Critical Loads of copper, nickel, zinc, arsenic, chromium and selenium for terrestrial ecosystems at a European scale

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Critical Loads of copper, nickel, zinc, arsenic, chromium and selenium for terrestrial ecosystems at a European scale

A preliminary assessment

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ABSTRACT

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This reports provides a preliminary assessment of critical loads of Cu,Ni,Zn,Cr, As and Se for Europe. Critical loads were computed according to existing methods, for forest soils and agricultural soils. Critical loads were assessed aiming at groundwater protection and for avoiding ecotoxilogical effects on soil organisms. Methods and input data for the models are described as well as critical limits used. Maps are provided showing the geographical distribution of 5 percentile critical loads for Europe for each metal and effect seperately. Results of the study are discussed in terms of geographical patterns and critical load ranges, and some indication of uncertainties and possible improvements of the applied methods and data is provided.

Keywords: arsenic, chromium, copper, critical limits, critical loads, Europe, heavy metals, nickel, selenium, zinc

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Preface

The 1998 Heavy Metal Protocol under the Convention on Long-range Transboundary Air Pollution entered into force 29 December of 2003 implying the start of the review of the Protocol. The focus of the review is on the sufficiency and effectiveness of the Protocol including the assessment of effects of deposition of Heavy Metals (HM).

One way of assessing these effects is by looking whether present en future deposition loads exceed critical loads. For the three priority HM, cadmium (Cd), lead (Pb) and mercury (Hg), critical loads and critical load maps for Europe have been developed under the Convention's Working Group on Effects, International Cooperative Programme Mapping and Modeling. For another 6 HM, Arsenic (As), Chromium (Cr), Copper (Cu), Nickel (Ni), Selenium (Se) and Zinc (Zn), for which emission and deposition data are available, it is also valuable to determine whether critical loads are exceeded or not. To be able to perform comparisons between depositons and critical loads for these other 6 HM, Alterra has been commissioned by the ministry of Housing Spatial Planning and the Environment to derive first order European critical loads maps for each of these 6 HM.

With this initiative, critical loads and European maps for these 6 HM can be scrutinised and further developed under the Convention on Long-range Transboundary Air Pollution. More important for the short term is that, with these 6 HM critical loads maps for human health and environmental receptors, a first evaluation can be made to see if these receptors are at risk due to depositions that are caused by current emissions. Furthermore, an assessment is possible whether the risk of these adverse effects could be diminished by projected reduced future emissions.

Therefore, it is my pleasure to draw your attention to this report. I hope that this novel information on European critical loads and critical loads maps of As, Cr, Cu, Ni, Se and Zn can contribute to the review of the HM Protocol and its possible revision.

Hans Bolscher
Director Climate Change and Industry
VROM

Summary

Concern about the input of metals on terrestrial ecosystems is mainly related to the impact on soil organisms and bioaccumulation in the organic layer. In several countries, there is also concern about the excess input of metals in agriculture as it may cause agricultural products with unacceptable levels of heavy metals and even reduced crop production. Furthermore, international standards exist to prevent heavy metal contamination of groundwater. So far, critical loads for Cd, Pb and Hg have been assessed by several European countries within the framework of the UNU-ECE LRTAP Convention. Critical loads express the maximum allowable input of metals below which significant harmful effects on sensitive elements of the ecosystem do not occur according to present knowledge.

End 2006, the Executive Body (EB) of the LRTAP Convention will decide whether the Heavy Metals Protocol must be revised, and whether other metals than Cd, Pb and Hg have to be included. Therefore a preliminary assessment was made of critical loads for Cu, Ni, Zn, Cr, As and Se.

To compute critical loads of Cu, Ni, Zn, Cr, As and Se, the internationally accepted methods described in the mapping manual (UBA, 2004) were applied, aiming at (a) ecosystem functioning protection and (b) human health protection through groundwater quality protection. Both types of critical loads were computed for forest ecosystems as well as agricultural systems. Critical loads were computed for about 800000 receptors, obtained from an overlay of digital maps on soil, vegetation, climate and yield- or administrative regions on a 2.5×2.5 km grid throughout Europe. Input data for the model were obtained from existing, detailed databases on soil characteristics, forest growth, crop yield and meteorology.

A literature survey was carried out to obtain critical limits for Cu, Ni, Zn, Cr, As and Se in view of ecotoxicological effects as well as drinking water protection. Furthermore, metal contents in agricultural crops and trees were obtained from the literature. For Cu, Ni and Zn, critical limit functions could be derived that provide a critical concentration as a function of soil pH and dissolved organic carbon, analogue to the existing functions for Cd and Pb. For Cr, As and Se only a fixed critical concentration could be used.

Results indicate that due to the higher metal uptake and metal leaching, critical loads for agricultural systems are somewhat higher than for forest systems, irrespective of the protection target chosen. For Cu and Se, critical loads aiming at groundwater protection are much higher than for ecosystem protection, due to the high allowable concentration in drinking water for these metals. Critical loads for Cr and Ni aiming at drinking water protection and ecosystem functioning are comparable. For As, the drinking water standard is more strict than the ecotoxicological limit, resulting in lower critical loads for drinking water protection. Patterns in critical loads are mostly determined by the precipitation surplus pattern in Europe, because metal leaching is,

for most metals, the dominant term in the critical load. Only for metals that are essential nutrients, such as Cu and Zn, uptake is important. For these two metals, critical load patterns are also affected by patterns in forest growth (for natural ecosystems) and crop yield (for agricultural systems). Critical concentrations for Ni strongly depend on soil pH: at low pH values critical concentrations are high, leading to high critical loads in those areas in Europe were acid, sandy soils dominate.

For Zn also a critical load was assessed for three different soil types, related to fodder quality. This was only possible for Zn as a relationship between the metal content in the crop and the metal concentration in the soil is required. First results reveal that these critical loads are much higher than critical loads related to ecosystem protection due to the high allowable Zn content in fodder crops, which leads to large allowable uptake quantities.

Results from this study should be interpreted with care as they stem from a preliminary assessment. Uncertainties are substantial, mainly because there was only limited information available on critical limits. Especially for Cr, As en Se, critical concentrations stem from very few sources and are therefore highly uncertain. For more robust assessments of critical metal loads for ecosystem protection, a thorough review of existing ecotoxicological data for these elements is needed. Furthermore, metal contents in crops and stemwood are obtained from few sources only and show a large variation. Some uncertainty also exist in the modeled precipitation surplus, but this uncertainty is minor compared to the uncertainty in critical limits. For Ni, results are strongly affected by soil pH. As soil pH was related to soil type and soil texture alone, pH estimates on the local scale may not always be accurate.

For Cr there are some doubts whether the critical load concept is applicable. If present as a hydroxide (which seems often to be the case) there will not be a direct relation between the amount of Cr in soil and Cr in soil solution. The concentration in soil solution is determined by the solubility product of the hydroxide and hence there will also not be a steady state concentration related to the input flux of Cr to soil. This is in contradiction with the steady state assumption of the critical load approach which means that if the Cr concentration in soil solution are regulated by the solubility of a chromium precipitate, the current critical load concept does not apply for Cr.

1 Introduction

Description of the problem

Terrestrial environments receive metals from natural and anthropogenic sources. Deposition from the atmosphere is the most significant input in remote areas. Atmospheric sources range from volcanoes to emissions from industries and mining. Direct inputs occur via land application of materials such as biosolids, composts and fertilizers. Terrestrial environments can also serve as sources of contamination to aquatic environments.

Concern about the input of metals on terrestrial ecosystems is, amongst others, related to the impact on soil organisms and the occurrence of bioaccumulation in the organic layer (Bringmark & Bringmark, 1995; Bringmark et al., 1998; Palmborg et al., 1998). This holds specifically for cadmium; lead and mercury. In several countries, there is also concern about the excess input of metals (specifically cadmium, copper and zinc) in agriculture (e.g. Moolenaar & Lexmond, 1998) as it may cause agricultural products with unacceptable levels of heavy metals and even reduced crop production (Alloway, 1990; Fergusson, 1990). The concern in aquatic ecosystems is related to the impact of heavy metals (specifically cadmium and mercury) on aquatic organisms and bioaccumulation in fish, which may result in a violation of food quality criteria.

Risks due to contaminating metals in the terrestrial environment are often assessed by comparing current concentrations against concentrations above which adverse effects are considered likely to occur. The definitions of these acceptable limits (critical concentrations or levels) depend on the receptor at risk and may, for example, be concentrations in soils, soil solution, plants, animals and humans. While this approach is appropriate where risks due to past contamination require management, it does not permit the assessment of future risk due to current inputs. To do this, we need to combine knowledge of the critical concentrations of metals with knowledge of their sources, cycling, and fate. The critical loads approach is a method for assessing (future) risks of input metals to terrestrial ecosystems. The approach has been successful in international negotiations on the reduction of atmospheric deposition of nitrogen and sulphur as it presents the maximum level 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 optimize the protection of the environment for a given international investment in pollution control by minimizing the difference between present loads and critical loads on a regional scale.

The critical load concept for heavy metals

In the mid–nineties, the concept of critical loads for metals was introduced (De Vries & Bakker, 1998) and preliminary critical load maps for Cd, Pb and Cu were derived for European forest soils (Van den Hout et al., 1999). Since then methodologies have been developed, discussed and eventually accepted within the framework of activities of the Coordination Center for Effects (CCE) of the ICP Modelling & Mapping under the Convention on Long-range Transboundary Air Pollution (LRTAP). A state of the art methodological manual, developed under the LRTAP Convention, has been adopted for the metals Cd, Pb and Hg (UBA, 2004; De Vries et al., 2005), and the critical loads maps of these metals have been published, based on results by the various countries (Slootweg et al., 2005; 2006). The focus was on these "priority metals" as they are part of the Heavy Metals Protocol that has been signed since 1998 by 24 countries, and came into force end 2004. Unlike the previous publication by Van den Hout et al. (1999), the attention was not only focused on ecotoxicological risks to forests, where metal deposition is the only external source, but also includes human toxicological risks by including agricultural systems where the load refers to the input by both fertilizers/animal manure (sometimes also sewage sludge) and atmospheric deposition. Until now, the risk of exceedances is however limited to the risk that deposition of these metals causes (Slootweg et al., 2005; 2006).

