below

Possible transfer functions

Transfer functions are regression relations which describe the partitioning of metals between soil and soil solution, while accounting for the impact of soil properties. Transfer functions relating soil metal concentrations in the (soil) solid phase to soil solution either refer to the free metal ion concentration or to the total dissolved metal concentration. The latter concentration includes metals bound to inorganic complexes and dissolved organic matter, but excludes metals bound to suspended particulate matter. Possibilities for the calculation of a dissolved concentration from solid phase data are presented in Figure 2.

Data on present metal contents are mostly (pseudo) total contents, $[M]_{\text{tot}}$, based on aqua regia destruction $[M]_{\text{AR}}$ or a concentrated nitric acid destruction $[M]_{\text{1N-HNO}_3}$. Chemically, it is the reactive metal content in soil, $[M]_{\text{re}}$, that interacts with the metal concentration in soil solution. Possible calculations of either a total (free and complexed) concentration of metals in solution ($[M]_{\text{ss}}$) or the free metal ion concentration or activity ($[M]_{\text{free}}$) from a total concentration in the solid phase ($[M]_{\text{tot}}$) are therefore considered inappropriate (see also Groenenberg et al. (2003). Instead, transfer functions for solid-solution partitioning can thus best be derived on the basis of reactive metal contents, based on mild HNO_3 (0.43N), EDTA or DTPA extractions (Römkens et al. 2004).

In this context, we make the assumption that effects data from ecotoxicological investigations in laboratory can also be related to a “reactive” heavy metal concentration in the soil, since the heavy metal applied in such tests is in a well

available form. This implies that solid phase transfer functions are needed to transfer reactive metal contents (NOEC data) to pseudo- total contents (*relation 1* in Figure 2).

Regarding the soil-solution, a distinction can be made between transfer functions relating free ion metal activity or concentration in solution (*relation 2* in Figure 2) or total metal concentration in solution with reactive metal concentrations (*relation 3* in Figure 2). Groenenberg et al. (2003) showed for metals which form strong complexes with DOC, such as Pb and Cu, the transfer functions with free ion metal activities or concentrations are always much better than the transfer functions with total concentrations. Therefore, the use of free metal activity or free metal concentration relations (*relation 2* in Figure 2), in combination with a chemical speciation model to calculate the total dissolved metal concentration from the free metal concentration (*relation 4* in Figure 2) is recommended. The latter aspect is discussed in Section 2.4.2.

Transfer functions to derive total metal soil metal concentrations from reactive soil metal concentrations

In this study, (pseudo)total soil metal concentration, $[M]_{\text{tot}}$, (extracted with Aqua Regia), were derived from reactive metal concentration, $[M]_{\text{re}}$, assumed to be equal to added metal concentrations in laboratory toxicity data, according to:

$$\log \text{ctM}_{\text{tot}} = \beta_0 + \beta_1 \cdot \log \text{ctM}_{\text{re}} + \beta_2 \cdot \log \text{OM} + \beta_3 \cdot \log \text{clay} \quad (1)$$

where:

ctM_{tot} = the total metal content in the solid phase ($\text{mg}\cdot\text{kg}^{-1}$)

- ctM_{re} = the reactive metal content in the solid phase (mg.kg⁻¹)
- OM = organic matter content in the soil (%)
- clay = clay content in the soil (%)

Regression relations were derived from a Dutch dataset containing 630 soil samples which were both extracted with 0.43 Mol.l⁻¹ HNO₃ and Aqua Regia (Römkens et al. 2004). The dataset consists of large variety of soil types with a relative wide variety in soil properties as the organic matter (median of 4% and 95% of 14%) and clay content (median of 13% and 95% of 36%). The dataset comprises both polluted and unpolluted soils. Results are shown in Table 3.

<Table 3>

When deriving the total critical metal concentration from a critical reactive metal concentration, using Eq. (1), it should be kept in mind that the critical soil metal concentrations are frequently higher than ambient soil concentrations, even for polluted soils. Therefore, the transfer function should preferably not be used outside its range of soil metal concentrations. The maximum values for the total (aqua regia extracted) concentrations of Cu, Zn, Cd and Pb were approximately 330, 3100, 40 and 1600 mg.kg⁻¹, respectively, whereas the maximum reactive (0.43 mol.l⁻¹ HNO₃ extracted) concentrations of Cu, Zn Cd and Pb were approximately 310, 2800, 20 and 1400 mg.kg⁻¹, respectively.

Transfer functions to derive relate free metal ion concentrations from reactive metal contents

There are various transfer functions in the literature that relate free metal ion concentrations to reactive metal contents, while accounting for the effect of soil properties, such as pH, organic matter content and clay content. For example, Sauvé et al. (1997b) found that the free Cu^{2+} concentration in a sample of urban, agricultural and forest soils could be described well as a function of pH and reactive soil Cu content alone, while Groenenberg et al. (2003) found that inclusion of both organic matter content and clay content was necessary to describe Cd^{2+} and Pb^{2+} in a dataset of Dutch soils. The transfer function used in this study was based on datasets comprising soils with a large variability in organic matter (<1% to >90%) and both the pH and organic matter content were significant variables in the transfer function that was described as:

$$\log [M]_{\text{free}} = a + b \cdot \text{pH}_{\text{ss}} + c \cdot \log \text{OM} + d \cdot \log \text{ctM}_{\text{re}} \quad (2)$$

where:

$[M]_{\text{free}}$ = the free metal ion concentration (mol.l^{-1})

ctM_{re} = the reactive metal content in the solid phase (mol.kg^{-1})

pH_{ss} = soil solution pH

This is entitled a c-Q relation (a relation calculating c from Q), where c stands for the free metal ion concentration and Q stands for the reactive soil metal content. For calibration of direct transfer functions for Cd, Pb, Cu and Zn data were drawn from seven sources:

- Sauv   et al. (1997a). Soil Pb and labile Pb in Pb-contaminated soils of various origins. Free Pb²⁺ concentrations were estimated by measurement of labile Pb using differential pulse anodic stripping voltammetry (DPASV) and speciation calculations. Metal contents in soil were determined using a concentrated HNO₃ extraction.
- Sauv   et al. (1997a). Soil Cu and free Cu²⁺ in Cu-contaminated soils of various origins – urban, forest and agricultural. Free Cu²⁺ was measured by ion-selective electrode (ISE). Soil Cu was determined using a concentrated HNO₃ extraction.
- Sauv   et al. (2000). Soil metal and labile Cd in Cd-contaminated soils of various origins. Free Cd concentrations were estimated by measurement of labile Cd using DPASV and speciation calculations. Soil Cd was determined using a concentrated HNO₃ extraction.
- Tambasco et al. (2000). Soil Zn and free Zn²⁺ in soils of various origins – urban and forest. Free Zn²⁺ was measured using DPASV. Soil Zn was measured by extraction with 0.01M EDTA at pH 8.6.
- Weng et al. (2001; 2002). Soil metal and free ion concentrations in sandy Dutch soils. Weng et al. (2001; 2002) measured free Cu, Zn, Cd and Pb concentrations by the Donnan membrane technique. Metal contents in soil were determined using a 2M HNO₃ extraction by Weng et al. (2001) and using Aqua Regia by Weng et al. (2002).
- Tipping et al. (2003). Soil metal and free ion concentrations in UK upland soils. Free Cu, Zn, Cd and Pb were estimated by using the WHAM6 speciation model (Tipping 1998) to speciate the soil solution. Metal contents in soil were determined using 0.43 mol.l⁻¹ HNO₃ extraction.

For the transfer functions derived here we have used the free ion concentration, since some of the data used (Sauvé et al. 1997a; Sauvé et al. 2000; Weng et al. 2002) express the free ion as a concentration rather than an activity. Actual differences between free activities and concentrations in soil solutions will be small compared to the expected variation in the activity or concentration with soil properties. Calculated values of the parameters in Eq. (1) are given in Table 4. According to the transfer functions, the effect of organic matter on Cu and Pb is higher than for Cd and Zn, but the effect is smaller than expected. The impact of pH and reactive metal concentration on the free metal ion concentration is, however, much higher for Cu and Pb than for Cd and Zn. More information is given in Lofts et al. (2004).

<Table 4>

2.3 The methodology used to derive critical metal concentrations in soil and soil solution

2.3.1 Derivation of critical free metal ion concentrations and reactive soil metal concentrations as a function of soil properties

Methodology to calculate toxic metal concentrations

The methodology used to calculate toxic metal concentrations was based on the evidence that toxic effects upon many soil organisms are mediated via the activity of free metals in soil solution. The principle of the free ion activity model (FIAM) is that the entry of the metal into the organism, resulting in toxicity, is considered to occur by binding to a receptor site, followed by transport into the body of the

organism. If the binding step is rapid in comparison with the transport step, then the toxic effect is proportional to the amount of metal bound to the receptor, which is itself proportional to the free metal ion concentration (FMI) in bulk solution. Other cations (e.g. H^+ , Na^+ , Ca^{2+}) would be expected to compete with the toxic metal for the receptor site (Morel 1983). Therefore, while in a single system the toxic effect on the organism would be expected to relate to the FMI alone, when considering equivalent toxic effects across a set of systems with varying chemical composition the concentrations of these competing cations must also be considered.

Binding of the metal to the receptor is thus considered to occur in competition with other solution cations (e.g. H^+ , Ca^{2+} , Mg^{2+}), so that the FMI concentration exerting a given toxic effect depends upon the concentrations of these cations in bulk solution. An increase in the concentration of any competing cation will result in an increase in the concentration of FMI required to exert a given level of toxic effect, due to increased FMI–cation competition at the receptor site. Experimentally, this would be observed as an apparent ‘protective’ effect of solution cations against the toxic effects of the FMI.

