

Critical limits for cadmium, lead and mercury related to ecotoxicological effects on soil organisms, aquatic organisms, plants, animals and humans

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1 Introduction

Available methodologies to derive critical loads and critical limits

In 2001, a “Guidance for the calculation of critical loads for cadmium and lead in terrestrial and aquatic ecosystems” was published describing the methodologies to calculate critical loads of cadmium (Cd) and lead (Pb) for terrestrial and aquatic ecosystems (De Vries et al., 2001). This was done to respond to the first official call (on voluntary basis) for data concerning critical loads for those metals by the CCE. This guidance document was based on:

- Two manuals, presenting guidelines for calculation methods, critical limits and input data for the calculation of critical loads of heavy metals for terrestrial ecosystems (De Vries and Bakker, 1998) and aquatic ecosystems (De Vries et al., 1998).
- A recommended set of critical limits and of transfer functions, describing the interaction of metals between the soil solid phase and the soil solution, and described in De Vries et al. (2002).

The recommended set of critical limits and of transfer functions was based on the results of two international expert groups on those topics, which were initiated at the 17th Task Force on ICP Modelling and Mapping in 2001. The report “Proposed harmonised critical limits and transfer functions for the calculation of critical loads for lead and cadmium (De Vries et al., 2002) includes the results of the first phase of work of the two experts groups. It was at the same time the scientific basis for critical limits and transfer functions, which were recommended in the guidance document for use in mapping exercises for calculating critical loads (De Vries et al., 2001). Here we report on further research related to critical limits. More detailed and updated information on transfer functions is provided by Römken et al. (2003) and in a background document by Groenenberg et al. (2003).

Approach of the expert group on critical limits

The expert group on critical limits was asked to provide a set of recommended critical limits, based on a harmonised approach, which is crucial for a harmonised critical load approach. The expert group was also asked to include and review critical limits provided at former international workshops on heavy metals in Bad Harzburg 1997 (Gregor et al., 1997) and in Schwerin 1999 (Gregor et al., 1999) and specifically the meeting of the Ad-hoc International Expert Group on Effects-based Critical limits for Heavy Metals in Bratislava 2000 (Curlík et al., 2000).

The expert group on critical limits started its work in a first phase (June 2001 - Nov 2001) with the prior aim to provide the NFCs of ICP Mapping and Modelling and the CCE with a harmonised set of critical limits to be used in a first call for data on critical Loads of Cd and Pb in 2001/2002. For that period it was agreed to focus the discussion and derivation of critical limits on:

- The metals cadmium (Cd) and lead (Pb).

- Direct ecotoxicological impacts on soil organisms and plants in terrestrial ecosystems (Results for aquatic ecosystems were taken from the literature).
- Mineral soils.

The harmonised approach that was chosen to derive critical limits was the methodology that has been recommended in the frame of EU and OECD risk assessment studies, which has also been included in the two manuals mentioned above. The results of working phase 1 were reported in an internal UN-ECE working paper (De Vries et al., 2002) including suggested critical limits with a preliminary status.

Next to direct effects on soil organisms, heavy metals may cause indirect effects through bioaccumulation, which stands for the phenomenon that a chemical accumulates in species through different trophic levels in a food chain (secondary poisoning). This may cause toxic effects on: (i) humans by affecting food quality of crops and animal products and (ii) animal health through the accumulation in target organs of cattle, birds and mammals (secondary poisoning). Impacts of metals on human health (specifically by effects on food quality of crops and animal products) were not considered in the first phase. In the second phase (Jan 2002 - Nov 2002), the expert group extended its focus by including:

- New findings with respect to organic soils/Organic layers as far as available.
- Methods to derive critical limits for mercury (Hg) and results obtained.
- Impacts of metal accumulation on human health, in co-operation with the UN/ECE Joint Task Force on Health, and the health of crops and animals.

Furthermore, agreements and assumptions related to the critical limits methodologies adopted in the first phase are further discussed.

Agreements and assumptions related to critical limits methodologies

The following agreements and assumptions were made within the first phase that also holds for the work carried out in the second phase by the expert group:

- The methods for derivation of critical limits (Cd, Pb, and Hg) should be in line with the EU/OECD methodologies.
- HC₅ values (protecting 95 % of the population, with a confidence level of 50 %) derived from statistical analysis of effects data (plants, microbiological processes, invertebrates) are recommended to be the scientific basis of critical limits for both soil and soil solution.
- The major route of exposure on plants and micro-organisms is pore water (apart from rock-eating fungi and mycorrhizae), while for hard bodied invertebrates the adsorbed (“reactive”) content is most important, due to exposure through ingestion. Following this assumption, critical limits for heavy metals in soil solution and for the reactive heavy metal content can preliminary be considered without further distinction to soil type and soil properties.
- The effect data from laboratory investigations can best be related to reactive metal content. The comparability of extraction methods, used in different countries to describe the reactive pool, should however be provided.

A critical evaluation of those assumptions is given in Section 6.

Aim and contents of this background document

This background document includes the results obtained in the second phase (Jan 2002 - Nov 2002) of the expert group, including (i) available results of ecotoxicological research on direct impacts on soil organisms and plants for Cd and Pb distinguishing between mineral soils and organic layers, (ii) critical limits for Hg for both mineral soils and organic layers and (iii) impacts of metals on human health and on animal health due to potential accumulation in the food chain, with a focus on food quality aspects.

First the receptors and related critical limits that are considered relevant are described (Section 2). Section 3 focuses on critical limits related to direct ecotoxicological effects on soil organisms and plants. This includes: (i) an overview of main methodological aspects, (ii) a summary of critical limits for Cd and Pb suggested in the first call for data and (iii) a preliminary overview of possible critical limits for Hg. The effects of bioaccumulation have been considered in deriving critical limits for soil, by the use of food chain models. Methods and results thus obtained in view of human health effects are described in Section 4, while distinguishing between (i) impacts on food quality of crops and (ii) impacts on food quality of animal products, concentrated on grazing cows and sheep. Section 5 focuses on critical limits related to impacts on animal health, while distinguishing between (i) simple food chain models on birds and mammals feeding on worms and/or plants and (ii) elaborated food chain models including birds and mammals of prey. The document ends with a critical evaluation of the assumptions related to the derivation and use of the critical limits and recommendations (Section 6).

2 Relevant receptors and related critical limits

2.1 Relevant receptors

With respect to risks on terrestrial and aquatic ecosystems, a major distinction can be made in risks/effects on (i) the ecosystem (direct ecotoxicological risks), (ii) animal health (indirect ecotoxicological risks) and (iii) on humans that use ground water for drinking water or that consume crops, meat or fish (human toxicological risks). An overview of the pathways of metals in terrestrial and aquatic ecosystems and the pathways considered in this background document, in view of (i) direct impacts on the terrestrial or aquatic ecosystem and (ii) indirect impacts on human health or animal health, are summarised in Figure 1.

The receptors that are considered in this background document in terrestrial ecosystems, distinguishing arable land, grassland and non-agricultural land, and in aquatic ecosystems are presented in Table 1. Possible effects on soil life 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 cattle are relevant in grassland and non-agricultural land. A final critical limit can be based on the most sensitive receptor.

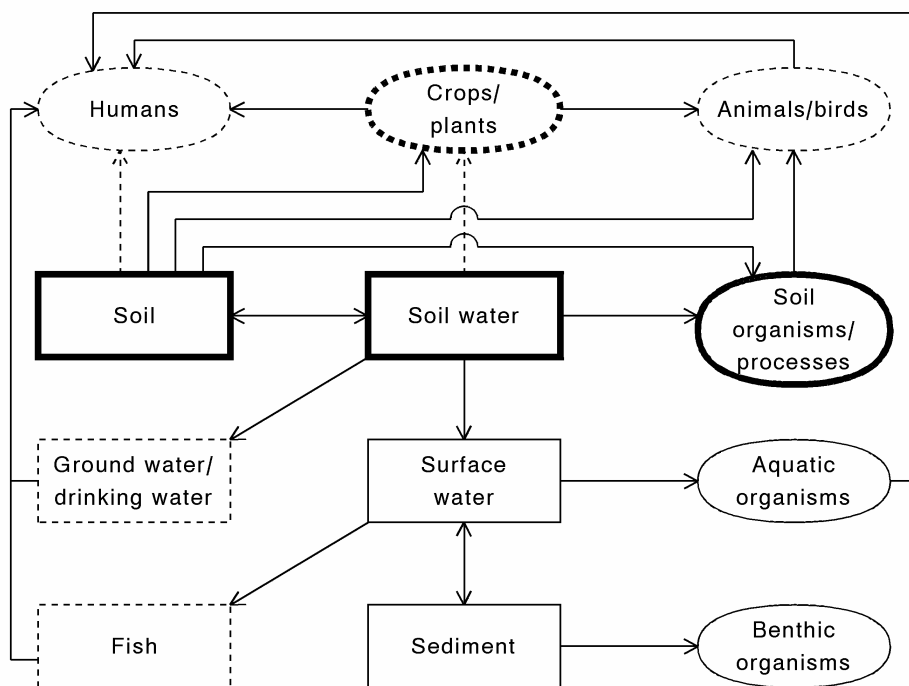


Figure 1 Overview of the relationships and fluxes of metals from the soil to other compartments. Compartments in black are related to direct impacts on the terrestrial ecosystem, normal compartments relate to direct impacts on the aquatic ecosystem and dotted compartments refer to indirect impacts on human health or animal health due to accumulation in the food chain.

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

Receptors of concern	Type of ecosystem			
	Arable land	Grassland	Non-agricultural land	Surface waters
<i>Ecosystem (direct effects)</i>				
- Soil micro-organisms	(+)	(+)	+	-
- Soil invertebrates	(+)	(+)	+	-
- Wild plants	-	-	+	-
- Algae, crustacea	-	-	-	+
<i>Human health/animal health (indirect effects)</i>				
<u>Plants</u>				
- Food crops (humans)	+	-	-	-
- Fodder crops (animals)	+	+	-	-
<u>Ground water</u> ¹ (humans)	+	+	+	-
<u>Animals</u>				
- Cattle (humans)	-	+	+	-
- Birds/Mammals	+	+	+	-
- Fish (humans)	-	-	-	+

¹ This refers specifically to ground water used as drinking water

Critical limits for soil are limited to direct ecotoxicological effects on soil organisms and plants and indirect effects on food crops, terrestrial fauna and humans (see Section 2.2). The effect on humans is assumed to be accounted for by food quality criteria for metals in food crops, animal products (cows/sheep), fish and drinking water (ground water) consumed by them (see Section 2.3).

2.2 Ecotoxicological and human toxicological effects

Ecotoxicological effects

With respect to Cd, Pb and Hg, no biological function is known. Specifically Cd and Hg and to a lesser extent Pb are thus toxic to various living organisms in a terrestrial ecosystem if certain concentration levels are exceeded. In order to judge the ecotoxicological risks associated with elevated heavy metal contents on terrestrial ecosystems, a further distinction should be made in the following receptors (Tyler, 1992):

- Soil organisms, including micro-organisms/macrofungi and soil fauna, especially invertebrates such as nematodes and earthworms. Effects on micro-organisms include reduced microbial biomass and/or species diversity, thus affecting c. Effects on soil fauna include a decrease in abundance, diversity and biomass. A review of these effects is given by Bengtsson and Tranvik (1989).
- Vascular plants including agricultural crops and trees. Effects include reduced development and growth of roots and shoots (toxicity symptoms), elevated concentrations of starch and total sugar and decreased nutrient contents in foliar tissues (physiological symptoms) and decreased enzymatic activity (biochemical symptoms). A review of these phytotoxic effects is given by Balsberg-Påhlsson (1989)
- Terrestrial fauna, such as birds and mammals, and cattle in agricultural soils. Effects are heavy metal accumulation, followed by possible effects to essential organs. Those effects are specifically considered important with respect to Cd and Hg, since these metals can accumulate in the food chain.

Health effects

The possible health effects of exposure to cadmium, lead and mercury have been investigated for many years both for humans and for animals. Results of these studies have been summarized in several reports published by international organizations e.g. the World Health Organization, International Agency for Research on Cancer, or governmental agencies like U.S. Department of Health and Human Services or Centers for Disease Control.

Cadmium: The kidney, and to a lesser extent the lungs, are the critical organs in a long-term occupational or environmental exposure to cadmium. Cd affects the functioning of kidneys and bones and may cause cancer (Jakubowski, 2003). Järup (1998) mentions reports of a higher prevalence of kidney stones among cadmium-exposed workers. Painful bone disorders, including spontaneous bone fracture, have been observed in humans chronically exposed to cadmium in food (IPCS, 1992). In its latest evaluation of the carcinogenic risk from cadmium exposure (IARC, 1993), concluded that there was sufficient evidence to classify cadmium and cadmium compounds as human carcinogens. This assessment was, to a great extent, dependent on the significant relations between the risk of lung cancer and estimated cumulative exposure to cadmium reported by Thun et al. (1985) and Stayner et al. (1992) in their analyses of mortality among a cohort of workers from a single cadmium recovery plant in the United States. The existing evidence is inadequate to evaluate an association between inhalation exposure to cadmium and reproductive effects

(Jakubowski, 2003). The half-life time of cadmium in human tissue is long due to the near incapability of the body to excrete the metal. In the liver it is 7 years, in the kidney it is approximately 15 years, in muscle tissue and the brain probably more than 30 years. In bone it could probably be more than 100 years (Kjellström and Nordberg., 1978)

Lead: Pb may cause hematological and neurological effects, reproductive and developmental effects, hypertension and cancer (Jakubowski, 2003). Anemia is one of the most characteristic symptoms of high and prolonged exposures to lead, resulting from the damaging effects of lead on the formation and functioning of red blood cells. One of the major targets of lead toxicity in adults is the nervous system, including the central and peripheral nervous systems. A special concern for pregnant women is that some of the lead accumulated in bone is released into the blood during pregnancy. Several studies conducted concurrently in the United States and other countries provided evidence that even low maternal exposures to Pb may lead to intellectual and behavioral deficits in children. Furthermore, in males exposures to lead may cause decreased sperm count and abnormal sperm morphology. Chronic high exposures to lead that existed earlier in this century were associated with an increased incidence of hypertension. The International Agency for Research on Cancer (IARC) has further designated lead and inorganic lead compounds as possibly carcinogenic to humans. The biological half-time of lead in blood can be as short as 20-40 days (isotopic tracer data), although longer half-time values have been reported in lead workers, and these may depend on the lead body burden. The half-time of elimination from bones amounts to about 5-10 years (IPCS, 1995).

Mercury The first reports of occupational mercury poisoning was from Attic silver smelting using liquid mercury and later from general use of mercury in industrial colours, leather preparation, experiments in alchemy, gold and silver craft work and medicine. Mercury is very toxic and can cause severe neurological disorders and immune-deficiencies even at very low levels of long term exposure. Several epidemiologic studies in occupational settings were performed between 1989 and 1993. The study populations included chloralkali workers exposed to mercury vapour (Piikivi, 1989; Piikivi and Hanninen, 1989), dentists (Ngim et al., 1992), and workers in a fluorescent lamp factory (Liang et al., 1993). Numerous effects of exposure to mercury on the central nervous system were identified. Symptoms included sleep disorders, fatigue, hand tremor and increased memory impairments. The metal has a half-life time of 2-3 months in the blood, 5-10 months in the liver and kidneys and 0.5-2 years in the brain.

2.3 Related critical limits

Type of limits

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 direct effects on soil organisms (micro-organisms and soil invertebrates) and plants (mg.kg⁻¹).

- Plants/terrestrial fauna: critical limits in plant tissue, animal products (meat) or target organs, such as kidney, related to direct effects on plants and/or animals and indirect effects on humans by consumption (food quality criteria) ($\text{mg}\cdot\text{kg}^{-1}$).
- Ground water: critical limits in drinking water related to indirect 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.

The aim of this background document is to present or derive critical limits for soil, soil solution, ground water or surface water, to be used in critical load models, distinguishing between:

- Soil and soil solution related to direct effects on soil organisms and plants
- Soil and ground water (drinking water) related to indirect effects on terrestrial fauna and/or humans.
- Surface water related to direct effects on aquatic organisms and indirect effects on human health.

Critical limits related to human-toxicological effects

Critical limits for soil related to human-toxicological effects can be derived from critical limits for humans (ADI values) with an integrated model in which all relevant exposure pathways have been included. An example of such a model is CSOIL (Van den Berg and Roels, 1991; Rikken Lijzen et al., 2001), which derives a critical limit for soil from a given ADI value. This model includes many exposure routes to humans, such as intake by crops, meat, drinking water, air and direct soil ingestion. Application of the CSOIL model for a standard soil (Lijzen et al., 2001) showed that critical limits for the soil based on human toxicological effects are generally much higher than those related to ecotoxicological effects. The derivation of a critical soil limit related to an ADI depends strongly on many assumptions regarding the intake of food. In this background document, it is therefore assumed that critical soil limits related to human-toxicological effects are adequately covered by back calculating food and drinking water quality criteria. In chapter 4, focusing on impacts on humans, information is included how data on acceptable daily intakes are back calculated to food and drinking water quality criteria.

In deriving critical limits for the soil or soil solution and of surface water related to ecosystem effects, use has been made of direct effects data for soil organisms or processes and plants and of aquatic organisms, respectively (Chapter 3). In deriving critical soil limits related to human health (Chapter 4) and animal health (Chapter 5) effects, use has been made of quality criteria or target values in crops and terrestrial fauna, which have been back calculated to the soil using soil-plant, soil-invertebrate, plant-animal and invertebrate-animal relations, as discussed in detail in those chapters.