This study

End 2006, the Executive Body (EB) of the LRTAP Convention will decide whether the present Protocol must be revised, and whether other metals than Cd, Pb and Hg have to be included. To decide whether policy measures are needed to reduce emissions of other metals (more specifically copper, zinc, nickel, arsenic, chromium and selenium; Cu, Zn, Ni, As, Cr en Se) insight is neccesary whether present loads of those metals can lead to risks for humans and ecosystems. This report thus presents an overview of preliminary critical loads of those metals for agricultural and non-agricultural soils in Europe, in view of impacts on soil organisms and soil processes and water quality. Impacts on food quality and crop health are only dealt with in terms of calculation examples, since there are hardly any food quality criteria available for the considered metals. The occurrence of actual risks is not part of this study but will be assessed in a parrelel study that compares results from deposition scenario's for 1990,2000,2010 and 2020 with the critical loads in this report and the critical loads for Cd, Pb and Hg as described in Slootweg et al. (2005).

Although As and Se can not be considered metals, the group of elements dealt with in this study, Cu, Zn, Ni, As, Cr en Se, will be referred to as 'metals' in the rest of the report for reasons of convenience.

Content of the report

Chapter 2 of this report described the methodologies applied in this study. It provides an overview of the model applied and the critical limits used. In chapter 3 an overview is provided of the input data used in the critical load computations. It describes the geographical information obtained from maps as well as non-georeferenced input data such as soil data obtained from existing data bases. Results from this study are given in Chapter 4: for each metal, maps with critical loads for forests and agricultural land are presented and dicussed. Furthermore, an example calculation for critical loads for Zn related to food quality is given in this chapter. In Chapter 5, conclusions are drawn and some recommendations for possible improvements and further research are given.

2 Methodology

2.1 General aspects

The concept of critical metal loads has been described extensively in De Vries and Bakker (1998). It is defined as the load that will not lead to concentrations of heavy metals above critical limits in defined compartments (e.g. soil/soil solution, ground water, surface water, plants or animal organs) in a steady-state situation. Examples are critical limits for the soil or soil solution in view of impacts on: (i) agriculture (food quality or crop health), (ii) ecology (e.g. soil organisms in view of impacts on nutrient cycling processes) and (iii) water quality (e.g. quality of ground water in view of impacts on drinking water or surface water due to impacts on aquatic organisms). Under the approach, an input–output mass balance is constructed for the system under consideration. The critical load is then the input rate (e.g. from atmospheric deposition) that balances the other inputs and outputs for a given critical metal concentration in a given compartment. A steady state assumption is central to the approach.

2.2 Simple mass balance

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 steady state situation. The assumption of a future steady state situation signifies that the concentration in the system does not change in time because the amount of heavy metal entering the system is equal to the amount that leaves the system. To keep the method simple and compatible with the approach for nitrogen, internal cycling of elements and weathering are neglected. For more information see de Vries et al. (2005).

2.2.1 Model

The critical load of a metal can be calculated from the sum of tolerable outputs from the considered system in terms of net metal uptake and metal leaching. The critical load equals the net uptake by forest growth or agricultural products plus an acceptable metal leaching rate, according to:

$$\mathrm{CL(M)} = \mathrm{M_u} + \mathrm{M_{le(crit)}} \tag{1}$$

where:

$\mathrm{CL(M)}$ = critical load of a heavy metal M ($\mathrm{g.ha^{-1}.yr^{-1}}$)

$\mathrm{M_u}$ = Metal net uptake in harvestable parts of plants under critical load conditions ($\mathrm{g.ha^{-1}.yr^{-1}}$)

$\mathrm{M_{le(crit)}}$ = critical leaching flux of heavy metal M from the considered soil layer ($\mathrm{g.ha^{-1}.yr^{-1}}$), whereby only the vertical drainage flux is considered

The critical leaching flux of a heavy metal from the topsoil can be calculated according to the equation

$$M_{le(crit)} = c_{le} \cdot Q_{le} \cdot [M]_{tot,sdw(crit)} \qquad (2)$$

where:

$M_{le(crit)}$ = critical leaching flux of heavy metal M from the considered soil layer (see Eq. 1) ($g.ha^{-1}.yr^{-1}$)

Q_{le} = flux of drainage water leaching from the considered soil layer ($m.yr^{-1}$)

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

c_{lo} = factor for appropriate conversion of flux units from $mg.m^{-2}.yr^{-1}$ to $ga.ha^{-1}.yr^{-1}$ (10 $g\ mg^{-1}\ m^{2}\ ha^{-1}$).

2.2.2 Metal removal by net growth and harvest

The removal of metals by net growth and harvest (Equation 1) at the critical load refers to the steady state level at critical load. For many metals however there is no clear relationship between concentrations in soil solution and concentrations in the harvestable parts in plants (both agricultural crops and trees). For metals and plants for which there is no good relation between soil solution concentration and plant concentrations we calculate the uptake from an average metal content in plants as found in relatively unpolluted areas. For agricultural crops these metal concentrations have to be below quality criteria for food and fodder crops.

To calculate the net element uptake the average yield (or growth increment) of harvestable biomass has to be multiplied with the element content in harvestable plant parts and with a factor to account for the element uptake fraction from the soil layer considered relative to that from the total soil (Eq. 3):

$$M_u = f_{Mu,z} \cdot Y_{ha} \cdot [M]_{ha} \qquad (3)$$

where:

M_u = metal net uptake in harvestable parts of plants under critical load conditions ($g.ha^{-1}.yr^{-1}$) (see Eq. 1),

f_{Mu} = fraction of metal net uptake within the considered soil depth (z_b or z), accounting also for metal uptake due to deposition on vegetation surfaces (–),

Y_{ha} = yield of harvestable biomass (dry weight) ($kg.ha^{-1}.yr^{-1}$),

$[M]_{ha}$ = metal content of the harvestable parts of the plants ($g.kg^{-1}$ dw), including also metals deposited on vegetation surfaces.

We used a root uptake factor ($f_{Mu,z}$) of 1 for all critical loads for all ecosystem types. For the calculation of critical loads related to drinking water, the leaching flux below the root zone has to be calculated which implies the use of $f_{Mu,z} = 1$. This is also the case if CL's are to be calculated related to critical concentrations in crops. For CL related to ecotoxicological effects we assumed that most uptake of nutrients and pollutants occurs in the top soil. In forests values around 80% have been reported for uptake from the humus layer alone (based on lead isotopes in Scots pine, Bindler et al., 2004). Thus, for calculations referring to the humus layer, $f_{Mu,z}$ may be 0.8, but, if the top of the underlying mineral soil is included in the calculations, $f_{Mu,z}$ is likely to approach 1, also in forests.

Because site specific data on metal contents are not available at a European scale we use default values for metal contents in trees and crops. Table 1 gives an overview of the selected default values. Species which are hyper accumulators i.e. Douglas-fir for As (Haug et al., 2004), were not used to set default values for element contents in vegetation.

Table 1 Element contents in biomass for various species (harvestable parts) used in the calculations. Ranges and sources are given in Appendix 1

Land use	Species	Element content in harvestable plant parts, $[M]_{ha}$ (mg.kg^{-1} dw)					
		Cu	Ni	Zn	As	Cr	Se
Grassland	mixed grassland species	10	0.7	71	0.21	0.8	0.08
Arable land	wheat (grains)	5.15	-	50	0.05	-	0.06-0.6
	maize	5.15	0.7	59	0.15	-	-
Coniferous forest	pine, fir, douglas spruce	5	1	20	0.01	0.6	-
Deciduous forest	oak, beech, birch, poplar	5	1	20	0.02	0.6	-

Relations between metal contents in crops and soil or soil solution were only used in example calculations for Zn in fodder crops and are discussed in chapter 4.

2.3 Critical limits

Critical concentrations of the metals As, Cr, Cu, Ni, Se and Zn in soil drainage water, $[M]_{dis,sdw(crit)}$, depend on the target to be protected. These values have to be derived from critical limits for (see Table 1):

- Metal contents in plants in view of human health or animal health effects through intake of plant products.
- Concentrations of free metal ions or total concentrations in soil solution (As, Cr, Cu, Ni, Se and Zn) in view of ecotoxicological effects on soil micro-organisms, plants and invertebrates.
- Metal concentrations (total dissolved concentration) in ground water in view of human health effects through intake of drinking water.

The critical metal concentrations in soil solution water and in plants, which are (in principle) interrelated, are calculated depending on the target to be protected as shown in Table 2. In this table we give also an overview of the relations needed to calculate the total dissolved concentration in drainage water.

Table 2 Calculations that are required to assess critical crop contents, needed to calculate the critical metal uptake, and critical dissolved soil metal concentrations, needed to calculate the critical metal leaching rate, in dependence of the receptor and effect considered.

Critical limit	Ecosystem[1]	Type of effect	$[M]_{crop}$	$[[M]_{le}$(crit)
Water quality				
Soil solution[2]	All	Ecotoxicological	Soil solution-plant	Free metal to total dissolved metal concentration in soil drainage water or no further calculations
Ground water[3]	All	Human – toxicological	Soil solution-plant	Requires no further calculations
Food quality				
Plant[4]	Arable land,	Human – toxicological or animal toxicological	Requires no further calculations	Plant-(soil total-soil reactive)-soil solution
Animal organ[5]	Grassland	Human – toxicological	Animal organ-soil-plant	Animal organ-soil-soil solution

[1] Includes grassland, arable land and non agricultural land (grassland, heathland and forests).

[2] A critical free metal ion concentration in soil solution in view of impacts on soil organisms and plants, derived from NOEC data for soil and transfer functions to estimate the free metal ion concentration (if available).