The approach that we used was based upon the theory of solution cations ‘protecting’ the organism from the effects of the toxic FMI, using an empirical formulation according to Lofts et al. (2004):

$$\log [M]_{\text{free,toxic}} = \alpha \cdot \text{pH}_{\text{ss}} + \sum \beta_i \cdot \log C_i + \gamma \quad (3)$$

where $[M]_{\text{free,toxic}}$ is the FMI concentration at the toxic endpoint, pH_{ss} is the soil solution pH, C_i is the concentration of a ‘protecting’ free cation and α , β and γ are empirical coefficients. Since concentrations of ‘protecting’ cations such as Ca^{2+} and Mg^{2+} would be expected to co-vary with pH_{ss} , as a first approximation the expression may be simplified to

$$\log [M]_{\text{free,toxic}} = \alpha \cdot \text{pH}_{\text{ss}} + \gamma \quad (4)$$

If toxic endpoints were available as the soil solution FMI, Eq. (4) would be directly applicable. However, literature studies routinely express the endpoint as a concentration of metal added to the soil at the start of the experiment, or as a soil metal concentration measured at the end of the experiment by chemical extraction. Therefore, Eq. (2) was used to convert the toxic soil metal concentrations to the FMI. FMI concentrations could then be calculated from the soil metal endpoints using Eq. (2), and regressed against pH_{ss} using Eq. (4). But since pH_{ss} is a variable in Eq. (4), this approach is not statistically valid. However, Lofts et al. (2004) presented a methodology to calculate critical limits preserving the underlying toxicological theory of Eq. (4) while avoiding statistically invalid regression steps. At the toxic endpoint,

$$\log [M]_{\text{free,toxic}} = a + b \cdot \text{pH}_{\text{ss}} + c \cdot \log \text{OM} + d \cdot \log \text{ctM}_{\text{re,toxic}} = \alpha \cdot \text{pH}_{\text{ss}} + \gamma \quad (5)$$

Rearranging gives:

$$\log \text{ctM}_{\text{re,toxic}} + (c/d) \cdot \log \text{OM} = \phi \cdot \text{pH}_{\text{ss}} + \psi \quad (6a)$$

or

$$F = \phi \cdot \text{pH}_{\text{ss}} + \psi \quad (6b)$$

where F represents the term $\log \text{ctM}_{\text{re, toxic}} + (c/d) \cdot \log \text{OM}$ and ϕ and ψ are new empirical coefficients being equal to:

$$\phi = (\alpha - b)/d \quad (7a)$$

$$\psi = (\gamma - a)/d \quad (7b)$$

Note that the term $[c/d]$ is derived from Eq. (2) and is therefore known. This expression gives the theoretical endpoint reactive soil metal, as a function of soil solution pH and % soil organic matter, and can be regressed against toxicity data to provide a function for the variation in $\log \text{ctM}_{\text{re, toxic}}$ with pH_{ss} and OM.

In literature toxicity experiments, soil pH has been estimated by chemical extraction (with H_2O , KCl or CaCl_2). In order to estimate the soil solution pH (pH_{ss}), relationships between pH by extraction with H_2O and pH_{ss} , and between pH by extraction with KCl and pH_{ss} , were established according (De Vries et al. 2005):

$$\text{pH}_{\text{ss}} = e \cdot \text{pH}_x + f \quad (8)$$

where the subscript X denotes the type of extraction used for pH (H₂O, KCl or CaCl₂) and e, f are coefficients. Results are given in Table 5. For conversion from pH extracted with H₂O or with KCl, a good general relationship is found. For conversion from pH extracted with CaCl₂, a poorer relationship is found, but data for which such a conversion is required are uncommon in the toxicity database.

<Table 5>

Equation (9) can be applied to give $ctM_{re,toxic}$ for a single effect on a single organism, as a function of soil solution pH and OM, by plotting F (Eq. 6b) against soil solution pH, for a series of soils of known pH and %soil organic matter. In principle, therefore, Eq. (6) can be applied to different sets of single-species data to calculate expressions for $\log ctM_{re,toxic}$ for a range of pH and OM. A set of $\log ctM_{re,toxic}$ values for a specific soil can then be calculated and used to define a critical limit for the soil following the methodology in Section 2.1.

Methodology for calculating critical limit functions for soil and soil solution

In practice, the toxicity databases for Cu, Zn, Cd and Pb are not sufficiently comprehensive to allow for the use of the approach suggested above. Instead, a simplified approach has been used, which calculates a single critical limit function applicable to any soil. This approach centres on the theory that if the theoretical toxicity function (Eq. 6a) holds for many species and processes, then by regression of the equation against lumped multiple–endpoint data, ‘ecosystem average’ values of the coefficients ϕ and ψ may be calculated. These coefficients then describe the apparent overall influence of soil chemistry on the endpoints. The scatter of points

around the regression can be ascribed to the intrinsic variability in the sensitivity of species or processes to the toxicant, and can therefore be analysed by a distributional approach, giving a critical limit function of the form:

$$F_{\text{crit}} = \phi \cdot \text{pH}_{\text{ss}} + \psi + \delta \quad (9)$$

where δ is a value calculated from the regression residuals for the desired level of ecosystem protection.

Lofts et al. (2004) presented in detail a method to calculate critical limit functions for Cu, Zn, Cd and Pb, using a bootstrapping technique to incorporate uncertainty in input data and parameters and to provide a convenient method to calculate a function at a given level of confidence. Briefly, a large number (10,000) samples of each toxicity dataset and of the parameters c and d (Table 4) were taken and used to calculate 10,000 pairs of ‘ecosystem average’ ϕ and ψ coefficients using Eq. (6a), and a corresponding value of δ by taking the 5%–ile of the regression residuals in F . These sets of coefficients were used to calculate 10,000 values of F (Eq. 8) at a series of pH_{ss} values and, by linear interpolation of the median F values, the critical limit function (with 50% confidence) was calculated:

$$F_{\text{crit}} = \log \text{ctM}_{\text{re}(\text{crit})} + (c/d) \cdot \log \text{OM} = \phi_{\text{crit}} \cdot \text{pH}_{\text{ss}} + \psi_{\text{crit}} + \delta \quad (10)$$

where \mathcal{E} is the constant term in the critical limit function, and the subscript CRIT refers to the critical value of a variable or the values of a coefficient in the critical limit function. Equation (12) can be rearranged to :

$$\log \text{ctM}_{\text{re}(\text{crit})} = \phi_{\text{crit}} \cdot \text{pH}_{\text{ss}} - (c/d) \cdot \log \text{OM} + \psi_{\text{crit}} + \delta \quad (11)$$

The critical limit function may also be expressed in terms of the free metal ion:

$$\log [\text{M}]_{\text{free}(\text{crit})} = \alpha_{\text{crit}} \cdot \text{pH}_{\text{ss}} + \gamma_{\text{crit}} \quad (12)$$

by calculation of critical values of α and γ according to (see Eq. 7):

$$\alpha_{\text{crit}} = b + d \cdot \phi_{\text{crit}} \quad (13a)$$

$$\gamma_{\text{crit}} = a + d \cdot (\psi_{\text{crit}} + \delta) \quad (13b)$$

Toxicity database used

Data sets including both NOEC or EC_{10} soil data and soil properties were used to derive NOEC soil solution data. Following procedures in the EU Risk Assessments, EC_{10} was considered equivalent to NOEC for the purposes of data gathering. NOEC and EC_{10} endpoints were used from major organisms, that represent different and significant ecological functions in the ecosystem, including: (i) decomposers, comprising micro-organisms or microbe-mediated soil processes (e.g. enzymatic activity), (ii) consumers, such as invertebrates (earthworms and

arthropods) and (iii) primary producers, specifically plants. Data for soil invertebrates were limited to soft bodied invertebrates which are exposed to the metal via the soil solution.

In order to provide as far as possible consistency between the critical limits derived here and those derived under parallel EU Risk Assessment procedures for soils and surface waters, the databases used were drawn from several draft reports for these metals (EU Risk Assessment Report Cadmium, Draft report 2003; EU Risk Assessment Report Zinc, Draft report 2004; Environmental Risk Assessment Pb and Pb-compounds, Draft report 2004 and Environmental Risk Assessment Cu, CuO, Cu₂O, CuSO₄ and Cu₂Cl(OH)₃, Draft report 2005). All these reports are still drafts since all limits mentioned in these reports are still under discussion by the EU. The only modification of the databases required was the removal of those endpoints for which the soil organic matter content was not provided. Metal concentrations in the control soils were not considered in deriving toxic endpoints, i.e. the added metal endpoint was used. This was the most suitable approach since the transfer functions that were applied to derive free metal ion concentrations are based on reactive soil metal contents. Added metal is likely to be reactive whereas some of the metal already present in the soil is likely to be in a non-bioavailable form. Furthermore, the toxic endpoint (NOEC/EC10) is always calculated by considering the effect on the organism relative to the effect in the control soil, i.e. the soil containing the background metal concentration. So the effect endpoint is effectively expressed as an added metal dose. This introduces some error because of the non linearity of the solid solution partitioning. In case the added metal concentration is large compared to the metal already present in the soil this error is likely to be very small. In field

conditions, these limits should be considered as critical elevations about the natural background concentration. The ecotoxicological datasets used to derive critical free metal ion concentrations for Cd, Pb Cu and Zn as a function of pH are summarized in Table 6.

<Table 6>

The ranges in the chemical parameters in the toxicological test soils for these metals are summarized in Table 7.

<Table 7>

2.3.2 Assessment of critical total metal concentrations in soil solution

Defining the critical total metal concentration in soil solution

To calculate critical loads for soils from the critical limit functions, it necessary to know the critical total metal concentration of in soil drainage water, $[M]_{\text{tot,sdw(crit)}}$, that corresponds to the free ion critical limit. Knowledge of $[M]_{\text{tot,sdw (crit)}}$ permits calculation of the leaching loss of the metal at its critical limit, by combination with the leaching. Critical total metal concentrations in soil drainage water (solution and suspended particles) are determined as the sum of the critical concentration of the free metal ion M^{2+} , $[M]_{\text{free(crit)}}$ and the metals bound to: (i) dissolved inorganic complexes such as MOH^+ , HCO_3^+ , MCl^+ , $[M]_{\text{DIC}}$, (ii) dissolved organic matter, $[M]_{\text{DOM}}$, and (iii) suspended particulate matter, $[M]_{\text{SPM}}$, according to:

$$[M]_{\text{tot,sdw(crit)}} = [M]_{\text{free(crit)}} + [M]_{\text{DIC}} + [M]_{\text{DOC}} \cdot [\text{DOM}] + [M]_{\text{SPM}} \cdot [\text{SPM}] \quad (14)$$

where:

$[M]_{\text{tot,sdw(crit)}}$ = critical total metal concentration in soil drainage water ($\text{mg}\cdot\text{m}^{-3}$)

$[M]_{\text{free(crit)}}$ = critical free metal ion concentration ($\text{mg}\cdot\text{m}^{-3}$)

$[M]_{\text{DIC}}$ = concentration of metal bound to dissolved inorganic (carbon) species ($\text{mg}\cdot\text{m}^{-3}$)

$[M]_{\text{DOM}}$ = concentration of metal bound to dissolved organic matter in equilibrium with the critical free ion concentration ($\text{mg}\cdot\text{kg}^{-1}$)

$[\text{DOM}]$ = concentration of dissolved organic matter ($\text{kg}\cdot\text{m}^{-3}$)

$[M]_{\text{SPM}}$ = concentration of metal in suspended particulate matter in equilibrium with the critical free ion concentration ($\text{mg}\cdot\text{kg}^{-1}$)

$[\text{SPM}]$ = concentration of suspended particulate matter ($\text{kg}\cdot\text{m}^{-3}$)

Note that all concentrations given above refer to soil drainage water (sdw), although it has only been mentioned specifically for the total metal concentration. In soil drainage water, the concentration of suspended particulate matter is generally very small. Assuming that $\text{SPM} = 0$, the total metal concentration in soil drainage water is equal to the dissolved concentration ($[M]_{\text{dis,sdw(crit)}}$, being equal to the critical concentration in soil solution, $[M]_{\text{ss(crit)}}$, according to:

$$[M]_{\text{ss(crit)}} = [M]_{\text{free(crit)}} + [M]_{\text{DIC}} + [M]_{\text{DOM}} \cdot [\text{DOM}] \quad (15)$$

By assuming geochemical equilibrium, the partitioning and speciation of metals over the various fractions can be calculated.