3 Critical limits related to direct ecotoxicological effects on terrestrial and aquatic organisms

There are two possible types of critical limits for soil and for surface water:

- A critical reactive metal concentration in the solid phase (soil or sediment)
- A critical dissolved metal concentration (soil solution or surface water)

The standard approach is the derivation of critical reactive metal concentration in the soil and critical dissolved metal concentration in surface water based on NOEC toxicity data for terrestrial or aquatic species. For both soils and surface waters, the use of critical dissolved metal concentrations is most adequate in view of deriving critical loads, but this requires NOEC data for soil solution that are either directly based on measurements or derived from NOEC soil data.

In this chapter we first describe the methodological approaches to derive critical soil and surface water limits from laboratory data and the possibility to derive critical soil solution limits including the limitations of the approaches (Section 3.1). We then present critical limits for reactive metal concentrations in soil and dissolved metal concentrations in soil solution and surface water (Section 3.2). Finally, a proposal is made for the critical limits for Cd, Pb and Hg to be used in soils, soil solution and surface water, based on those results (Section 3.3).

3.1 Methodological approach

Below we describe the:

- Approach that was used to derive critical soil limits from NOEC data, focusing on a statistical extrapolation method
- Approach that was used to derive critical soil solution limits from NOEC soil data, using transfer functions relating dissolved and solid phase metal concentrations, while accounting for the impact of soil properties.
- Limitations of both approaches

3.1.1 The methodology to derive critical limits for soil and surface water

Relevant toxicity data

An international framework, in which much work has been done on the subject of critical limits, is the Organisation for Economic Co-operation and Development (OECD). Within this framework a methodology has been developed for the calculation of Maximum Permissible Concentrations (MPC's) or critical limits of substances in the soil (OECD, 1989) and the aquatic environment (OECD, 1992). In this context, a distinction is made in acute toxicity data based on short-term ecotoxicological experiments (< 1 day) and chronic toxicity data, based on long-term ecotoxicological experiments (1 day - 1 month). Acute toxicity is defined by the EC₅₀ or LC₅₀ value which is equal to the concentration at which 50% of the considered organism is either affected (EC₅₀ with EC = effect concentration) or even dead (LC₅₀

with LC = lethal concentration). Chronic toxicity is defined by No Observed Effect Concentrations (NOEC's), sometimes referred to as No Observed Effect Levels (NOEL's), of several species in an ecosystem. From a range of NOEC data an HC_p can be derived, being the hazardous concentration at which p% of the species in an ecosystem is potentially affected, or 100-p % is protected.

Organisms considered in the effect assessments

Derivation of critical limits related to direct ecotoxicological effects requires the use of test results from major organisms that represent different and significant ecological functions in the ecosystem, including:

- Decomposers, comprising micro-organisms that play an important role in food webs and in mineralisation of organic matter, allowing nutrient cycling in the ecosystem.
- Consumers, such as invertebrates, that play a significant role in creating and maintaining a good soil structure.
- Primary producers, specifically plants, which provide food for all other heterotrophic organisms.

The protection of the soil community requires protection of all these organisms playing a leading role in the structure and the functioning of the ecosystem. Consequently, the organisms or taxonomic groups that are considered in deriving L(E)C₅₀ or NOEC data for terrestrial ecosystems are micro-organisms or microbe-mediated soil processes (e. g. enzymatic activity), invertebrates (earthworms and arthropods) and plants.

The organisms or taxonomic groups that are considered in deriving L(E)C₅₀ or NOEC data for surface water include algae, crustacea and fish.

Calculation of critical limits using statistical extrapolation techniques

If only (i) acute toxicity data or (ii) chronic toxicity data for less than the above mentioned taxonomic groups are available, a method is applied, in which the MPC is derived from those data while using arbitrary safety factors varying from 10 to 1000 (OECD, 1992). If chronic NOEC's for all the above mentioned different taxonomic groups in the considered compartment are available, which is generally the case for Cd, Pb and Hg in soil and surface water, the MPC is derived from an HC_5 , being the Hazardous Concentration for 5% of the species, assuming a log-logistic or log-normal distribution. In this context, a statistical extrapolation method according to Aldenberg and Slob (1991; 1993) is used to derive a critical limit.

Statistical extrapolation methods are based on the assumption that the “species sensitivities distribution” (SSD) in natural ecosystems approximates a postulated statistical frequency distribution. Different distributions like e.g. log logistic, log normal or others could be used (Aldenberg and Slob, 1993; Aldenberg and Jaworska, 2000). The log-normal or log-logistic distribution is a pragmatic choice because of its mathematical properties. From the estimated distribution, a concentration can be derived which is assumed to protect a predefined number of species in the ecosystem. The method of Aldenberg and Slob (1991; 1993), that assumes a log-

logistic distribution of the available NOEC toxicity data, is most well known in this context.

A concentration of a certain compound is 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 MPC (MPC =HC₅). Pragmatically, it has thus been decided that the 5% of the SSD using a 50% confidence (this means that there is 50% chance that the true value is below this estimated value and 50% chance that it is above it) equals the MPC or critical limit. The confidence interval of this value should also be estimated

A log-logistic distribution implies that the fraction (or percentage) of unprotected (or potentially affected) species (denoted as the percentage unprotected species, p, or the potentially affected fraction, PAF), can be approximated from the logarithmic concentration value of a certain heavy metal. The latter concentration is denoted as HC_p, being the Hazardous Concentration for p% of the species. The relation between HC_p and p can be described according to (Aldenberg and Slob, 1991) as:

$$\log HC_p = \mu - \beta \cdot \ln\left(\frac{100-p}{p}\right) \quad (1)$$

where:

- p = percentage of unprotected or potentially affected species at a given logarithmic concentration value of a certain compound.
- u = mean value of the log-logistic distribution (the value where p = 50%).
- β = scale parameter, which determines the width or shape of the log-logistic distribution.

As an example, Fig. 2 presents NOEC data for Pb and Cd from four taxonomic groups (micro-organisms, microbe-mediated processes such as mineralisation, nitrification and respiration, earthworms and plants) with a fitted log-logistic distribution. The data are based on Klepper and Van de Meent (1997), which in turn based their data on various literature compilations. Results of the fits were very good with an adjusted coefficient of variation of the fit varying between 0.97 and 0.99.

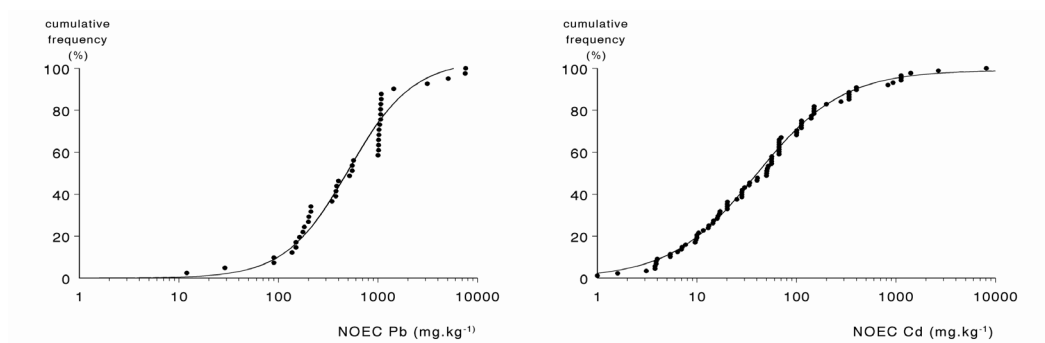


Figure 2 Fitted log-logistic distribution functions through NOEC data for Cd and Pb in soil.

3.1.2 The methodology used to derive critical soil solution limits

General approach

Apart from using NOEC data for Cd and Pb in soil solution, critical soil solution limits can also be based on literature information on NOEC soil data of organisms that are affected through the soil solution (plants and micro-organisms). This can be done by the application of transfer functions, relating dissolved and solid phase metal concentrations while accounting for the impact of soil properties, on the NOEC solid phase data. This requires the availability of data on those soil properties (at least pH and organic matter content and preferably also clay content) in laboratory experiments. Data sets including both NOEC soil data and soil properties thus allow calculation of NOEC soil solution data that can again be evaluated by a statistical approach deriving limits based on a 95% protection level, as described in Section 3.1.1.

Use of transfer functions to derive critical limits for total and free metal ion

There are various transfer functions to calculate dissolved metal concentrations from solid phase metal contents. A summary of those functions is given below. More information is given in Groenenberg et al. (2003).

Most straightforward is a direct approach relating dissolved to solid phase metal concentrations, while accounting for the impact of soil properties, according to:

$$\log[C_{Me}] = a + b \cdot \log[\text{SOM}] + c \cdot \log[\text{clay}] + d \cdot \text{pH} + e \cdot \log[\text{DOC}] + m \cdot \log[Q_{Me}] \quad (2)$$

and in the case of activities as:

$$\log(a_{Me}) = a + b \cdot \log[\text{SOM}] + c \cdot \log[\text{clay}] + d \cdot \text{pH} + m \cdot \log[Q_{Me}] \quad (3)$$

where:

C_{Me}	= dissolved metal concentration in soil solution (here in mol. m ⁻³)
a_{Me}	= free metal ion activity in soil solution (here in mol. m ⁻³)
Q_{Me}	= reactive metal concentration in soil (here in mol.kg ⁻¹)
DOC	= dissolved organic carbon concentration in soil (g.m ⁻³)
SOM	= soil organic matter content (weight %)
Clay	= clay matter content (weight %)

The principle of expressing the critical limit as the free ion concentration is that this form of metal is believed to be available for interactions with organisms (Lanno et al., 1999). Most recent results of regression coefficients thus obtained for the concentration – reactive metal content relationship (Eq. 2) and the activity– reactive metal content relationship (Eq. 3) are given in Table 2 and 3, respectively. More information is given in Groenenberg et al. (2003).

Table 2 Values for the regression coefficients for the concentration – reactive metal content relationship (Eq.2) and statistical measures R² and se(Y) based on results of studies carried out in the Netherlands and the UK (after Groenenberg et al., 2003).

Metal	Datasets	A	<i>b</i>	<i>C</i>	<i>D</i>	E	<i>m</i>	se(Y)	R ²
			(SOM)	(clay)	(pH)	(DOC)	(Q _{Me})		
Cd	Dutch	1.91	-0.73	-0.48	-0.39	0.08	1.27	0.53	0.67
	Dutch	2.05	-0.69	-0.48	-0.40	-	1.26	0.54	0.67
Pb	Dutch	*	-0.75	-0.33	-0.21	0.33	0.72	0.63	0.50
	Dutch	-2.49	-0.54	-0.30	-0.26	-	0.70	0.65	0.48
Cd	UK	-2.65	-0.61	-	-0.20	0.28	0.78	-	0.55
Pb	UK	-3.90	-0.47	-	-0.20	0.79	0.89	-	0.81

Table 3 values for the regression coefficients for the activity– reactive metal content relationship (Eq.3) and statistical measures R² and se(Y) based on results of studies carried out in the Netherlands and the UK (after Groenenberg et al., 2003).

Metal	Datasets	a	<i>b</i>	<i>c</i>	<i>d</i>	<i>m</i>	se(Y)	R ²
			(SOM)	(Clay)	(pH)	(Q _{Me})		
Cd	Dutch	2.27	-0.87	-0.42	-0.46	1.31	0.53	0.70
Pb	Dutch	-1.33	-0.90	-0.23	-0.70	0.68	0.62	0.78
Cd	UK	-0.28	-0.69	-	-0.42	0.97	0.36	0.76
Pb	UK	0.90	-0.53	-	-1.14	0.87	0.45	0.95

Groenenberg et al. (2003) also present a direct approach relating the reactive metal content to either the totals dissolved concentration or the free metal ion activity, according to:

$$Q_{Me} = K_{f,C} \cdot C_{Me}^n \text{ or } Q_{Me} = K_{f,a} \cdot a_{Me}^n \quad (4)$$

K_f can thus be calculated according to:

$$K_{f,C} = \frac{Q_{Me}}{C_{Me}^n} \text{ or } K_{f,a} = \frac{Q_{Me}}{a_{Me}^n} \quad (5)$$

where:

K_f = Freundlich coefficient for either a concentration or activity relationship
n = Freundlich exponent (-)

Results for the coefficients relating these Freundlich coefficients and soil properties (organic matter and clay content, pH and DOC concentration) are presented in Groenenberg et al. (2003). Here we used the results of the direct approach to transfer NOEC solid phase data results to soil solution concentrations or free metal ion activities.

3.1.3 Uncertainties in the calculation of critical soil and soil solution limits

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.

There are several motivations for introducing “Species Sensitivity Distributions” (SSDs) into the MPC (critical limit) derivation, the main one being that it makes use of all available data when deriving a critical limit. Main underlying assumptions of the statistical extrapolation methods are (OECD, 1992):

- The species sensitivities distribution follows a theoretical distribution function;
- The species tested in the laboratory is a random sample of this distribution.

Furthermore, in case of ecotoxicological tests for organisms in or on soils, the bioavailability to the tests organisms used is assumed to be comparable. These assumptions have important consequences. The methods should be applied on NOECs from chronic/long term studies, preferably on full life time or multi-generation test studies. Furthermore, as far as possible, toxicity tests should be conducted in conditions where the substances are bioavailable to the test organisms. Since bioavailability of the test compound, and therefore the toxicity found, is influenced by soil properties, the medium should be comparable in organic matter and clay content, soil pH and soil moisture content. Finally, MPC derivation based on statistical extrapolation requires that the database contains preferably more than 20 NOECs, for different species covering major taxonomic groups. The data of the most sensitive end-point should be used as the representative for the species. The most common drawbacks of the method, put forward in this context, are the question of representativity of the selected test species, the comparability of different endpoints and the arbitrary choice of a specific percentile and a statistical confidence level.

The critical limits thus derived suffer from several uncertainties due to extrapolations of single-species toxicological NOEC data to a Maximum Permissible Concentration. These areas have been adequately discussed in other papers (e.g. Forbes and Forbes, 1993), and may best be summarised under the following headings (See also De Vries and Bakker, 1998):

- Intra- and inter-laboratory variation of toxicity data;
- Intra- and inter-species variations (biological variance);
- Laboratory data to field impact extrapolation, such as differences between the metal availability in the laboratory and the field situation.
- Additive, synergistic and antagonistic effects arising from the presence of other substances.

Due to these uncertainties, arbitrary safety (or assessment) factors have been suggested to extrapolate from single-species laboratory data to a multi-species ecosystem. The size of the safety 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 safety factors can be used with larger and more relevant long-term data sets. In this study no use has been made of safety factors when sufficient NOEC data were available from major taxonomic groups to avoid the derivation of unrealistically low critical

limits. Furthermore, comparison of field and laboratory data do not show a consistently lower result for the field data (..).

3.2 Critical limits for reactive metal concentrations of cadmium, lead and mercury in soil

Critical limits on the basis of NOEC soil data

It is assumed that effects data from ecotoxicological tests are related to the reactive fraction, because in those tests the metals are added in a well available form. Besides, the reactive fraction is better related to the concentration in soil solution than total contents (Römkens et al., 2003). As reactive fraction, the adsorbed fraction of metals can be regarded. This share of the total content may be determined by extraction using weak acids like e.g. 0.43N HNO₃ or complexing agents like EDTA, DTPA.

A first approximation of critical limits of reactive metal contents was derived by:

- Combining the available data by Schütze and Throl (2000), an EC Risk assessment in support of regulation (CEE) 793/93 on existing substances 2002 in preparation (Farret and Magaud, pers. comm.) and Crommentuijn et al. (1997).
- Using only the NOECs data for soil fauna that mainly get their intake through soil ingestion; specifically the hard bodied. In reality the impact will occur by two pathways (partly soil and partly solution) but the data can be used by assuming the extreme case of soil ingestion only. In this case one does not have to correct for soil type effects.
- Apply a log-logistic fit and calculate the critical limits (HC5)

Enclosed is Table 4, summarising the results with soil fauna data. Using all data, this table suggests a critical limit of 0.9 mg.kg⁻¹ for Cd, 30 mg.kg⁻¹ for Pb and of 0.03 mg.kg⁻¹ for Hg.

Table 4. Fitted parameter values and resulting critical limits for reactive metal concentrations in soil based on a compilation of NOEC data for soil invertebrates.

Metal	N ¹	μ	B	R ² _{adj}	Critical limit HC ₅ (mg.kg ⁻¹)	Data source
Cd	13	1.10	0.41	93	0.78	Crommentuijn et al. (1997)
	30	1.82	-0.35	93	6.0	Schütze and Throl (2000)
	12	1.64	-0.41	90	2.7	(Farret and Magaud, pers. comm.)
	67	1.57	-0.46	91	0.9	All
Pb	13	2.71	0.30	93	66	Crommentuijn et al., (1997)
	10	2.94	-0.48	87	34	Schütze and Throl (2000)
	12	2.48	-0.37	93	33	(Farret and Magaud, pers. comm.)
	52	2.64	-0.41	90	30	All
Hg	5	0.109	-0.8223	92	0.03	Schütze and Throl (2000)

¹ N is the number of experiments

Normalisation of critical limits to organic matter content

Most forest soils, at least in Northern and Central Europe, are covered by an organic 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 direct consequences for the mineralisation of nutrients in forest soils and ultimately for forest growth.

The critical limits derived in Table 4 above are all related to mineral soil. There is, however, a difference between the sensitivity of organism, in the Organic layer and the mineral soil. To illustrate this difference, the NOEC data for micro-organisms exposed to metals in both Organic layer 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 and Pb are presented in Table 5. For the sake of comparison, results for Cu and Zn were also added.

Table 5. Fitted parameter values and resulting critical limits for reactive 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	M	B	R ² _{adj}	Critical limit (mg.kg ⁻¹)		
						5%	20%	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

The results show that the HC5 values for mineral soil for Pb are comparable to those given in Table 4 (30 and 32), but the results for the organic layer are 4 times as high 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. The results for Cd are quite opposite. Here the HC₅ is comparable for the organic layer and mineral soil but the HC₂₀ and HC₅₀ are is approximately 1.5 and 4 times as high. For Cu and Zn, the results for the organic layer are consistently a factor 2-4 higher than for the mineral soil. The different results for the ratio of critical limits in organic layer and mineral soil for the various metals imply that it is not simply possible to normalise the results of the mineral soil to the organic matter content. Instead, it seems reasonable to use comparable values for Cd in both organic layer and mineral soil, while for Pb, one can best use a four times higher value for the organic layer than for the mineral soil.