[3] A critical total dissolved concentration in ground water in view of drinking water quality (or a target value when critical limits are not available)

[4] A critical metal concentration in plants based on food quality criteria. This target is relevant for arable land only in case of human health and also to grassland in case of animal health

[5] A critical metal concentration in target organisms of grazing animals (liver and kidney of cows and sheep) based on food quality criteria and animal health. This target is relevant for grassland only.

Below, we give an overview of available critical limits for the various metals divided in ecotoxicological effects, human health effects and animal health effects.

Critical concentrations related to ecotoxicological effects of Cd and Pb in the manual are derived as a critical limit function of the free metal concentration in solution depending on pH, based on a methodology described in Lofts et al. (2004). For Cu, Zn and Ni, it was possible to find a critical limit function that was derived in the same way as described in the manual. For the other metals, use was made of an estimated fixed critical free or total metal concentration in soil solution, based on literature data, as described below. The calculation of a total dissolved concentration from a critical free ion concentration is discussed in paragraph 2.4.

Critical concentrations related to human health effects are limited to drinking water limit values, since there are no food quality criteria for the metals considered in this study There are however, standards for As, Cu, Se and Zn in fodder crops in view of animal health effects The derivation of a critical concentration in soil solution based on critical plant metal contents is discussed in Chapter 4 by an example calculation for Zn, being the only metal with an acceptable reliable soil-plant relationship.

Arsenic

In oxidized environments the stable form of As is As(V), therefore we limit ourselves to As(V) in this study. As(V) is present in soils as an anion and strongly sorbed to soils. As is not known to be an essential element for living organisms.

Ecotoxicological effects

For ecotoxicological effects there is not a critical limit function. Doyle et al. (2003) reported an expected no effect value (ENEV) for the total concentration in soil pore water of 70 $\mu g.l^{-1}$. The reported ENEV for fresh water is 21 $\mu g.l^{-1}$ which is very similar to the HC_5 of 25 $\mu g.l^{-1}$ published by Crommentuijn et al. (1997) for fresh water organisms. We used the concentration of 70 $\mu g.l^{-1}$ as derived for the soil solution.

Human health effects

There are no food quality criteria for As concentrations in agricultural products. The critical concentration in drinking water according to EU regulation (98/83/EC) and a provisional guideline of WHO is 10 $\mu g.L^{-1}$.

Animal health effects

For animal health, critical limits are set for fodder crops. According to the EU guideline (EU 70/524/EEC) the maximum concentration is 2 $mg.kg^{-1}$. This is equal to the Dutch critical concentration in fodder crops of 2.3 $mg.kg^{-1}$ for grass and maize (dry weight). There are however no plant soil or plant soil solution relations available to calculate a critical solution concentration from the critical crop content which means a critical load cannot be computed.

Chromium

Chromium can be present in the environment in different oxidation states of which Cr(III) and Cr(VI) are stable forms. In soil the predominant species is Cr(III) however Cr(VI) can be present in significant amounts as well. The ratio between Cr(III) and Cr(VI) is the result of the rates of reduction and oxidation which depends on several factors as pH, presence of Fe and organic matter etc.. Reduction of Cr(VI) is favoured by low pH and the presence of organic matter, Fe(II) and S. Oxidation of Cr(III) is favoured by alkaline pH and the presence of Mn-oxides. In neutral and acidic soils in the presence of organic matter Cr(VI) is readily transformed to Cr(III) (Bartlett & Kimble, 1976; Cary et al., 1977; Grove & Ellis, 1980). Because the critical load approach is applied to top soils which in general contain organic matter we assume Cr to be present in soil as Cr(III).

Ecotoxicological effects

For Cr no critical limit functions are available for ecotoxicological effects. We were not able to find critical concentration for Cr in soil solution. Therefore we have looked for critical concentrations in surface waters. Official limit values do not distinguish between Cr(III) and Cr(VI) and are therefore based on the most toxic form which is Cr(VI). Therefore we have looked for toxicological data specifically related to Cr(III). Crommentuijn et al. (1997) report a HC_5 of 34 $\mu g.l^{-1}$ based upon statistical extrapolation of toxicity data for freshwater species. The lowest NOEC value they report is 48 $\mu g.l^{-1}$ for a fish species. For Daphnia magna (a fresh water invertebrate) a similar concentration of 44 $\mu g.l^{-1}$ is reported as an effect concentration (fecundicity) which we have chosen as the critical limit.

Human health:
There are no food quality criteria for Cr concentrations in agricultural products. Both the EU and WHO set the drinking water limit at 50 $\mu g.l^{-1}$ total chromium.

Animal health effects
There are no standards for Cr concentrations in animal food, so critical loads for animal health can not be assessed. In general mammals are rather insensitive to Cr(III); Cr(III) is an essential element for them.

Copper

Ecotoxicological effects
For Cu there is a critical limit function (Lofts et al, 2003 and De Vries et al., 2006) which relates the critical concentration to the pH according to:

$$\log[Cu]_{free(crit)} = -1.23 \cdot pH_{ss} - 2.05$$

Doyle et al. (2003) also reported a critical free metal ion concentration in solution. Their expected no effect value (ENEV) does not depend on pH and is fixed at 40 $\mu g.l^{-1}$. This value is at the high end of the critical limit function which gives critical concentrations around this value at pH 3. At higher pH values, critical Cu concentrations are lower, with values being more than a factor thousand lower at pH 6.

Human health effects
There are no food quality criteria for Cu in crops. There is however a critical limit for Cu in residues of pesticides in crops in the Netherlands of 24 $mg.kg^{-1}$. There are, however, no relations available applicable to the field scale between concentrations in crops and concentrations in soil or soil solution (see below). The limit for drinking water: 2 $mg.l^{-1}$ (EU and WHO).

Animal health effects
In the Netherlands there are critical limits in fodder crops for cattle to protect animal health. For grass and maize the maximum concentration for cows is 40 $mg.kg^{-1}$. For sheep, that are more sensitive to copper, the maximum concentration is 17 $mg.kg^{-1}$.
There are, however, no relations available applicable to the field scale between concentrations in crops and concentrations in soil or soil solution. We have not used relations derived from pot experiments because these are generally different (predict higher metal concentrations) from relations derived from field data. Also the data on which these relations are derived are often very limited with regard to variation in soil type and pH.

Nickel

Ecotoxicological effects

For Nickel there is a critical limit function (De Vries et al., 2006):

$$\log[\mathrm{Ni}]_{\mathrm{free(crit)}} = -0.64 \cdot \mathrm{pH}_{\mathrm{ss}} - 2.59 \tag{5}$$

Doyle et al. (2003) report a critical free metal concentration of 0.2 $\mathrm{mg.l^{-1}}$.

Human health effects

There are no food quality criteria for Se concentrations in agricultural products. for drinking water, we used a critical limit of 20 $\mu\mathrm{g.l^{-1}}$ (EU + provisional value WHO).

Animal health effects

For animal health there is not a critical Ni concentration in fodder crops.

Selenium

Se is present in soils as Se(V) as selenate under oxidized conditions. Se is an essential element for living organisms, however at higher concentrations Se becomes toxic and there seems to be a narrow window for optimal Se concentrations.

Ecotoxicological effects

There are hardly any effect concentrations, expressed as solution concentrations, available for Se in terrestrial systems. We have used 1 $\mu\mathrm{g.l^{-1}}$ as a limit (Meili, pers. comm.).

Human health effects

There are no food quality criteria for Se concentrations in agricultural products. EU and WHO keep a drinking water standard of 10 $\mu\mathrm{g.l^{-1}}$

Animal health effects

For animal health there is not a critical Se concentration in fodder crops. However, according to EU regulation, the maximum content in animal food after addition of Se to animal food is 0.5 $\mathrm{mg.kg^{-1}}$ (EU guideline 70/524/EC).

Zinc

Ecotoxicological effects

For Zn we used the critical limit function according to De Vries et al. (2006):

$$\log[\mathrm{Zn}]_{\mathrm{free(crit)}} = -0.31 \cdot \mathrm{pH}_{\mathrm{ss}} - 4.63$$

Doyle et al. (2003) give a critical free ion concentration of 280 $\mu\mathrm{g.l^{-1}}$

Human health effects

Zn is an essential element for living organisms. There are no critical limits for Zn in food crops and neither a limit for Zn in drinking water.

Animal health effects

In the Netherlands there is a maximum concentration for Zn in fodder crops of 250 mg.kg^{-1} (fresh weight), recalculated to dry weight this gives a limit of 284 mg.kg^{-1} (De Vries et al., 2006b). According to the EU guideline on additives to fodder crops the maximum concentration in Zn is 250 mg.kg^{-1} (EU guideline 70/524/EC).

Summary

Table 3 provides an overview of the various limits used for the different protection targets. For most metals, critical loads were computed for both drinking water and ecotoxicology, both for forests as well as for agricultural soils. Only for Zn, critical loads for drinking water could not be computed because not limit for drinking water exists. Critical loads for animal health could be computed for Zn only as this is the only metal for which both a critical limit in fodder crops exists as well as a tranfer function to related Zn content in the crop to Zn content in the soil solution.

Table 3 Critical limits used for concentrations of As,Cr,Cu,Ni,Se and Zn related to drinking water quality and ecotoxicological effects

	Critical concentration in $\mu g.l^{1}$		*Critical content mg.kg^{-1}*
Metal	*Human health:drinking water*	*Ecotoxicology*	*Animal health*
Cr	50	44	
Ni	20	± 25 – 700 (pH and DOC function)	
Cu	2000	± 1 – 50 (pH and DOC function)	
Zn	-	± 20 - 90 (pH and DOC function)	285 (example calculation only)
As	10	70	
Se	10	1	

2.4 Calculation of total dissolved metal concentrations from free metal ion concentrations.

To calculate critical loads for soils from the critical limit functions, it is necessary to know the total concentration of metal in soil drainage water that corresponds to the free ion critical limit. The metal in soil drainage water comprises the following metal species:

Metal free ion M^{2+}	$[M]_{free}$
Inorganic complexes	MOH^+, $MHCO_3^+$, MCl^+ etc. $[M]_{DIC}$
Metal bound to DOM	$[M]_{DOM}$
Metal bound to SPM	$[M]_{SPM}$

Here, DOM is dissolved organic matter, and SPM is suspended particulate matter. The total concentration of metal in soil drainage water does not refer simply to dissolved components ($[M]_{free}$, $[M]_{DIC}$, and $[M]_{DOM}$), but also includes $[M]_{SPM}$. Data on SPM concentration in soil drainage waters are scarce, and in many cases the contribution of SPM to the metal leaching is only small. Therefore we neglected this component.