Calculating the critical total metal concentration in soil solution

Given the activity or free concentration of $[M]_{\text{free}}$ the concentrations of the other metal species were estimated by applying the equilibrium speciation model WHAM6 (Windermere Humic Aqueous Model, Version 6, Tipping 1994, 1998). The calculation takes into account the dependence of the metal speciation on pH and competitive effects due to major cationic species of Mg, Al, Ca and Fe (Tipping et al. 2002; Tipping 2005). A customised program (W6-MTC), based on WHAM 6 was used. Use of W6-MTC allows to calculate critical total dissolved metal concentrations from critical pH dependent free metal ion activities, for various combinations of pH, concentrations of soil organic matter, dissolved organic matter (DOM) or dissolved organic carbon (DOC) and suspended particulate matter (SPM) and partial CO_2 pressure (pCO_2). Calculations were made with DOC concentrations of 10, 15, 20 and 35 mg.l^{-1} used as average values for arable land, grassland, forest mineral topsoil (0-10 cm) and forest organic layer (O horizon), respectively (De Vries et al. 2005). (DOM=20, 35, 40 and 70 mg l^{-1}), pCO_2 of 15 x atmospheric value and ($[\text{SPM}] = 0$ (values thus equal the total concentration in soil solution). The calculations refer to a temperature of 10°C.

The W6-MTC program was applied by carrying out the following steps to calculate values of $[M]_{\text{ss(crit)}}$ (see Eq. 15 for its definition):

1. The concentration (g.l^{-1}) of “active” fulvic acid (FA) as used in WHAM is obtained by multiplying $[\text{DOC}]$ in mg.l^{-1} by 1.3×10^{-3} . This conversion factor is based on application of the WHAM6 model to field and laboratory data for waters and soils

involving Al (Tipping et al. 1991; Tipping et al. 2002), Cu (Dwane and Tipping 1998; Vulkan et al. 2000; Bryan et al. 2002), and Cd (Tipping 2002).

2. The critical free ion concentration, $[M]_{\text{free(crit)}}$, is computed from the soil solution pH and the Critical Limit Function (Eq.12 with critical values of α and γ according to Table 10).

3. The activity of Al^{3+} is calculated from the pH, using equations derived by Tipping (2005). One equation applies to soils low in Al, and high in organic matter. A second equation applies to high-Al mineral soils. In the present exercise, soils with less than 20% organic matter are considered to be high in Al, and those with more than 20% organic matter are considered low in Al.

4. The activity of Fe^{3+} is obtained by assuming a solubility product of $10^{2.5}$ (at 25°C) and an enthalpy of reaction of $-107 \text{ kJ}\cdot\text{mol}^{-1}$ (Tipping et al. 2002).

5. As a starting-point, Na is assumed to be present in the soil solution at a concentration of $0.001 \text{ mol}\cdot\text{l}^{-1}$, balanced by equal concentrations, in equivalents, of the three major acid anions Cl^- , NO_3^- and SO_4^{2-} . Thus, the concentrations of Cl^- and NO_3^- are each $0.000333 \text{ mol}\cdot\text{l}^{-1}$, while that of SO_4^{2-} is $0.000167 \text{ mol}\cdot\text{l}^{-1}$.

6. The concentration of $[M]_{\text{free}}$ and the activities of Al^{3+} and Fe^{3+} are fixed at the values obtained in steps 1-3, and the activity of H^+ is fixed from the pH. The WHAM6 model is then run to make an initial computation of inorganic solution speciation and metal binding by FA. As part of the computation, concentrations of carbonate species are obtained from pH and pCO_2 . Possible metal inorganic complexes are with OH^- , Cl^- , SO_4^{2-} , HCO_3^- and CO_3^{2-} .

7. If the result from Step 6 gives an excess of positive charge, which occurs for acid solutions, the total concentrations of NO_3^- and SO_4^{2-} are increased to compensate. Then the WHAM6 program is run again.

8. If the result from Step 6 gives an excess of negative charge (less acid to alkaline solutions), it is assumed that Ca provides the required additional positive charge. The WHAM6 model is run iteratively to find the total concentration of Ca that gives the correct charge balance.
9. The binding of metal to SPM is computed, by applying multiple regression equations (“transfer functions”) derived for soils. The transfer function used here is Eq. (2) with the parameters mentioned in Table 4.
11. The concentrations of dissolved inorganic metal species (including $[M]_{\text{free}}$) and metal bound to dissolved organic matter, $[M]_{\text{DOM}}$, are added to obtain $[M]_{\text{ss (crit)}}$.

3 Derived critical limits for cadmium, lead, copper and zinc concentrations in soil and soil solution

3.1 Critical limits for reactive and total metal contents in the soil

Critical limits for reactive and total metal contents

Figure 3 shows results from the toxicity data set assessment for Cd, Pb, Cu and Zn by plotting $F(\log [M]_{\text{re(crit)}} + c/d \cdot \log [\text{OM}])$ against pH_{ss} . The regression slope is positive, indicating that $\log [M]_{\text{re(crit)}}$ increases with increasing pH_{ss} , with the exception of Cu where the slope is not significant. The statistical significance of the slopes was tested at the 95% confidence level. Furthermore $\log [M]_{\text{re(crit)}}$ increases with increasing soil organic matter. The relationship between $\log [M]_{\text{re(crit)}}$ and $\log [\text{OM}]$ is determined by the transfer function via the coefficient c/d . The results lead to the following relationships between the critical reactive metal concentration versus

the organic matter content and pH in soil solution, with the reactive metal concentrations in mol.g⁻¹:

$$\log \text{ctCd}_{\text{re(crit)}} = 0.33 \cdot \text{pH}_{\text{ss}} + 1.00 \cdot \log [\text{OM}] - 10.32 \quad (16)$$

$$\log [\text{Pb}]_{\text{re(crit)}} = 0.11 \cdot \text{pH}_{\text{ss}} + 0.66 \cdot \log [\text{OM}] - 7.74 \quad (17)$$

$$\log [\text{Cu}]_{\text{re(crit)}} = 0.02 \cdot \text{pH}_{\text{ss}} + 0.68 \cdot \log [\text{OM}] - 7.54 \quad (18)$$

$$\log [\text{Zn}]_{\text{re(crit)}} = 0.14 \cdot \text{pH}_{\text{ss}} + 1.07 \cdot \log [\text{OM}] - 8.56 \quad (19)$$

The value for the dependence of the critical limits on soil organic matter, [OM], follows directly from the results of the regression coefficients c and d for the free metal ion– reactive metal content relationship (see Eq. 11 and Eq. 2 and the results for c and d in Table 4). The effect of organic matter on the critical limit for the reactive metal content is largest for Cd and Zn and lowest for Cu and Pb, whereas the reverse is true for the pH effects. Inversely, the effects on organic matter on the partitioning between reactive metal content and free metal ion concentration are largest for Cu and Pb and lowest for Cd and Zn, whereas the pH effects are largest for Cd and Zn and lowest for Cu and Pb (see Table 4).

To illustrate the impacts of pH and organic matter content on the critical reactive metal contents, results of the various critical limit functions (Eqs. 16-19) are presented in Table 8 for mineral soils and organic soils, with a representative organic matter content of 5% and 80%, in a pH range of 4-7. Results show that it is essential

to make a distinction in soil types, considering their difference in those soil properties. In acid mineral soils, such as forest top soils, the critical reactive metal content is calculated to be nearly 10 (Cu and Pb) to more than 50 (Cd and Zn) times as low compared to highly organic soils with a high pH (Table 8). Note that these critical limits refer to reactive metal contents, i.e. they do not include the immobile metal content. Calculated critical total metal contents, using the relationship between reactive and pseudo-total (aqua regia) soil concentrations of Cd, Pb, Cu and Zn (Eq. 1) and the coefficients β_0 - β_3 in Table 4 are also given in Table 8 for a soil with an assumed clay content of 5%.

<Table 8>

Results show that the critical total metal concentrations are close to the reactive metal concentrations in organic layers. In mineral layers the ratio between reactive and total metal concentrations is much lower for Cu and Zn than for Cd and Pb. When using a clay content of 25%, values are approximately 20% to 50% higher depending on the metal considered.

In comparing the results with present metal concentrations, one has to be aware that the critical concentrations are related to added metal. The values in Table 8 should thus be added to a natural background concentration before comparing them with present concentrations. Furthermore, there are indications that toxicity risks in the field situation are lower, thus leading to higher critical limits (see discussion).

Normalisation of critical limits to organic matter content

The relationships derived above suggest that the critical reactive metal concentration increases with increasing soil organic matter. This has important consequences for forest soils because most forest soils, at least in Northern and Central Europe, are covered by an organic layer (mor) in which many deposited pollutants are efficiently retained. Since plant root systems and fungi are located in this layer, there is an immediate risk of biological disturbance. Reduced decomposition of organic matter may have consequences for the mineralization of nutrients in forest soils and ultimately for forest growth.

This is in line with observations on the sensitivity of soil organisms in the organic layer and the mineral soil of forests. To test the relationship of the critical limit with organic matter, it was compared with field observations on the sensitivity of soil organisms to Cd, Pb, Cu and Zn in the organic layer and the mineral soil of forests. The NOEC data for micro-organisms exposed to metals in both organic layers and mineral soil compiled by Bååth (1989) were evaluated with a log-logistic fit to calculate the critical limits. Results refer to effects on enzyme synthesis and activity, litter decomposition and soil respiration. Results for Cd, Pb, Cu and Zn are presented in Table 9. Apart from the HC₅, results are also included for HC₂₀ and HC₅₀ to show the impact of organic matter content on these percentiles.