Unlike the other metals, mercury concentrations in soils and sediments, river and lake waters, and in biota are recommended to be normalised to organic matter, being the dominating carrier of this metal (Meili, 1991, 1997; Meili et al., 2003). This applies in particular to the biologically active layers of forest soils, which are considered as critical receptor systems to Hg pollution (Meili et al., 2003), which are typically rich in organic matter. In soils with appreciable organic matter content

(tentatively >10% dw), organic matter dominates the Hg cycling (transport, dilution, and toxicity). Even conceptually the Hg content of total organic matter is quite directly related (although not equal) to the Hg content in living organic matter (Meili, 1997), and thus to the toxicity of soil Hg. If the organic content is very low, other matrices are likely to control the cycling of Hg, and in particular the soil content of iron and aluminium (oxyhydroxides, reactive) and clay should be taken into account to set the critical limit.

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). These findings suggest a lowering of effect levels for Hg (as well as Pb) in soils considerably below known values. A tentative critical limit is that the Hg concentration in the Organic layer (O-horizon) of podzolic forest soils should not exceed the present mean level in the most contaminated regions of south Sweden, where further increase should be avoided. This level is about $0.4 \text{ mg} \cdot (\text{kg dw})^{-1}$, which after normalisation with respect to organic matter content corresponds to a more robust value of $0.5 \text{ mg} \cdot (\text{kg org})^{-1}$ in these highly organic soils (see also Meili et al., 2003 and references therein).

This limit might be applied to mineral soils, in which the critical limit per unit dry weight will decline with the organic content to much lower levels. Using the value of $0.5 \text{ mg} \cdot (\text{kg org})^{-1}$ for mineral layers with an organic matter content of 5-10% leads to a critical content of $0.025\text{--}0.05 \text{ mg} \cdot \text{kg}^{-1}$, being the range in which the values for soil invertebrates are found.

3.3 Critical limits for metal concentrations of cadmium, lead and mercury in soil solution

3.3.1 Critical limits for cadmium and lead concentrations in soil solution

Critical limits for total dissolved Cd and Pb on the basis of NOEC soil data and transfer functions

The recommended critical limits for Cd and Pb in soil solution are based on literature information on NOEC soil data that are: (i) limited to organisms from which you can be sure that the effect is only through the soil solution (certainly plants and micro-organisms), (ii) accompanied by data on soil properties (pH, clay and organic matter content) to allow calculation of NOEC soil solution data using harmonised transfer functions and (iii) evaluated by a statistical approach deriving limits based on a 95% protection level, as described in Section 3.1.

The above mentioned approach has been applied to derive the critical limits for Cd and Pb by:

- Combining available data by Schütze and Throl (2000), Farret and Magaud, pers.comm.) and Klepper and Van de Meent (1997), who mainly included data from Crommentuijn et al. (1997).
- Separating them in NOECs for soil for plants and micro-organisms.

- Applying harmonised general transfer functions for Cd and Pb (Römken et al., 2003) to calculate related NOECs for soil solution.
- Applying a log-logistic fit to derive the HC₅, being the critical limit.

Results are given in Table 6, with the number of measurements plus the results of the fit. The values of 0.8 ug.l⁻¹ for Cd and 8 ug.l⁻¹ for Pb are in the centre of the range of calculated critical limits for soil solution. More detailed information is given in De Vries et al. (2002).

Table 6 Fitted parameter values and resulting critical limits for dissolved Cd and Pb concentrations in soil, based on a compilation of NOEC data for various receptors

Metal	Receptor	N ¹	μ	B	R ² _{adj}	Critical limit HC ₅ (ug.l ⁻¹)
Cd	Micro-organisms	83	2.802	-0.9893	95	0.78
	Plants	86	1.869	-0.8143	86	0.30
	All	169				0.6 (0.3-0.8)
Pb	Micro-organisms	31	1.369	-0.8270	91	1.7 ² (0.09)
	Plants	10	2.739	-0.5280	90	15 ² (1.5)
	All	41				8 (2-15)

¹ N is the number of experiments

² Values presented for Pb are HC₂₀ values. HC₅ values (given in brackets) are likely to be too low, especially for micro-organisms and plants since the transfer function for lead is unreliable at low concentrations.

Critical limits for free Cd and Pb on the basis of NOEC soil data and transfer functions

Current work on soil critical limits for heavy metals (Cu, Zn, Cd, Pb) in the UK has focused on deriving limits expressed as the free metal ion concentration, following the recommendations of the Bratislava workshop (Curlík et al., 2000). The principle of expressing the critical limit as the free ion concentration is that this form of metal is believed to be available for interactions with organisms (Lanno et al., 1999). However, it has been shown that the acute toxicity of metals to freshwater organisms is not a function of the free ion concentration alone, but also of the concentrations of other cations present (e.g. H⁺, Ca²⁺, Mg²⁺) (Meyer et al., 1999). This approach has been used in formulating the Biotic Ligand Model (BLM), which postulates uptake of metal at a receptor site on an organism, in competition with other cations. The BLM 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).

In deriving critical limits, expressed as different soil pools of metal (total reactive, soil solution, free ion), we would expect the most appropriate pool to give the smallest variance in endpoint concentrations, for a range of soils of differing chemical composition. Our present work on the derivation of critical limits has shown that contrary to existing theory, endpoints expressed as the free ion show a greater variance among different soils than do endpoints expressed as the reactive soil metal. Endpoints expressed as the free ion show, however, strong relationships with pH, the concentrations becoming lower as pH increases. The endpoint-pH relationship can be expressed as:

$$\log[M^{2+}]_{\text{toxic}} = a.\log[H^+] + b \text{ or } \log[M^{2+}]_{\text{toxic}} = m.\text{pH} + c \quad (6)$$

This is consistent with the theory of competition among cations for receptor sites as encapsulated in the Biotic Ligand Model, with the proton (H^+) competing with the free metal ion for uptake by the organism. We can define an index of free ion toxicity, $\phi_{M,H}$, which accounts for the effects of competition from H^+ on free ion toxicity:

$$\phi_{M,H} = \frac{[M^{z+}]_{\text{toxic}}}{[H^+]^{-m}} \text{ or } \log_{10} \phi_{M,H} = \log_{10}[M^{z+}]_{\text{toxic}} - m\text{pH} \quad (7)$$

Endpoints expressed as $\log_{10} \phi_{M,H}$ (see Examples) show smaller variance than do endpoints expressed as the free ion or the reactive soil metal. In calculating endpoint concentrations as the free metal ion, transfer functions were used relating reactive soil metal and free ion concentration derived by Tipping et al. (2003a) from 98 UK upland soils. The free ion concentrations used to derive the functions were estimated using the WHAM / Model VI chemical speciation model. Examples of the approach are given in Annex 1 and 2.

In this report we do not yet present final results obtained for free metal ion concentrations as a function of pH. In Section 6, we discuss, however, the possibility to derive such pH dependent critical limits for the free metal ion concentrations, including some illustrating material for Cd and Pb.

3.3.2 Critical limits for mercury concentrations in soil solution

Critical limits for total Hg in soil solution on the basis of NOEC soil solution data

Very few studies are available on mercury toxicity to trees and microorganisms in the forest ecosystem. Studies on trees indicate that methylmercury has a toxic effect on tree root growth, possibly there would be a similar effect on biomass decomposition. Godbold et al. (1987) did experiments on the tolerance of tree roots to methyl mercury. Effects at very low levels were reported. A Hill-type retardation model was adapted to the data ($h(\text{Hg}) = 1/(1 + k.[\text{Hg}]^m)$), the parameters are $k=3.10^{15}$ and $m=1.75$ when the concentration is expressed as kmol/m^3 . This implies that for no effect the limit is 0.08 ug.l^{-1} and for an effect of 20% it is 0.3 ug.l^{-1} .

Critical limits for total Hg in soil solution on the basis of NOEC soil data and DOC

Critical total mercury concentrations in soil solution can be calculated by 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:

- As with soil, the Hg concentration in solution can (should) be expressed on an organic matter basis, since virtually all dissolved Hg is bound to dissolved organic carbon (DOC) in a concentration range between $10\text{-}60 \text{ mg.l}^{-1}$ (e.g. Meili, 1997). The distribution coefficient suggests that 95-99% of all Hg in soil solutions is bound by organic substances if considering dissolved species alone, and far more if considering the whole soil (99.999%).

- If the binding properties of particulate 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 = 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.

Using the limit Hg max 0.5 mg.kg⁻¹ org) and a relatively DOM concentration of 20 mg.l⁻¹ (DOC = 10 mg.l⁻¹), the critical steady state concentration of total Hg in soil solution is 10 ng.l⁻¹ or 0.01 ug.l⁻¹. This is similar to peak values observed in streams (Johansson and Iverfeldt, 1994) and other freshwaters (Meili, 1997). Note that this value is much lower than the above derived critical limit of 0.08 ug.l⁻¹.

Critical limits for free Hg in solution on the basis of NOEC soil data and distribution coefficients

The concentration of “bioreactive” Hg (analog to “free ion” concentration) can be calculated by dividing the critical concentration of “organically sorbed” Hg by the distribution coefficient for Hg on (dissolved) organic matter. Field and laboratory studies using biota to determine the bioreactive (“free”) species, and involving different types of soil and lake organic matter, suggest that the value for this distribution coefficient is around 10⁶ (one million) l.kg⁻¹. This value seems to be fairly independent of the soil or water from which the organic matter originates (Meili, 1997). Note that this distribution coefficient is operationally defined for ecotoxicological purposes by using biota to determine the “free” Hg, and that chemical Hg binding considered here may involve any constituent associated with natural organic matter.

Given the limit above for Hg bound to organic substances (0.5 mg kg⁻¹ org), the critical free bioreactive Hg concentration in soils is in the order of 0.5 ng.l⁻¹. Since virtually all dissolved Hg is bound to dissolved organic matter, the concentration of both free Hg (ug.l⁻¹) and Hg bound organic substances (mg.kg⁻¹) liberated from soils are fairly independent of the concentration of DOM or DOC in the soil solution.

3.4 Critical metal concentrations of cadmium, lead and mercury in surface water

Critical limits for surface water for Cd, Pb and Hg were derived from a literature compilation given in Crommentuijn et al. (1997). In Table 7 results are given of a fitted log-logistic distribution based on these results.

Table 7 Fitted parameter values and resulting critical limits for Cd, Pb and Hg concentrations in surface water at different protection percentages, based on a compilation of NOEC data for various taxonomic aquatic groups (data after Crommentuijn et al. (1997)).

Metal	N ¹	μ	β	HC _p (ug.l ⁻¹)		
				p = 5%	p = 20%	p = 50%
Cd	87	1.2	0.56	0.36	2.7	16
Pb	42	2.2	0.39	11	46	158
Hg	38	0.8	0.49	0.23 ²	1.3	6.3

¹ N is the number of experiments

² This value is nearly equal to ‘official’ MPC values derived in the Netherlands.

The data refer to various taxonomic groups (including algae, crustacea, macrophyta and oligochaeta). In an EC Technical Guidance document on risk assessment 2002 in prep; (Farret and Magaud, pers. comm.), an HC₅ of 0.31 µg.l⁻¹ was derived. Consequently, a value of 0.3 µg.l⁻¹ is suggested for Cd, 11 µg.l⁻¹ for Pb and 0.23 µg.l⁻¹ for Hg. Comparison with the limits for soil solution, shows that the critical limit for Cd in surface water is lower, whereas the critical limit for Pb is higher.

Critical Limits for Cd and Pb heavy metals have also been discussed at the Workshop on Heavy Metals (Pb, Cd and Hg) in Surface Waters; Monitoring and Biological Impact, March 18 – 20, 2002 in Lillehammer, Norway (Skjelkvåle and Ulstein, 2002). It was stressed that the chemical conditions of the surface waters are important for the toxicity of the metals. Further studies should aim at critical limits, which are related to specific conditions (“quasi free ion activities”). Recommended ranges for critical limits, expressed as total concentration in the surface water, were 0.1 - 1.0 µg.l⁻¹ for Cd and 1 - 11 µg.l⁻¹ for Pb. Similar ranges in environmental quality criteria, i.e. 0.1 - 1.5 µg.l⁻¹ for Cd and 1 - 15 µg.l⁻¹ for Pb, are recommended for Sweden (SEPA, 2000). These values are in reasonable accordance with those presented in Table 7.

4 Critical limits for soil related to impacts on human health

4.1 Methodological approach

In chapter 2, we mentioned the use of food quality criteria as an alternative to using exposure limits (e.g., ADIs) and deriving critical soil limits based on a comprehensive model on human exposure pathways. In Berlin we agreed to use food quality criteria of Cd and Pb in food crops (specifically Cd in wheat) and Hg in fish as being the exposure routes for which critical loads related to human health have to be derived.

In this section, an overview and discussion is first presented of: (i) the dominant exposure pathways of humans (food and to a small extent drinking water), (ii) the way in which quality criteria can be derived from ADI values, (iii) critical limits for major food chains (the food quality criteria for Cd, Pb, Hg in food crops and for Hg in fish) and (iv) the approach to calculate critical soil limits from food quality criteria.

Health risks and dominant exposure pathways

The major routes for human exposure are consumption of food, drinking of water and inhalation of air and to a lesser extent soil (children). An overview of “Health risks of heavy metals from long range transboundary air pollution” was presented to the Executive body at the nineteenth session of the working group of effects in august 2000 (EB.AIR/WG.1/2000/12). In this document it was concluded that food is the dominant route of exposure of Cd and Pb of non-smokers (tobacco smoking can at least double the Cd intake), while the intake of fish is an important route of Hg intake. The most sensitive (and therefore important) target organism to protect is

the kidney in case of Cd and inorganic Hg. The target site for Pb toxicity is cognitive impairment associated with Pb levels in blood above 100 $\mu\text{g.l}^{-1}$.

In principle, critical limits for soil related to human-toxicological can be derived from critical limits for humans (ADI values) with an integrated model in which all relevant exposure pathways, but in this background document human-toxicological effects are considered to be adequately covered by food quality criteria (see also section 2). Considering the important role of food intake, this document follows the recommendations of the document on “Health risks of heavy metals from long range transboundary air pollution” (EB.AIR/WG.1/2000/12) by focusing on the relationships between metal (Cd, Pb and Hg) contents in food crops and soil.

Derivation of food quality criteria from acceptable daily intakes

Below we illustrate how food quality criteria can be derived from acceptable daily intakes (ADI) with the example of Cd in grain (wheat) and Hg in fish, being the most important food pathways to humans for these metals, at least for citizens in countries with a relatively large fish consumption, such as Scandinavia.

Dose response data for symptoms incidence by humans for Cd and Hg exposure are presented in Sverdrup (2002). For Cd, the symptom is expressed as % incidence of tubular proteuria at the age of 40 years, whereas for Hg, the % incidence refers to neurological disorders and immunodeficiencies. For both metals, the ADIs are given as microgram per day for adult persons. Table 8 shows how the ADI values, related to incidence levels varying between 0.01% and 0.2% for Cd and Hg, can be transferred to food quality criteria for grain and fish respectively, depending on the percent incidence accepted. For comparison, the WHO 1972 recommendation for methylmercury exposure limits given as 5 $\mu\text{g.kg}^{-1}$ body weight per week, being equal to 50 $\mu\text{g.d}^{-1}$ for an adult person with a body weight of 70kg.

Table 8. Possibility to derive food quality criteria for grain and fish based on acceptable daily intakes

Symptom incidence percentage	Cd limits		Grain content ¹ (mg.kg^{-1})	Hg limits		
	ADI _{total} ($\mu\text{g.d}^{-1}$)	ADI _{grain} ($\mu\text{g.d}^{-1}$)		ADI _{total} ($\mu\text{g.d}^{-1}$)	ADI _{fish} ($\mu\text{g.d}^{-1}$)	Fish content ² (mg.kg^{-1})
0.2	40	20	0.33	40	20	0.70
0.05	28	14	0.23	26	13	0.46
0.02	15	7.5	0.12	19	9.5	0.34
0.01	9	4.5	0.08	15	7.5	0.26

¹ Based on dividing the ADI by a net grain intake of 60 g.d^{-1} (400 g.d^{-1} times a body uptake efficiency of 15%)

² Based on dividing the ADI by a fish intake of 200 g. week^{-1} or 60 g.d^{-1}

To perform the calculations for Cd and Hg, it is assumed that the diffuse background exposure due to other exposure pathways is approximately equal to the exposure caused by eating grain (bread) or fish. For Cd, another important pathway is drinking water. For Hg another significant source has historically been dental fillings, but this problem is rapidly decreasing with the increased use of polymer and silicate based materials in dentistry. In performing the calculations to derive a critical Cd content in grain, the daily intake of grain is taken at 400 g and the body uptake efficiency, defined as the ratio between the total amount taken up by the body to the total

administered dose, is assumed to equal 15%. Actually, the uncertainty in this range is large and can vary from 5-20% (Friberg et al., 1979). To derive a critical Hg content in fish, a weekly intake of 200 g of fish is assumed.

When one takes for both Cd and Hg an symptom incidence of 0.01% only, being the standards of risk accepted for generic medical preparates, the acceptable Cd content in grain equals 0.08 mg.kg⁻¹ and the acceptable Hg content in fish equals 0.26 mg.kg⁻¹. When one assumes for both metal a ten times higher risk (0.1%) the contents increase to 0.28 mg.kg⁻¹ for Cd and to 0.60 mg.kg⁻¹ for Hg. The recommended food quality criterion for Cd in grain is 0.10 mg.kg⁻¹, whereas it varies between 0.3 mg.kg⁻¹ (EPA) and 0.50 mg.kg⁻¹ (WHO) for fish, showing that the calculated levels are in the range of those values.