Given the free metal concentration of M^{2+}, the concentrations of the other metal species can be estimated by applying an equilibrium speciation model. The calculation has to take into account the dependence of the metal speciation on pH and competitive effects due to major cationic species of Mg, Al, Ca and Fe. For this purpose we used custom version of the Windermere Humic Aqueous Model version 6 (WHAM6, Tipping, 1998) speciation model, termed W6S-MTC3, kindly provided by E. Tipping.

The W6-MTC program carries out the following steps to calculate values of $M_{tot,SDW,crit}$.

1. The inputs to the calculation are: pH, % soil organic matter, pCO_2, [DOC] in $mg.l^{-1}$, and [SPM] in $mg.l^{-1}$. The relevant concentrations of DOC and SPM are those in water draining from the soil zone of interest. The calculations refer to a temperature of 10°C.
2. The concentration ($g.l^{-1}$) of "active" fulvic acid (FA) is obtained by multiplying [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 & Tipping, 1998; Vulkan et al., 2000; Bryan et al., 2002), and Cd (Tipping, 2002).
3. The critical free ion concentration - M_{free} - is computed from the soil pH and the Critical Limit Function.
4. The activity of Al^{3+} is calculated from the pH, using equations derived by Tipping (2004). 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.
5. The activity of Fe^{3+} is obtained by assuming a solubility product at 25°C of $10^{2.5}$ and an enthalpy of reaction of -107 $kJ.mol^{-1}$ (Tipping et al., 2002).
6. As a starting-point, Na is assumed to be present in the soil solution at a concentration of 0.001 $mol.l^{-1}$, 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 $mol.l^{-1}$, while that of SO_4^{2-} is 0.000167 $mol.l^{-1}$.
7. The concentration of M^{2+} and the activities of Al^{3+} and Fe^{3+} are fixed at the values obtained in steps 2-4, 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-}.
8. If the result from Step 7 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.
9. If the result from Step 7 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.
10. The binding of metal to SPM is computed, by applying multiple regression equations ("transfer functions") derived for whole soils. These equations

describe metal binding as a function of free ion concentration, pH, and organic matter. The transfer function used here is Equation (A7.4) with the parameters mentioned in Table A7.5.

11. The concentrations of dissolved inorganic metal species (including M^{2+}), metal bound to dissolved organic matter, and metal bound to SPM, are added together to obtain $M_{tot,SDW,crit}$.

Because of competition effects between metals when the model is used for all metals simultaneously, we made separate model runs for the metals for which the critical concentration had to be calculated.

3 Input data

3.1 Geographical data

Geographical input data for the critical load model include precipitation surplus, soil organic matter content, soil pH, DOC concentration in the top soil, forest growth and crop yield. These input data vary as a function of location and/or ecosystem type.

Maps with computational units (receptors) that hold the required information to derive the input data for the model, were constructed by overlaying maps with a grid resolution of 2.5 × 2.5 km. Two map overlays were made, one that holds the spatial distribution of receptors for forests and one for agricultural soils.

The receptor map for forests was made by overlaying:
- The harmonised land cover map produced by the CCE and SEI by combining the Corine land cover map with the SEI land cover map (Posch et al., 2005)
- A soil map at scale 1:1,000,000 for all European countries (Eurosoil, 1999); except for Russia, Belarus, Ukraine and Moldova, for which the FAO 1:5,000,000 soil map (FAO, 1981) was used.
- Average forest growth derived from an updated data base of the European Forest Institute (EFI), which contains growth data for a variety of species and age classes in about 250 regions in Europe (Schelhaas et al., 1999).
- A map with EMEP grid cells of 50×50 km^2, for reference with deposition data.

The receptor map for agriculture was constructed by overlaying the maps mentioned above, but without the forest growth map that was replaced by a map containing the EU administrative regions (NUTS regions) and by adding a map with the so-called 50 × 50 km MARS grid.

The soil maps are composed of so-called soil associations, each polygon on the map represents one association. Every association, in turn, consists of several soil typological units (soil types) that each covers a known percentage of the soil association. The soil typological units on the maps are classified into more than 200 soil types (Eurosoil, 1999).

For each soil typological unit information is available, of which soil texture and drainage classes are used here to derive other input data. Six texture classes are defined from clay and sand content.

The resulting receptor maps including all detailed soil information contains about 1.000.000 receptors larger than 1 km^2 for forests and 600.000 units larger than 1 km^2 for agriculture.

Regarding tree species, a distinction was made between coniferous, mixed and deciduous forests since data on the geographical distribution of various tree species (e.g. pine, fir, spruce, oak, beech and birch) is not available.

3.2 Precipitation surplus

3.2.1 Forests

To compute the leaching of metals in forest soils, the annual water flux through the soil has to be computed using meteorological data and soil hydraulic properties. Long-term (1961-1990) average monthly temperature, precipitation and cloudiness were derived from a high resolution European data base (Mitchell et al., 2004) that contains monthly values for the years 1901-2001 for land-based grid-cells of 10'×10' (approx. 15×18 km in central Europe). For sites east of 32° a 0.5°×0.5° global database from the same authors was used.

Actual evapotranspiration was calculated according to a model used in the IMAGE global change model (Leemans & van den Born, 1994) following the approach by Prentice et al. (1993). Potential evapotranspiration was computed from temperature, sunshine and latitude. Actual evapotranspiration was then computed using a reduction function for potential evapotranspiration based on the available water content in the soil, described by Federer (1982). Soil water content is in turn estimated using a simple bucket-like model that uses water holding capacity (derived from the available soil texture data) and precipitation data. A complete description of the model can be found in Annex 4 of Reinds et al. (2001).

The available water content (AWC) was estimated as a function of soil type and texture class according to Batjes (1996) who provides texture class dependent AWC values for FAO soil types based on an extensive literature review.

3.2.2 Agricultural soils

Leaching from agricultural soils was computed by subtracting the water consumption of wheat in the growing season computed on a daily basis by a detailed agricultural crop growth model from the yearly rainfall for the 50 × 50 km MARS grid. Details on this procedure are provided in Micale & Genovese (2004) and Lazar & Genovese (2004).

3.3 Metal uptake

3.3.1 Forests

Uptake of metals by forests was computed by multiplying the estimated annual average stem growth with the heavy metal contents in the wood (cf. section 2.2.2).

Wood densities of 450 kg/m3 and 650 kg/m3 for coniferous and deciduous trees, respectively, have been used. For mixed forests the average of these values were applied.

Forest growth was derived from the EFI database mentioned above (Schelhaas et al., 1999). Growth was assessed by taking from the database the average growth over all age classes for the specific combination of region and tree species group (conifers/ deciduous/mixed). The area weighted cumulative frequency distribution of the average growth is provided in Figure 1a, for all computational units. The figure shows that stem growth mostly varies between 1.5 – 8 $m^3.ha^{-1}.yr^{-1}$. Occasionally in high productive areas, yields up to 15 $m^3.ha^{-1}.yr^{-1}$occur. To compute uptake, also the stemwood density is needed; averaged stemwood densities were set at 450 $kg.m^{-3}$ for conifers trees and to 650 $kg.m^{-3}$ for deciduous trees (e.g. Wagenfuhr & Schreiber, 1989).

3.3.2 Agriculture

Uptake of metals by wheat was computed by multiplying the crop yield, derived from agricultural statistics, with the estimated heavy metal contents (cf. section 2.2.2).

Crop yield for wheat were derived using the average of the reported national yields from EUROSTAT for the period 1987-2003 (Genovese & Bettio, 2004). The cumulative frequency distribution of average wheat yields is provided in Figure 1b. Yields vary between about 2-6 $ton.ha^{-1}.yr^{-1}$. Average yields around 2-3 $ton.ha^{-1}.yr^{-1}$ are found in countries like Spain, Portugal and the Baltic states, whereas yields between 5.5 and 6.5 $ton.ha^{-1}.yr^{-1}$ occur in north-western Europe (Germany, Netherlands, Belgium, France, Ireland)

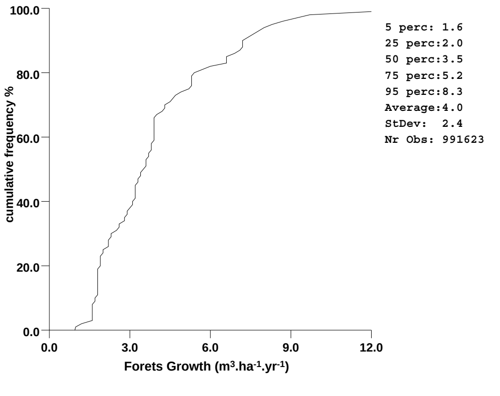


Figure 1a Cumulative distribution of stem growth

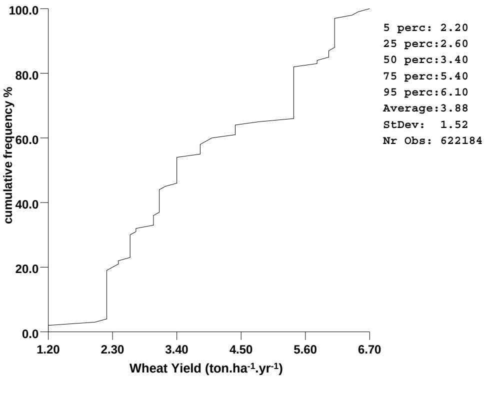


Figure 1b Cumulative distribution of wheat yield for EU-25

3.4 Dissolved organic carbon and soil pH

For the computation of critical concentrations of Cu, Zn and Ni, the concentration of dissolved organic carbon (DOC) and the soil pH are required.