<Table 9>

The results show that the HC₅ values for the organic layer are 4 times as high for Pb compared to the mineral soil in case of the HC₅. This is comparable to results from

Sweden, reporting a critical value of 34 mg.kg⁻¹ in the mineral soil and a range of 50-144 mg.kg⁻¹ for the organic layer (Bringmark, pers. comm.). The HC₂₀ and HC₅₀ is approximately 2 and 1.5 times as high. For Cd, however, the HC₅ is comparable for the organic layer and mineral soil but the HC₂₀ and HC₅₀ are approximately 1.5 and 4 times as high for the organic soil. For Cu and Zn, the results for the organic layer are consistently a factor 2-4 higher than for the mineral soil. Focusing on the HC₅, the results indicate comparable values for Cd in both organic layer and mineral soil, while for Pb, Cu and Zn the values are 3-5 times higher for the organic layer than for the mineral soil. Results in Table 8 for 80% OM (representative for an organic layer) and 5% OM (representative for a mineral layer) at pH 4 (typical for forest soils) show that the calculated values suggest ratios near 5-7 for Pb, Cu and Zn and even near 10 for Cd. The similar trends for the critical limit trends with the results of Bååth are a reasonable verification of the derived critical limit functions except for Cd. It should be noted that many of the effect concentrations given in Bååth (1989) are from field pollution gradients containing mixtures of metals so it is not really possible to ascribe observed toxic effects to a single metal. These mixture effects could partly explain why the results for Cd are not comparable with those in Table 8.

3.2 Critical limits for free and total dissolved metal concentrations in soil solution

Critical limits for free metal ion concentrations

Figure 4 shows the Cd, Pb, Cu and Zn toxicity dataset expressed as $\log [M]_{\text{free,toxic}}$, plotted against pH. The regression slope is negative; $\log [M]_{\text{free,toxic}}$ decreases with

increasing pH. Results of the coefficients in the critical limit function (Eq. 12) are given in Table 10.

<Table 10>

Lofts et al. (2004) presented critical limits based on a somewhat different set of toxicity data than that used here, which has been harmonised with the data used in the EU Risk Assessment process. The previous derived critical limit functions are shown together with the critical limit functions derived in this article in Table 10 and Figure 4 for comparison. For Cu, Zn and Pb the new limit function gives higher critical free ion concentrations. Particularly for Pb the difference is appreciable, with the new function giving limits almost one order of magnitude (factor 10) higher at pH 3, dropping to half an order of magnitude (factor 3) at pH 8.

The new function for Cu gives limits between about 0.3 to 0.6 orders of magnitude (factor 2-4) higher, and that for Zn gives limits up to 0.3 orders (factor 2) higher. The new limit function for Cd intersects the old one at about pH 6, giving a limit 0.4 orders of magnitude lower (factor 2.5) at pH 3 and 0.2 orders (factor 1.6) higher at pH 8. The large difference in functions seen for Pb is largely due to the removal of several sensitive endpoints relating to plant effects in tropical soils; data on such non-European soils were explicitly rejected for use under the EU Risk Assessment procedures.

Critical limits for total dissolved metal concentrations

Critical total metal concentrations in soil solution for Cd, Pb, Cu and Zn as a function of pH and DOC, based on calculations with the WHAM6 (W6-MTC) model, are presented in Figure 5. Results show that total metal concentrations increase specifically below pH 5 when DOC concentrations are below 20 mg.l⁻¹. For Cu, this is even the case below pH 4. At high DOC concentrations, such as in forest organic layers, the increase is generally more regular from pH 6 onwards, except for Cd, where a decrease is predicted between pH 6 and 5.

The variations in the total concentrations arise from the interplay between several factors, as follows: (i) the critical free metal ion concentration decreases with pH and this will tend to make the total critical concentration decrease with pH, (ii) the complexation of the metal with DOC and with inorganic ligands, notably carbonate species and OH⁻, increases with pH, thereby tending to increase the total concentration, (iii) calcium ions compete with the toxic metals for binding by DOC; this is most significant for the weaker-binding metals (Zn, Cd) at higher pH, i.e. where the Ca concentration is increasing and (iv) Al and Fe(III) species compete with the toxic metals for binding. The calculations assume that free concentrations of Al species are lower in organic soils than in mineral soils (Tipping 2005), and so there is stronger binding of metal by DOC (less competition), and therefore the total dissolved metal concentrations are higher, in the organic horizon of the forest soil. The combination of these effects generates the complex pH dependences shown in Figure 5.

4 Derived critical limits for mercury concentrations in soil and soil solution

Unlike Cd and Pb, the cycling of Hg in soils is controlled almost entirely by its extremely strong association with the thiols of natural organic matter (Skylberg et al. 2003), also in soil solution where the presence of dissolved humic substances leaves virtually no free ions. The exposure of biota to Hg is thus mainly controlled by the competition between biotic and other organic ligands, and the degree of contamination of all types of natural organic matter is determined by the supply of organic matter relative to the supply of Hg at a given site (Meili 1991, 1997). Therefore, unlike the other metals, the critical limit for Hg in soils can best be set for the organically bound Hg content rather than for the free Hg ion concentration or total dissolved Hg concentration. The latter concentrations can however be derived from critical limits for mercury contents in organic soil layers, as illustrated below.

Critical limits for mercury contents in organic soil layers

With respect to Hg, critical soil limits presented in this study refer specifically to effects on soil micro-organisms and invertebrates in the humus layer of forests, which are considered as critical receptor systems to Hg pollution (Meili et al. 2003b). Recent field studies show some observational and experimental indications of a reduced respiration in forest soils at Hg concentrations close to those encountered in rural areas of south Sweden (Bringmark and Bringmark 2001a, b). A tentative critical limit is that the mean Hg concentration in the organic top layer (O-horizon) of podzolic forest soils should not exceed the present mean level in the mentioned

regions to avoid further increase. Since mercury concentrations in biologically active soils and sediments are recommended to be normalised to organic matter, OM) for the reasons mentioned above, this yields a critical limit of $0.5 \text{ mg} \cdot (\text{kg OM})^{-1}$ in these highly organic soils (Meili et al. 2003b and references therein).

It should be stressed that this result applies to the biologically active layers of forest soils (tentatively organic matter content $>10\%$), in which organic matter dominates the Hg cycling (transport, dilution, and toxicity). Conceptually the Hg content of total organic matter is also related (although not equal) to the Hg content in living organic matter (Meili 1997), and thus to the toxicity of soil Hg. In mineral soils where the organic matter content is generally lower than 10%, other matrices are likely to participate in controlling the cycling of Hg, and in particular the soil content of iron and aluminium (oxyhydroxides, reactive) and clay may need to be taken into account to set the critical limit. Mineral soil compartments are however considered less critical than the organic layer.

Critical limits for free mercury concentrations in soil solution

The concentration of free (bioreactive) Hg in soil solution can be calculated by dividing the critical concentration of “organically sorbed” Hg by the apparent distribution coefficient for Hg on (dissolved) organic matter. Field and laboratory studies, using biota to determine the concentration of bioreactive species and involving different types of soil and lake organic matter, suggest that the value for this distribution coefficient is at least $10^6 \text{ l} \cdot \text{kg}^{-1}$. The value seems to be fairly independent of the soil or water quality at the source from which the organic matter originates (Meili 1997). Since virtually all dissolved Hg is bound to and mobilized

together with dissolved organic matter (DOM), the concentration of “free” Hg is also fairly independent of the concentration of DOM in the soil solution. Note that this distribution coefficient is operationally defined for ecotoxicological purposes by using biota to determine sum of bioavailable “free” Hg forms (which may even include organic forms), and that chemical Hg binding considered here may involve any constituent associated with natural organic matter (thiols, iron, etc). Given the limit above for Hg bound to organic substances ($0.5 \text{ mg kg}^{-1} \text{ OM}$), the critical “free” (bioreactive) Hg concentration in soil solution is below 1 ng.l^{-1} , possibly even far below that.

Critical limits for total mercury concentrations in soil solution

Critical total mercury concentrations in soil solution can be calculated by using a transfer function for Hg from soil to soil solution, while assuming a similar critical Hg/org ratio in the solid phase and in the liquid phase, at least in oxic environments where binding to sulphides is negligible. The following reasoning supports this (see also Meili 1991; 1997; De Vries et al. 2003; Meili et al. 2003a; Åkerblom et al. 2004):

- As with soil solids, the Hg concentration in solution can (should) be expressed on an organic matter basis, since virtually all dissolved Hg is bound to dissolved organic matter (see above). Given a typical concentration range of $10\text{-}60 \text{ mg.l}^{-1}$ for dissolved organic carbon (DOC, \approx half of DOM) in organic forest top soils, the distribution coefficient suggests that at least 95-99% of all Hg is bound by organic substances if considering dissolved species alone, and far more if considering the whole top soil ($>99.999\%$).

- If the binding properties of solid and dissolved organic matter are similar, we would expect a similar Hg/org ratio in soils and stream waters, which is indeed supported by field data (Meili 1991, 1997).
- Organic carbon concentrations in boreal stream runoff typically peaks at DOC concentrations of 15-20 mg.l⁻¹. This is well within the range found in soil solutions, which supports the assumption that there are no fundamental differences between the two waters.

The critical leaching of Hg from the humus layer is related to the mobility and Hg content of dissolved organic matter because of the strong affinity of Hg for living and dead organic matter and the resulting lack of competition by inorganic ligands in this layer (e.g. Meili 1991, 1997). Therefore, Hg/OM ratios are a useful tool for calculating critical limits and loads and associated transfer functions (Meili et al. 2003b). This is the basis of the transfer function to derive total Hg concentrations in percolating (top) soil solution as follows:

$$[\text{Hg}]_{\text{ss}(\text{crit})} = [\text{Hg}]_{[\text{OM}](\text{crit})} \cdot f_f \cdot [\text{DOM}]_{\text{ss}} \quad (20)$$

where

$[\text{Hg}]_{\text{ss}(\text{crit})}$ = Critical dissolved Hg concentration in soil solution (mg.m⁻³).

$[\text{Hg}]_{[\text{OM}](\text{crit})}$ = Critical limit for Hg concentration in soil organic matter [OM], or the Hg/OM ratio in organic (top)soils (0.5 mg.kg⁻¹ OM).

f_f = Fractionation ratio, describing the Hg contamination of organic matter in solution (DOM) relative to that in solids (OM) (-).