Critical limits for cadmium, lead and mercury in food, drinking water and air

The major routes for human exposure are consumption of food, drinking of water and inhalation of air. In Table 9, an overview is given of relevant critical limits for Cd, Pb and Hg in this context, focusing on wheat in the case of food. Food is the main source of cadmium exposure in the general population (about 94 -99 % of the total intake in non-smokers). In this context, wheat is an important food product and furthermore, wheat is one of the most strongly accumulating crops, thus leading to the most sensitive critical limit for soil (see Section 4.2).

Table 9. Overview of food, drinking water and air quality criteria for Cd, Pb and Hg in view of human health effects

Receptor	Unit ¹	Critical limit			Source
		Cd ¹	Pb ¹	Hg ¹	
Wheat	mg.kg ⁻¹	0.10	0.2	0.03	(food quality criteria, EU, 2001)
Vegetables ²	mg.kg ⁻¹	0.10	0.3	0.03	(food quality criteria, EU, 2001)
Fish	mg.kg ⁻¹	-	-	0.3-0.5	(Lindqvist et al., 1991)
Drinking water	µg.l ⁻¹	3	10	1	(WHO, 1993)
Air	µg.m ⁻³	0.005	0.5	1.0	(WHO, 2000)

¹ All critical limits for food and fish are in mg.kg⁻¹ fresh weight

² Examples are endive, spinach, lettuce etc.

In Sweden, critical limits for mercury in aquatic ecosystems have been based on international regulations, field evidence, and experimental studies (Meili et al., 2003 and references therein). In the early 1990's, the Swedish Environmental Protection Agency has suggested the following environmental quality objectives: For the protection of human health and a sustainable management of natural resources the concentration of total Hg in fish must not exceed 0.5 mg.(kg fw)⁻¹ (fresh weight); for the protection of biological diversity and a sustainable management of natural resources further large-scale accumulation of metals in the Organic layer of forest soils must stop.

The critical limit adopted for fish is based on recommendations by the WHO/FAO and is the same as in many other countries (Lindqvist et al., 1991); it should be noted, however, that the US Environmental Protection Agency now recommends a lower fish Hg limit of 0.3 mg.(kg fw)⁻¹ referring to methyl-Hg alone, which constitutes

virtually all Hg in fish-eating freshwater fish (US-EPA, 2001). The Swedish Food and Health Administration is at present evaluating the relevance of a new limit at 0.3 mg.kg⁻¹. Japan has already adopted a 0.3 mg.kg⁻¹ guideline (Dickman and Leung, 1998). These limits are largely based on the potential exposure of fish consumers, but recent studies suggest behavioural effects of low-level methyl-Hg exposure also in fish (Matta et al., 2001; Hammerschmidt et al., 2002). Critical Limits for Hg have also been discussed at the Workshop on Heavy Metals in Surface Waters in Lillehammer, Norway (Skjelkvåle and Ulstein, 2002). At this workshop the above mentioned Hg limits were adopted (0.3 - 0.5 mg.kg⁻¹ according to EPA or WHO, respectively). Models for estimating critical loads of Hg for aquatic ecosystems should thus address the basic question: What is the maximum load that will keep the mercury level in fish below 0.3 or 0.5 mg Hg.kg⁻¹.

General approach to critical soil limits from food quality criteria

In general, bioaccumulation, which stands for the phenomenon that a chemical accumulates in species through different trophic levels in a food chain. To indicate the transfer of chemicals in food chains both bioaccumulation factors (BAFs) and bioconcentration factors (BCFs) are used. The following terminology is used, according to Jongbloed et al. (1994):

BAF: defined as the ratio of the test chemical concentration in (a part of) an organism (e.g. mammal) to the concentration in its food (e.g. fodder, plants) at steady state. BAFs are generally used for accumulation by birds and mammals and are expressed on wet weight basis.

BCF: defined as the ratio of the test chemical concentration in (a part of) an organism (e.g. plant, earthworm) to the concentration in a medium (e.g. water, soil) at steady state. BCFs are generally used for plants and invertebrates (worms) and are expressed in wet weight tissue and dry weight soil.

In the following sections, target values in crops have been back calculated to the soil using soil-plant relations, while accounting for the possible impacts of organic matter and clay content and of soil pH on these relationships (Section 4.2). Furthermore, target values for metals in animal products are used and back calculated to the soil using soil-plant and plant-animal relations, including the effects of soil properties on these relationships (Section 4.3).

4.2 Derivation of critical limits for soil from food quality criteria for crops

Approach

Figure 3 shows how critical limits for the soil have been derived from critical limits in crops, distinguishing between food quality criteria in view of human health, fodder quality criteria in view of animal health and phytotoxic level in view of toxic effects on the crop itself. The latter aspect is not related to human health but was included to be sure that the food quality criteria do not lead to situations where food crops are adversely affected. Since the kind of crop influences the soil limit, it is necessary to derive relationships for the most sensitive crops to assess critical soil limits. In this

document a distinction has been made between the food crops wheat, potato, lettuce and endive (use of food quality criteria), the fodder crops grass, maize and sugarbeet (fodder criteria). Furthermore, critical limits for all those crops were derived from the literature in view of phytotoxic effects on the crop itself. The mathematical approach to calculate critical soil limits, the used critical metal contents in plants and the results obtained are described separately below. More information on the approach is given in De Vries et al. (2003).

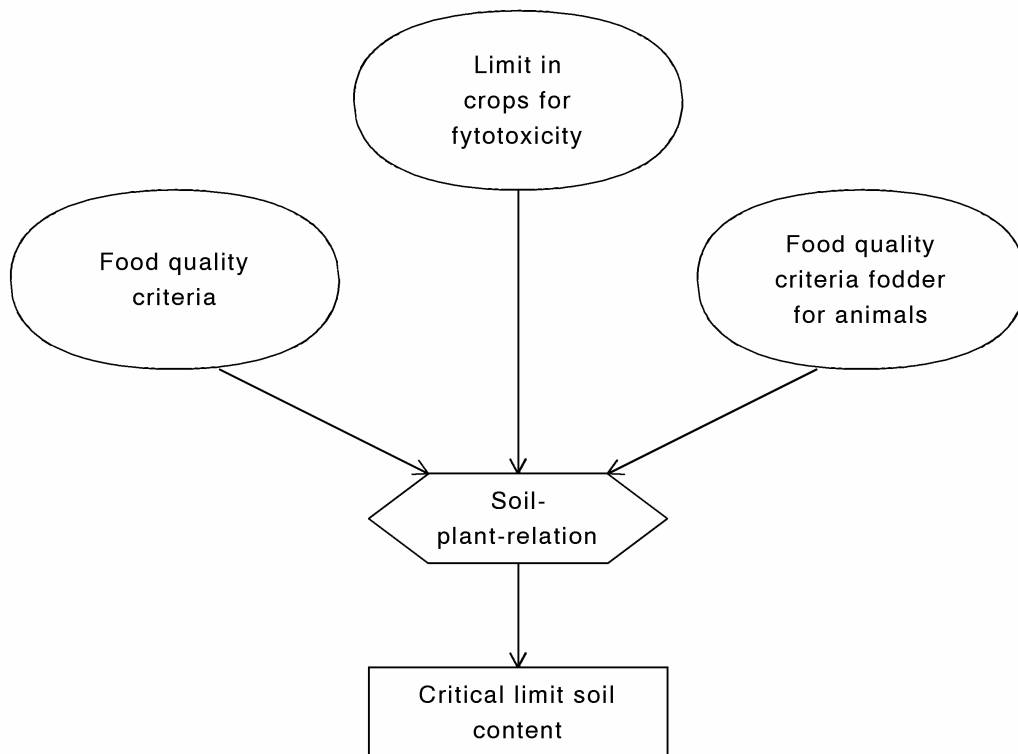


Figure 3 Procedure that has been applied to derive critical limits for heavy metals in the soil from quality criteria in food crops in view of effects on humans (arable land) and in fodder in view of effects on animals (grassland) and from critical limits in crops in view of phytotoxic effects (grassland and arable land).

Calculation of critical limits in soil from critical limits in crops

In most bioaccumulation models, including the model CSOIL calculating critical soil limits from an acceptable daily intake by humans, a simple bioconcentration factor (often denoted as bioaccumulation factor) is used to calculate a critical limit for heavy metals in soil from a critical metal content in plant according to:

$$[\text{Me}]_{s(\text{crit})} = [\text{Me}]_{p(\text{crit})} / \text{BCF}_{\text{sp}} \quad (8)$$

where:

$[\text{Me}]_{p(\text{crit})}$ = limit for metal concentration in plant (mg.kg^{-1})

$[\text{Me}]_{s(\text{crit})}$ = limit for metal concentration in soil (mg.kg^{-1})

BCF_{sp} = bioconcentration factor from soil to plant, being the ratio of metal concentration in plant to metal concentration in soil (-)

Such an approach is only acceptable if there is somehow a (linear) relationship between plant and soil content. This is hardly ever the case. Often, use is therefore made of a median BCF value based on many plant and soil data. This is, however, not acceptable to derive a critical soil limit since the plant content might hardly be influenced by the soil content but by other factors such as above ground uptake of deposited metals. Furthermore, the crop may exclude metals from the soil solution thus making use of any soil plant relationship irrelevant. In this situation, it is simply impossible to derive critical limits for soil from critical plant limits.

If a significant relationship exists between plant and soil content, the relationship can often be improved by including the impact of soil properties (content of organic matter and clay and the soil pH). In such a situation the metal content in plants can be described by a non-linear relationship with the metal content in the soil and soil properties according to (Römken and de Vries, 2003):

$$[\text{Me}]_p = K_{sp} \cdot [\text{Me}]_s^n \quad (9)$$

where:

- $[\text{Me}]_{p(\text{crit})}$ = metal concentration in plant ($\text{mg}\cdot\text{kg}^{-1}$)
- $[\text{Me}]_{s(\text{crit})}$ = metal concentration in soil ($\text{mg}\cdot\text{kg}^{-1}$)
- K_{sp} = transfer constant from soil to plant ($\text{mg}\cdot\text{kg}^{1-n}$)
- n = coefficient describing the non-linear relationship (-)

in which the value of K_{sp} depends on the content of organic matter and clay and the soil pH according to:

$$\text{Log } K_{sp} = a + b \cdot \text{pH} - KCl + c \cdot \log(\text{clay}) + d \cdot \log(\text{SOM}) \quad (10)$$

where:

- SOM = soil organic matter content (%)
- Clay = clay content (%)

Using a critical limit in a crop (food quality criteria, fodder criteria or phytotoxicity limit), a critical soil limit can thus be calculated from the inverse non-linear soil-plant relationship according to:

$$[\text{Me}]_{s(\text{crit})} = ([\text{Me}]_{p(\text{crit})} / K_{sp})^{1/n} \quad (11)$$

A relationship was considered significant when $R^2 > 0.5$. Furthermore, inverse application is only warranted when maximum measured metal contents in plants, used in deriving the relationship, do approach (and preferably exceed) the critical limits in plants. Otherwise, the derivation of critical soil limits from critical plant contents implies that the relationship is applied outside its range of derivation, which may lead to highly unreliable results (De Vries et al., 2003).

Critical metal contents in crops in view of food quality and phytotoxicity

Critical metal contents in crops in view of fodder and food quality are only available for Cd, Pb and (until recently) for Hg, being the priority metals considered in this document. An overview of those criteria for the considered land uses and fodder and food crops is given in Table 10. An overview of limits in view of phytotoxic effects on crops is also given in Table 10, based on literature information. In De Vries et al. (2003), more detail information is given on the background of all the criteria. This document also contains the original food quality criteria given as fresh weight. As expected food and fodder quality criteria are much more stringent than limits in view of phytotoxic effects on crops. However, for Hg the food quality criteria are not considered applicable recently.

Table 10 Overview of fodder and food quality criteria for Cd, Pb and Hg in view of animal health and human health and limits in view of phytotoxic effects on crops. All limits are given on the basis of dry weight.

Land use	Crop	Fodder or food quality criteria (mg.kg ⁻¹ dry weight)					
		Cd ¹	Pb ¹	Hg ¹	Cd ²	Pb ²	Hg ²
Grassland	Grass	1.1	11	0.11	30 ^d	67 ^h	3 ^h
Fodder crops	Maize	1.1	11	0.11	25 ^d	38 ^h	0.6 ^h
	Sugarbeet	1.1	11	0.11	5 ^a	-	1 ^a
Arable land	Wheat	0.12	0.24	0.035	4 ^d	-	4.6 ^h
	Potato	0.42	0.42	0.13	5 ^a	13 ^h	1 ^a
	Lettuce	4.0	6.0	0.60	10 ^c	140 ^{ch}	1 ^a
	Endive	3.3	5.0	0.50	15 ^d	17 ^h	1 ^a

¹ The fodder quality criteria of Cd, Pb and Hg for grass, maize and sugarbeet are originally given as 1, 10 and 0.1 on the basis of 12% moisture content. These data have been back calculated to dry weight. The food quality criteria for wheat, potato, lettuce and endive are originally given as fresh weight (see also Table 9). In back calculating to dry weight, the following moisture percentages were applied: wheat 85% for the grain (the edible part), potato: 24%, lettuce: 5% and endive: 6%. For the food quality criteria are not considered applicable recently.

² For all crops, values are lower limits of ranges in phytotoxic contents based on:

- a Kabata-Pendias and Pendias (1992), general crop-unspecific overview.
- b Mortvedt et al. (1991).
- c Smilde (1976).
- d MacNicol and Beckett (1985), content at 10% reduction in yield
- e Dijkshoorn et al. (1979), content at 10% reduction in yield
- f Chang et al. (1992), content at 50% reduction in yield
- g Sheppard (1992), content at different percentages reduction in yield
- h Sauerbeck (1983), content at different percentages reduction in yield

Soil-plant relationships

To illustrate the absence of a simple direct relationship between metal contents in plants and soil, Figure 4 gives an overview of relationships between Cd, Pb and Hg contents in crops (grass and wheat respectively) and soil. Only for Cd in wheat some relationship can be discerned. For all other combinations, the BCF concept does not work, since there is simply not such a relationship.

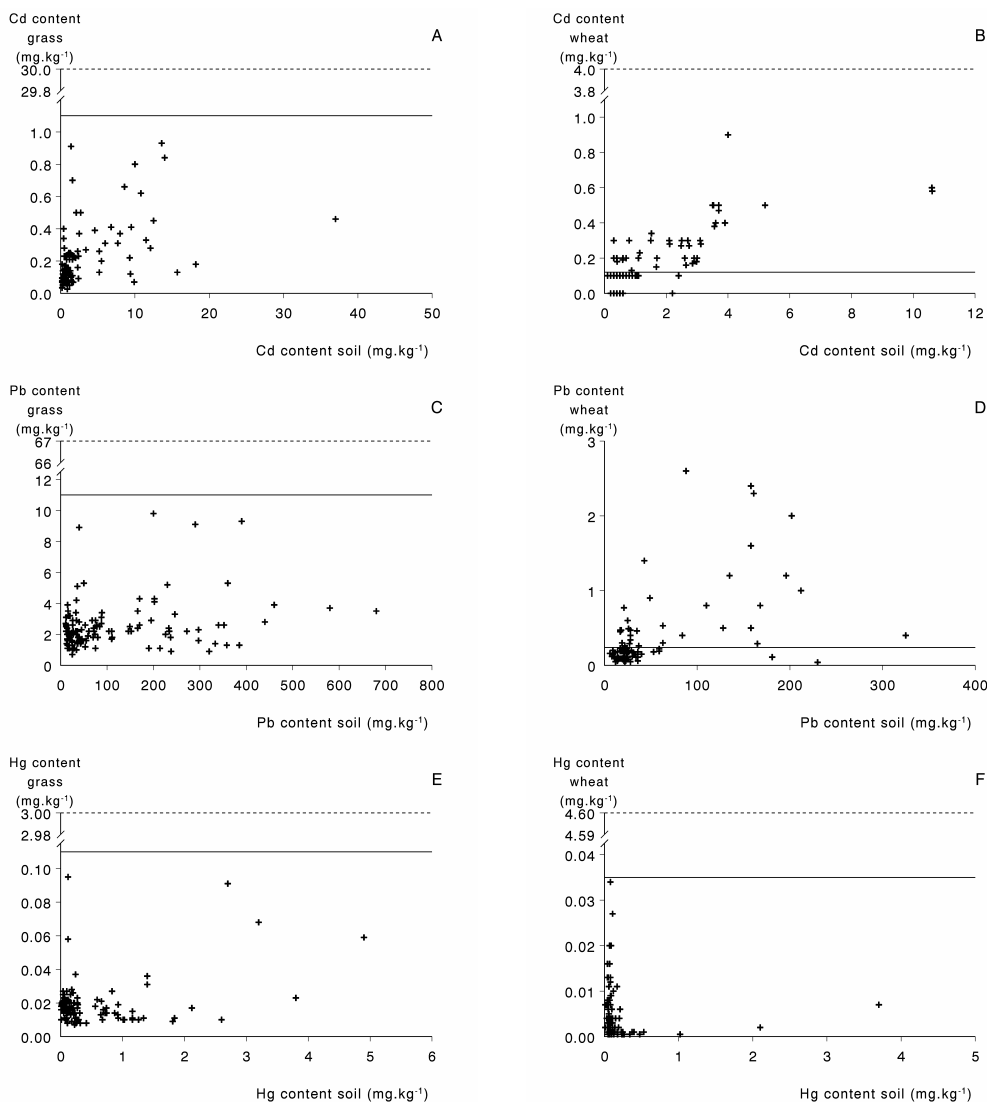


Figure 4 Relationships between Cd, Pb and Hg contents in grass and soil (A, C and E) and in wheat and soil (B,,D,F). The solid line represents the fodder or food quality criteria and the dashed line represents limits in view of phytotoxic effects on crops.