3.4.1 Forests

For forests the DOC concentration was estimated from a linear regression with soil pH and texture using data from European Intensive Forest Monitoring plots according to:

$$DOC = 54.02 + a - 6.67*pH$$

With:
a = texture dependent constant, being 0 for sand,-12.7 for light clay,-8.1 for löss and -11.8 for heavy clay.

pH values for each soil type were derived from a European database on forest soils (Vanmechelen et al., 1997) that hold pH measurements for about 5000 sites in Europe.

3.4.2 Agriculture

The DOC concentration in agricultural soils was obtained from a relationship with pH and organic matter content according to (Römkens et al., 2004):

$$DOC = 10^{**}(-0.1757*pHs + 0.728453*\log10(Om) + 2.0416) \qquad (6)$$

With:
DOC = DOC concentration (mg.l^{-1})
pHs = soil pH
OM = organic matter content (in %)
This relationship is based on 840 samples from various soil profiles.

Topsoil pH values for agricultural soils were obtained as a function of soil type and topsoil texture from a global soil data set (Batjes, 2002) that provides pH values for about 180 different soil types and 3 texture classes based on 9607 soil profiles.

4 Results

4.1 Introduction

European wide computations of critical loads for metals where carried of for:

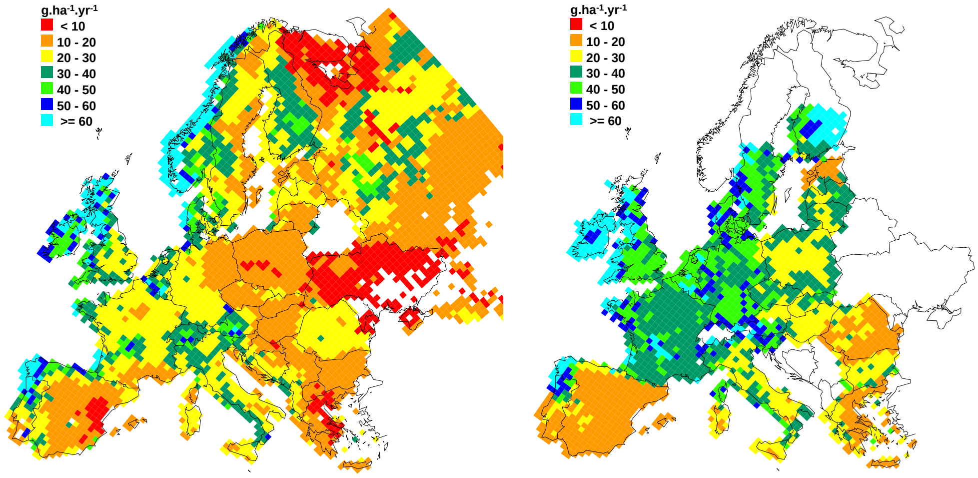
- Ecosystem functioning by avoiding negative effects on soil microorganisms and invertrabrates
- Human health effects by aiming at groundwater protection

Both critical loads approaches were applied for forests as well as for agricultural soils. For Cu, Ni and Zn critical concentrations for ecosystem functioning were computed as a function of pH and DOC concentration to account for complexation (so-called critical limit functions, Lofts et al., 2004) using the WHAM model. For the other metals, pH and DOC independent values were used. Critical limits for drinking water protection refer to total metal concentrations, so complexation does not play a role. An overview of the limits used, is provided in Chapter 2 of this report.

4.2 Copper

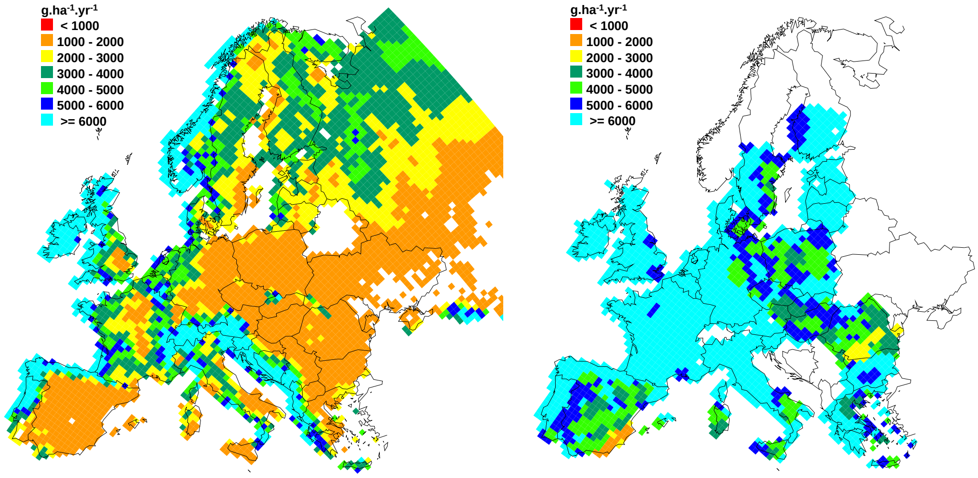
The spatial distribution of the critical loads for copper is provided in Figure 2 that shows the 5 percentile critical load for each EMEP 50×50 km cell. The 5 percentile critical load is the critical load value below which 5 percent of the critical loads lie. This implies that a deposition equal to the 5 percentile critical load will protect 95% of the ecosystems in the grid cell. Critical loads for agricultural soils are only computed for the EU 25 countries, as yield data from EUROSTAT are available for these countries only. Furthermore, parts of Scandinavia have no critical loads as wheat does not occur in this region.

Figure 2 shows that 5 percentile critical loads for copper per EMEP 50 × 50 cell related to ecosystem functioning, range between 5 and 200 $g.ha^{-1}.yr^{-1}$. Highest critical loads are found in areas with a high precipitation surplus such as south-western Norway and Scotland, whereas low critical loads are found in areas with a very low precipitation surplus, such as central Spain. In general critical loads are higher for agriculture than for forests because of higher leaching fluxes under annual crops compared to forests (part of the year the soil is bare when growing annual crops) and because of the higher uptake of Cu by wheat that is about twice as high as the uptake by forests due to its higher yield. Because copper is a nutrient, a substantial part (up to about 50%) of the critical load in areas with low leaching consist of uptake. This is reflected in Map 1 D that shows lower critical loads in Spain than in France, not only because of lower leaching, but also because of lower uptake; wheat yields for France are about 6 $ton.ha^{-1}.yr^{-1}$ and about 2.6 $ton.ha^{-1}.yr^{-1}$ for Spain. Because yields were used on a country level, this creates a somewhat artificial, sharp, transition in critical load map between Spain and France.



(A) CL(Cu), Forest, Ecosystem

(B) CL(Cu), Agriculture, Ecosystem



(C) CL(Cu), Forest, Drinking Water

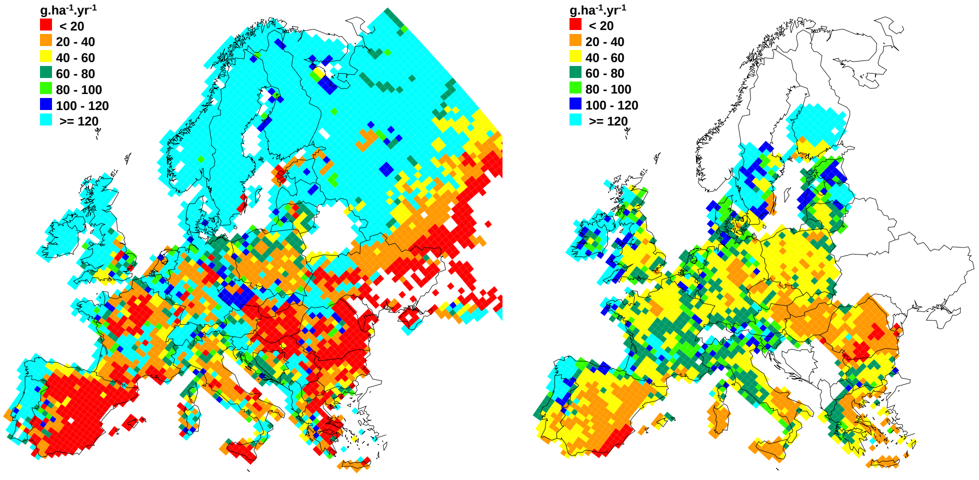
(D) CL(Cu), Agriculture, Drinking Water

Figure 2 Critical loads for Copper; please note the difference in legend between the two effects (A and B versus C and D)!

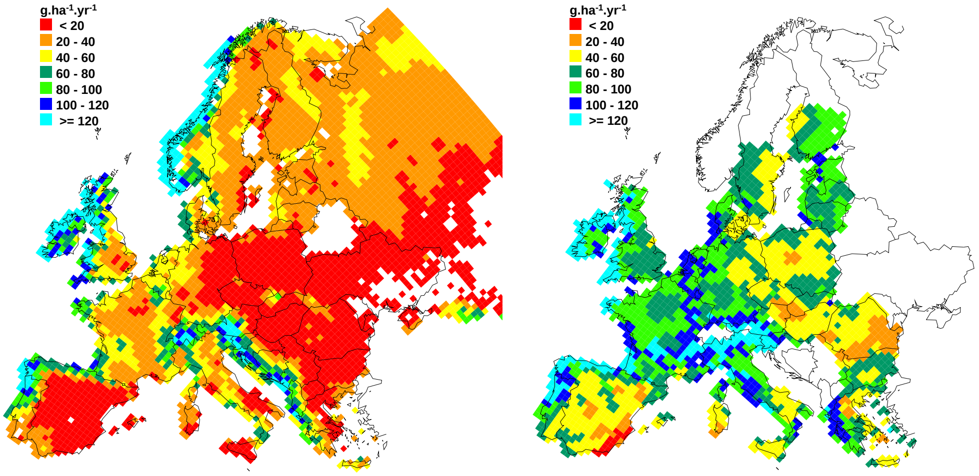
For drinking water (Figures 2B and 2C) critical loads are much higher than for ecosystem functioning due to the high critical concentration of Cu in drinking water of 2000 mg.l$^{-1.}$ This critical concentration is about a factor of 200 higher than the critical concentration for ecosystem functioning which varies between 2 and 20 mg.l^{-1} depending on pH and DOC concentration. Critical loads for drinking water protection vary between 3000 – 10000 g.ha^{-1}.yr^{-1} and are thus unlikely to be ever exceeded by atmospheric inputs.