$[\text{DOM}]_{\text{ss}}$ = Dissolved organic matter concentration in soil solution (kg.m⁻³).

The scale-invariant fractionation or transfer factor f_f describes the Hg partitioning between organic matter in solids and organic matter in solution and is defined as the ratio between the Hg content of DOM and that of OM (Meili et al. 2003a; Meili et al. 2003b). Preliminary studies in Sweden suggest that both are of similar magnitude and that 1 may be used as a default value for f_f until deviations from unity prove to be significant (Åkerblom et al. 2004).

Based on the Hg limit of 0.5 mg.kg^{-1} OM and a typical DOM concentration of 70 mg.l^{-1} (or 0.07 kg.m^{-3} ; $\text{DOC} = 35 \text{ mg.l}^{-1}$) in biologically active top soils, the critical steady state concentration of total Hg in soil solution is 0.035 mg.m^{-3} or 35 ng.l^{-1} (see Eq. 21). This concentration is consistent with that derived by a different approach at the watershed scale (Meili et al. 2003b) and is similar to high-end values presently observed in soil solutions and surface freshwaters (Meili 1997; Meili et al. 2003a; Åkerblom et al. 2004). Note that this ecosystem limit for soil water is much lower than the drinking water limit for Hg, but higher than that for surface freshwaters where Hg limits for fish consumption usually are exceeded at surface water concentrations of $1\text{-}5 \text{ ng.l}^{-1}$.

5 Discussion and conclusions

Comparison of derived critical limits with limits for other effects

Critical limits for phytotoxic effects on plants based on NOEC soil solution data: Critical limits for metals in soil solution can also be derived on the basis of NOEC soil solution

data for phytotoxic effects. Results of a literature review by Lijzen et al. (2002), including data on phytotoxic effects of the metals Cd, Pb, Cu, Zn and Hg on plants based on laboratory studies with solution culture experiments, are summarized in Table 11. A comparison of those HC₅ values with the range in critical dissolved concentrations derived for soil solution in the complete pH (3.5-8) and DOC range (10-35 mg.l⁻¹), as presented in Figure 5) shows that critical Cd concentrations of:

- Cd are comparable in the low pH range (below 4) and even up to a pH of 7 when DOC values are high (35 mg.l⁻¹).
- Pb are comparable in a relatively high pH range (above 5) for low DOC values (up to 20 mg.l⁻¹)
- Cu are comparable in a large pH range (above 4) but only for low DOC values
- Zn due to phytotoxic effects are slightly lower than those due to ecotoxicological effects in any pH and DOC range, but most comparable in the high pH range (above 5.5) but only at low DOC values.

In Table 11, the median and 95% range in HC₅ values in view of ecotoxicological effects are given for a pH range between 5 and 7, assuming that the phytotoxicity experiments are mainly carried in this pH range. A comparison of these ranges shows that ranges are comparable. The median HC₅ values in view of ecotoxicological effects of Cd and Zn are slightly lower and higher, respectively, compared to phytotoxic effects (Table 11). These results at least indicate that the modelled critical total dissolved metal concentrations as shown in Figure 5 are in agreement with the above mentioned literature study. For Hg the HC₅ for phytotoxic effects is higher than the value derived from an Hg limit of 0.5 mg.kg⁻¹ OM critical soil. The values

only overlap at the lower end of the HC₅ concentrations derived for phytotoxic impacts (Table 11).

<Table 11>

Critical limits for ecotoxicological effects on aquatic organisms based on NOEC surface water data:

For aquatic ecosystems, critical limits for total dissolved metal (mg.m⁻³) have been suggested on the basis of chronic toxicity data for a variety of organisms, including the major taxonomic groups, i.e. algae(unicellular and multicellular), crustacea, macrophyta, molluscs and fish. In the effects assessment chronic NOEC or L(E)C10 values are used rather than acute LC50 or EC50 values to derive PNEC values. As with soils, the 95% protection level calculated with 50% confidence is regarded as the MPC (MPC =HC₅).

A summary of effect-based critical limits, based on various EU Risk Assessment Reports for Cd, Pb, Cu, Zn and Hg, is presented in Table 12. Values of the HC₅ are based on the 5-percentile cut-off value of various chronic toxicity data calculated with the methods described in Section 2.1 (Aldenberg and Slob 1993; Aldenberg and Jaworska 2000). For all metals, an assessment factor was used, being a safety factor related to aspects such as the: (i) endpoints covered, (ii) diversity and representativity of the taxonomic groups covered and the (iii) statistical uncertainties around the 5th percentile estimate and (iv) validation of the HC₅ with of multi-species mesocosm or field data. The necessity of such a factor, varying from 1-4 for the various metals, can be disputed. The limits for Cd, Zn, Cu and Pb are still under discussion by the EU.

<Table 12>

A comparison of the critical dissolved concentrations derived for soil solution at high pH (Figure 5) and surface water (Table 12) shows the critical concentration in surface waters is:

- generally much lower for Cd and Zn, even when the assessment factor of 2 is neglected. Values are in the same order of magnitude at low DOC levels.
- comparable for Pb when the assessment factor of 3 is neglected, but lower when included (a value near $1.6 \text{ mg}\cdot\text{m}^{-3}$ is derived for soil solution at a pH near 5.5 and a DOC concentration of $10 \text{ mg}\cdot\text{l}^{-1}$).
- comparable for Cu, for which an assessment factor of 1 is used in the official risk assessment report. Both the values of $8.2 \text{ mg}\cdot\text{m}^{-3}$ (worst case physicochemical situation) and $30.3 \text{ }\mu\text{g mg}\cdot\text{m}^{-3}$ (typical European physicochemical situation) are in the range encountered in soil solution between pH 4 and 8 and a DOC concentration of 10 to $35 \text{ mg}\cdot\text{l}^{-1}$.
- almost equal for Hg when the assessment factor of 4 is included. A value of $0.036 \text{ mg}\cdot\text{m}^{-3}$ is also similar to high-end values presently observed in soil solutions and surface freshwaters (Meili 1997; Meili et al. 2003a; Åkerblom et al. 2004).

The differences observed between soil and surface water critical limits can be questioned. Analysis of aquatic ecotoxicological data by Lofts et al. (unpublished) suggested overlap between aquatic and terrestrial toxic endpoint concentrations at a given pH. Hence one might think of using common critical limits for both soils and freshwaters, by using the critical limit functions derived before for toxic effects on

the soil ecosystem. However, although there is no theoretical reason why the sensitivities of soil and water organisms to metals should not be similar (assuming that uptake of the free ion from the aqueous phase is the significant mechanism leading to toxicity) this approach can not yet be advocated because the aquatic toxicity data for covered a more restricted pH range than for the terrestrial toxicity data. More research is needed to study the possibility to use similar limits for waters and soil solution.

Overall comparison: In Table 13, an overall comparison of median critical limits is given, including WHO data for drinking water limits. The comparison shows that the limits for ecotoxicological and phytotoxic effects are generally comparable with the HC5 for surface waters being most stringent for Cd and Zn. The drinking water limit is comparable to these limits for Cd, but is 5 times to even 100 times higher in the case of Pb and Hg, respectively (Table 13).

Uncertainties in the calculation of critical limits from NOEC data

Assumptions in extrapolating single-species toxicity data to ecosystem effects: The function of risk assessment is the overall protection of the environment. Certain assumptions are made to allow extrapolation from single-species toxicity data to ecosystem effects, such as: (i) ecosystem sensitivity depends on the most sensitive species and (ii) protecting ecosystem structure protects community function. It is thus assumed that protection of the most sensitive species protects ecosystem structure and function. The main motivation for introducing “Species Sensitivity Distributions” (SSDs) into the MPC (critical limit) derivation is that it makes use of all available data when deriving a critical limit. The main underlying assumption of the statistical

extrapolation method is that the species tested in the laboratory are a random sample of the actual “Species Sensitivity Distributions” (OECD 1992).

In general, critical limits derived from extrapolations of single-species toxicological NOEC data to a Maximum Permissible Concentration include several uncertainties due to (e.g. Forbes and Forbes 1993); (See also De Vries and Bakker 1998):

- Lack of representativity of the selected test species, incomparability of different endpoints.
- Species sensitivities distribution not following a theoretical distribution function.
- Occurrence of intra- and inter-species variations (biological variance).
- Laboratory data to field impact extrapolation, such as differences in metal availability in the laboratory and the field situation and in the exposure time.
- Occurrence of intra- and inter-laboratory variation of toxicity data.
- Additive, synergistic and antagonistic effects arising from the presence of other substances.

In deriving critical limits in this study, we tried to overcome several of those uncertainties. First of all, the MPC derivation was based on a statistical extrapolation of approximately 50 to 90 NOECs from different species covering major taxonomic groups. Considering this amount, the data of the most sensitive end-point might be seen as representative. Secondly, we did not assume an a priori theoretical distribution function. Thirdly, we quantified the intrinsic variability in the sensitivity of species or processes to the toxicant in terms of the scatter of points around the regression described in Eq. (14). Finally, the differences between metal availability in the laboratory and field situation were accounted for in the transfer functions used.

Regarding exposure time, the NOECs from chronic/long term studies were mainly based on full life time or multi-generation test studies. The other error-derived sources of scatter in the data, such as intra- and inter-laboratory variation of toxicity data, cannot be assessed quantitatively.

Due to the various above mentioned uncertainties, arbitrary assessment (or safety) factors have been suggested to extrapolate from single-species laboratory data to a multi-species ecosystem, related to aspects such as:

- The overall quality of the database and the endpoints covered, e.g., if all the data are generated from “true” chronic studies covering all sensitive life stages.
- The diversity and representativity of the taxonomic groups covered by the database, and the extent to which differences in the life forms, feeding strategies and trophic levels of the organisms are represented.
- Statistical uncertainties around the 5th percentile estimate, reflected in e.g. the goodness of fit or the size of confidence interval around the 5th percentile, and consideration of different levels of confidence.

The size of the assessment factor depends on the confidence with which a critical limit can be derived from the available data. This confidence increases if data are available on the toxicity to organisms at a number of trophic levels, taxonomic groups and with lifestyles representing various feeding strategies. Thus lower assessment factors can be used with larger and more relevant long-term data sets.

In this study no use has been made of assessment factors, since sufficient NOEC data were available for major taxonomic groups to avoid the derivation of unrealistically low critical limits. This approach is supported by the Scientific

Committee on Toxicity, Ecotoxicity and the Environment (CSTEE) who evaluated the risk assessment of cadmium in the framework of Council Regulation (EEC) 793/93 on the evaluation and control of risks of existing substances (CSTEE 2004).