In case of Cd, the concentrations in the plant could be significantly related to soil concentrations, while accounting for the impact of soil properties influencing metal availability, according to (see also Eq. 2 and 3, Römken and de Vries, 2003):

$$\log [Me_{\text{plant}}] = a + b \cdot \text{pH} + c \cdot \log(\text{clay}) + d \cdot \log(\text{OM}) + n \cdot \log[Me_{\text{soil}}] \quad (12)$$

Values for the various coefficients (the exponent n and the parameters a , b , c and d) were derived for Cd, Pb and Hg in grass, maize, wheat, potatoes, lettuce, endive and spinach, being the main crops in the Netherlands (De Vries et al., 2003). In general, relationships were reasonable to good for Cd, relatively poor for Pb and absent for Hg. As an example, results for Cd and Pb for grass, maize, wheat and lettuce are presented in Table 11. For grass and maize no relationships were found for Pb. In most cases, the sign of the coefficients (pH-KCl, clay and OM) is negative, implying

that an increase in pH, clay content and organic matter content leads to a lower metal content in crops.

When one requires a minimum R² value of 0.5, the relationships derived for Pb in wheat and lettuce are also not acceptable for application. This implies that only for Cd significant relationships are available. Furthermore, the maximum plant contents in the data set used for the derivation do approach or exceed the critical limit, thus allowing to convert food quality criteria to soil criteria for this metal alone.

Table 11 Overview of selected soil– plant relationships for Cd and Pb.

Crop	Soil– Plant relationship ¹	R ²
<i>Grass</i>		
Cd	$\log(\text{Cd}_{\text{plant}}) = 0.17 - 0.12 \cdot \text{pH} - 0.28 \cdot \log(\text{OM}) + 0.49 \cdot \log(\text{Cd}_{\text{b}})$	0.53
Pb	No relationship found	-
<i>Maize</i>		
Cd	$\log(\text{Cd}_{\text{plant}}) = 0.9 - 0.21 \cdot \text{pH}^2 - 0.32 \cdot \log(\text{clay}) + 1.08 \cdot \log(\text{Cd}_{\text{soil}})$	0.62
Pb	No relationship found	-
<i>Wheat</i>		
Cd	$\log(\text{Cd}_{\text{plant}}) = 0.35 - 0.15 \cdot \text{pH} - 0.39 \cdot \log(\text{OM}) + 0.76 \cdot \log(\text{Cd}_{\text{soil}})$	0.72
Pb	$\log(\text{Pb}_{\text{plant}}) = -0.25 \cdot \text{pH} - 1.42 \cdot \log(\text{OM}) + 1.14 \cdot \log(\text{Pb}_{\text{soil}})$	0.24
<i>Lettuce</i>		
Cd	$\log(\text{Cd}_{\text{p}}) = 2.55 - 0.33 \cdot \text{pH} - 0.19 \cdot \log(\text{clay}) - 0.39 \cdot \log(\text{OM}) + 0.85 \cdot \log(\text{Cd}_{\text{soil}})$	0.71
Pb	$\log(\text{Pb}_{\text{p}}) = -0.65 + 0.59 \cdot \text{pH} - 0.30 \cdot \log(\text{OM}) + 0.59 \cdot \log(\text{Pb}_{\text{soil}})$	0.40

¹ pH is pH_{KCl}, clay is clay content in % and OM is organic matter content in %

Critical limits for cadmium

As an example of the applicability of the methodology, critical Cd contents have been calculated using the food quality criterion for lettuce and the relevant soil-plant relationship presented in Table 11. The example refers to a sandy soil with 2% clay and a clay soil with 20% clay, with organic matter contents varying between 2 and 10% and pH-KCl varying between 5 and 7. Results show that it is essential to make a distinction in soil types considering their difference in soil properties. In acid sandy soils, the critical Cd content approaches the critical reactive Cd content related to direct impacts on soil invertebrates (Table 12).

Table 12 Calculated critical Cd contents in soil in which the food quality criterion for lettuce was not exceeded as a function of soil properties.

Clay content (%)	Organic matter content (%)	Critical Cd content in soil (in mg.kg ⁻¹)		
		pH 5	pH 6	pH 7
2	2	0.61	1.4	3.3
2	5	0.88	2.1	4.8
2	10	1.2	2.7	6.4
20	2	1.9	4.4	10
20	5	2.8	6.5	15
20	10	3.7	8.6	20

To present critical limits for major soil types, critical soil contents have been calculated on the basis of food quality criteria for Cd for the following three soil types in agriculture:

- Sandy soil with an organic matter content of 3%, a clay content of 3% and a pH-KCl of 5.5.

- Clay soil with an organic matter content of 3%, a clay content of 25% and a pH-KCl of 6.5.
- Peat soil with an organic matter content of 30%, a clay content of 15% and a pH-KCl of 6.0.

Results thus obtained for all major crops show that wheat is most sensitive to Cd, thus causing the lowest critical Cd contents in soil (Table 13). For this crop the critical total content is comparable to the reactive metal content presented in Table 5, although it is slightly lower for most soil types (Compare Table 5 and 13).

Table 13 Calculated critical Cd contents in soil in which the food quality criteria for different crops were not exceeded.

Land use	Crop	Cd content (mg.kg ⁻¹)			
		Sand	Clay	Peat	All soils
Grass land	Grass	9.3	37	14	37
Arable land	Maize	2.6	7.6	5.3	6.1
	Sugar beet	0.94	3.3	2.0	2.2
	Wheat	0.46	0.72	1.9	1.1
	Potato	5.3	9.3	14	10
	Lettuce	1.5	5.8	9.5	6.4
	Endive	0.93	5.3	8.3	5.8

4.3 Derivation of critical limits from food quality criteria for animal products

Approach

Figure 5 shows how critical limits for the soil have been derived from food quality criteria in animal products/organs related to human health and from acceptable daily intake by animals related to animal health. The latter aspect was included to be sure that the food quality criteria for humans do not lead to situations where animal health is adversely affected. The derivation was limited to grazing animals (cows and sheep), which are most sensitive due to ingestion of soil in addition to grass intake. The figure shows that such a derivation thus derives information on grass and soil intake and on soil-plant and plant-animal product relationships. The presentation in the figure is based on the implicit assumption that the transfer of metal in (mixed) plant and soil to animal products is equal. The mathematical approach to calculate critical soil limits, the used critical metal contents in animal products and organs and the results obtained are described below. More information on the approach is given in De Vries et al. (2003).

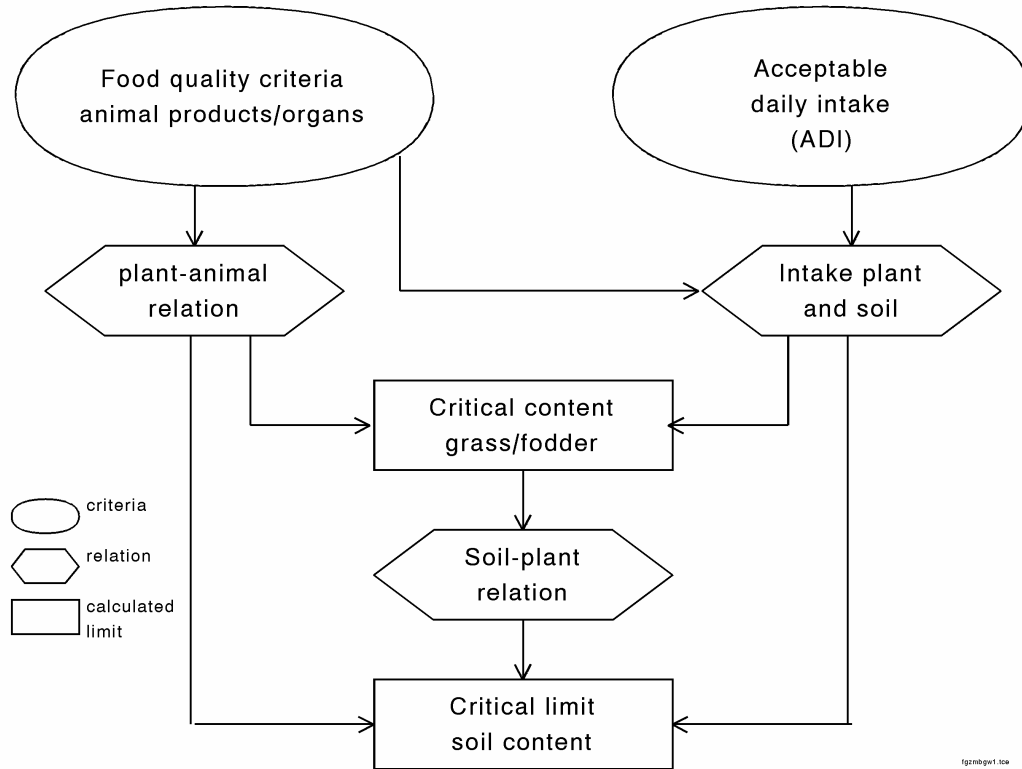


Figure 5 Procedure that has been applied to derive critical limits for heavy metals in the soil (on grassland) from food quality criteria in animal products/organs in view of effects on humans and from acceptable daily intakes in view of toxic effects on animals.

Calculation of critical limits in soil from critical limits in animal products/organs and from acceptable daily intakes

When information is available on acceptable daily intakes (ADI) of metals, this can be used to get information on critical metal contents in fodder (grass) and soil according to:

$$[\text{Me}]_{p(\text{crit})} \cdot I_p + [\text{Me}]_{s(\text{crit})} \cdot I_s = \text{ADI} \quad (13)$$

where:

- ADI = Acceptable daily intakes of metals (mg.dag⁻¹)
- I_p = Intake of plants (fodder) (kg.dag⁻¹)
- I_s = Intake of soil (kg.dag⁻¹)

A combination of Eq. (13) and Eq. (9) gives:

$$K_{sp} \cdot [\text{Me}]_{s(\text{crit})}^n \cdot I_p + [\text{Me}]_{s(\text{crit})} \cdot I_s = \text{ADI} \quad (14)$$

From Eq. (14), the value of [Me]_{s(crit)} can be solved iteratively on the basis of a given ADI and given values of K_{sp}, I_p and I_s. When a significant soil-plant relationship does not exist, e.g. due to strong buffering on metal contents in plants, a plant metal

content that is not related to the soil content (by using the median value in available data sets) and calculating the soil content, according to:

$$[\text{Me}]_{\text{s(crit)}} = (\text{ADI} - [\text{Me}]_{\text{p}} \cdot I_{\text{p}}) / I_{\text{s}} \quad (15)$$

When information is available on food quality criteria in animal organs/products, this can be used to calculate an ADI by assuming that:

- The transfer coefficient of metals from soil to animal product and from plant to animal product is equal (see also Fig. 5). This allows the calculation of an average concentration of metal in fodder, based on a certain intake of grass and the inevitable additional ingestion of soil.
- There is a direct linear relationship between metal content in animal organs/products and metal content in fodder (use of a BCF_{pa}).
- The intake of metals by other sources (like intake of water and air) is negligible.

Using these assumptions the relation between metal content in animal organs/products and in soil can be approximated as:

$$[\text{Me}]_{\text{ao(crit)}} = \left(\frac{[\text{Me}]_{\text{p(crit)}} \cdot I_{\text{p}} + [\text{Me}]_{\text{s(crit)}} \cdot I_{\text{s}}}{I_{\text{p}} + I_{\text{s}}} \right) \cdot \text{BCF}_{\text{pa}} \quad (16)$$

where:

$$\begin{aligned} [\text{Me}]_{\text{ao(crit)}} &= \text{Food quality criteria for metal content in animal organ (mg.kg}^{-1}\text{)} \\ \text{BCF}_{\text{pa}} &= \text{Bioconcentration factor from van plant to animal} \\ &\quad \text{organ/product (-)} \end{aligned}$$

A combination of Eq. (13) and (16) gives:

$$\text{ADI} = [\text{Me}]_{\text{ao(crit)}} \cdot (I_{\text{p}} + I_{\text{s}}) / \text{BCF}_{\text{pa}} \quad (17)$$

This again allows the calculation of $[\text{Me}]_{\text{s(crit)}}$, either iteratively from Eq. (14) or directly from Eq. (15).

Critical metal contents in animal products and target organs, plant-animal relationships and acceptable daily intakes

Calculation of critical soil limits requires information on food quality criteria in animal products/organs or ADIs, plant- animal product (target organ) relationships (in addition to soil-plant relationships) and intake data of grass and soil. In Table 14, an overview is given of the critical contents of Cd, Pb and Hg in animal products and animal organs of cows and sheep in view of food safety (food quality criteria) and animal health. An estimate of the acceptable daily intake based on these criteria is given in Table 15 using Eq. (17) and the plant-animal bioconcentration factors given in the same table. The intake of grass by cows and sheet was assumed to be equal to 16.9 and 2.5 kg.d^{-1} , respectively and 0.41 and 0.10 kg.d^{-1} of additional soil, assuming that the animals are always in the field ("worst case scenario", see De Vries et al., 2003 and references therein).

Table 14 Critical contents of Cd, Pb and Hg in animal products and animal organs of cows and sheep in view of food safety (food quality criteria, EU, 2001) and animal health (Puls, 1988).

Animal	Organ	Critical limit (mg.kg ⁻¹)					
		Food safety			Animal health		
		Cd	Pb	Hg ¹	Cd	Pb	Hg
Cow	Kidney	1.0	0.5	0.05	5	3	14
	Liver	0.5	0.5	0.05	1.4	2	2
	Meat	0.05	0.1	0.05	0.02	-	-
Sheep	Kidney	1.0	0.5	0.05	4	5	1
	Liver	0.5	0.5	0.05	2	5	4
	Meat	0.05	0.1	0.05	-	0.1	-

¹ For Hg, the food quality criteria have recently been abandoned. For sheep, the food quality criteria have been assumed equal to those for cows.

Table 15 Plant-animal bioconcentration factors and calculated acceptable daily intake (ADI) of Cd, Pb and Hg in cows and sheep in view of impacts on food safety and animal health.

Animal	Organ	BCF _{pa} ^{1,2}			ADI food safety (mg.d ⁻¹)			ADI animal health (mg.d ⁻¹)		
		Cd	Pb	Hg	Cd	Pb	Hg	Cd	Pb	Hg
		Cow ¹	Unspecific	-	-	-	-	-	-	63
	Kidney	2.99	0.086	0.638	5.8	101	1.4	29	604	380
	Liver	0.554	0.0404	0.158	16	214	5.5	44	857	219
	Meat	3.3.	1.3.	9.2.	262	1332	941	105	-	-
	Min.	10 ⁻³	10 ⁻³	10 ⁻⁴						
	Min.	-	-	-	5.8	101	1.4	29	604	28
Sheep ²	Kidney	2.08	-	0.468	1.25	-	0.28	5	-	5.6
	Liver	1.85	-	0.0572	0.70	-	2.3	2.8	-	182
	Meat	2.9.	-	9.4.	45	-	138	-	-	-
	Min.	10 ⁻³		10 ⁻⁴						
	Min.				1.25		0.28	2.8		5.6

¹ Estimates for BCF_{pa} for cows are based on Van Hooft (1995).

² Estimates for BCF_{pa} for sheep are based on Beresford (1999). The values used are the upper estimates of the ranges given in this publication.

Results

In Table 16, an overview is given of critical soil limits of Cd, Pb and Hg based on acceptable daily intakes avoiding an excess of target values for the kidney (the most sensitive animal organ) and in view of impacts on animal health. Results show that those contents are generally much higher than those derived from impacts on soil organisms (see before). More detailed information is given in De Vries et al. (2003).

Table 16 Overview of critical metal contents in soil on grassland in view of food safety (effects on kidney) and animal health.

Metal	Type of cattle	Food quality (kidney)	Animal health
Cd	Cow	8.8	65
	Sheep	7.3	25
Pb	Cow	155	1382
Hg	Cow	2.6	68
	Sheep	2.4	55

5 Critical limits related to impacts on animal health

Approaches (food web models) to derive critical limits for soil based on accumulation in the food chain to animals (specifically Cd and Hg) were not considered in the first phase of the expert group. This was partly because of lack of time and partly since those critical limits are generally considered less reliable (see also Crommentuijn et al., 1997). Since critical limits for Cd and Hg related to impacts on terrestrial fauna may be lower than those related to soil organisms (see also De Vries and Bakker, 1998) it seems crucial to give attention to them and therefore this aspect is discussed in more detail in this section.

5.1 Simple food-chain models: impacts on birds and mammals fed on worms and plants

Approach

Bioaccumulation of chemicals from soil to small birds and mammals takes place in at least two steps, namely a transfer (e.g. a BCF) from soil to food (plants and/or invertebrates), followed by a BAF to small birds and mammals. Figure 6 shows the indicator- and target animals that have been used in this background document to calculate critical soil limits from target values in animal organs in view of animal health impacts.

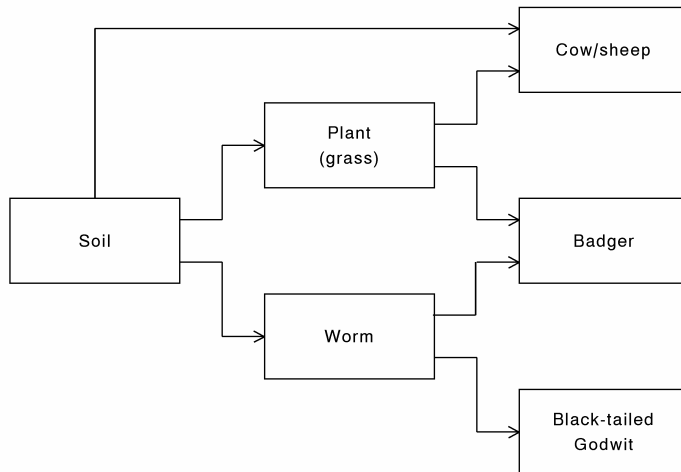


Figure 6 Indicator and target organism and procedure that has been applied to derive critical limits for heavy metals in the soil from criteria in animal organs in view of toxic effects on animals.