4.3 Nickel

Figure 3 shows the 5 percentile critical load for Ni for each EMEP 50×50 km cell.



(A) CL(Ni), Forest, Ecosystem *(B) CL(Ni), Agriculture, Ecosystem*



(C) CL(Ni), Forest, Drinking Water *(D) CL(Ni), Agriculture, Drinking Water*

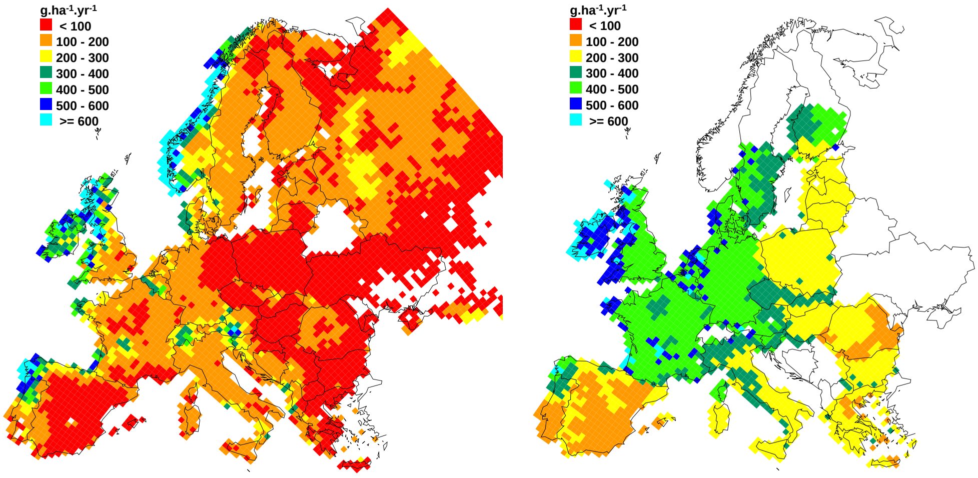
Figure 3 Critical loads for Nickel

Figure 3 shows that the 5 percentile critical loads for Ni for protecting ecosystem functioning, vary between 10 and 200 g.ha^{-1}.yr^{-1}. As with copper, highest critical loads are found in areas with a high precipitation surplus and lowest critical loads are found in dry areas. Although Ni is a (minor) nutrient, uptake does not significantly contribute to the critical load as even in areas with low leaching (critical loads < 20 g.ha^{-1}.yr^{-1}), the percentage of the critical loads that consist of uptake is lower than 20%. The critical concentration of Ni related to ecosystem protection is strongly dependent on pH: at very low pH's (< 4) the critical concentration is high compared to values at higher pH. The maps therefore also show high critical loads in areas with acid soils such as Scandinavia, the eastern parts of the Netherlands and Germany, central France and the Czech Republic.

Critical loads related to drinking water protection are generally somewhat lower than the critical loads for ecosystem protection, because the drinking water standard of 20 mg.l^{-1} is mostly lower than the critical concentration for ecotoxological effects that varies between 25 and 700 mg.l^{-1} (with a median value of about 80 mg.l^{-1}) for forests depending on pH and DOC concentration.

4.4 Zinc

Figure 4 provides the 5 percentile critical loads for Zinc per EMEP 50×50 km grid cell.



(A) CL(Zn), Forest, Ecosystem *(B) CL(Zn), Agriculture, Ecosystem*

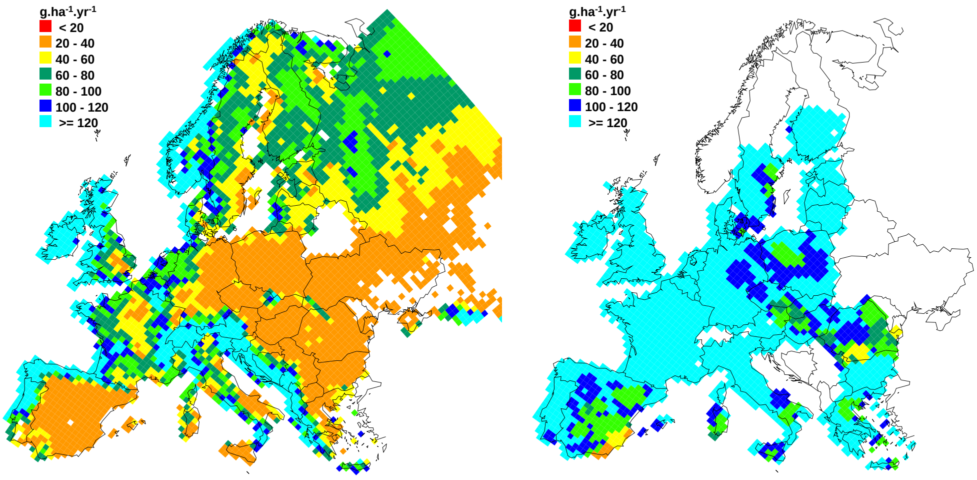
Figure 4 Critical loads for Zinc

For zinc, only critical loads related to protection of ecosystem functioning were computed as no WMO drinking water standard is available for zinc. For the Netherlands a limit of 3000 mg.l^{-1} is used for drinking water, but, as with copper, this would lead to critical loads of several kg.ha^{-1}.yr^{-1} and no exceedance by atmospheric deposition is likely to occur.

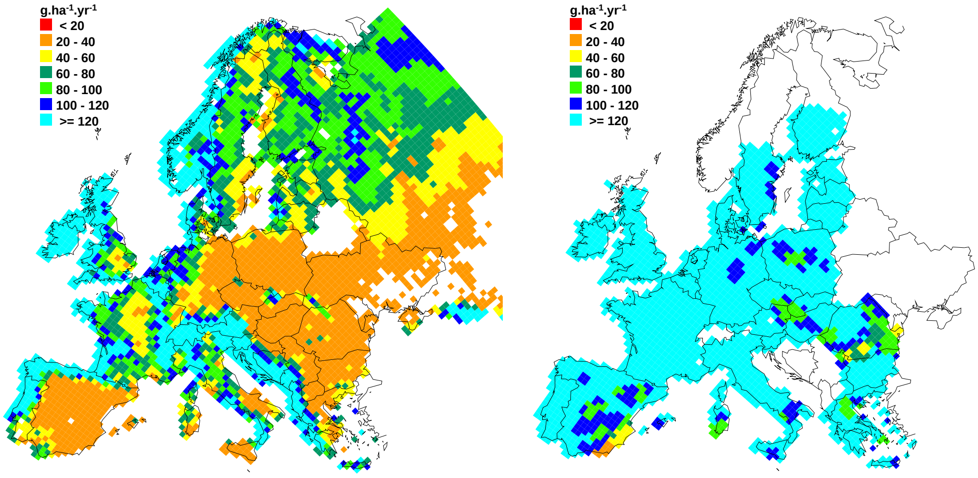
Critical loads related to ecosystem functioning, range from 70 – 400 g.ha^{-1}.yr^{-1}. Critical concentrations were computed as a function of DOC and pH and vary between 20 and 90 mg.l^{-1}. For the lowest critical loads (< 80 g.ha^{-1}.yr^{-1} coinciding with areas with low leaching rates), about half of the critical load consist of leaching an the other half of uptake, so that apart from the spatial pattern in the leaching flux, also the patterns in forest growth and crop yield are reflected in the critical load pattern. Since these patterns are to some extend correlated, they cannot be easily distinguished on the map, except for the transitions between France and Spain and Germany and Poland for agricultural critical loads.

4.5 Chromium

Figure 5 provides the 5 percentile critical loads for Chromium per EMEP 50×50 km grid cell.



(A) CL(Cr), Forest, Ecosystem *(B) CL(Cr), Agriculture, Ecosystem*



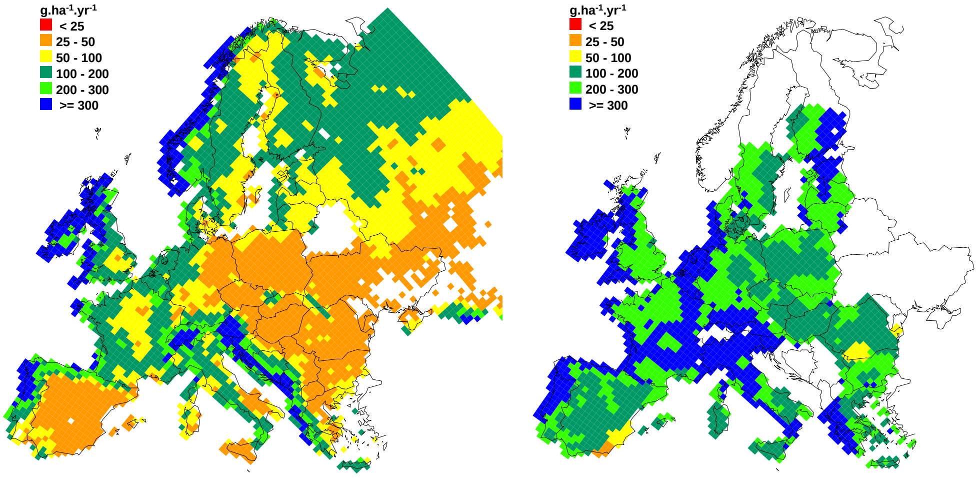
(C) CL(Cr), Forest, Drinking Water *(D) CL(Cr), Agriculture, Drinking Water*