Differences in metal toxicity of laboratory spiked soil and field-contaminated soils: Comparison of field and laboratory NOEC soil data in the EU Risk Assessment Reports for Cu, Pb and Zn showed consistently higher result for field data. Consequently, laboratory to field factors were used that increase the critical limit by a factor of 2 for Cu, 3 for Zn and 4 for Pb. An important cause for this difference is the higher availability of added metals in laboratory spiked soil compared to field-contaminated soils due to: (i) metal-induced acidification due to hydrolysis of the metal in solution and displacement of protons from the solid phase, (ii) higher ionic strength of the soil solution, reducing the sorption of cationic metals in soil and (iii) the slow ageing reactions which metals undergo in the field (McLaughlin et al. 2004). The increased solubility of metals in the laboratory compared is clearly demonstrated by Smolders et al. (2004), who found that Zn concentrations in soil pore water were several times higher in Zn salt-spiked samples compared to equivalent field-contaminated samples, at the same total Zn concentration. Furthermore, part of the toxicity response is likely to be from salt toxicity due to osmotic stress induced by the counter ion (Cl, NO₃, SO₄), especially at high concentrations (Stevens et al. 2003). The possible decrease in pH during the experiment is not accounted for in our calculation of the dissolved metal concentration and furthermore, the transfer function used is not derived at high ionic strengths. Only the ageing factor is accounted for in our approach, by assuming that all added metal is in the reactive form, which is likely to be an overestimate. These aspects imply that the derived critical limit functions for

soil and soil solution may lead to an underestimate of the critical metal concentrations.

Lack of including the competition of base cations: In the approach used, the competition of ‘protecting’ cations such as Ca^{2+} and Mg^{2+} in binding the metal to the receptor was neglected by assuming that these concentration co-vary with pH. This causes an uncertainty in the critical limits derived. Competition from other cations is formally considered in the Biotic Ligand Model (BLM), which has been used to explain variability in acute toxic endpoints for several freshwater species, as a function of water chemistry (Santore et al. 2001; De Schamphelaere and Janssen 2002). At present a BLM for terrestrial systems (TBLM) is under development (Thakali et al. 2005).

Uncertainties in transfer functions predicting free metal ion concentrations: The transfer functions that have been used in deriving pH dependent critical limits for the FMI in soil solution need improvements since:

- The dataset from which these transfer functions were derived is not consistent. Metal contents in soil were derived using different extraction techniques.
- The coefficient m for the metal content in the relation for Cd is <1 which means that when the equation is written according to a Freundlich equation, $n > 1$. This means that adsorption increases with an increasing concentration.
- Critical concentrations of soil metal in the ecotoxicological experiments were higher than those used in deriving the transfer functions. This holds specifically for Cd, in which in the maximum metal content in the transfer function dataset (44 mg.kg^{-1}) is much lower than in the ecotoxicological data set (2989 mg.kg^{-1}).

For Pb, the difference is much less (max Pb is 14860 mg.kg⁻¹ while ecotox is 16573 mg.kg⁻¹).

Another drawback is that the transfer function is based on a direct approach in which the metal concentration in soil solution is the explained variable and the soil metal content is the explaining variable, which is often referred to as c-Q relations. In this case Q stands for the reactive metal content (ctM_{re}) and c for the dissolved (free) metal concentration in soil solution ([M]_{free} or [M]_{ss}). Results of regression coefficients thus obtained deviate from those in which the metal content in the solid phase is the explained variable and the solution concentration is the explaining variable (together with soil properties), which is often referred to as Q-c relations. Another approach is to assume Freundlich adsorption, derive the n value by optimization and relate Freundlich adsorption constants (K_f) to soil properties (further referred to as the K_f approach). With the K_f approach calculations can be done in both directions. Furthermore the parameters derived using the K_f approach are more stable with respect to the data used in the derivation (Groenenberg et al. (2003)). Use of this approach is thus favourable in deriving critical limit functions.

Conclusions

Despite the various uncertainties involved in the derivation, the following major conclusions that can be derived from this overview paper:

1. Critical reactive and total metal concentrations in soils should be considered as a function of soil properties, like pH organic matter and clay content. Since these soil properties vary widely between soil types, the range in critical metal contents can be large. Comparison with present metal concentrations

in the rural area shows that critical metal concentrations might be exceeded at low pH and low organic matter and clay content (acid sandy soils) due to the high metal bioavailability.

2. The derivation of a pH depending critical limit function for FMI activity is an appropriate tool for describing the effects of Cd, Pb, Cu and Zn. It incorporates the effect of an increase of concentrations of competing cations in the soil solution, specifically of protons, as an increase in the concentration of the FMI required to result in a toxic effect. The pH dependence, expressed as the slope between pH and the logarithmic free metal ion concentration, is larger for Pb and Cu (slope near -1) than for Cd and Zn (slope near -0.3). The dependence of critical total metal concentrations in soil solution on pH is more complex, as since the relationship is affected by DOC binding and the interaction with competing ions like Ca, Al and Fe(III) species. Chemical speciation models, such as WHAM, are useful to derive such relationships.
3. The FMI approach is not applicable for Hg, because nearly all Hg is bound to soil organic matter. Critical concentrations of Hg in soil solution related to effects on microbiota and invertebrates living in the humus layers of forest soils can be derived based on a limit set for the Hg content of solid organic matter and assuming a similar Hg/OM ratio in the solid phase and in the liquid phase.
4. A comparison of the critical dissolved concentrations derived for soil solution at high pH and surface water shows that critical concentrations in surface waters are generally lower for Cd and Zn but comparable for Pb, Cu and Hg.

In summary, this review shows that critical metal concentrations in soil and soil solution related to ecotoxicological effects should be derived as a function of soil and soil solution chemistry. Most important are pH and organic matter concentrations in soil and soil solution. Future work should focus on diminishing uncertainties in the derived critical metal concentration functions by: (i) further assessment of relevant NOEC data combined with soil properties, (ii) improvement and validation of transfer functions, calibrated over a range of soil metal concentrations which covers the range found in the toxic endpoint NOEC data and (iii) including the metal that is present before the start of the experiment to allow direct comparison of the critical limits thus derived with present concentrations. Finally, most important would be to assess direct relationships between measured (free) metal ion concentrations and ecotoxicological effects.

Summary

Risk assessment for metals in terrestrial ecosystems, including assessments of critical loads, require appropriate critical limits for metal concentrations in soil and soil solution. This paper presents an overview of methodologies used to derive critical (i) reactive and total metal concentrations in soils and (ii) free metal ion and total metal concentrations in soil solution for Cd, Pb, Cu, Zn and Hg, taking into account the effect of soil properties in view of ecotoxicological effects. Most emphasis is given to the derivation of critical free and total metal concentrations in soil solution, using available NOEC soil data and transfer functions relating solid phase and dissolved metal concentrations. This approach is based on the assumption that impacts on test organisms (plants, micro-organisms and soil invertebrates) are mainly related to the soil solution concentration (activity) and not to the soil solid phase content. Critical

Cd, Pb, Cu, Zn and Hg concentrations in soil solution vary with pH and DOC level. The results obtained are generally comparable to those derived for surface waters based on impacts to aquatic organisms. Critical soil metal concentrations, related to the derived soil solution limits, can be described as a function of pH and organic matter and clay content, and varying about one order of magnitude between different soil types.

Key words: soil properties, critical limits, metals, soil, ecotoxicological effects, free metal ion, complexation

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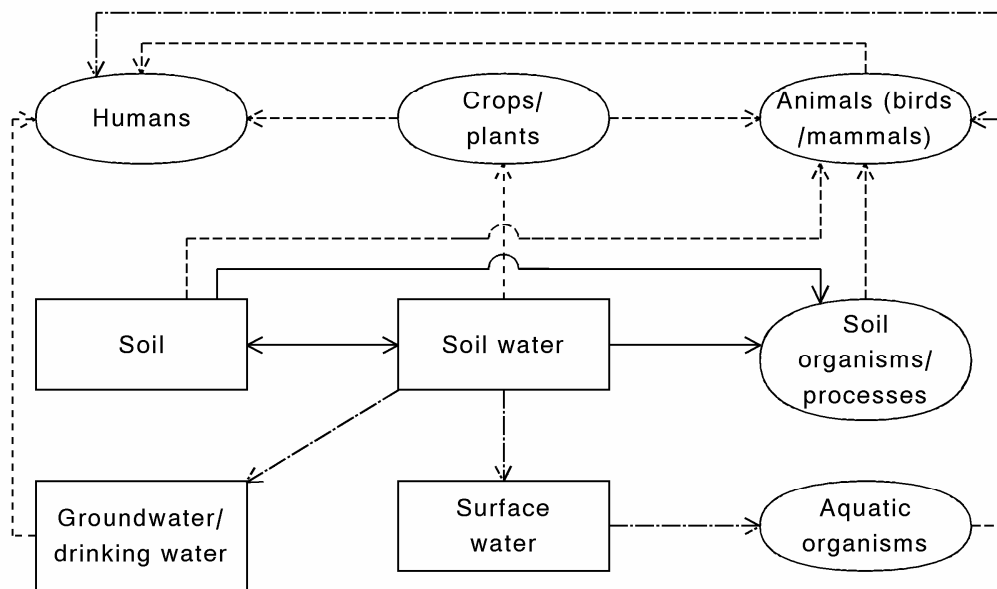
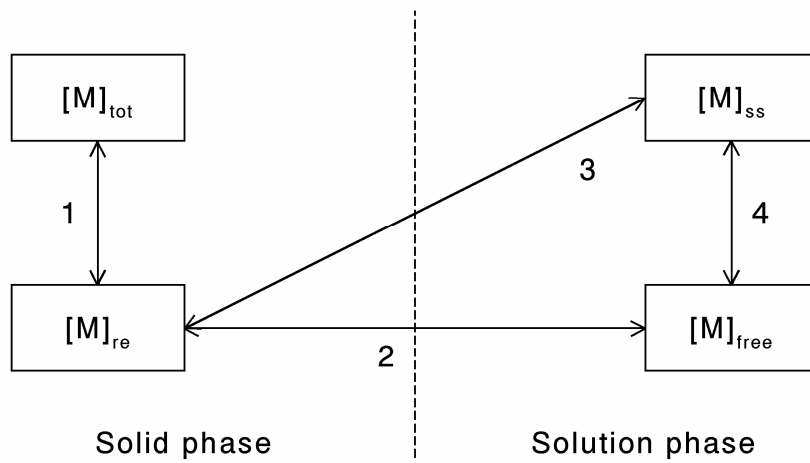


Figure 144.tce

Fig. 1 Overview of the fluxes and impact pathways of metals from the soil to other compartments in terrestrial and aquatic ecosystems. Boxes are key "pools" and ovals are key "receptors". Solid arrows are related to fluxes/impacts within the soil ecosystem, discussed in this paper, whereas the dotted arrows refer to impacts on the health, productivity or food quality of animals and humans due to accumulation in food chains, discussed in the subsequent paper (De Vries et al. 2006). Even though plants are also included in ecotoxicological tests for soils, dotted arrows are used from soil solution to plants/crops, referring to crop uptake and subsequent impacts on food quality. The hatched arrows are not considered in both papers, which focus on terrestrial ecosystems, and impacts on aquatic organisms in surface water are only discussed in this paper to compare results with those obtained for soil solution.