The food chain: soil ---> plant (grass) ---> cattle has been described in the previous chapter for agricultural soils. This food chain is also relevant for cows and sheep grazing in nature. In this case the parameterisation of the model described in Section 4.2 (e.g. the intake of grass and soil and the body weight of the cow) is slightly different, but the overall result is comparable to that presented in Table 16. In this section we do thus focus on the food chain: soil ---> soil invertebrate ---> mammal/bird. Assuming that the mammal or bird only feeds on soil invertebrates

(e.g. worm-eating birds or mammals) the simplest model to calculate a critical metal content in the soil, $[Me]_{s(crit)}$, based on this food chain is (Romijn et al., 1991a, b):

$$[Me]_{s(crit)} = [Me]_{in(crit)} / BCF_{sin} \quad (18)$$

in which:

$[Me]_{in(crit)}$ = Critical limits in terms of No Observed Effect Concentrations (wet weight) of the food (invertebrate), corrected for the species of concern (mammal or bird: $mg \cdot kg^{-1}$)

BCF_{sin} = Bioconcentration factor, representing the ratio between the concentration in the invertebrate (the food of the species of concern) and the concentration in soil ($kg_{dry\ soil} / kg_{wet\ food}$)

The methodology described above, has been used by Van de Plassche (1994) to derive critical soil metal contents for Cd, Cu and methyl-Hg, using the formula in the general sense of invertebrates (not only worms). Van de Plassche applied extra correction factors in Eq. (18) to extrapolate the results from toxicity studies in the laboratory to field conditions. This refers to differences in metabolic rate (energy demand), caloric food content, food assimilation efficiency, pollutant assimilation efficiency and species sensitivity to the pollutant in the laboratory and the field situation. BCF's used by Van de Plassche (1994) have, however, not been corrected for soil characteristics, thus leading to one single critical limit value for Cd, Cu and methyl-Hg.

A more sophisticated approach based on the simple food chain: soil --> earthworm --> mouse is presented by Ma and Van der Voet (1993). First of all, a BCF is used, which depends on soil characteristics and the Cd concentration in the soil according to:

$$\ln BCF_{Cd} = b_0 + b_1 \cdot pH + b_2 \cdot SOM + b_1 \cdot \ln Cd_{soil} \quad (19)$$

where:

BCF_{Cd} = the ratio of Cd in the earthworm (dry weight) and Cd in the soil (dry weight) ($kg \cdot kg^{-1}$)

Furthermore, the accumulation factor from the earthworm to the mouse is not implicitly put to 1, as assumed by Romijn et al. (1991a; 1991b), but modelled as a function of uptake (constant) and elimination (first order reaction). Using this approach, EC_{50} values were derived for Cd in the soil as a function of pH and organic matter content, using a NOEC value of $120 \text{ mg} \cdot \text{kg}^{-1}$ dry weight in the kidney of mouse (Ma and van der Voet, 1993). The dependence of critical limits for soil on soil characteristics implies that impacts of Cd on earthworms occur through the soil solution, since the partitioning of Cd from the soil to the soil solution is influenced by the same soil characteristics. In this section, an updated approach of Ma and Van der Voet (1993) is used to calculate metal contents in worms from metal contents in soil.

Below we first describe the approach to calculate critical metal contents in soil from critical metal contents in target organs and acceptable daily intakes, distinguishing

between the black-tailed godwit, feeding on worms only, and the badger feeding on both plants and worms. We then describe the results based on this approach using data for soil-plant and soil-worm relations and available target values for the kidney of the godwit and badger.

Calculation of critical metals contents from critical metal contents in target organs or acceptable daily intakes

Black-tailed godwit: vermivores

The black-tailed godwit is taken as a representative of the vermivores, of which the intake of earthworms is considered to be the dominant source of metal intake. When information on the ADI of such a vermivore (here the godwit) is available, this can be used to derive a critical metal content in the earthworm (the food) according to:

$$[\text{Me}]_{\text{w(crit)}} = \text{ADI}/I_{\text{w}} \quad (20)$$

where:

$$\begin{aligned} [\text{Me}]_{\text{w(crit)}} &= \text{Critical limit for metal concentration in worm (mg.kg}^{-1}\text{)} \\ I_{\text{w}} &= \text{Daily intake of earthworms (kg.d}^{-1}\text{)} \end{aligned}$$

Eq. (20) is based on the assumption that the godwit eats earthworms only. As with the soil-plant relations, the metal content in earthworms can be related to the metal content in soil and soil properties according to:

$$[\text{Me}]_{\text{w(crit)}} = K_{\text{sw}} \cdot [\text{Me}]_{\text{s(crit)}}^m \quad (21)$$

where:

$$K_{\text{sw}} = \text{transfer constant from soil to worm (mg.kg}^{-1}\text{-m)}$$

in which the value of K_{sw} depends on the content of organic matter and clay and the soil pH according to (compare Eq. 10; (after Ma, 1983):

$$\text{Log } K_{\text{sw}} = a_0 + a_1 \cdot \text{log(CEC)} + a_2 \cdot \text{log(OM)} + a_3 \cdot \text{pH} \quad (22)$$

where:

$$\text{CEC} = \text{cation exchange capacity (mmol}_c\text{.100g}^{-1}\text{)}$$

By combining Eq. (21) and (22), a critical soil limit can thus be calculated from an ADI using an inverse non-linear soil-worm relationship according to:

$$[\text{Me}]_{\text{s(crit)}} = (\text{ADI}/I_{\text{w}})/K_{\text{sw}}^{1/m} \quad (23)$$

Direct information on the acceptable daily metal intake is generally not available, but this information can be derived from a critical metal content in the kidney of the vermivore and the critical time period in which this critical content is reached. The kidney is used since this is the most sensitive organ for the intake of Cd, Pb and Hg. The critical time period is set equal to the reproductive phase of the species. For

both Cd and Pb, there is enough information available to derive an ADI according to (De Vries et al., 2003):

$$[\text{Me}]_{\text{org (crit)}} = [\text{Me}]_{\text{w(crit)}} \cdot I_w \cdot f_{\text{ass,org}} \cdot T_{\text{dy}} \cdot T_{\text{crit}} / M_{\text{org}} \quad (24)$$

which by combination with Eq.(20) leads to:

$$\text{ADI} = \frac{M_{\text{org (crit)}} \cdot M_{\text{org}}}{f_{\text{ass,org}} \cdot T_{\text{dy}} \cdot T_{\text{crit}}} \quad (25)$$

where

- $[\text{Me}]_{\text{org (crit)}}$ = critical limit for metal content in target organ (kidney) (mg. kg⁻¹)
- M_{org} = dry weight of the organ (g)
- $f_{\text{ass,org}}$ = assimilation fraction of the metal in food to the (target)organ (-)
- T_{dy} = number of days that the species is exposed to polluted food (d.yr⁻¹)
- T_{crit} = critical time period (reproductive phase of the species), in which the metal content in the target organ should stay below the critical limit (jr)

Badger: Omnivores

The badger is taken as a representative of the omnivores, of which the intake of earthworms (*Lumbricus terrestris*) form the largest part of the diet, in which well-grazed pastures are preferred. Badgers eat also grass, fruits and nuts, cereals like wheat or oats, bulbs and tubers etc. In short, badgers are opportunists and will take whatever is available, but earthworms are the preferred food item. In this document the badger is assumed to live on worms and grass only. When information on the ADI of an omnivore like the badger is available, this can be used to derive a critical metal content in the earthworm and the plant (the food) according to:

$$[\text{Me}]_{\text{p(crit)}} \cdot I_p + [\text{Me}]_{\text{w(crit)}} \cdot I_w = \text{ADI} \quad (26)$$

A combination of Eq. (9), (21) and (26) leads to:

$$I_p \cdot K_{\text{sp}} \cdot [\text{Me}]_{\text{s(crit)}}^n + I_w \cdot K_{\text{sw}} \cdot [\text{Me}]_{\text{s(crit)}}^m = \text{ADI} \quad (27)$$

From Eq. (14), the value of $[\text{Me}]_{\text{s(crit)}}$ can be solved iteratively on the basis of a given ADI and given values of K_{sp} , K_{sw} , I_p and I_w . When a significant soil-plant relationship does not exist, a constant plant metal content (e.g. a median or 95 percentile value) should be used to calculate the soil content, according to:

$$[\text{Me}]_{\text{s(crit)}} = ((\text{ADI} - I_p \cdot [\text{Me}]_p) / (I_w \cdot K_{\text{bw}}))^{1/m} \quad (28)$$

As with the vermivores, the value of ADI can be derived from a critical metal content in the kidney of the badger and the critical time period in which this critical content is reached, using Eq. (25).

Critical metal contents in target organs and acceptable daily intakes

In this study, the calculation of critical soil limits has been limited to Cd and Pb, since information for Hg needed to calculate ADI values and critical metal contents in worms was not available. Estimates of the ADI, using Eq. (25) and the needed parameters to perform the calculation are given in Table 17. From the ADI values, the critical metal content in worms was calculated assuming an intake of worms (wet weight) of 0.1 kg.d⁻¹ by the godwit and 0.5 kg.d⁻¹ by the badger and a dry matter percentage of 16 (84% moist).

Table 17 Calculated acceptable daily intake of Cd and Pb by the black-tailed godwit and the badger

Animal	[Me] _{org(crit)} (mg.kg ⁻¹)		M _{org} (kg)	f _{ass,org} (-)		T _{dy} (d.yr ⁻¹)	T _{crit} (yr)	ADI (mg.d ⁻¹)	
	Cd	Pb		Cd	Pb			Cd	Pb
Godwit ¹	200 ³	90 ⁴	3.85.10 ⁻³	5.10 ⁻³	1.5.10 ⁻⁴	122	5	0.253	0.114
Badger ²	200 ³	90 ⁴	65.10 ⁻³	5.10 ⁻³	1.5.10 ⁻⁴	365	4	1.781	0.801

¹ Apart from the critical metal content in the kidney, [Me]_{org(crit)}, all data are based on Klok and de Roos (1998).

² Apart from the critical metal content in the kidney, all data are based on De Vries et al. (2003).

³ The critical limit of Cd in the kidney of vertebrates varies between 100-350 mg.kg⁻¹ (Nicholson et al., 1983; Cooke and Johnson, 1996; Pascoe et al., 1996). In this study, we used a value of 200 mg.kg⁻¹.

⁴ This critical limit is based on Ma (1996)

Soil-worm relationships

Ma (1983) has given an overview of the uptake of Cd, Pb, Cu and Zn for earthworms in relation to soil metal contents and soil properties. He used a model in which the natural logarithm of the metal content in the worm was related to the natural logarithm of the metal content in the soil and the natural logarithm of the soil properties pH, organic matter content and CEC. In this study, a new analyses was carried out using a ¹⁰log relationship according to (see Eq. 22):

$$\log[\text{Me}_w] = a_0 + a_1 \cdot \log(\text{CEC}) + a_2 \cdot \log(\text{OM}) + a_3 \cdot \text{pH} + n \cdot \log[\text{Me}_s] \quad (29)$$

where:

[Me]_w = metal content in earthworm (mg.kg⁻¹)

[Me]_s = metal content in soil (mg.kg⁻¹)

The CEC has been derived from the clay and organic matter content according to (Helling et al., 1964):

$$\text{CEC} = ((3.0 + 0.44 \cdot \text{pH}) \cdot \text{clay} + (5.1 \cdot \text{pH} - 5.9) \cdot \text{OM}) / 10 \quad (30)$$

The results of this analysis for Cd and Pb, based on data for six soils with different levels of metal pollution, are given in Table 18, while including and excluding the organic matter content. Despite its lower value of R², the latter relationship was used to avoid unwanted effects of increased organic matter contents. Results with soil metal content and pH and CEC alone still show a reasonable to good fit of the relationship, implying that the metal content in worms can reasonably to well described by soil metal contents and these soil properties

Table 18 Overview of parameters in de transfer function for metal accumulation in earthworms, based on data by Ma (1983).

Metal	Parameters					
	a ₀	a ₁ (CEC) mmol.c.100 gr ⁻¹	a ₂ (OM) %	a ₃ (pH)	n mg kg ⁻¹	R ²
Cd	2.28	-0.70	0.61	-0.09	0.25	0.80
Pb	1.88	-1.49	1.21	-0.09	0.62	0.72
Cd	2.69	-0.38	-	-0.14	0.51	0.72
Pb	1.92	-0.99	-	-0.22	1.16	0.61

Critical soil contents for cadmium and lead based on acceptable daily intakes of those metals by the godwit and badger

Results of the critical limits for Cd and Pb in soil based on acceptable daily intakes of those metals by the godwit and badger (determined by the target values for those metals in the kidney) are given in Table 19. A distinction has been made in agricultural and non-agricultural soil based on the expected difference in pH. With respect to clay and organic matter content, use was made of the values presented before in Section 4.2. The pH values used are:

- Sandy soil: 5.5 for agriculture and 4.5 for nature.
- Clay soil: 6.5 for agriculture and 6.0 for nature.
- Peat soil: 6.0 for agriculture and 4.5 for nature.

Results show that critical Cd and Pb contents do become very low, specifically on sandy soils and peat soils (Table 19).

Table 19 Overview of critical Cd and Pb contents in the soil based acceptable daily intakes of those metals by the godwit and badger.

Soil use	Soil type	Black-tailed godwit		Badger	
		Cd content (mg.kg ⁻¹)	Pb content (mg.kg ⁻¹)	Cd content (mg.kg ⁻¹)	Pb content (mg.kg ⁻¹)
Agriculture	Sand	0.14	123	0.28	165
Agriculture	Clay	0.66	534	1.3	718
Agriculture	Peat	1.0	1024	2.0	1378
Nature	Sand	0.067	69	0.13	92
Nature	Clay	0.47	412	0.92	554
Nature	Peat	0.33	426	0.65	573

5.2 Detailed food-chain models: impacts on birds and mammals of prey

A more detailed food web model has been used by Jongbloed et al. (1994) as shown in Fig. 7. Jongbloed et al. (1994) used this model to calculate MPC values of Cd and MeHg. As shown in Fig. 7, there are four possible main routes going from soil to birds or beasts of prey (soil-plant-bird, soil-invertebrate-bird, soil-plant-mammal, and soil-invertebrate-mammal). This number increases exponentially when different plant parts and invertebrate groups are distinguished as quantitatively important food items for small birds and mammals.

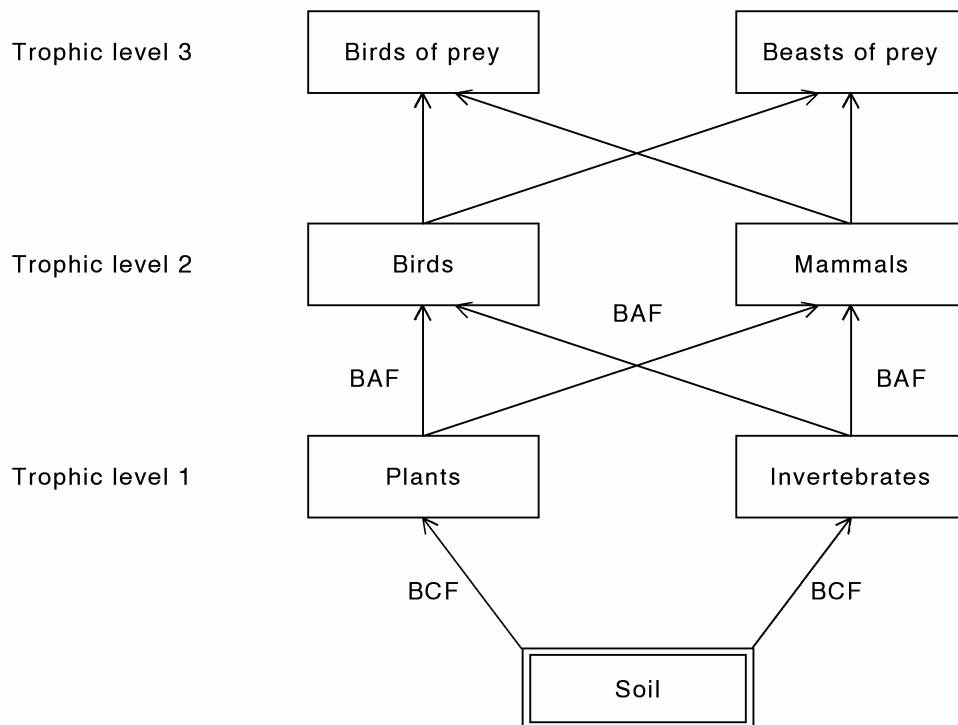


Figure 7 Scheme of a terrestrial food web used for modelling bioaccumulation. The compartments plants and invertebrates can be split up in several groups, depending on the availability and variation among bioaccumulation data.

For plants a distinction can, for example, be made between leaves, seeds, fruits and tubers. The group of invertebrates may comprise earthworms, gastropods, larvae of insects, caterpillars, insects, isopods and spiders. Jongbloed et al. (1994) made a distinction between leaves and seeds with respect to plants and between worms and insects with respect to invertebrates, thus leading to a total of 16 exposure routes going from soil to both birds and beasts of prey.

Jongbloed et al. (1994) calculated a critical soil limit according to Eq. (18). The BCF value, being the total bioaccumulation of a contaminant from the soil to the food of the considered top predator, was calculated from (i) the BCF's of each considered plant part and invertebrate group, (ii) the fraction of each group in the diet of the considered bird or mammal, (iii) the BAF's of the considered bird or mammal and (iv) the fraction of birds or mammals in the diet of the top predator (see Fig 7). Critical limits were derived from cumulative frequency distributions of NOEC values, corrected for differences between laboratory and field conditions and BCF values using a Monte Carlo approach (critical limit is 5 percentile of resulting frequency distribution).