Figure 5 Critical loads for Chromium

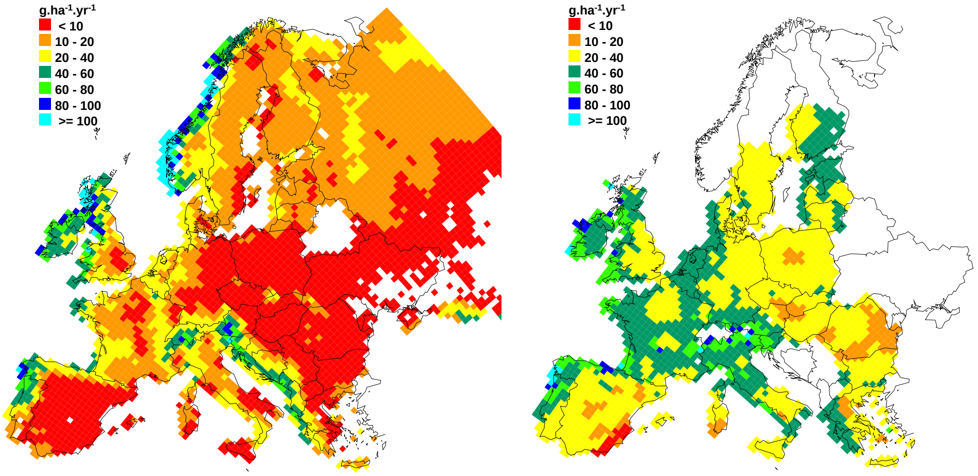
Critical loads for chromium related to ecotocicological effects, were computed using a fixed critical concentration of 44 mg.m^{-3}. Because this critical concentration is almost identical to the drinking water standard of 50 mg.m^{-3}, critical loads and the patterns therein are very similar for the two effects. This can be clearly seen in Figure 5 (compare (A and C) and (B and D)). Critical loads for forests range from about 20 g.ha^{-1}.yr^{-1} in dry areas to about 150 g.ha^{-1}.yr^{-1} in areas with high leaching. Patterns of critical loads follow the patterns of leaching, as uptake contributes less than 2.5% to the total critical load. The critical load for Cr is thus about equal to a fixed concentration × the leaching flux for all effects and receptors. Critical loads for agriculture range from about 80 g.ha^{-1}.yr^{-1} in dry areas to about 300 g.ha^{-1}.yr^{-1} in areas with high leaching. They exceed the critical loads for forests because of the higher leaching fluxes in agricultural land.

4.6 Arsenic

Figure 6 shows the 5 percentile critical loads for Arsenic for each EMEP 50×50 km cell.



(A) CL(As), Forest, Ecosystem *(B) CL(As), Agriculture, Ecosystem*



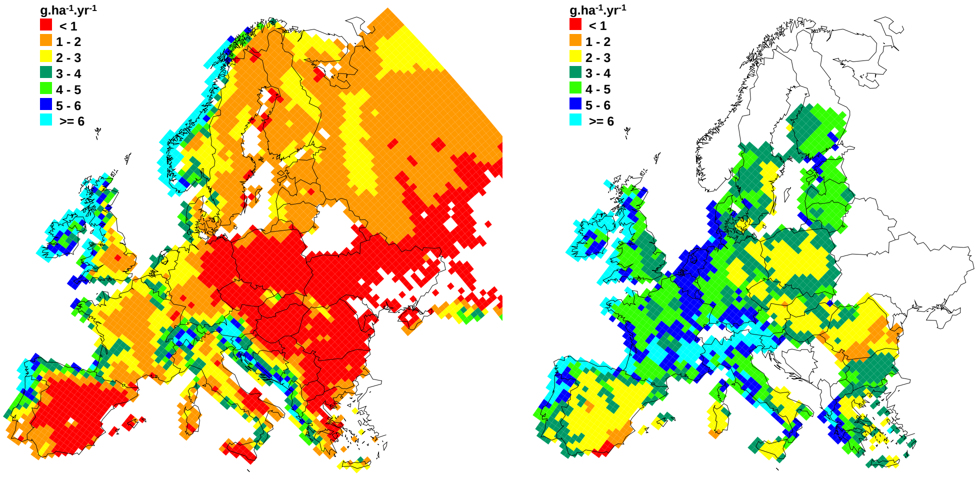
(C) CL(As), Forest, Drinking Water *(D) CL(As), Agriculture, Drinking Water*

Figure 6 Critical loads for Arsenic

Because a fixed critical concentration was used to compute critical loads for ecosystem protection, the critical load patters follow, as with chromium, the patterns of the precipitation surplus: high critical loads are found in areas with a high precipitation surplus, low critical loads are found in areas with low rainfall. The critical concentration for ecotoxilogical effects was set at 70 $mg.m^{-3}$ which is much higher than the drinking water standard of 10 mg.m^{-3} used to compute critical loads related to human health effects shown in Figure 6 (A,B). As a consequence, critical loads for arsenic related to ecotoxilogical effects are much higher than those for human health effects (compare maps (A and B) to (C and D)): critical loads for ecotoxicology vary between 40 – 400 g.ha^{-1}.yr^{-1} and between 5 - 70 g.ha^{-1}.yr^{-1} for drinking water. Because the arsenic contents in crops and trees are very low (0.1 and 0.02 mg.kg^{-1} respectively), uptake does hardly contributes to the critical load: less than 2% for critical loads for agriculture and less than 0.4% for forests.

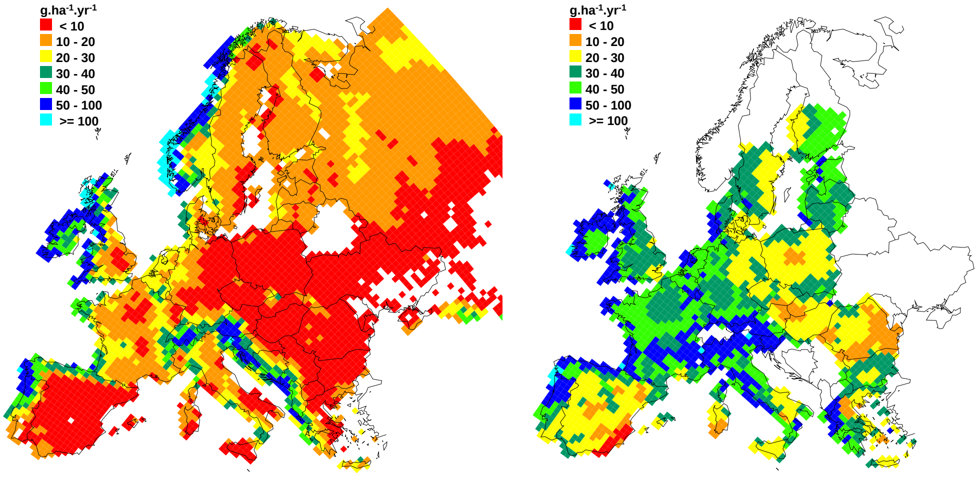
4.7 Selenium

Figure 7 shows the 5 percentile critical loads for Selenium for each EMEP 50×50 km cell.



(A) CL(Se), Forest, Ecosystem

(B) CL(Se), Agriculture, Ecosystem



(C) CL(Se), Forest, Drinking Water

(D) CL(Se), Agriculture, Drinking Water

Figure 7 Critical loads for Selenium

For selenium a critical concentration related to ecosystem protection of 1 $mg.m^{-3}$ was used. For drinking water, the critical concentration was ten times higher: 10 $mg.m^{-3}$. This is directly reflected in the critical loads: critical loads for drinking water range from 5 – 70 $g.ha^{-1}.yr^{-1}$ whereas critical loads for ecosystem protection range from 0.8 - 6 $g.ha^{-1}.yr^{-1}$. As with the other metals, patterns in critical loads follow the patterns in precipitation excess. Uptake of selenium is generally low; only with the lowest ecotoxicological critical loads, uptake accounts for about 30% of the critical load.

Summary of results

Table 4 summarizes the critical loads computed for forests and agricultural soils, related to ecotoxilogical effects and based on drinking water standards. The ranges of critical loads given represent the range between the 5 and 95 percentile. Table 4 shows that for Cu and Se critical loads related to ecotoxilogical effects are lower than those for drinking water protection. For Ni and Cr critical loads are comparable for the two effects, whereas for As critical loads for drinking water are lower than those related to ecotoxilogical effects. Noteworthy is the wide range of critical loads for Ni related to ecotoxilogical effects, due to the strong effect of pH on the critical limit. This effect is most pronounced for forest soils, where the pH range is wider than for agricultural soils.

Table 4 Ranges in critical loads for the various receptors and effects

Critical Loads $g.ha^{-1}.yr^{-1}$				
	Ecotoxilogical effects		Drinking water standards	
	Forests	Agriculture	Forests	Agriculture
metal				
Cu	12-70	15-100	1000-11000	3700-14000
Ni	27-1700	30-770	13-110	39-140
Zn	70-440	190-620		
Cr	24-230	80-300	27-270	95-340
As	35-370	130-480	5-53	19-70
Se	0.8-6	2-7	5-54	19-69

4.8 Example calculations critical limits agriculture.

Because not enough data were available to calculate critical loads related to animal health on a European scale we evaluate the use of critical loads for animal health with some example calculations. We have chosen 3 characteristic soil types for this evaluation i.e. (i) a humic poor sandy soil, (ii) a clay soil and (iii) a peat soil.

Critical loads can be calculated for metals for which there is a critical concentration in food crops related to animal health and for which there is a relation between metal contents in soil and or soil solution and contents in plant.