- 1 Immobile metal correction
- 2, 3 Solid solution partitioning
- 4 Speciation in solution



Fig. 2 Overview of relations between metal concentrations in soil solid phase and soil solution

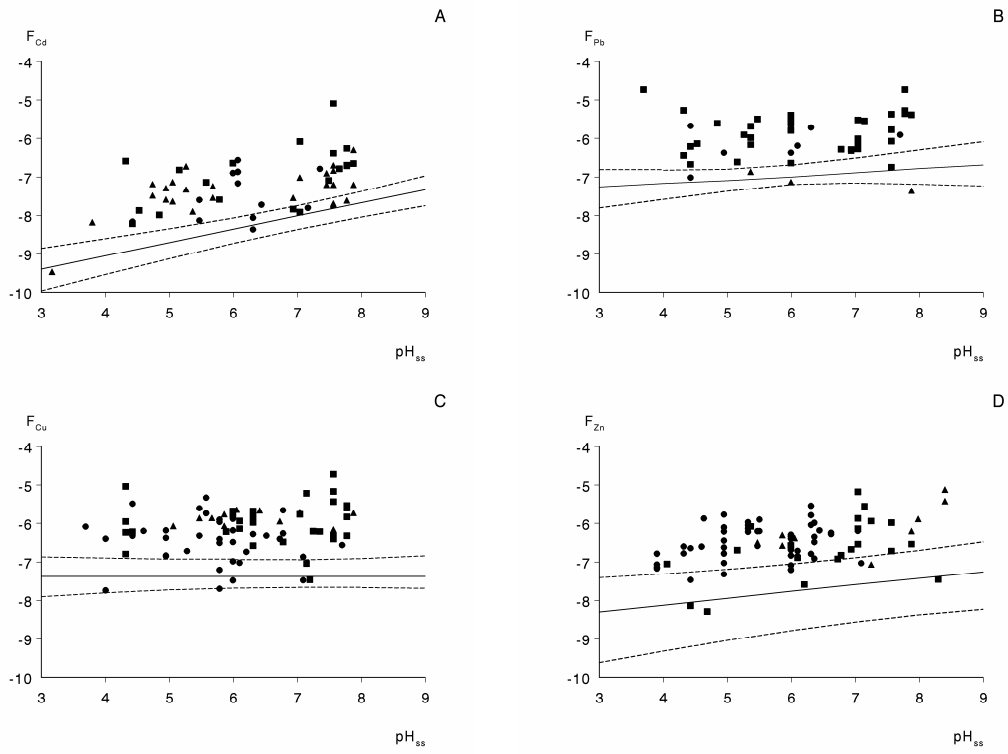


Fig. 3 Plots of F against pH_{ss} for cadmium (A), lead (B), copper (C) and zinc (D). Triangles: Toxicity endpoints for plants; circles: toxicity endpoints for invertebrates; squares: toxicity endpoints for microbial processes. Solid line: median critical limit function (50% confidence); dotted lines: critical limit functions with 90% confidence. (5% and 95%)

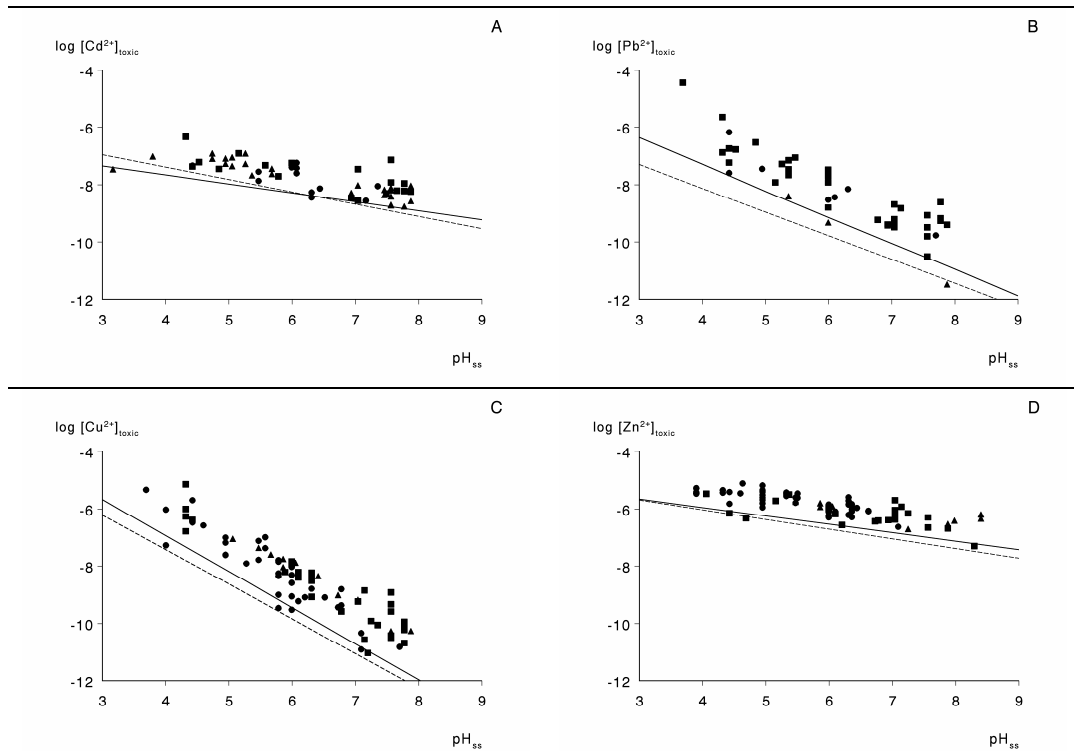


Fig. 4 Toxicity data and associated ecotoxicological critical limit functions for cadmium (A), lead (B), copper (C) and zinc (D). Data and limits are expressed as the logarithmic free metal concentration in soil solution in $\text{mg}\cdot\text{m}^{-3}$. Triangles: Toxicity endpoints for plants; circles: toxicity endpoints for invertebrates; squares: toxicity endpoints for microbial processes. Solid line: median critical limit function (50% confidence); dash-dot line: critical limit functions previously calculated by Lofts et al. (2004).

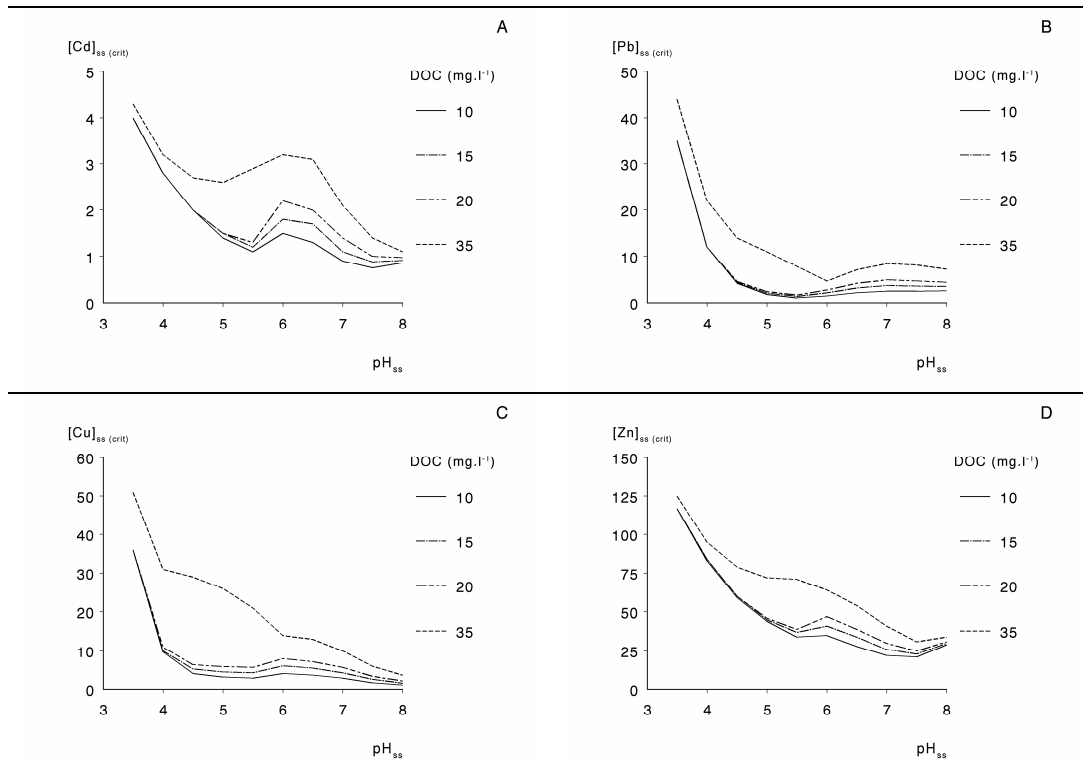


Fig. 5 Estimated total critical concentrations of cadmium (A), lead (B), copper (C) and zinc (D) in soil solution in mg.m^{-3} at DOC concentrations of 10, 15, 20 and 35 mg.l^{-1} , considered representative for arable land, grassland, forest mineral topsoil and forest organic layer.

Table 1 Receptors of concern in three main types of terrestrial ecosystems.

Receptors of concern	Type of ecosystem		
	Arable land	Grassland	Non-agricultural land
Ecosystem			
- Soil micro-organisms	+	+	+
- Soil invertebrates	+	+	+
- Agricultural plants	+	+	-
- Wild plants	-	-	+
<i>Human health/ animal health</i>			
Plants			
- Food crops (human health)	+	-	-
- Fodder crops (animal health)	-	+	-
Ground water ^a (human health)	+	+	+
Animals			
- Cattle (human and animal health)	-	+	+
- Birds/Mammals (animal health)	+	+	+

^a This refers specifically to ground water used as drinking water

Table 2 Critical limits for Cd and Pb for ecotoxicological effects in soils (mg/ kg soil), calculated by (a) assuming a log-logistic distribution of toxic endpoints and (b) assuming no statistical distribution of endpoints and calculating critical limits by bootstrapping.