To illustrate the results of such an approach, the results obtained for Cd are presented in Table 20. Results show that for Cd (i) birds of prey are always more sensitive than beasts of prey and (ii) bioaccumulation is lowest in the food chain soil -> leaf --> bird/mammal and highest in the food chain soil --> worm --> bird/mammal. The latter food chain to birds of prey is by far the most critical

pathway for Cd exposure, leading to very low critical limits for soil (approximately 0.1 mg.kg⁻¹). When one aims to protect the most sensitive species, the latter limit seems appropriate.

Table 20 MPC values for Cd in soil, based on 8 different exposure pathways.

Food chain	Critical Cd limit in soil (mg.kg ⁻¹)	
	Birds of prey	Beasts of prey
Soil --> leaf --> bird	2.3	37
Soil --> seed --> bird	0.44	7.2
Soil --> worm --> bird	0.08	1.5
Soil --> insect --> bird	0.40	6.4
Soil --> leaf --> mammal	3.6	48
Soil --> seed --> mammal	0.68	9.4
Soil --> worm --> mammal	0.12	1.9
Soil --> insect --> mammal	0.61	8.3

6 Discussion and conclusions

Recommended set of critical limits and discussion

A recommended set of critical limits for Cd, Pb and Hg for the assessment of critical loads, including ranges for uncertainty assessment, is given in Table 21. More information on the derivation of those limits has been given before (see also De Vries et al.,(2002). For the sake of comparison, the drinking water limits are also included (see also Section 4.1). Those data can be use as an upper limit for groundwater. Apart from Pb, those data are much higher than the results obtained from ecotoxicological tests for soil organism and aquatic organisms (see Table 21).

Table 21 Recommended set of critical limits including ranges for uncertainty assessment

Metal	Critical limit soil content reactive (mg.kg ⁻¹)	Critical limit soil solution (µg.l ⁻¹)	Critical limit in surface water (µg.l ⁻¹)	Critical limit drinking water (µg.l ⁻¹)
Cd	0.9 (0.7 – 1.1)	0.6 (0.3 – 0.8)	0.3 (0.15-0.6)	3
Pb	30 (25 – 35) ¹	8 (2 – 15)	11 (5-18)	10
Hg _{inorganic}	0.1 (0.03-0.3)	0.2 (0.08-0.3)	0.23 (0.09-0.49)	1
Hg _{methyl}	-	-	0.011 (0.001-0.042)	-

¹ For the humus layer, a value of 130 can best be used.

Critical soil limits related to impacts on animal health and human health can either not be derived for Pb and Hg, since soil-plant relationships do not exist, these critical limits are much higher than those related to direct impacts (in case of impacts on cattle in view of food quality aspects and animal health; see Table 16). The only metal in which indirect impacts due to accumulation in the food chain may cause lower critical soil metal contents can become lower is Cd. This is illustrated in Table 22, showing calculated critical total Cd contents in soil related to food quality criteria for wheat and to acceptable daily intakes of worm eating birds and mammals. Comparison of Table 21 and 22 shows that that critical total Cd content are mostly lower than the critical reactive metal content.

Table 22 Calculated critical total Cd contents in soil in which quality criteria for wheat and animal health of worm eating birds and mare exceeded.

Land use	Crop/animal	Cd content (mg.kg-1)		
		Sand	Clay	Peat
Arable land	Wheat	0.46	0.72	1.9
All land uses	Impacts on worm eating birds (godwit)	0.14	0.66	1.0
All land uses	Impacts on worm eating animals (badger)	0.067	0.47	0.33

Discussion aspects

At the end of the first phase of the expert group on critical limits (Nov 2001), there were still many suggestions for sophistication of the critical limits derivation and the further approach, which could not be agreed upon in the short time available. These points included (see also De Vries et al., 2002): (i) use of safety factors in addition to the statistical approach and other details of statistical analysis calculations, (ii) harmonisation of critical limits for soils and soil solutions with critical limits of aquatic ecosystems and ground water, (iii) derivation of critical limits for different soil categories in view of different sensitivities of biological communities in each soil category and (iv) use of data for free ion activity in the critical load calculation.

In the mean time, it was concluded that safety factors in addition to the statistical approach are not needed and the same is true for the harmonisation of critical limits for soils and soil solutions versus those for surface water and groundwater. Instead it is relevant to derive and compare critical limits for the various receptors of concern, to gain insight in the differences in sensitivity for the receptors. In this section, we thus focus on the latter two aspects and on additional relevant aspects by including a discussion on the:

- Validity of critical limits for reactive metal concentrations in soil
- Possible improvement of critical limits for soil solution and surface waters based on available ecotoxicological data
- Use of pH dependent critical limits for the free metal ion in soil solution.
- Derivation of critical loads from food quality criteria for lead and mercury for which soil-plant relationships do not exist.

These sections are followed by a discussion on relations between national critical soil limits and those included in this document, followed by possible options for the further approach, related to the experiences described.

Use of critical reactive metal concentrations in soil

In De Vries et al. (2002) the expert group agreed preliminarily on the assumption that effects data from ecotoxicological investigations in laboratory can be best related to a “reactive” heavy metal concentration in the soil, since the heavy metal applied in such tests is in a well available form. Furthermore, it was assumed that the effects on soil invertebrates can best be related to the “reactive” metal content of the soil, because these organisms partly eat soil, whereas the soil solution is relevant as pathway for effects of heavy metals for plants and micro-organisms. In view of those considerations only one critical limit (soil solution) as well as one critical limit (“reactive”) have been set for each of the two metals, Cd and Pb. Those critical limits

were directly or indirectly (by using transfer functions) derived from ecotoxicological databases as described in Section 3.2.

Within the expert group, the question arose, whether the assumptions behind the derived single critical limit for “reactive” metal in the soil is an appropriate reflection of the reality since:

- The critical limit “reactive” refers to the pathway soil – invertebrates, assuming that intake of heavy metals occurs by soil ingestion only. This is only a small part of the overall effects on soil functioning. There are indications that in general invertebrates are less sensitive than micro-organisms. The latter are more important, considering the number of individuals, living biomass (ca. 80 %) and share of the transformation processes in soils (> 80 %). Therefore the protection of the living conditions of soil micro-organisms should be emphasised.
- The reactive content of heavy metals differ for soil categories, not only due to the different ability to bind (anthropogenic) inputs but also caused by the composition of parent materials and status of weathering (natural processes). The meso-and macrofauna of the soils has adapted to the different heavy metal contents (and other soil conditions) during hundreds and even thousands of years. Therefore we cannot expect to find the same biocenosis in different soil types. Also the type of land use influences the composition of species. Different communities of organisms however, might be of different sensitivity. Although this is reasonable, the data basis to quantify the variable sensitivity is still missing. More related research is necessary.
- Also invertebrates are not only exposed by the “reactive” content of a heavy metal but might also be affected by metals in the soil solution (even certain species like e.g. nematodes are living in soil water and are thus only exposed to soil solution). It is even likely that, apart from the hard bodied invertebrates, soil solution is the major pathway for all soil organisms and plants.

Beside these scientific arguments, which make the uncertainties of this approach clear, there are practical limitations of the use of this type of critical limits in critical loads calculations: In former studies already came out that using one critical limit for “reactive” heavy metal content in soil and calculating critical loads on the basis of this limit, the most sensitive soils (soils with low binding capacity) get the highest critical load. The reason is that by the use of transfer functions the highest concentration in soil solution is expected in sensitive soils with low binding capacity which contributes to high leaching rates and consequently to high acceptable inputs, assuming a balance between inputs and harmless outputs (mainly via leaching). This aspect is discussed below.

Comparison of critical limits for soil and soil solution with background concentrations and official national critical limits

In Germany, the effects based critical limits for soil have been compared to background values in order to consider the different ability of soils to accumulate pollutants like heavy metals. The latter is an important argument. It means that e.g. soils with low binding capacity for metals, which are exposed only to a relatively low (ubiquitous) input rate of Cd will probably never reach the critical limit for Cd “reactive” (found in laboratory) because the metal is permanently washed out. On

the other hand the critical limit for Pb “reactive” is exceeded in soils with higher binding capacity because most of the Pb input is bound, but effects have not been proved under natural conditions.

First approximations of the reactive metal content for units of the General Soil Map of Germany (including 69 soil units) show that the critical limit “reactive” is often exceeded by background values for Pb, but seldom by background values for Cd (with background total contents being transformed into “reactive” background contents). Starting with the critical limit “reactive” and using the transfer function according to the guidance document (De Vries et al., 2001; De Vries et al., 2002) only about 25 percent of the more than one million grids (over all land use classes) had a related Pb concentration in the soil solution below or near by the critical soil solution limit of 8 mg.m⁻³, whereas for cadmium more than 75% exceeded the critical soil solution limit of 0,8 mg.m⁻³. These results show that that the two types of critical limits do lead to different results. This is to be expected, since the given critical soil solution limits are derived by applying transfer functions on the NOEC laboratory data, whereas the calculated critical limits for soil solution based on a given critical reactive metal content is derived by applying transfer functions in the field situation. The differences reflect the differences in soil properties in the NOEC experiments and the field situation.

While for Cd the calculated concentrations in soil solution on the basis of background values are in good agreement with measurement results (Bielert et al., 1999), the calculated concentrations of Pb in arable land were slightly higher, but also in the same order of magnitude as measurements. However the calculated concentrations (background) of Cd and Pb in poor and acidic soils are much higher as found in field investigations (e.g. results from measurements of concentration in leaching water at level II forest monitoring plots, Nagel et al., 2000). These results show that there may be high uncertainties in the transfer functions, especially for soils with low binding capacity. When using concentrations in soil solution (critical or present), which are calculated by these transfer functions, especially for poor and acidic soils the annual leaching rates of the metals may be overestimated and the critical loads become too high for these sensitive soils.

In Germany, the critical limits “reactive” for Cd and Pb have also been compared with precautionary soil values according to the German Federal Soil Protection and Contaminated Site Ordinance (Table 3). These values are provided with reference to aqua regia extraction. Using them, pH has to be considered also. Organic matter content is assumed to be not higher than 8 %.

Table 23 Precautionary values for Pb, Cd in soils, in mg/kg dry weight, aqua regia –decomposition.

Soils		Cd	Pb
Soil type clay	clay content > 25 %	1.5	100
Soil type loam/silt	clay content 12 to 25 % and silt content > 50 %	1	70
Soil type sand	clay content < 12 % and silt content < 50 %	0.4	40

The precautionary values are based on evaluation of ecotoxicological effects data. However, neither factor method nor statistical distribution method was used to set these values (Terytze, 2001). The precautionary values are set in a more empirically

way, using literature data on the ranges of NOECs and LOECs, assuming that in sandy soils effects occur at lower thresholds as in well binding soils like e.g. clay soils.

In order to get information, what the critical limit “reactive” means in terms of aqua regia and to compare these values with the German precautionary values a recalculation was done. The resulting aqua regia values differed only slightly for Cd (1.2 – 1.3 mg.kg⁻¹; 1.3 – 1.4 mg.kg⁻¹ for sandy or clay soils respectively) and little more for Pb (37 mg.kg⁻¹ up to 60 mg.kg⁻¹). Transforming the precautionary values to “reactive” contents by using the transfer functions of De Vries et al. (2002) there was good agreement with the critical limit “reactive” for Cd in clay soils (0.6 – 1.0 mg.kg⁻¹), but in sandy soils the precautionary value results in lower contents “reactive” (round about 0.25 mg.kg⁻¹). For lead, while there was good accordance to critical limit “reactive” for sandy soils (24 – 33 mg.kg⁻¹), the transformed values “reactive” for clay soils were too high (34 – 59 mg.kg⁻¹). The conclusion of these comparisons is that the transfer function from aqua regia to “reactive” does probably not enough differentiate the soil categories, especially with respect to Cd.

In Germany, the critical values for soils for official soil protection strategies have also been compared with data on background contents. The idea behind is, that in these background areas, harmful effects on soil organisms could not be detected up to now, although the contents partly exceed these effect thresholds. In these situations, the political aim is to protect the current soil quality, not to decrease the heavy metal content. The latter approach is only indirectly effect based. However it is well practicable and plausible for executive purposes.

Possible improvement of critical limits for soil solution and surface water

Derivation of critical limits for soil solution can be improved on the basis of NOEC soil solution data. Results on effects of Hg, measured for soil solution, on tree roots are available, but they only relate to seedlings, not to mature trees. There are also a limited number of data giving soil solution data in relation to sub-lethal effects for Cd from France. Furthermore, there is a Dutch literature review including data for Cd and Pb on phytotoxic effects on plants, mainly from laboratory studies. These data have been provided to the critical limits group and will be included in a future final report of the expert group.

Regarding the use of critical limits, it is questionable to relate (total) concentrations in soil solution and surface water to effects on soil organisms or aquatic organisms without accounting for the environmental chemistry. An applicable approach could be to look for pH, alkalinity and DOC to improve the relationships. The Swedish classification (report “Environmental quality criteria for lakes and water courses”), will in this context also be considered in the final report.

Use of critical limits expressed as free metal ion

There are clear and aimed suggestions to improve critical limits related to ecotoxicological effects, which can be easily applied. Critical limits for free and total metal (Cd, Pb and Hg) concentration in soil solution and surface water have to be derived as a function of pH and DOC (+ alkalinity for surface waters). For soils this

implies application of transfer functions on NOEC soil data as described before. It can be assumed that most or nearly all eco-toxicological data are related to soil solution effects. Therefore, we will test the use of pH and DOC dependent free and total metal ion concentrations, to set critical limits for soil solution only, based on NOEC-Data on soil. Derivation will be based on plants, microbiota and soil fauna (except the hard bodied) using one common database. If it works, the critical loads modelling will become easier. For comparison an analogous evaluation of critical limits for the reactive soil content will also be included. As a preliminary example, calculated values of $[M^{2+}]_{tox}$ are shown plotted against $\log[H^+]$ for Cd and Pb in the Figs. 8 and 9 using data compiled in the UK (Tipping et al., 2003b).

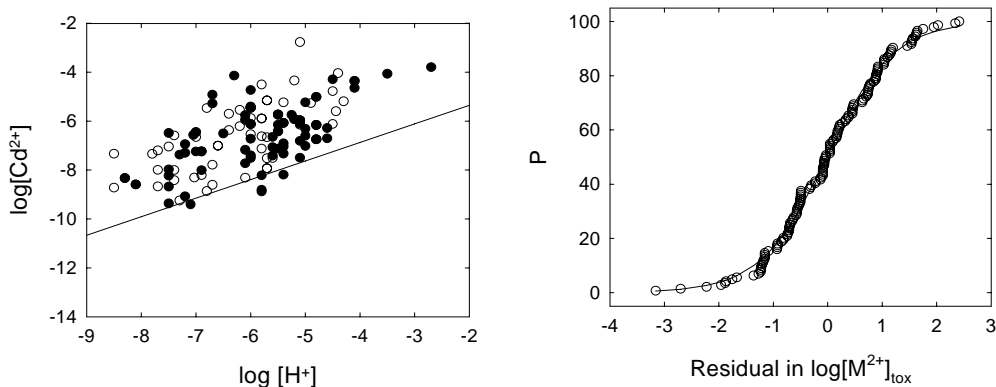


Figure 8 Left: $\log[Cd^{2+}]_{tox}$ plotted against $\log[H^+]$, showing the critical limit function (solid line) derived from weighted regression and the distribution of residuals in $\log[Cd^{2+}]_{tox}$ (right). Solid points in the left hand pane are for effects on plants and animals, open points are for effects on microbial processes. The critical limit function was calculated by combining the data on both types of effect.

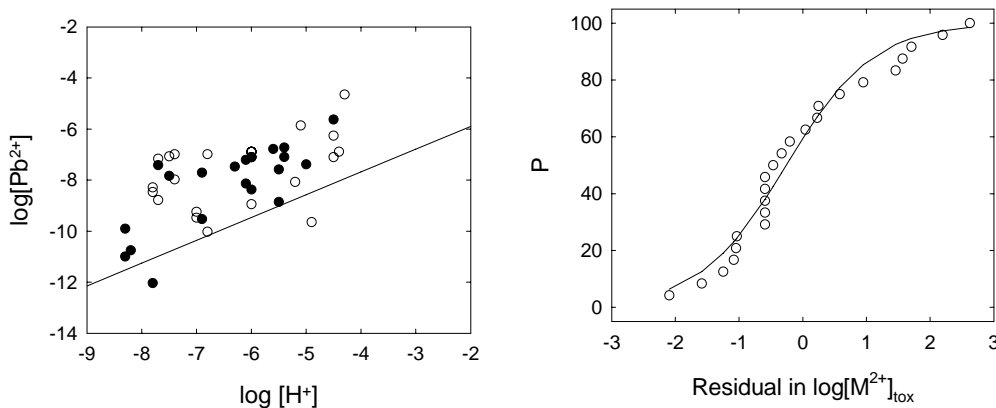


Figure 9 Left: $\log[Pb^{2+}]_{tox}$ plotted against $\log[H^+]$, showing the critical limit function (solid line) derived from weighted regression and the distribution of residuals in $\log[Pb^{2+}]_{tox}$ (right). Solid points in the left hand pane are for effects on plants and animals, open points are for effects on microbial processes. The critical limit function was calculated by combining the data on both types of effect.

For each metal, considering all species and effects endpoints together in a database compiled in the UK, a significant ($P < 0.001$) correlation between $\log[M^{2+}]_{tox}$ and $\log[H^+]$ was seen. It was not possible with the current data to determine any independent effects of Ca^{2+} or Mg^{2+} on $[M^{2+}]_{tox}$. Therefore critical limits for the free metal ion were expressed as functions of $\log[H^+]$ only. This was done using a method which is intended to combine the species sensitivity distribution approach of

Aldenberg and Slob (1991) with a description of the dependence of the critical limit, $[M^{2+}]_{crit}$, upon $\log[H^+]$.