For As, Cu and Zn there are maximum concentrations for fodder crops for the other metals discussed in this report no such criteria are available. From these metals only for Zn soil plant relations are available. For Zn a relation is available between metal contents in maize (used as fodder) and metal contents in the soil as a function of pH, clay and organic matter content. There are several possible pathways to calculate a critical concentration in solution from a critical metal content in the crop. The first path uses the available plant soil relationship: first a critical content in soil is calculated from the critical content in maize, the pH, the organic matter and clay content of the soil using the plant soil relationship. Then a critical concentration in soil solution is calculated from this soil content using transfer functions for solid solution partitioning of metals again using the pH, organic matter and clay content of the soil. Possible alternatives are to derive direct relations between the metal contents in the plant and the metal concentration in soil solution. In that case a distinction can be made between relations of plant contents with total concentrations in soil solution and relations with the free metal concentration in soil solution. In the last case as a final step total concentrations have to be calculated from the free metal concentrations using WHAM analogue to critical concentrations related to ecological effects.

From the data set which was used to derive the plant soil relationships we derived relationships which relate the plant content to total metal concentrations and free metal concentrations in soil solution directly. First we estimated reactive metal contents from the total metal contents in soil (aqua regia) as reported in the data set using regression relations between reactive metal contents and total metal contents (Römkens et al., 2004). Then total metal concentrations and free metal concentrations in soil solution were calculated from these reactive metal content and soil properties with transferfunctions (Römkens et al., 2004; Groenenberg et al., 2006). For both free metal concentrations and total concentrations we were able to derive plant-soil solution relations with a good explained variance (see Table 5) according to:

$$\text{Log}\,(Me_{plant}) = a + b\,\log\,(Me_{solution}) + c\,pH \qquad (7)$$

With:
Me_{plant} = metal content in crop ($mg.kg^{-1}$ dw)
$Me_{solution}$ = free or total metal concentration in soil solution ($mol.l^{-1}$).

Table 5 Coefficients for the soil plant soil solution relationships (Eq. 7) for Zn in maize

Type of relation	a	b	c	R^2	SE-y
total conc.	3.95	0.59	0.18	0.64	0.14
free metal conc.	4.28	0.58	0.11	0.67	0.13

The relationships for plant contents with soil solution concentrations are of a comparable goodness of fit as the relation for soil plant relationships. Relationships without pH give a clear less good fit (R^2 = 0.3). The effect of pH is most likely due to the lower availability of metals at lower pH, this can bee seen as a competitive effect of other cations for uptake and is analogue to the pH effect in the critical limit functions for ecotoxicological effects (Lofts et al., 2004). Because of the almost similar good fit for relations with total concentrations and relations for free metal concentrations, we used the relation between metal contents and total concentrations in solution because the use of the relation with free metal ions needs an extra calculation step introducing additional error.

Combining the critical metal content of 285 mg.kg^{-1} Zn with equation (8) for total concentrations in solution yields the following equation to calculate the critical concentration in solution:

$$\text{Log}\ (\text{Me}_{\text{solution, crit}}) = -2.51\ -0.30\ \text{pH} \qquad (8)$$

With:

$\text{Me}_{\text{solution,crit}}$ = the total concentration in soil solution (mol.l^{-1}).

The critical load can then be calculated as the sum of the critical leaching flux and the uptake of Zn at the critical concentration. The critical leaching is the critical concentration multiplied with the precipitation excess.

Tabe 6 gives an overview of critical loads of Zn calculated for ecotoxicological effects and animal health according to the methodology described above for 3 major soil types including relevant soil properties. For all soils we used a precipitation excess of 300 mm and a yield of 45 ton maize.ha^{-1}.yr^{-1}.

Table 6 Overview of critical loads of Zn calculated for animal health and ecotox effects ecotox effects

soil type	pH	%OM	%clay	critical leaching g.ha^{-1}.yr^{-1}	uptake g.ha^{-1}.yr^{-1}	CL g.ha-^{1}.yr^{-1}	Critical leaching g.ha-^{1}.yr-^{1}	uptake g.ha-^{1}.yr-^{1}	CL g.ha-^{1}.yr-^{1}
				animal health			ecotox		
sand	5.5	3	3	13576	12825	26401	123	858	981
clay	6.5	3	25	6804	12825	19629	132	1354	1486
peat	6	30	15	9611	12825	22436	351	1960	2311

The calculated critical loads related to animal health for Zn are (far) above the critical loads related to ecotoxicological effects that ranges from 190 – 620 g.ha^{-1}.yr^{-1}, especially for clay and peat soils. The critical limit for Zn in fodder crops of 285 mg.kg^{-1} is rather high. Normal concentrations of Zn in maize range from 28-174 mg.kg^{-1} with a median value of 59 mg.kg^{-1}. The critical leaching calculated for ecotoxicology is very small compared to the uptake at the critical concentration calculated with equation 7. The calculated metal contents in maize range from 19-44 mg.kg^{-1}, with the lowest metal contents in sand, which are below the range measured for maize (Table 1).

5 Conclusions

Because of its intrinsic simplicity, the critical load concept could also be applied to the metals Cu, Zn, Ni, Cr, As and Se. For Cu, Zn and Ni, critical limit functions could be derived that provide critical concentrations of free metal ions related to ecotoxicological effects as a function of pH. Using WHAM critical concentrations of total metal were calculated from these critical limit functions depending on pH and DOC. For the other metals only a fixed total concentration was used, independent of pH and DOC. It is likely however, that for the cationic metals the toxic effects are better related to free metal ions, so critical total concentrations also depends on pH and DOC. For more accurate assessments of critical concentrations, it should be investigated if critical limit functions can be derived for these metals as well. As and Se are present in soil solution as anions. Possibly other factors play a role in the toxicity of these elements than for the cationic metals. Phosphate maybe important in the chemistry and toxicity of As because of the similar chemistry. It is recommended that the chemistry and toxicity of anionic species is further investigated. For Ni there is a very strong pH effect on the critical concentrations (e.g. the critical concentration at pH 3.5 is 5 times higher than at pH 4.3 at the same DOC level), which means that the estimated soil pH is of importance. Because pH was related to soil type and texture alone, local pH may deviate from this average and critical loads for Ni at local scale may thus not be represented well.

Results show that for most metals and receptors investigated, leaching is the dominant term in the critical load. As a consequence, both the critical metal concentration and the leaching flux are important parameters. Leaching was estimated from detailed rainfall data and modelled water consumption using a simple water balance model. Modelled leaching fluxes are uncertain, as no calibration or validation of the model has been carried out at the European scale. However, it has been shown that even such simple models can perform rather well when looking at the plausibility of the simulated leaching using chloride budgets at Intensive Monitoring plots (De Vries et al., 2003).

This study showed that critical loads for forests are normally lower than for agricultural soils because of lower leaching fluxes and lower metal uptake. The leaching flux for annual crops is somewhat underestimated as soil evaporation from base soil outside the growing season was not accounted for. Metal uptake forms a significant part of the critical load for the nutrients Zn and Cu only. For these metals, crop yields and forest growth data are of importance as well. Forest growth was available at reasonable level of detail, but crop yield only at country level. Existing within-country differences in crop yield and thus in associated metal uptake, are therefore not reflected in the results. Differences in uptake between forests and annual crops stem from differences in yield as well as differences in estimated metal contents. The latter parameter, however, is rather uncertain as expressed by the wide ranges in metal contents provided in chapter 2. More insight in metal contents in crops and stemwood in relatively unpolluted areas could improve uptake estimates.

Most of the uncertainty in the critical loads for ecosystem protection stems from the uncertainty in the critical concentrations used. Especially for Cr, As en Se, critical concentrations stem from very few sources and are therefore highly uncertain. For more robust assessments of critical metal loads for ecosystem protection, a thorough review of existing ecotoxicological data for these elements is needed.

Chromium in soils is likely to be present as Cr(III)-hydroxides or in precipitates of Fe-hydroxides or adsorbed to organic matter. Data on chromium solubility in non contaminated soils in the Netherlands show a clear correlation between the concentration of the free chromium ion and the pH, a relation of chromium in solution with reactive chromium in the soil solid phase was absent (Groenenberg, unpublished results). These data substantiate the presence of chromium as a precipitate. If present as a hydroxide there will not be a direct relation between the amount of Cr in soil and Cr in soil solution. The concentration in soil solution is determined by the solubility product of the hydroxide and hence there will also not be a steady state concentration related to the input flux of Cr to soil. This is in contradiction with the steady state assumption of the critical load approach which means that if Cr concentrations in soil solution are regulated by the solubility of a chromium precipitate, the current critical load concept does not apply for Cr.

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Appendix 1 Element contents in biomass

Element content in harvestable plant parts $[M]_{ha}$ *(mg.kg*$^{-1}$ *dw)*

metal	crop	min	max	median	remark	ref
As	wheat	0.01	0.34	0.05		1
As	maize	0.06	0.47	0.15		1
As	grass	0.07	1.11	0.21		1
Cu	wheat	3.8	6.17	5.15		2
Cu	maize	1.9	7	4.0		2
Cu	grass	6.4	21.5	12.2		2
Zn	wheat	33	94	50		2
Zn	maize	28	174	59		2
Zn	grass	38	176	71		2
As	Spruce	0.04	0.13	-	3 samples contaminated soil, contents wet weight basis	3
As	Spruce	0.002	0.02	0.011		5
As	Scots pine	0.4	31	-	Contaminated soils	4
Se	rye grass	0.06	0.4	0.08	field	5
Se	wheat					
Ni	Rye grass	-	-	50	lowest concentration pot experiment	5
Ni	Corn	-	-	0.7	Field experiment	6
Ni	Grass	0.1	4.3	0.99	Field (peat soils)	7
Ni	Dactylis Glomerata	-	-	0.4	Field soil in pot	5
Cr	Grass	0.12	4.2	0.8	Field (peat soils)	7
Ni						
Cr						

1 Wiersma, et al. (1986)
2 Van Driel et al. (1987)
3 Haug et al. (2004)
4 Anonymous
5 Bechtel Jacobs company LLC (1998)
6 Granato et al. (2004).
7 Groenenberg et al. (2003)