Metal	Critical limits from a log-logistic distribution		Critical limits from bootstrapping	
	50% ile confidence	95% ile confidence	50% ile confidence	95% ile confidence
Cd	4.5	2.8	3.8	2.9
Pb	63	48	75	21

Table 3 Values for the coefficients β_0 - β_3 in the relationship between total (aqua regia, being pseudo-total) and reactive (0.43N HNO₃) soil concentrations of Cd, Pb, Cu and Zn (Eq. 1) and the statistical measures R²_{adj} and se(Y) using a Dutch dataset (Römkens et al. 2004). Relationships hold with ctM_{tot} and ctM_{re} in mg.kg⁻¹.

Metal	β_0	β_1 ctM _{re}	β_2 OM	β_3 clay	R ² _{adj}	Se(Y) ^a
Cd	0.028	0.877	0.009	0.081	0.96	0.10
Pb	0.323	0.810	0.035	0.136	0.92	0.13
Cu	0.318	0.761	0.044	0.191	0.94	0.10
Zn	0.614	0.753	-0.107	0.275	0.96	0.12

^a The standard error of the y-estimate on a logarithmic basis

Table 4 Values for the regression coefficients a-d for the FMI – reactive metal content relationship (Eq. 5) for Cd, Pb, Cu and Zn and the statistical measures R² and se(Y) based on results of studies carried out in Canada, the Netherlands and the UK Values in brackets are the standard errors for the coefficients.

Metal	a	b pH _{ss}	c OM	d log ctM _{re}	R ²	se(Y)
Cd	-0.14 (0.65)	-0.53 (0.031)	-0.60 (0.076)	0.60 (0.062)	0.62	0.53
Pb	4.33 (0.49)	-1.02 (0.032)	-0.69 (0.074)	1.05 (0.056)	0.85	0.60
Cu	4.99 (0.63)	-1.26 (0.035)	-0.63 (0.090)	0.93 (0.091)	0.90	0.61
Zn	0.55 (0.62)	-0.45 (0.027)	-0.61 (0.077)	0.57 (0.071)	0.62	0.46

Table 5 Results of linear regression analyses of the pH in soil solution against pH-H₂O and pH-KCl

Explaining variable	N	e	f	se (pH _{ss})	R ² _{adj}
pH-H ₂ O	1145	1.05	-0.28	0.45	0.84
pH-KCl	905	0.97	0.62	0.49	0.80
pH-CaCl ₂	413	0.88	1.32	0.74	0.49

All coefficients are significant at $p > 0.999$.

Table 6 Numbers of ecotoxicological datasets used for copper, zinc, cadmium and lead

Type of study	Cadmium	Lead	Copper	Zinc
Plants				
Studies	6	4	7	4
Species/Groups	7	5	6	5
Endpoints	26	5	11	9
Invertebrates				
Studies	7	6	29	15
Species/Groups	5	3	14 ^b	7 ^c
Endpoints	13	8	43	55
Microbial processes^a				
Studies	9	14	14	10
Processes	4	10	7	7
Endpoints	18	35	33	21
Total				
Studies	22	24	50	29
Species/Processes	16	18	27	19
Endpoints	57	48	87	85

^a Respiration and substrate-induced respiration considered as one process, and all nitrogen transformation processes considered as one process.

^b Including two community studies on nematodes and one community study on micro-arthropods.

^c Including one community study on nematodes.

Table 7 Ranges of chemical parameters in toxicological test soils. Values in brackets are the medians of the parameters.

Metal	pH	OM (%)	ct M _{soil,toxic} (mg/kg soil)
Cd	3.17–7.88 (6.07)	1.2–80 (4.2)	1.8–2989 (29)
Pb	3.69–7.88 (5.99)	1.0–80 (6.2)	10–16573 (767)
Cu	3.69–7.88 (5.99)	0.2–80 (5.0)	3.2–3313 (120)
Zn	3.90–8.40 (5.99)	0.3–85 (5.0)	10–1621 (158)

Table 8 Calculated critical reactive metal contents in soil as a function of pH and organic matter content. Values in brackets are the critical total metal concentrations for a sandy soil with 5% clay.

Metal	Organic matter content (%)	Critical reactive metal content in soil (in mg.kg ⁻¹)			
		pH 4	pH 5	pH 6	pH 7
Cd	5	0.56 (0.74)	1.2 (1.4)	2.6 (2.8)	5.5 (5.5)
	80	9 (9)	19 (19)	41 (41)	88 (88)
Pb	5	30 (44)	39 (54)	50 (66)	64 (81)
	80	187 (212)	241 (260)	311 (319)	400 (400)
Cu	5	6.6 (13)	6.9 (13)	7.2 (14)	7.6 (14)
	80	43 (60)	45 (63)	48 (65)	50 (67)
Zn	5	3.7 (14)	5.1 (18)	7.0 (23)	9.6 (30)
	80	71 (99)	98 (127)	135 (161)	187 (206)

Table 9 Fitted parameter values for u and β according to Eq. (1) and resulting critical limits for total metal contents in organic layers and mineral soil, based on a compilation of NOEC data for micro-organisms by Bååth (1989).

Metal	Layer	N ¹	u	β	R ² _{adj}	Critical limit (mg.kg ⁻¹)		
						HC ₅	HC ₂₀	HC ₅₀
Cd	Organic layer	17	2.070	-0.8715	92	0.3	7.3	118
	Mineral soil	53	1.510	-0.6152	97	0.5	4.5	32
Pb	Organic layer	16	2.989	-0.2914	76	135	385	976
	Mineral soil	56	2.839	-0.4511	96	32	164	690
Cu	Organic layer	42	2.678	-0.4032	98	31	132	477
	Mineral soil	62	2.296	-0.5205	98	5.8	38	198
Zn	Organic layer	30	2.994	-0.4387	97	50	243	986
	Mineral soil	49	2.652	-0.4706	94	19	100	449

Table 10 Coefficients in the median critical limit functions (Eq. 12) for free metal ion concentrations.

Metal	α_{CRIT}		γ_{CRIT}	
	This study	Lofts et al (2004)	This study	Lofts et al (2004)
Cd	-0.32	-0.43	-6.34	-5.66
Pb	-0.91	-0.83	-3.80	-4.80
Cu	-1.23	-1.21	-2.05	-2.57
Zn	-0.31	-0.34	-4.63	-4.66

Table 11 HC₅ concentrations for dissolved Cd, Pb, Cu, Zn and Hg in solution experiments related to phytotoxic impacts on plants (Values in brackets are the 'lower limit' and 'upper limit' of the 95% confidence limit) as compared to ranges in HC₅ values derived from NOEC data and WHAM modelling.

Metal	Nr of data	HC ₅ concentration	
		phytotoxicity (mg.m ⁻³)	ecotoxicity (mg.m ⁻³)
Cd	19	2.6 (0.5-07)	1.6 (1.3-3.2)
Pb	11	1.4 (0.09-7.0)	2.2 (0.5-9.2)
Cu	12	4.0 (0.3-20)	5.2 (1.7-25)
Zn	6	15 (0.3-90)	37 (18-65)
Hg	11	0.08 (0.01-0.27)	0.01-0.04

Table 12 Recommended critical limits for dissolved Cd, Pb, Cu, Zn and Hg concentrations in surface waters (based on various EU risk assessment reports).

Metal	Data sources	HC ₅ concentration (mg.m ⁻³)	Assessment factor	Critical limit (mg.m ⁻³)
Cd ^a	168 single species studies 9 multi species studies	0.38	2	0.19
Pb ^b	19 freshwater NOECs/EC10s 11 saltwater NOECs/EC10s	5.0	3	1.6
Cu ^c	22 freshwater species specific NOECs/EC10s 4 multi species studies	8.2	1	8.2
Zn ^d	18 freshwater NOECs/EC10s	15.6	2	7.8
Hg ^e	30 freshwater and saltwater NOECs/EC10s	0.142	4	0.036

^a Values based on the EU Risk Assessment Report for Cd, Draft 2003 (Risk assessment Cadmium metal CAS-No. 7440-43-9, EINECS-No.: 231-152-8: 2003). For Cd, a relationship with water hardness has been reported in the Report. The influence of hardness on the toxicity of cadmium can be taken into account, using 3 hardness classes (with hardness H in mg CaCO₃.l⁻¹) according to 0.16 mg.m⁻³ if H <100, 0.30 mg.m⁻³ if 100 < H < 200 and 0.50 mg.m⁻³ if H > 200, when using no assessment factor.

^b Values based on “Environmental Risk Assessment Pb and Pb-compounds - Effects Assessment to the Aquatic Compartment. Draft report 2004”. Report Compiled by P. Van Sprang et al.

^c Values based on “Environmental Risk Assessment Cu, CuO, Cu₂O, CuSO₄ and Cu₂Cl(OH)₃. Effects Assessment to the Aquatic Compartment. Draft report 2005”. Report Compiled by P. Van Sprang et al. The value of 8.2 mg.m⁻³ is based on a worst case physicochemical situation. For a typical European physicochemical situation, a value of 30.3 mg.m⁻³ is calculated.

^d Values based on the EU Risk Assessment Report for Zn, Draft 2004 (Risk assessment Zinc metal CAS-No.: 7440-66-6, EINECS-No.: 231-175-3: 2004).

^e Value based on: Final Report of the Study: Identification of quality standards for priority substances in the field of water policy. Towards the Derivation of Quality Standards for Priority Substances in the Context of the Water Framework Directive (2003).

Table 13 Comparison of ranges in HC₅ values for Cd, Pb, Cu, Zn and Hg derived from NOEC soil data in this with HC₅ concentrations related to phytotoxic impacts on plants, impacts on aquatic organisms and drinking water limits.

Metal	HC ₅ concentration ecotoxicity (mg.m ⁻³)	HC ₅ concentration phytotoxicity (mg.m ⁻³)	HC ₅ concentration surface waters (mg.m ⁻³)	Drinking water limit (mg.m ⁻³)
Cd	1.6	2.6	0.19	1
Pb	2.2	1.4	1.6	10
Cu	5.2	4.0	8.2	-
Zn	37	15	7.8	-
Hg	0.02	0.08	0.036	3