First, a weighted linear regression of $\log[M^{2+}]_{tox}$ was carried out against $\log[H^+]$. The weighting of data points was done to compensate for the differing number of data points from different studies. Data points from the same study which referred to the same species or effect were grouped together. Each point was assigned a weight n_{max}/n , where n was the number of data points within the group and n_{max} was the largest group size for that metal. The best fit regression line was found by minimising the sum of squares in the term $\Sigma[(\log[M^{2+}]_{tox} - \log[M^{2+}]_{tox, regression})^2 \cdot n_{max}/n]$. For each metal this gave a best fit regression of the form described in Eq. (6). The critical limit, $\log[M^{2+}]_{crit}$, was assumed to be a linear function with the form

$$\log[M^{2+}]_{crit} = a \cdot \log[H^+] + b + B \quad (31)$$

where a and b are the terms in Eq. (6) and the term B was calculated by assuming the residuals in $\log[M^{2+}]_{tox}$ to be log-logistically distributed, and applying the expression of Aldenberg and Slob (1991):

$$B = \mu - \beta \cdot \log [(100 - p) / p] \quad (32)$$

with $p = 95$. The value of B was found by optimising the variables μ and β , minimising the term $\Sigma[(p - p_{calc})^2 \cdot n_{max}/n]$. This procedure gave the following expressions for $\log[M^{2+}]_{crit}$:

$$\log[Cd^{2+}]_{crit} = 0.76\log[H^+] - 3.87 \quad (33)$$

$$\log[Pb^{2+}]_{crit} = 0.66\log[H^+] - 5.47 \quad (34)$$

Plots of $\log[M^{2+}]_{tox}$ against $\log[H^+]$, and distributions of residuals in $\log[M^{2+}]_{tox}$ (Figures 8 and 9) do show the possibility of using a pH dependent critical limit for the free metal ion concentration. More information is given in Tipping et al, (2003b).

Derivation of critical loads for lead and mercury from food quality criteria

Food quality criteria can be back-calculated to critical limits in soils from Cd content in crops, and to waters for Hg in fish. The pathway of Cd via wheat is most important for human health and a special critical soil Cd limit for arable soils is relevant. The critical limit wheat - arable soil should be used including the formula to calculate soil - plant transfer.

For Pb and Hg in food crops, back calculation to soil content is, however, not possible. Because there are no relationships between content of soil and contents in plants for Pb and Hg, direct uptake from atmosphere to plant has to be considered. It is assumed that uptake of Hg is completely due to direct uptake from atmosphere. For Pb, direct uptake is specifically relevant for vegetables. As an example, Figure 10 shows the relationship between Pb and Cd deposition and Pb and Cd content of endive and lettuce, respectively based on results for one growing season in the year 2001 (De Temmerman and de Witte, 2003a).

The resulting linear regression relationships that were derived are:

$$\begin{aligned} \text{Cd deposition} &= -15 + 456 \text{ Cd content endive} & R^2 &= 0.81 \\ \text{Cd deposition} &= -1.8 + 139 \text{ Cd content lettuce} & R^2 &= 0.92 \\ \text{Pb deposition} &= 39 + 240 \text{ Pb content endive} & R^2 &= 0.58 \\ \text{Pb deposition} &= 42 + 50 \text{ Pb content lettuce} & R^2 &= 0.52 \end{aligned}$$

Those kind of relationships can be used to directly derive critical limits from food quality criteria. For example, using a critical Cd limit of 0.2 mg.kg^{-1} fresh weight for vegetables (Table 9) leads to a critical Cd deposition of approximately $75 \text{ ug.m}^{-2}.\text{d}^{-1}$ for endive and of $25 \text{ ug.m}^{-2}.\text{d}^{-1}$ for lettuce. Similarly, using a critical Pb limit of 0.3 mg.kg^{-1} fresh weight for vegetables (Table 9) leads to a critical Pb deposition of approximately $110 \text{ ug.m}^{-2}.\text{d}^{-1}$ for endive and of $60 \text{ ug.m}^{-2}.\text{d}^{-1}$ for lettuce (see also De Temmerman and de Witte, 2003a)

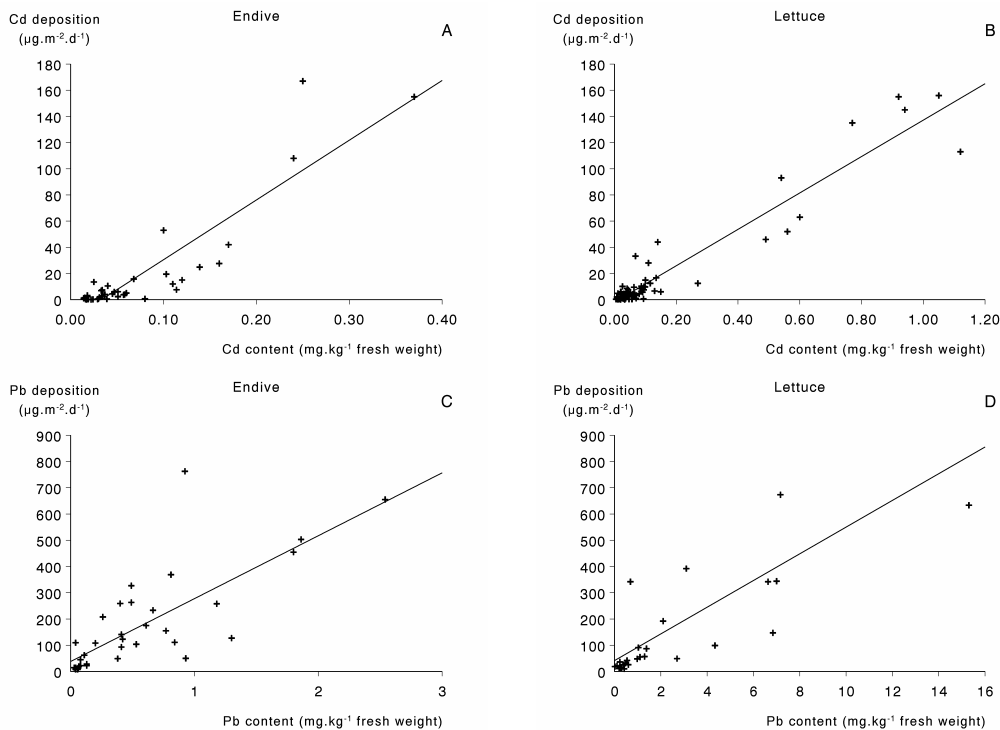


Figure 10 Relationships between inputs from the atmosphere in $\text{ug.m}^{-2}.\text{d}^{-1}$ and plant contents in mg.kg^{-1} for Cd in endive (A) and lettuce (B), Pb in endive (C) and lettuce (D).

Similarly, figure 11 shows results of the relationship between Hg content in grass and the concentration of mercury in the atmosphere (after De Temmerman and de Witte, 2003b). Applying a critical metal content in grass of 0.1 mg.kg^{-1} (fresh weight) implies a critical Hg concentration in air of approximately 12 ng.m^{-3} . In general the concentration in leafy vegetables are approximately half the Hg concentrations in grass (De Temmerman et al., 1986), but the critical limits are three times as low. Assuming a comparable relationship between Hg immission concentrations and Hg contents in plants for grass and vegetables, the critical Hg concentration in air should not be higher than approximately 10 ng.m^{-3} .

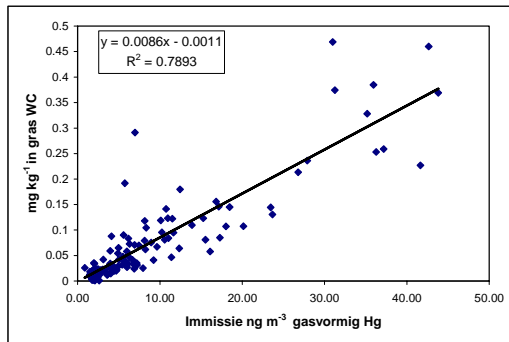


Figure 11 Relationships between inputs from the atmosphere and plant contents for Hg in grass.

Consequences and options for the further approach

There are many limitations and uncertainties in the use of the critical limit “reactive” in critical loads calculations for heavy metals. In general, critical loads based on this type of critical limits are higher than critical loads based on critical limits for soil solution. There are the following options for the further approach:

- 1) Using the minimum of critical limits “soil solution” and critical limits “reactive” for critical loads calculations. For soils with low clay and/or humus content, and low pH the critical loads will become high when using critical limits “reactive”. On the other hand, soils with high binding capacity will have low critical loads. There are thus regions where the critical loads, based on critical limits “reactive” are lower than critical loads based on critical limits “soil solution”, being the regions with high binding capacity and low or moderate metal contents in the soil. Using the minimum of both types of critical loads, the soils with high binding capacity would be presented as the most sensitive ones, what is the opposite to the common imagination of a soil, sensitive against heavy metal input. Regarding the uncertainties of this method, its use for emission reduction purposes should be handled carefully.
- 2) Calculating critical loads for heavy metals on the basis of critical limits “soil solution” only. The advantage of this approach is that uncertainties of the transfer functions are excluded from the critical load calculation. The calculation model is very easy and has been used already by eleven countries up to now. However we have to be aware of the fact that the critical limit (soil solution), which is used in this method, is also based on one of these transfer functions. At present, the critical loads are mainly determined by the precipitation excess, except for regions where this flux is very low. However,, when using a pH, and possibly also DOC, dependent critical limit, the critical load will also depend on those factors. Despite some shortcomings of this method it is considered the surest way of effects based critical loads calculations at the moment, although test of the new methodologies still have to be done.

Aspects of human health have to be considered in future for the agricultural types of land use and again the most sensitive critical load should be the measure for emission reduction strategies. In the future, in view of dynamic modelling, it is also relevant to calculate a stand-still critical load. The uncertainties of the transfer functions have the same influence on the calculations of a stand-still critical load as in the effects based approach using critical reactive metal contents. The difference is that the calculations are based on measured values for the heavy metal content in the soil. When dynamic

models are applied it might become also relevant to calculate a target load for a finite period with a (simple) dynamic approach. A target load includes an acceptable net accumulation in the soil (based on the difference from background values of total contents to Critical Limits for total contents) as presented in De Vries and Bakker (1998) and de Vries et al. (2001). Such a load implies that the soils with high binding capacity would be presented as the least sensitive ones. This is according to the imagination of a soil, being insensitive against heavy metal input.

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Annex 1 Impact of pH on cadmium toxicity to *Folsomia candida*

Crommentuijn et al. (1997) determined LC₅₀, EC₅₀ (weight) and EC₅₀ (individuals) of cadmium for *F. candida* in 12 artificial soils (pH 3.12-7.29, % O.M. 2.0-10.0). The LC₅₀ was determined for eight soils only. Endpoint free ion concentrations were calculated using the transfer function:

$$\log_{10}[\text{Cd}^{2+}] = -0.42\text{pH} - 0.69\log_{10}[\% \text{O.M.}] + 0.97\log_{10}[\text{M}_{\text{SOIL}}] + 2.63 \quad (35)$$

calculated by Tipping et al. (2003a). The following expressions were derived for the endpoint free Cd concentration as a function of pH:

$$\text{LC}_{50}: \log_{10}[\text{Cd}^{2+} \text{LC}_{50}]_{\text{toxic}} = -0.38\text{pH} - 3.12 \quad r^2 = 0.97 \quad (36)$$

$$\text{EC}_{50\text{-weight}}: \log_{10}[\text{Cd}^{2+} \text{EC}_{50\text{-weight}}]_{\text{toxic}} = -0.34\text{pH} - 3.63 \quad r^2 = 0.94 \quad (37)$$

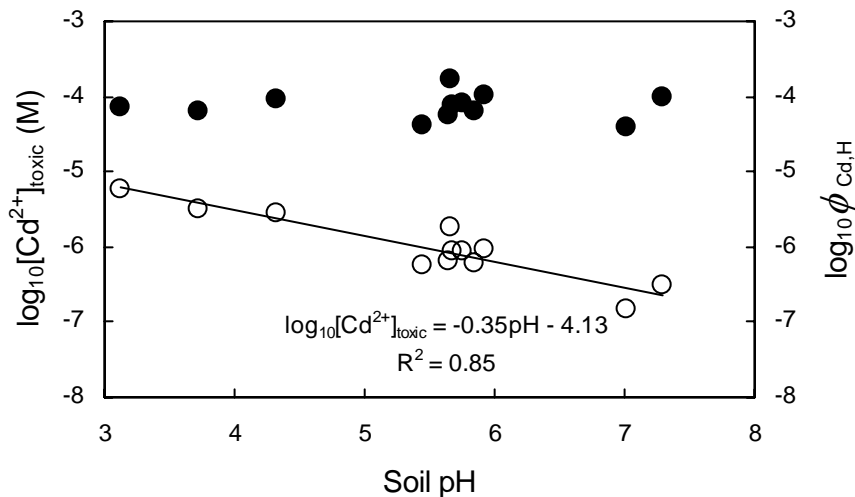
$$\text{EC}_{50\text{-individuals}}: \log_{10}[\text{Cd}^{2+} \text{EC}_{50\text{-individuals}}]_{\text{toxic}} = -0.35\text{pH} - 4.13 \quad r^2 = 0.85 \quad (38)$$

Variances in the endpoints, expressed as log₁₀[total added Cd], log₁₀[Cd²⁺]_{toxic} and log₁₀ φ_{Cd,H}, are given in Table 1. log₁₀ φ_{Cd,H} consistently gives the lowest variance of the three endpoints. Free ion endpoints (EC₅₀ individuals), unadjusted and adjusted for pH, are shown in Figure 2.

Table 1. Variances of endpoints for the data of Crommentuijn et al. (1997).

	LC ₅₀	EC ₅₀ -weight	EC ₅₀ -individuals
log ₁₀ [total added Cd]	0.04	0.03	0.05
log ₁₀ [Cd ²⁺]	0.17	0.18	0.20
log ₁₀ φ _{Cd,H}	0.01	0.01	0.03

Figure A1. Cadmium toxicity to *F. candida*. EC₁₀ values expressed as the free ion (open symbols), and as the index of free ion toxicity (closed symbols).



Annex 2 Impact of pH on copper toxicity to alfalfa

González (1991) determined EC₁₀ (relative yield) concentrations of copper for alfalfa in ten Chilean soils (pH 5.3-7.5, %O.M. 0.3-14.5). The endpoint concentrations ranged from 32 mg Cu.(kg soil)⁻¹ to 1253 mg Cu.(kg soil)⁻¹, expressed as the reactive (added) Cu concentrations. Endpoint free ion concentrations were calculated using the transfer function

$$\log_{10}[\text{Cu}^{2+}] = -1.15\text{pH} - 0.40\log_{10}[\%O.M.] + 0.54\log_{10}[\text{M}_{\text{SOIL}}] + 1.34 \quad (39)$$

calculated by Tipping et al. (2003a). The calculated free ion concentrations are shown in Figure 1 and are clearly strongly dependent upon the pH. The relationship between pH and the endpoint expressed as the free ion concentration is described by the expression

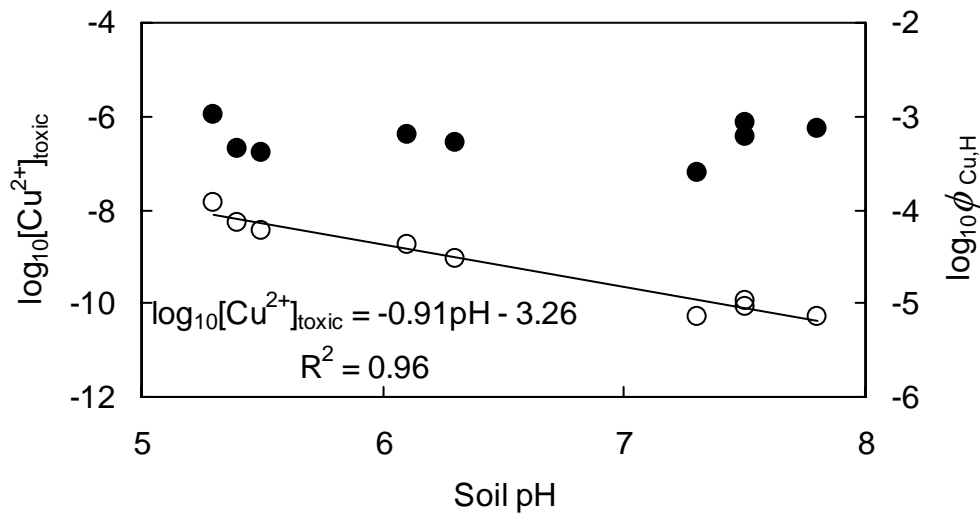
$$\log_{10}[\text{Cu}^{2+}]_{\text{toxic}} = -0.91\text{pH} - 3.25 \quad r^2 = 0.96 \quad (40)$$

which then gave the following expression for $\phi_{\text{Cu,H}}$:

$$\phi_{\text{Cu,H}} = \frac{[\text{Cu}^{2+}]_{\text{toxic}}}{[\text{H}^+]^{0.91}} \quad \text{or} \quad \log_{10} \phi_{\text{Cu,H}} = \log_{10}[\text{Cu}^{2+}]_{\text{toxic}} + 0.91\text{pH} \quad (41)$$

The endpoints expressed as \log_{10} [total added Cu], $\log_{10}[\text{Cu}^{2+}]_{\text{toxic}}$ and $\log_{10} \phi_{\text{Cu,H}}$ had variances of 0.44, 0.89 and 0.03 respectively. Thus, expressing the endpoint as $\log_{10} \phi_{\text{Cu,H}}$ gave a much lower variance than did total metal or the free ion.

Figure A2. Copper toxicity to Alfalfa. EC₁₀ values expressed as the free ion (open symbols), and as the index of free ion toxicity (closed symbols).



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